
Photocatalytic Degradation of Polluted Water in Presence of Copper Hexacyanoferrate (II)

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ABSTRACT

Photolabile property of ferrocyanide ion is well known. The electron generated by ferrocyanide ion on exposure of light may be utilized for the photoreduction of dye. In the present work use of photolabile nature of ferrocyanide ion was made for the photocatalytic degradation of erythrosine B dye. For this purpose, we used Copper hexacyanoferrate (II) as a photocatalyst. Effect of different parameters like pH, concentration, light intensity etc. was studied on the rate of reaction. A suitable mechanism for the photocatalytic degradation of erythrosine B dye has been proposed.

Keywords: Photoreduction, degradation, Erythrosine B, Copper Hexacyanoferrate (II).

Introduction

The existence of life on earth essentially depends on solar energy and the study of reactions induced by light covers the area of the photochemistry of which plays a great role in many chemical and biological processes. The chemistry of excited electronic states of a molecule is known as photochemistry. These excited states are generated by excitation of compounds, atoms or molecules by absorption of appropriate wavelength from light in an ultraviolet or visible region of the spectrum. Photochemical reactions i.e. dissociation, isomerization and optical electronic excited species are the central features of photochemistry. The photoredox reactions may take place either between the central metal ion and one of its ligand (intramolecular type) or between the complex and another species present into the solution (intermolecular type). Exhaustive researches in the field of photocatalysis have shown various fascinating applications of photocatalytic reactions based on the use of semiconductors.^{1,2} Photodegradation of dye pollutants on silica gel supported TiO₂ particles under visible light has been studied by Chen et al.³ Butts et al.⁴ Hermann et al.⁵ have used heterogeneous photocatalysis for waste water treatment. The photosubstitution reactions of [Fe(CN)₆]⁴⁻ complex has been studied by Barbieri and Cavicchi⁶ [Fe(CN)₆]⁴⁻ is an extremely stable in acid i.e. medium, where exists in its extensively protonated form. The photosensitivity of [Fe(CN)₆]⁴⁻ was already known long back⁷⁻⁹, but there are conflicting opinions^{10,11} regarding the photocatalytic exchange between [Fe(CN)₆]⁴⁻ and CN ions. It is evident that a lot of attention has been paid on the role of iron complexes in number of chemical and photochemical reactions and same attention has been paid on the use of potassium hexacyanoferrate (II) as a homogeneous photocatalyst for the degradation of dyes and in developing photochromic systems¹²⁻¹⁴, but its use has contained limitations as potassium hexacyanoferrate is highly soluble in water and gives a pale yellow solution, which does not utilise sunlight (visible portion) to the desired extent. Therefore, it was proposed to prepare the insoluble and stable copper hexacyanoferrate, which is reddish brown in colour. As difference metal hexacyanoferrates have been used as a probiotic catalyst and must have played a major role in chemical evolution, it seems very important, whether compound like copper hexacyanoferrate (II) can be used as a photocatalyst for the degradation of waste water pollutants particularly dyes.

In spite of many uses, the dyes are toxic and carcinogenic also. Environmental contamination by these toxic chemicals has emerged as a serious global problem. Coloured solutions containing dyes from

industrial effluents of textile, dyeing and printing industries may cause skin cancer due to photosensitization and photodynamic damage. On the other hand, bleached dye solution is less toxic. Secondly, coloured water containing dyes is of almost no use, but if this coloured solution is bleached to give colourless water, then it may be used for washing, cooling, irrigation and cleaning purposes.

Experimental

Section(A)

0.878 g of erythrosine B was dissolved in 100.0 mL of doubly distilled water so that the concentration of dye solution was 1.0×10^{-3} M. It was used as a stock solution. This solution was further diluted as desired. The optical density of this dye solution was determined with the help of a spectrophotometer. Then, it was divided into four parts.

- (i) The first beaker containing only dye solution was kept in dark,
- (ii) The second beaker containing only dye solution was kept in sunlight.
- (iii) 0.10 g of semiconductor copper hexacyanoferrate (II) was added to the third beaker containing dye solution and was kept in dark, and
- (iv) In the fourth beaker containing dye solution with 0.10 g of the semiconductor was added and exposed to sunlight.

