PHOTOCATALYTIC DEGRADATION OF RHODAMIN-B USING METAL COMPLEXES AND HYDROGEN PEROXIDE

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ABSTRACT

The photocatalytic degradation has been considered to be an efficient process for degradation of organic pollutants, which are present in the effluents released by industries. The photocatalytic bleaching was carried out on rhodamin-B (cationic dye) in the presence of iron (III) complex, hydrogen peroxide and was observed spectrophotometrically. The effect of various operating variables like pH, concentration of complex and dye, amount of H_2O_2 and light intensity etc. was also observed on the efficiency of the reaction. A tentative mechanism has also been proposed for this photocatalytic degradation of rhodamin-B.

Keywords: *Photocatalytic degradation, rhodamin-B, metal complexes, hydrogen peroxide.*

INTRODUCTION

Textile industries generate waste water with different characteristic. The waste characteristic varies according to the process employed. Discharge of waste water into water sources causes pollution and affects water quality including temperature, turbidity, pH, alkalinity, acidity BOD, COD and colour. Colour in waste water is imparted by the dyes used in dyeing and printing industries.

Most of the dyes are toxic in nature and their high concentration causes many water borne diseases and increases the BOD of water. The presence of carcinogens have also been reported in waste water of dyeing and printing units. As the dyes present in waste water degrades very slowly under normal conditions, some treatment methods to remove the dyes from the water have to be employed. Several methods of treatment of effluents have been undertaken from time to time, the most common of which are chemical precipitation and biological methods. However, these methods suffer from many disadvantages, but photocatalytic degradation seems to be the most promising technique, since it is of low cost and less time consuming.

Photochemical degradation of dyes employing Fenton reagent provides a newer method for the treatment of waste water containing dyes effluents. Fenton reaction involves the formation of hydroxyl and perhydroxyl radicals. Fenton reagent is an established reagent for degradation of dyes but main demerit of the reagent is that the reaction stops after complete consumption of Fe^{+2} ions, whereas, in photo-Fenton reaction, Fe^{+2} ions are regenerated from Fe^{+3} ions with an additional requirement of light. This makes the process cyclic in nature and photochemical degradation proceeds smoothly. “Photocatalysis” is an emerging and frontline area of researchers since it is a cost effective and ecofriendly technique.

A number of Fenton and photo-Fenton reaction involving degradation of dyes and other pollutants have been reported from time to time [1-4]. Pignatello *et al.* [5] reported the degradation of PCBs by ferric ion, hydrogen peroxide and UV light. Chen *et al.*[6] investigated the photo-Fenton degradation of malachite green catalyzed by aromatic compounds under visible light irradiation. Xie *et al.*[7] studied the photoassisted degradation of dyes in the presence of Fe^{+3} and H_2O_2 under visible irradiation. Oxidative degradation of malachite green by Fenton generated hydroxyl radicals in aqueous acidic media was studied by Dutta *et al.*[8] Nerud *et al.*[9] reported the decolorization of synthetic dyes by the Fenton-reagent and the Cu/Pyridine/H_2O_2 system. Kavitha *et al.* [10] studied the degradation of 2-chlorophenol by Fenton and photo-Fenton process - a comparative study. Chen *et al.* [11] observed the electrochemical degradation of bromopyrogallol red in the presence of cobalt ions. Verma *et al.* [12] investigated the decolorization of synthetic dyes using a copper complex with glucaric acid. Feng *et al.* [13] studied the photodegradation of 17 β-estradiol in water by UV-vis / Fe (III) / H_2O_2 system.

From the literature survey it was observed that no attention has been paid on the photocatalytic degradation of rhodamin-B by a modified photo-Fenton reagent made of metal complexes, e.g., $[Fe (SCN)]^{+2}$, $[Cu (SCN)]^{+}$ and H_2O_2. Therefore, a comparative study of photocatalytic degradation of rhodamin-B (Fig. 1) using these complexes and H_2O_2 has been reported.

