



USE OF COPPER HEXACYANOFERRATE (II) AS A PHOTOCATALYST FOR DEGRADATION OF BISMARK BROWN

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ABSTRACT

Photolabile property of ferrocyanide ion is well known. The electron generated by ferrocyanide ion on exposure to light may be utilized for the photoreduction of dye. In the present work, use of photolabile nature of ferrocyanide ion has been made for photocatalytic bleaching of bismark brown dye. Copper hexacyanoferrate (II) was synthesized and used for this purpose. Effect of different parameters like pH, concentration, light intensity etc. has been observed on the rate of photocatalytic bleaching. A suitable mechanism for the photocatalytic degradation of bismark brown dye has been proposed.

Key words: Photocatalyst, Reduction, Bismark brown, Copper hexacyanoferrate (II).

INTRODUCTION

Water is one of the fundamental requirements of life and any undesired addition of chemical substances lead to its contamination and make it unfit for human utility. The main purpose of waste water treatment is the removal of these toxic substances and colour and to make the water useful for industrial and domestic use. Semiconductor photocatalysis is a rapidly expanding subject that, combined with nanotechnology, has led to some striking new products in the market, such as self-cleaning glass (e.g. Active from Pilkington Glass), tiles, fabrics, paint and concrete. Here, light is used to excite a semiconductor material, which is then able to carry out a wide range of reactions including the mineralisation of organics, destruction of bacteria, viruses and moulds, clearing the 'fog' associated with misted windows, generation of fuels (such as hydrogen via water splitting) and driving novel organic reactions. Photocatalysis with semiconductor has recently become an area of

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intensive investigation. In addition to the more extensively studied use of electron transfer reactions at semiconductors for inducing the photolysis of water as a means of solar energy storage, recent attention has been paid to the use of semiconductors for initiating electron transfer.

The photocatalytic degradation of methylene blue, rhodamine-B and methyl orange in presence of CdS as photocatalyst has been reported.^{1, 2} Kominami et al.³ investigated photodegradation, decolourisation and mineralization of malachite green in aqueous suspension of TiO₂ nanoparticles under aerated conditions. Semiconductor iron (III) oxide has been used for the photocatalytic bleaching of some dyes like malachite green, methylene blue and crystal violet.⁴ Photodegradation of dye pollutants on silica gel supported TiO₂ particles under visible light has been studied by Chen *et al.*⁵

The photoaquation reaction, hexacyanoferrate (II) ion has been studied by various workers from time to time⁶⁻⁹. The effect of light on trioxalatoferrate (III) was observed by Dobereiner¹⁰. Draper¹¹ suggested that this kind of system can be used for the purpose of photometry. The photochemistry of aqueous solutions of [Fe(CN)₆]³⁻ has been investigated by different workers. A number of products like aquapentacyanoferrate (III)¹², HCN¹³, Fe(OH)₃¹⁴, cyanogen¹⁵ and prussian blue¹⁶ were obtained under variable conditions, when aqueous solution of [Fe(CN)₆]³⁻ was irradiated. The photoelectron production from transition metal complexes is an example of intermolecular photoredox reaction, where the central metal undergoes oxidation.

EXPERIMENTAL

Photocatalytic degradation of bismark brown

0.4616 g of bismark brown R 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) 0.10 g of semiconductor copper hexacyanoferrate (II) was added to the fourth beaker containing dye solution and was 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. This experiment confirms that the reaction between bismark brown R and semiconductor powder is neither thermal nor photochemical but it is a photocatalytic reaction.

The stock solution (1.00×10^{-3} M) of bismark brown R 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 bismark brown R 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 bismark brown R was observed at $\lambda_{max} = 470$ nm. The plot of $1 + \log$ O.D. vs. exposure time was a straight line (Fig. 1), which indicates that the photocatalytic bleaching of bismark brown R follows pseudo-first order kinetics. The rate constant (k) for the reaction was determined using the expression -

$$k = 2.303 \times \text{slope} \quad \dots(1)$$

The results for a typical run are presented in Table 1 and graphically represented in Fig. 1.