These beakers were kept for 3-4 hours and then the optical density of solution in each beaker was measured with the help of a spectrophotometer. It was observed that the solutions of first three beakers had almost the same optical density, while the solution of fourth beaker had a reasonable decrease in its initial value of optical density. The reaction between erythrosine B and semiconductor powder is neither thermal nor photochemical but it is a photocatalytic reaction it is confirmed by this reaction.

The stock solution (1.00×10^{-3} M) of erythrosine B was prepared in doubly distilled water (100 mL). 0.10 g of copper hexacyanoferrate (II) was added to 50.0 mL of 1.50×10^{-5} M erythrosine B solution. The desired pH of the solution was adjusted by addition of previously standardized H_2SO_4 and NaOH solutions. The pH of the solution was measured by a digital pH meter (Cyberscan 1000).

A 200 W tungsten lamp was used for irradiation. The intensity of light was measured by a solarimeter (Surya Mapi CEL Model 201). A water filter was used to cut-off thermal radiations. The progress of the reaction was monitored using a spectrophotometer (Systronics Model 106). The solution was made free from copper hexacyanoferrate (II) particles and other impurities by centrifuging before measurement of absorbance. The photocatalytic bleaching of erythrosine B was observed at $\lambda_{max} = 525$ nm.

Section (B)

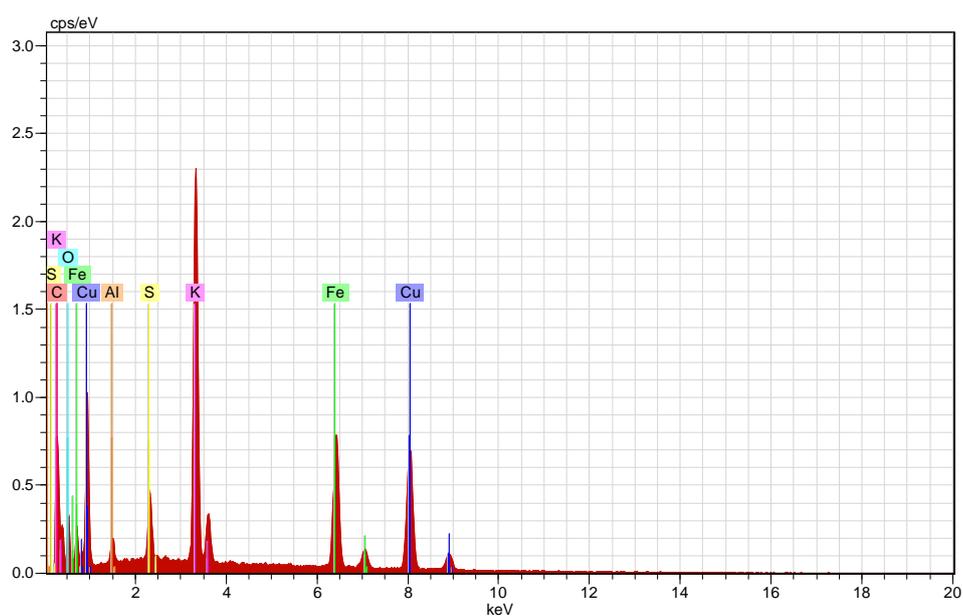
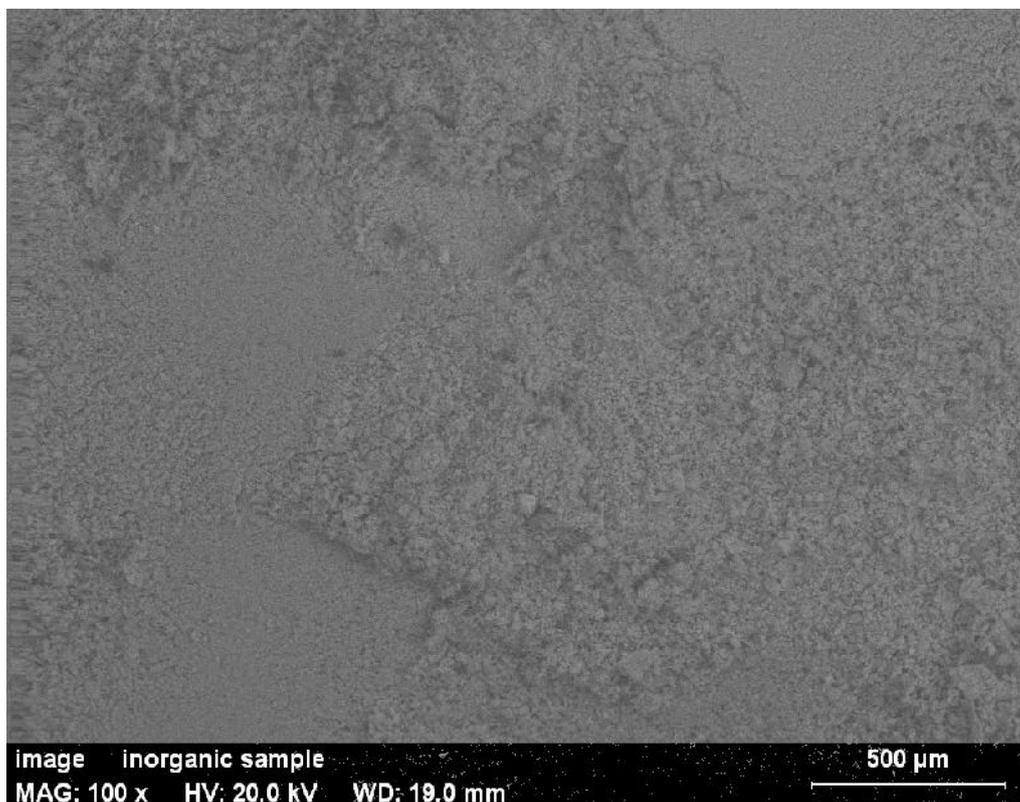
Copper ferrocyanide was prepared by adding potassium ferrocyanide (167 mL; 0.1 M) slowly to copper (II) chloride (500 mL; 0.1 M) solution with constant stirring following the method used by Kourim *et al.*¹⁵ The reaction mixture was heated on a water bath at 100°C for about 2-3 hrs. Chocolate brown precipitates were obtained. Then it was cured for 24 hrs. The reddish brown precipitates were washed and then dried at 60°C (99.4 % yield).