EXPERIMENTAL SECTION

$FeCl_3.6H_2O$ (Himedia), $CuCl_2$ (Merck), KSCN (Himedia), H_2O_2 (30%; Merck) and rhodamin-B (Himedia) were commercial products and were used as

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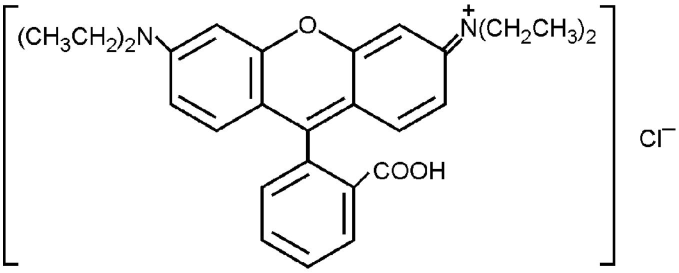

Fig 1. Structure of rhodamin-B

received. A 200 W tungsten lamp (Philips) was used for irradiation purpose. The intensity of light at various distances was measured by “Suryamapi” [CEL Model 201]. The pH of the solution was measured by a digital pH meter [Systronics Model 335]. The desired pH of solution was adjusted by the addition of previously standardised 0.1N sulphuric acid and 1N sodium hydroxide solution. A UV / VIS spectrophotometer [Systronics Model 106] was used for measuring absorbance of reaction at regular time intervals.

The photochemical degradation of rhodamin-B was studied in the presence of transition metal complexes {$[Fe(SCN)]^{+2}$, $[Cu(SCN)]^{+}$, H_2O_2 and light. Stock solution of rhodamin-B [1.0×10^{-3}M] was prepared in doubly distilled water. $[Fe(SCN)]^{+2}$ complex was prepared by mixing $FeCl_3$ (1.0×10^{-3}M) and KSCN (1.0×10^{-3}M) in 1:1 ratio. Similarly, $[Cu (SCN)]^{+}$ complex was prepared. A reaction mixture containing dye (⊗ 10^{-5} M), complex (⊗ 10^{-5} M) and hydrogen peroxide, was exposed to light for a certain period of time depending upon the complex used.

For the photocatalytic degradation of rhodamin-B, simple assembly of apparatus have been used. The required amount of reaction mixture was taken in a beaker of 100.0 mL capacity. A water filter having inlet and outlet for water was used for cutting off thermal radiations. The reaction mixture was then exposed to 200 W tungsten lamp.

RESULT AND DISCUSSION

An aliquot of 3.0 mL was taken out from the reaction mixture at regular time intervals and the absorbance was measured spectrophotometrically at λ_{max} = 560. It was observed that the absorbance of the solution decreases with increasing time intervals, which indicates that the concentration of rhodamin-B 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 following expression:

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

Graphically representation of typical run is given in Fig. 2.

For iron complex / H_2O_2 system, it was observed that reaction complexes in two phases. The first phase is an induction period, in which radicals are generated whereas major degradation of dye occurs in second step as shown by sharp decrease in absorbance, so only second step was considered in all variations.