Table 1: A typical run

[Bismark brown R] = 2.40×10^{-4} M	pH = 5.5	
Copper hexacyanoferrate (II) = 0.40 g	Light Intensity = 50.0 mW cm^{-2}	
Time (min)	Optical density (O.D.)	1 + log O.D.
0.0	0.724	0.8597
15.0	0.692	0.8401
30.0	0.646	0.8102

Cont...

Time (min)	Optical density (O.D.)	1 + log O.D.
45.0	0.616	0.7896
60.0	0.589	0.7701
75.0	0.552	0.7419
90.0	0.537	0.7340
105.0	0.506	0.7041
120.0	0.481	0.6821
135.0	0.460	0.6627
150.0	0.432	0.6355
165.0	0.414	0.6170
180.0	0.384	0.5843

$k = 5.69 \times 10^{-5} \text{ sec}^{-1}$

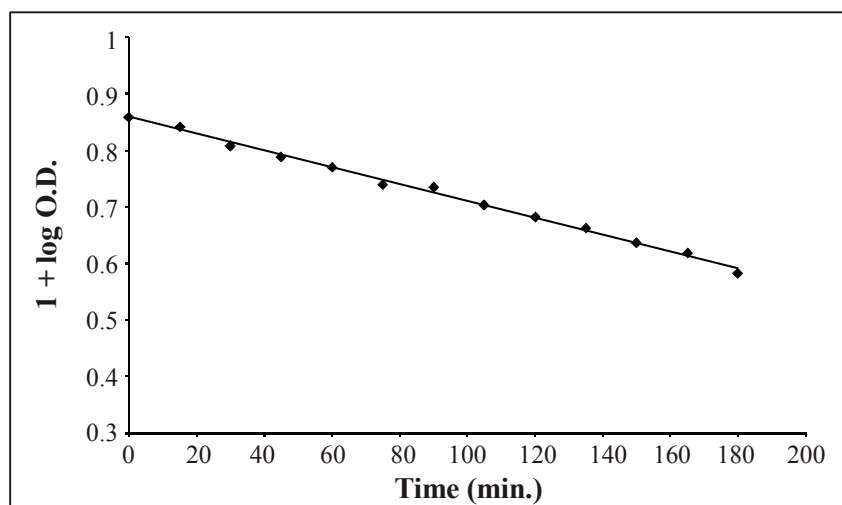


Fig. 1: A Typical run

RESULTS AND DISCUSSION

Effect of pH

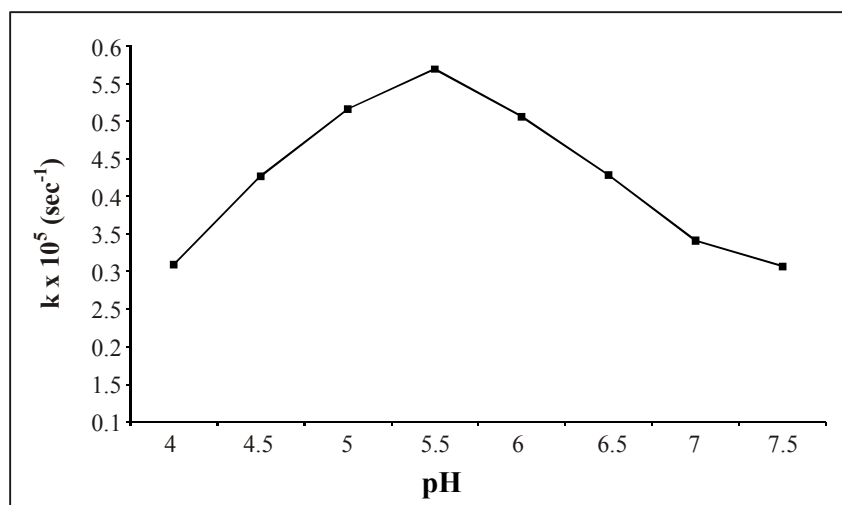
The effect of pH on the rate of photocatalytic bleaching of bismark brown R was investigated. The results are reported in Table 2 and graphically presented in Fig. 2.