The XRD data of the product were also recorded (Fig. 1.1). IR spectral data of this compound shows a broad peak about 3700 cm^{-1} , which is characteristic of OH group and water molecules. A sharp peak at 1601 cm^{-1} indicates the presence of cyanide and Fe-C stretching frequencies. An intense band at 2182 cm^{-1} may be attributed to the cyanide groups coordinated to a transition metal ion¹⁶⁻¹⁸. In the lower frequencies region, typical bands at 502, 471 and 436 cm^{-1} are observed¹⁹⁻²⁰. A sharp band is also present at 452 cm^{-1} , which may be due to the presence of metal-nitrogen bond due to polymerization.

The copper ferrocyanide is quite stable in presence of strong acids (nitric, sulphuric and hydrochloric acids), bases (sodium, potassium and ammonium hydroxides) as well as many salt solutions in the concentration range from 1.0 – 2.0 M. Such metallic ferrocyanides may have shown photosensitizing and photocatalytic activity in the primitive earth conditions. Thus, it is also possible to use them for the waste

water treatment or for the degradation of pollutants like dyes. With this idea in mind, it was proposed to prepare and use copper ferrocyanide as a photocatalyst for the degradation of dyes erythrosine B.

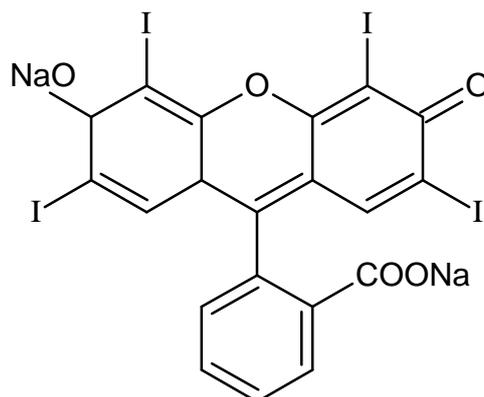
On the basis of XRD, elemental analysis and infra-red spectral data, the following structure of copper ferrocyanide was confirmed as – $\text{Cu}_2 [\text{Fe} (\text{CN})_6] \cdot 2\text{H}_2\text{O}$



Results and Discussion

ERYTHROSINE B

Erythrosine B is also known as acid red 51 and food red 14. Its colour index is 45430. It is a disodium salt of 3',6'-dihydroxy-2',4',5',7'-tetraiodospiro [isobenzofuran-1(3H), 9'(9H) xanthene]-3-one or 2',4,5',7'-tetraiodofluorescein. The structure of erythrosine B is –



Its molecular formula is $C_{20}H_6I_4Na_2O_5$ and molecular weight is 879.92. Its λ_{max} is 524 nm.

The plot of $1 + \log O.D.$ vs. exposure time was a straight line (Fig.), which indicates that the photocatalytic bleaching of erythrosine B follows pseudo-first order kinetics. The rate constant (k) for the reaction was determined using the expression

1.1 A TYPICAL RUN

[Erythrosine B] = 2.00×10^{-5} M

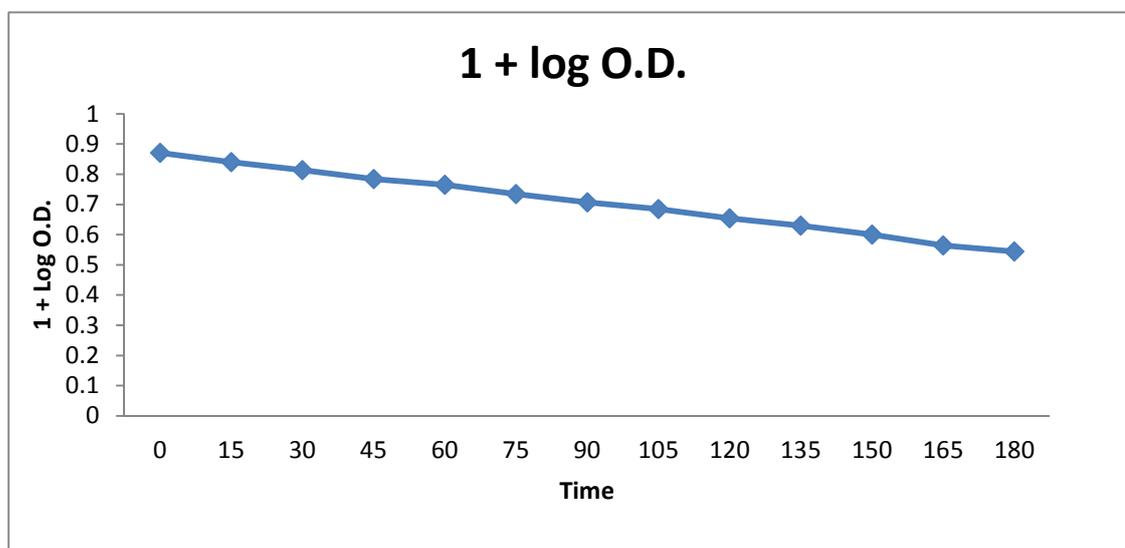
Copper hexacyanoferrate (II) = 0.40 g

pH = 4.5

Light Intensity = 50.0 mW cm^{-2}

Time (min)	Optical density (O.D.)	1 + log O.D.
0.0	0.743	0.8710
15.0	0.692	0.8401
30.0	0.652	0.8142
45.0	0.609	0.7846
60.0	0.582	0.7649
75.0	0.542	0.7340
90.0	0.509	0.7067
105.0	0.484	0.6848
120.0	0.451	0.6542
135.0	0.426	0.6294
150.0	0.398	0.5999
165.0	0.367	0.5647
180.0	0.350	0.5441