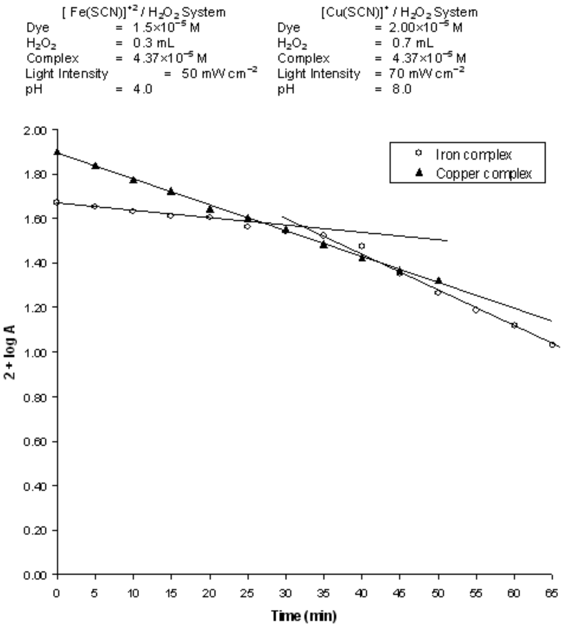

Fig 2. A typical run

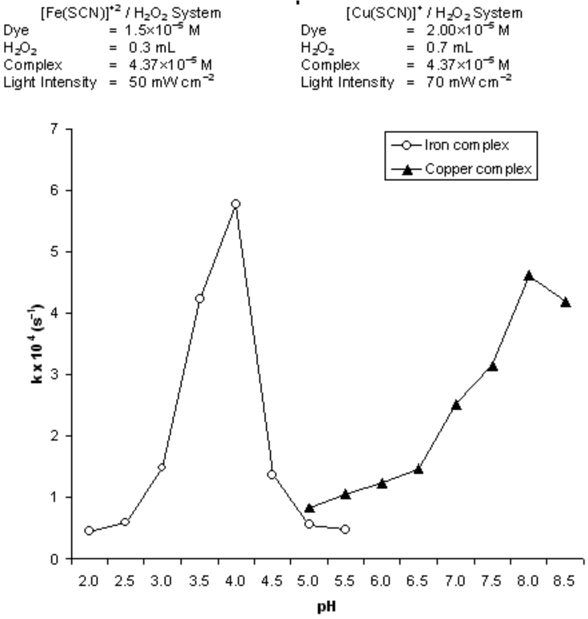

Fig 3. Effect of pH

Effect of pH

The effect of pH on photocatalytic degradation was investigated in the pH range 2.0 – 5.5, 5.0 – 8.5 for iron and copper complexes system, respectively. The results are reported in Fig 3.

Photochemical degradation of rhodamin-B was maximum at pH 4.0 and 8.0 for iron and copper

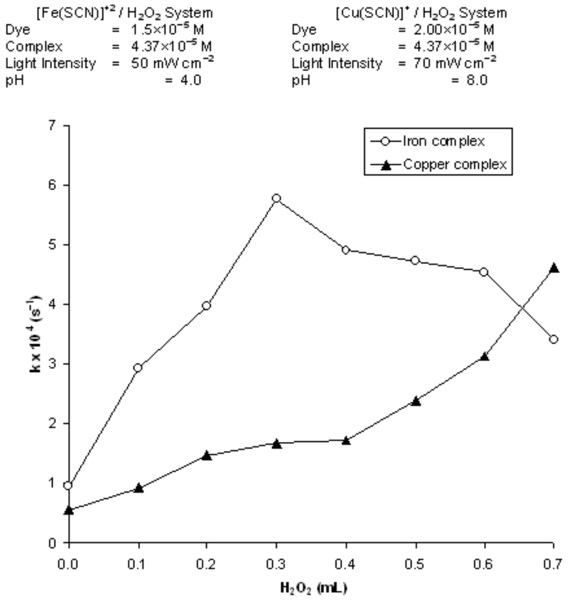

Fig 4. Effect of H_2O_2

complexes system, respectively. The photochemical degradation depends strongly on the pH of the reaction medium. In case of iron complex, it was observed that rate of degradation of dye increases on decreasing pH from 5.5 to 4.0. It may be due to dominance of eq. (2) over eq. (3), where $^{-}$OH ions are generated. These $^{-}$OH ions are removed by increasing H^+ ion concentration on decreasing pH. This will facilitate the eq. (2) forming more $^{\bullet}$OH radicals, which will be utilized for oxidative degradation of rhodamin-B 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. (3) starts dominating over eq. (2) as $Fe(OH)_3$ is less soluble than $Fe(OH)_2$ and generation of $^{\bullet}$OH radicals by eq. (3) is retarted at lower pH than 4.0 [14].

In case of copper complex, reaction proceeds faster in basic medium. The rate of degradation of dye increases on increasing pH from 5.0 to 8.0. It may be due to dominance of eq. (3) over eq. (2), where H^+ ions are generated. These H^+ ions are removed by increasing $^{-}$OH concentration on increasing pH. This will facilitate the eq. (3), forming more $^{\bullet}$OH radicals, which will be utilized for oxidative degradation of rhodamin-B as well as thiocyanate radical. Beyond pH 8.0, further increase in pH results is decreased rate of degradation, which can be attributed as the dominance of eq. (3) over eq. (2), where H^+ ions are generated.

Effect of hydrogen peroxide

The effect of amount of H_2O_2 on the rate of photocatalytic degradation of rhodamin-B was also investigated. The results are reported in Fig 4.