Table 2: Effect of pH

[Bismark brown R] = 2.40×10^{-4} M
 Copper hexacyanoferrate (II) = 0.40 g

Light Intensity = 50.0 mW cm^{-2}

pH	$k \times 10^5 \text{ (sec}^{-1}\text{)}$
4.0	3.09
4.5	4.27
5.0	5.16
5.5	5.69
6.0	5.06
6.5	4.28
7.0	3.41
7.5	3.07

**Fig. 2: Effect of pH**

It has been observed that the photocatalytic bleaching of bismark brown R 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 bismark brown R increases up to pH 5.5. On increasing the pH above 5.5, 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 remains in its neutral form. Thus, the reaction rate is adversely affected.

Effect of bismarck brown R concentration

The effect of bismark brown R concentration on the rate of reaction was also studied by using different concentrations of bismark brown R. The results are given in Table 3 and graphically presented in Fig. 3.

Table 3: Effect of bismarck brown R concentration

Copper hexacyanoferrate (II) = 0.40 g		Light Intensity = 50.0 mW cm ⁻²	
pH = 55			
[Bismark brown R] × 10 ⁵ M		k × 10 ⁵ (sec ⁻¹)	
0.4		2.00	
0.8		3.22	
1.2		4.06	
1.6		4.68	
2.0		5.22	
2.4		5.69	
2.8		5.00	
3.2		4.16	
3.6		3.02	
4.0		1.89	

It was observed that as the concentration of bismark brown R was increased, the rate of photocatalytic bleaching also increases, reaching a maximum at 2.40×10^{-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 bismark brown R was increased, more dye molecules were available for excitation and consecutive energy transfer. But as the concentration of bismark brown R was increased

above 2.40×10^{-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.

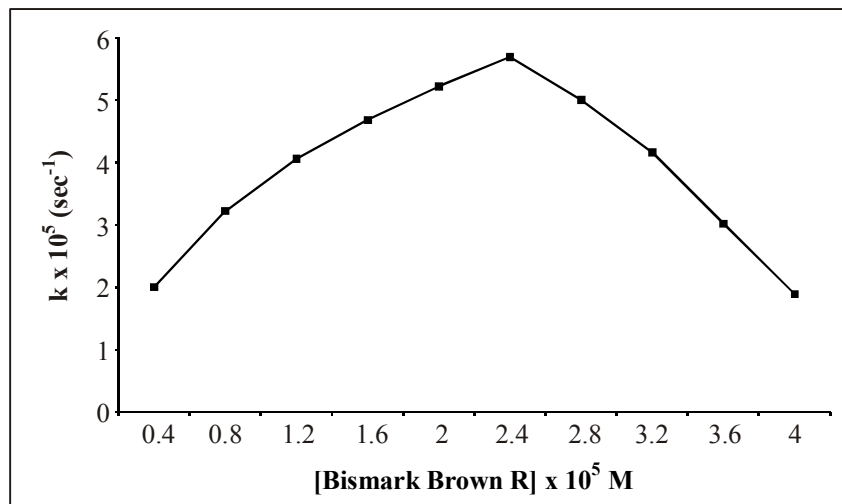


Fig. 3: Effect of dye concentration

Effect of amount of semiconductor

The effect of amount of copper hexacyanoferrate (II) powder on the rate of photocatalytic bleaching of the bismark brown R was also observed. The results are reported in Table 4 and graphically presented in Fig. 4.

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

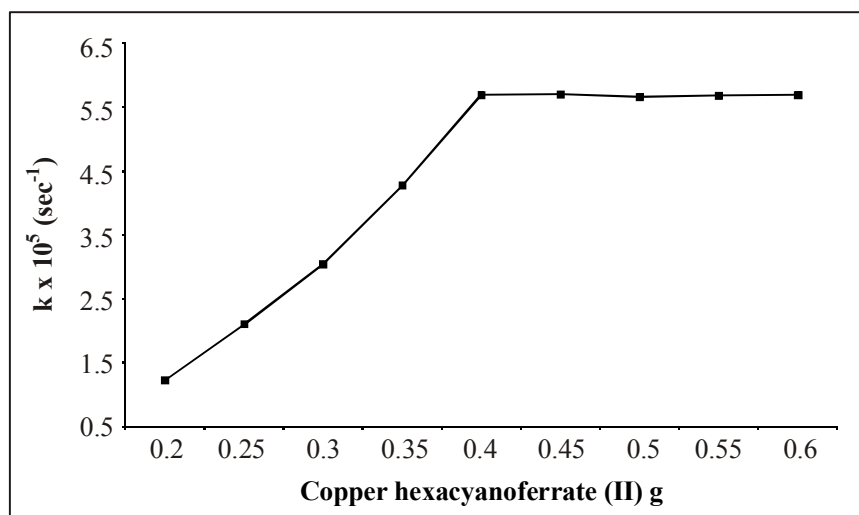
This may be due to the fact that as the amount of semiconductor was increased; in the initial stage, there is a corresponding increase in the exposed surface area of the semiconductor, but after this limiting value (0.40 g), any increase in the amount of semiconductor will not increase the exposed surface 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.