$$k = 6.87 \times 10^{-5} \text{ sec}^{-1}$$



1.2 EFFECT OF pH

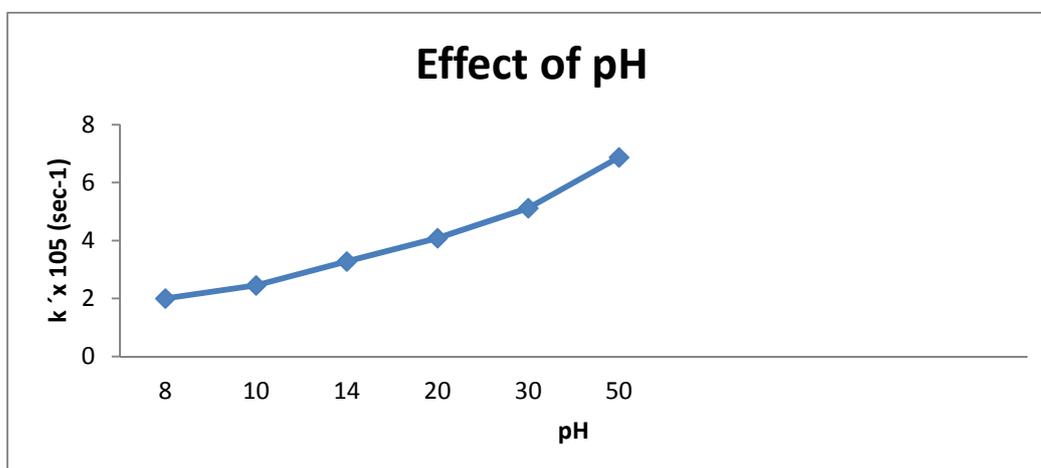
Table 1.3 EFFECT OF pH

[Erythrosine B] = 2.00×10^{-5} M

Light Intensity = 50.0 mW cm^{-2}

Copper hexacyanoferrate (II) = 0.40 g

pH	$k \times 10^5 \text{ (sec}^{-1}\text{)}$
3.5	5.32
4.0	6.10
4.5	6.87
5.0	6.02
5.5	5.41
6.0	4.80
6.5	4.43
7.0	3.70
7.5	3.27
8.0	3.01



It has been observed that the photocatalytic bleaching of erythrosine B decreases on lowering the pH of the medium. It may be due to the fact that at low pH, surface of the semiconductor is positively charged due to adsorbed H^+ ions and the dye may exist in its protonated form; thus, facing a force of repulsion between the two i.e. protonated dye and positively charged surface of the semiconductor. On increasing the pH, this effect decreases and rate of photodegradation of erythrosine B increases up to pH 4.5. On increasing the pH above 4.5, there is an adverse effect on the reaction rate. This may be explained on the basis that now more OH^- ions are available, which will make the semiconductor surface negatively charged due to adsorption of OH^- ions and the dye is an anionic dye; thus, again rate decreases due to repulsion between two negatively charged species i.e. OH^- adsorbed semiconductor surface and negatively charged dye, erythrosine B

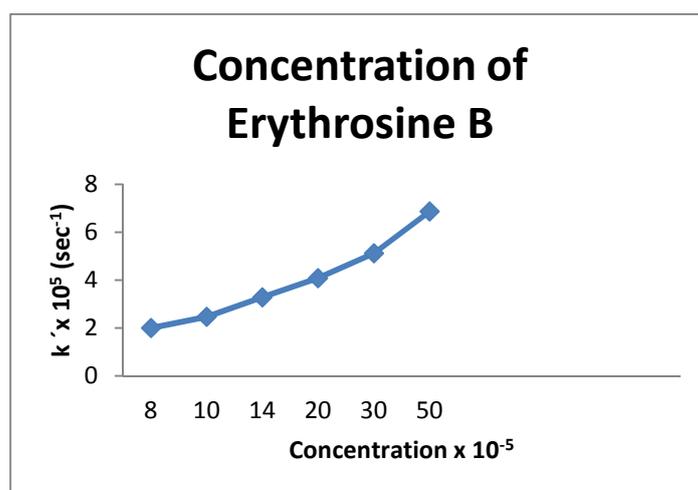
1.3 EFFECT OF ERYTHROSINE B CONCENTRATION –