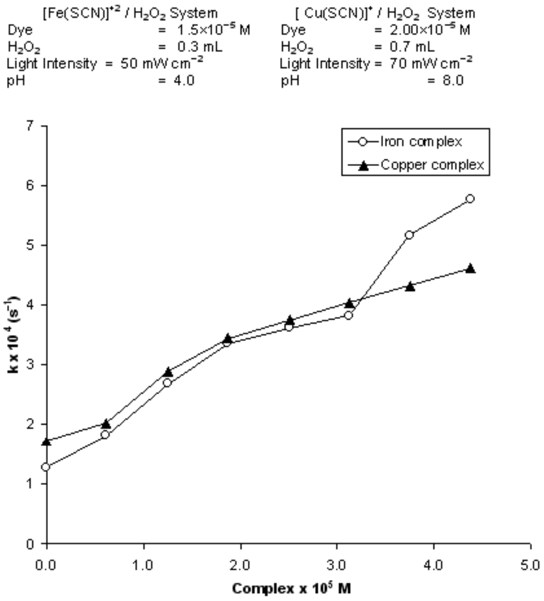

Fig 5. Effect of complex concentration

The rate photochemical degradation of rhodamin-B was maximum at 0.3 mL for iron complex, but the rate continuously increases from 0.0 – 0.7 mL H_2O_2 in case of copper complex system. It may be explained on the basis that the increasing amount of H_2O_2 will provide more $^{\bullet}$OH radicals responsible for oxidative degradation of rhodamin-B. But after a fixed amount of H_2O_2 (0.3 mL) further increment in amount of H_2O_2 will produce more $^{-}$OH ion along with $^{\bullet}$OH radicals and as a result, the pH of the medium increases, resulting into a decrease in the rate of degradation.

A different kind of behaviour for copper complex system was observed. In this case, a continuous increase for the rate of degradation of rhodamin-B was observed on increasing the amount of H_2O_2 from 0.0 to 0.7 mL. It may attributed to the fact that eq. (2) does not dominate over eq. (3) in this case and as such, no decrease in the rate was observed even on increasing the amount of H_2O_2.

Effect of concentration of complexes

The effect of concentration of complexes on the rate of photocatalytic degradation of rhodamin-B was observed by keeping all other factors identical. The results are reported in Fig 5.

It is clear from the data that the rate of photocatalytic degradation increases on increasing concentration of complexes. The rates were determined upto the concentration 4.37 × 10^{-5} M for iron and copper complexes system, respectively. Because beyond this limits the rates were extremely fast and it was not possible to record the observation correctly due to experimental limitations. This increasing trend may be explained on the basis that on