Table 4: Effect of amount of copper hexacyanoferrate (II)

[Bismark brown R] = 2.40×10^{-4} M
pH = 5.5

Light Intensity = 50.0 mW cm^{-2}

Copper hexacyanoferrate (II) (g)	$k \times 10^5 (\text{sec}^{-1})$
0.20	1.22
0.25	2.10
0.30	3.04
0.35	4.28
0.40	5.69
0.45	5.70
0.50	5.66
0.55	5.68
0.60	5.69

**Fig. 4: Effect of amount of semiconductor**

Effect of light intensity

The effect of light intensity on the rate of photocatalytic bleaching of bismark brown R was observed. The results are reported in Table 5 and graphically presented in Fig. 5.

Table 5: Effect of light intensity

Light intensity (mWcm ⁻²)	k × 10 ⁵ (sec ⁻¹)
8.0	1.44
10.0	2.22
14.0	3.04
20.0	4.16
30.0	5.02
50.0	5.69

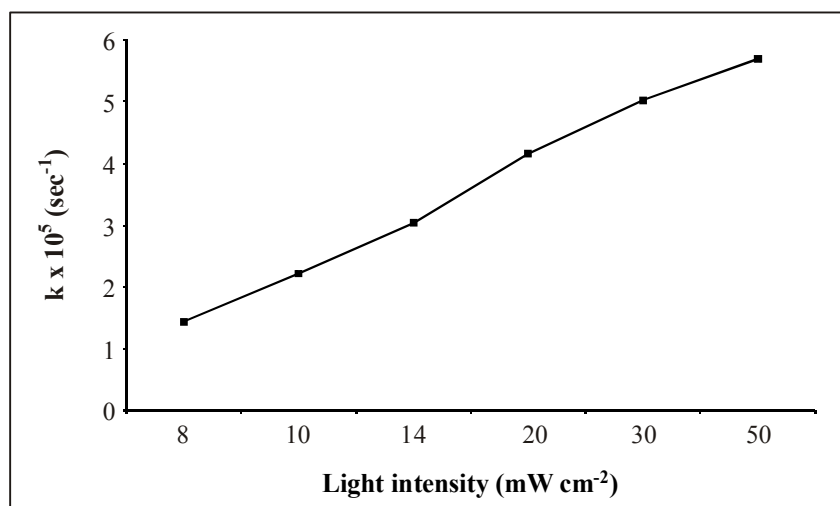


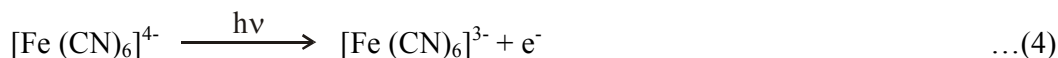
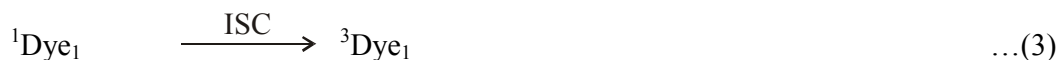
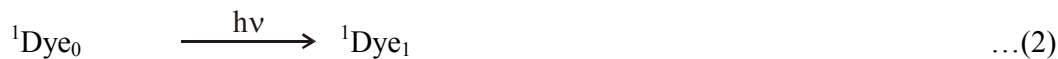
Fig. 5: Effect of light intensity

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

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.

Thus, these observations support the fact that copper hexacyanoferrate (II) acts as a photocatalyst quite effectively to photodegrade 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. This work further strengthens the opinion that copper hexacyanoferrate (II) not only works as a prebiotic catalyst as reported earlier, but also as an efficient photocatalyst. Thus, this work opens new avenues to search for more and more effective photocatalysts in years to come.

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