Table 1.4 EFFECT OF ERYTHROSINE B CONCENTRATION

Copper hexacyanoferrate (II) = 0.40 g
pH = 4.5

Light Intensity = 50.0 mW cm^{-2}

[Erythrosine B] $\times 10^5$ M	k $\times 10^5$ (sec^{-1})
0.40	1.88
0.60	3.00
0.80	4.04
1.00	4.68
1.25	5.26
1.50	6.09
1.75	6.53
2.00	6.87
2.25	6.41
2.50	6.03
2.75	5.46
3.00	4.62
3.25	4.08
3.75	2.89



It was observed that as the concentration of erythrosine B was increased, the rate of photocatalytic bleaching also increases, reaching a maximum at 2.00×10^{-5} M. Further increase in concentration of dye resulted into a decrease in the rate of photocatalytic bleaching. It may be explained on the basis of the fact that

as the concentration of the erythrosine B was increased, more dye molecules were available for excitation and consecutive energy transfer. But as the concentration of erythrosine B was increased above 2.00×10^{-5} M, the dye itself will start acting as a filter for the incident light. Thus, it will result in a decrease in the desired light intensity to reach the dye molecules near the semiconductor particles and thus; a decrease in the rate of photocatalytic bleaching was observed.

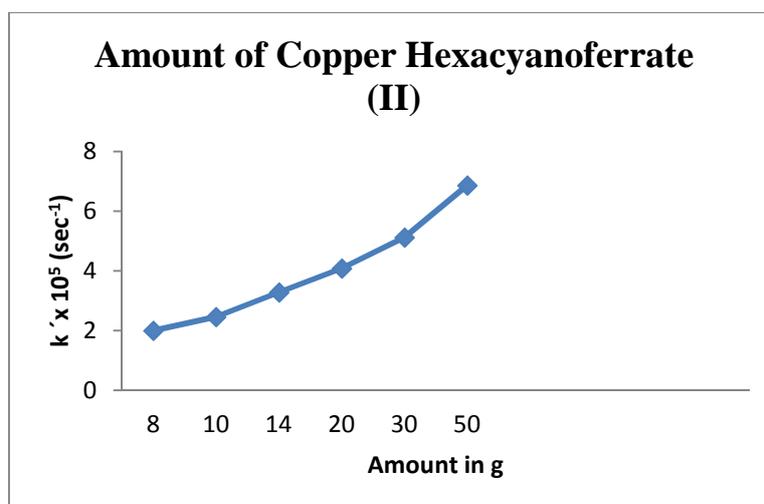
1.5 EFFECT OF AMOUNT OF SEMICONDUCTOR

Table 1.5 EFFECT OF AMOUNT OF COPPER HEXACYANOFERRATE (II)

[Erythrosine B] = 2.00×10^{-5} M
pH = 4.5

Light intensity = 50.0 mW cm^{-2}

Copper hexacyanoferrate (II) (g)	$k \times 10^5 \text{ (sec}^{-1}\text{)}$
0.04	1.06
0.08	2.08
0.12	3.20
0.16	4.02
0.20	5.17
0.25	5.53
0.30	5.80
0.35	6.16
0.40	6.87
0.45	6.79
0.50	6.84
0.55	6.82
0.60	6.86



It was observed that rate of reaction increases with increase in the amount of copper hexacyanoferrate (II) upto 0.40 g; but beyond 0.40 g, the rate of reaction becomes virtually constant.

This may be due to the fact that as the amount of semiconductor was increased in the initial stage there is a corresponding increase in the exposed surface area of the semiconductor, but after this limiting value (0.40 g), any increase in the amount of semiconductor will not increase the exposed surface area but only the thickness of the semiconductor layer. This was also confirmed by using reaction vessels of different dimensions, where there is a decrease in the point of saturation for smaller vessels and an increase in the case of larger reaction vessels.