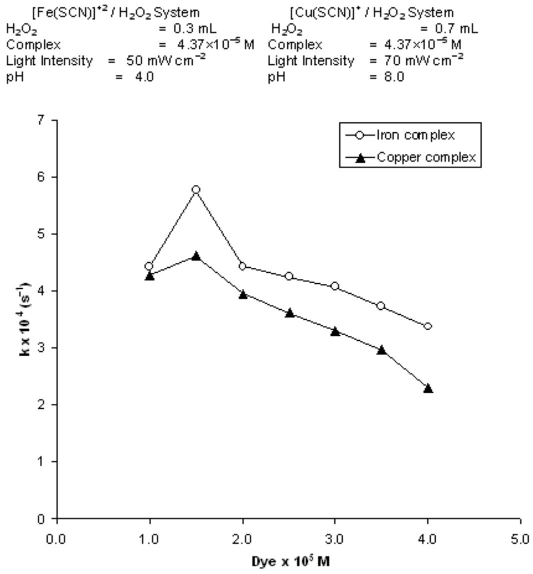

Fig 6. Effect of dye concentration

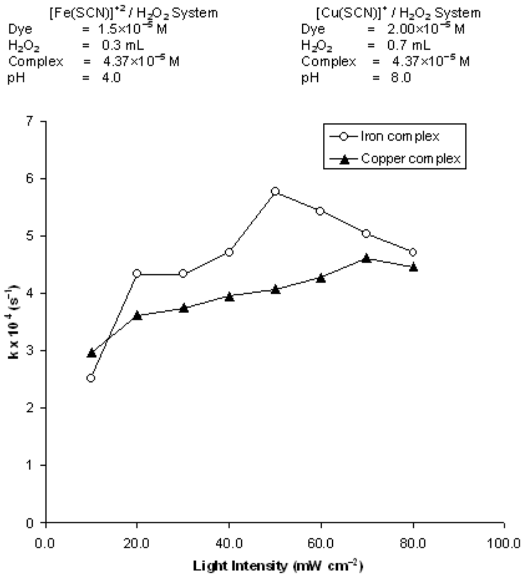

Fig 7. Effect of light intensity

increasing the concentration of complexes more molecules of complexes were available to take part in reaction. This results in an enhanced generation of the $^{\bullet}OH$ radicals and as a consequence, the rate of photocatalytic degradation of dye also increases.

Effect of rhodamin-B concentration

The effect of rhodamin-B concentration on the rate of photocatalytic degradation was also observed and the results are given in Fig 6.

The rate of degradation was found to increase with increasing concentration of rhodamin-B upto 1.50×10^{-5} M and 2.00×10^{-5} M for $[Fe(SCN)]^{+2}$ and $[Cu(SCN)]^{+}$ complex system, respectively. Further increase in concentration beyond these limits decreases the rate of degradation. This may be explained on the basis that on increasing the concentration of rhodamin-B, the reaction rate increases as more molecules of dyes were available for degradation. But further increase in concentration causes retardation of reaction due to number of collisions between dye molecules increase whereas, collisions between dye and $^{\bullet}OH$ radicals decrease. As a consequence, rate of reaction is retarded. Unsuitable steric orientation is also one of the factor for decrement in the rate of reaction.

Effect of light intensity

The effect of light intensity on the photocatalytic degradation of rhodamin-B was also investigated. The results are reported in Fig 7.

The data indicate that an increase in the light intensity increase the rate of reaction and maxima were found at 50 mW cm^{-2}, 70 mW cm^{-2} for iron and copper complexes system, respectively. 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 intensity beyond the maximum limits results in decrease in the rate of reaction. It may be probably due to thermal side reactions.

Mechanism

On the basis of the experimental observations and corroborating the existing literature, a tentative mechanism has been proposed for the degradation of rhodamin-B in presence of iron and copper complexes, H_2O_2 and light.

$$[M\,(SCN)]^{n+} \xrightarrow{h\nu} M^{n+} + {}^{\bullet}SCN$$

$$M^{n+} + H_2O_2 \longrightarrow M^{(n+1)+} + {}^{-}OH + {}^{\bullet}OH$$

$$M^{(n+1)+} + H_2O \xrightarrow{h\nu} M^{n+} + {}^{\bullet}OH + H^+$$

$${}^{\bullet}SCN + 8\ {}^{\bullet}OH \longrightarrow SO_4^{2-} + NH_4^+ + CO_2 + 2\,H_2O$$

$$\text{Dye} + {}^{\bullet}OH \longrightarrow \text{Products}$$

$${}^{\bullet}OH + {}^{\bullet}OH \longrightarrow H_2O_2$$

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$$

(M stands for iron and copper)

Photo-Fenton reaction is one of the example of classical photocatalytic process in homogeneous system that 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 $^{\bullet}OH$, ^{-}OH and Fe^{3+} ions. Fe^{3+} ion decomposes water photochemically to give $^{\bullet}OH$ radical and Fe^{2+} ions. Thiocyanate radical and dye are decomposed by hydroxyl radicals to simpler ions/molecules like sulphates and ammonium ion, carbon dioxide, water *etc.*

The above proposed mechanism for iron complex is also applicable for copper complex.

CONCLUSION

The rate of photocatalytic degradation of rhodamin-B is enhanced by metal complexes. The increasing order of the rate with different metal complexes is as follows – $[Fe(SCN)]^{+2}$ > $[Cu(SCN)]^{+}$

The hydroxyl radicals photocatalytically degrade the rhodamin-B. The participation of $^{\bullet}OH$ radicals as an active oxidising species was confirmed by using hydroxyl radical scavengers, where the rate of photodegradation was drastically reduced.

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

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