1.6 EFFECT OF LIGHT INTENSITY

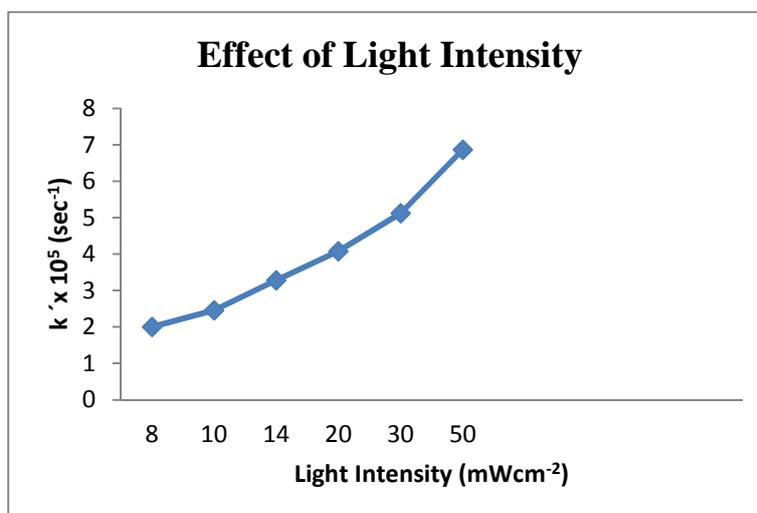
Table 1.6 EFFECT OF LIGHT INTENSITY

[Erythrosine B] = 2.00×10^{-5} M

pH = 4.5

Copper hexacyanoferrate = 0.40 g

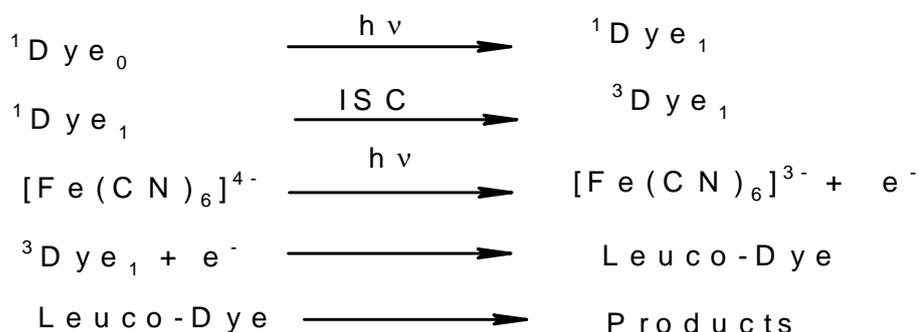
Light intensity (mWcm^{-2})	$k \times 10^5 (\text{sec}^{-1})$
8.0	2.00
10.0	2.46
14.0	3.28
20.0	4.08
30.0	5.12
50.0	6.87



It was observed that the rate of reaction increases on increasing the intensity of light upto 50.0 mWcm^{-2} . It 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. Higher intensity of light was avoided due to side thermal reactions.

(C) MECHANISM

On the basis of observations, a tentative mechanism for photocatalytic bleaching of dye in presence of copper hexacyanoferrate (II) has been proposed as –



The dye exists in its singlet ground state (${}^1\text{Dye}_0$). This dye will adsorb light of suitable wavelength and it is excited to its first excited singlet state (${}^1\text{Dye}_1$). It undergoes inter system crossing (ISC) to its first excited triplet state (${}^3\text{Dye}_1$). The semiconductor copper hexacyanoferrate (II) will eject a photoelectron in presence of light. This photoelectron reduces the dye molecule to its leuco form, which is unstable and degrades further to final products.

In this observation we say that photodegradation of different dye molecules to less toxic products and can help in combating against the water pollution created in water resources from the nearby industries like dyeing, printing and textile industries by copper hexacyanoferrate (II) acts as a photocatalyst quite effectively in this method. The copper hexacyanoferrate (II) not only work as prebiotic catalyst as reported earlier, but also as an efficient photocatalyst. Thus, this work open new avenues to search for more and more effective photocatalysts in years to come.

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