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PHOTOCATALYTIC DEGRADATION OF AZURE B USING COPPER HEXACYANOFERRATE (II) AS SEMICONDUCTOR

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ABSTRACT

The copper hexacyanoferrate (II) assisted photodegradation of azure B has been examined under visible irradiation (λ_{max} = 640 nm). The azure B is which undergoes degradation on irradiation with visible light. The rate of degradation of azure B was found to follow pseudo-first order reaction. After irradiation for 2 hours, 86% of azure B dye was degraded with addition of 0.05 g / 50 mL copper hexacyanoferrate (II) to solution 1×10^{-5} M of azure B. The influence of pH, semiconductor amount, azure B concentration, and light intensity were investigated and optimum conditions are recorded. The photodegradation was conducted in basic medium and at room temperature.

Key words: Photocatalyst, Azure B, Copper hexacyanoferrate (II), Semiconductor, Optical density.

INTRODUCTION

The presence of dye in wastewater has become a major issue all over the world. These dyes constitute largest group of organic compounds. Due to the high concentration of organics in the effluents and the higher stability of modern synthetic dyes, the conventional biological treatment methods are ineffective for complete colour removal and degradation of organics and dyes[1]. Dyes are designed to resist UV light and chemical and these criteria yield dyes that are not easily degraded in the environment[2]. According to Riu et al.[3], most commonly used azo dyes can be degraded to aromatic amines under anaerobic conditions and some of these amines are carcinogenic.

Conventional methods are not destructive but only transfer dye from one phase to another; hence, there is a need for developing treatment technologies for eliminating contaminants from wastewater. In this way, photocatalytic degradation by semiconductor is a new, effective and rapid technique for the removal of pollutants from water[4,5]. Gandhi et al.[6,7]

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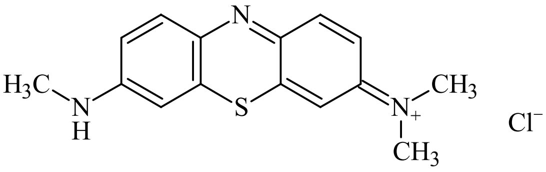
used CoS-ZnS (1 : 2) and CoS-ZnS (1 : 10) as semiconductor in the photocatalytic degradation of azure B and methylene blue, respectively.

Presently, different transition metal complexes play an important role in photocatalytic degradation of different dyes. Amido black-10 B and bismark brown-R were bleached using photo-Fenton reagent by Kumar et al.[8] and Sharma et al[9], respectively. Jhala et al.[10] studied the photocatalytic degradation of neutral red indicator using potassium trisoxalatoferrate (III). The effect of light on trisoxalatoferrate (III) was observed by Doberiner[11]. Draper[12] suggested that this kind of system can be used for the purpose of photometry. Degradation of rose Bengal dye in aqueous medium using heterogeneous photo-Fenton process has been assessed by Sharma et al[13]. Research studies using Fenton reagent have demonstrated its ability to oxidize pesticides[14]. Chen and Zhu[15] catalytically degraded orange-II by UV-Fenton with hydroxyl-Fe-pillared-bentonite in water. Sharma et al.[16] reported photocatalytic degradation of amido black-10B using copper hexacyanoferrate (II) as semiconductor.

In present work, copper hexacyanoferrate (II) was found good semiconductor for the photocatalytic degradation of azure B, It is chocolaty coloured powder and able to utilize sunlight efficiently. Azure B is a dye used in biological stain. The chemical structure of azure B is –



EXPERIMENTAL

Material and methods

The stock solution (1.0×10^{-3} M) of azure B was prepared in double distilled water (500 mL) and further diluted as and when required. The pH of the solution was adjusted by addition of previously standarised H_2SO_4 and NaOH solution and measured by digital pH meter (Systronics, Model 335). 0.05 g of copper hexacyanoferrate (II) was added to 50.0 mL for 1.2×10^{-5} M azure B solution. The solution was irradiated by a 200 W tungsten lamp (Philips). The intensity of light was measured by a solarmeter (Surya mapi CEL model 201). A water filter was used to remove thermal radiations. The optical density of solution was recorded at regular time interval by using spectrophotometer (Systronics-104). Before measuring OD, copper hexacyanoferrate (II) was removed by the help of centrifuge machine (Remi, Model 1258).

RESULTS AND DISCUSSION

Photocatalytic degradation of azure B was observed at λ_{max} = 640 nm. A graph, plotted between exposure time and 1 + log OD was obtained as straight line, which indicates that photocatalytic degradation of azure B follow pseudo-first order kinetics. The rate constant k for the reaction was determined using the expression : k = 2.303 × slope

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

Table 1: A typical run

[Azure B] = 1.2×10^{-5} M pH = 11.0
Copper hexacyanoferrate (II) = 0.05 g Light intensity = 51.0 $mWcm^{-2}$

Time (min.)	Optical density (O.D.)	1 + log O.D.
0	0.760	0.880
20	0.538	0.731
40	0.399	0.601
60	0.289	0.462
80	0.205	0.312
100	0.174	0.241
120	0.104	0.017
		k = 2.64×10^{-4} sec^{-1}

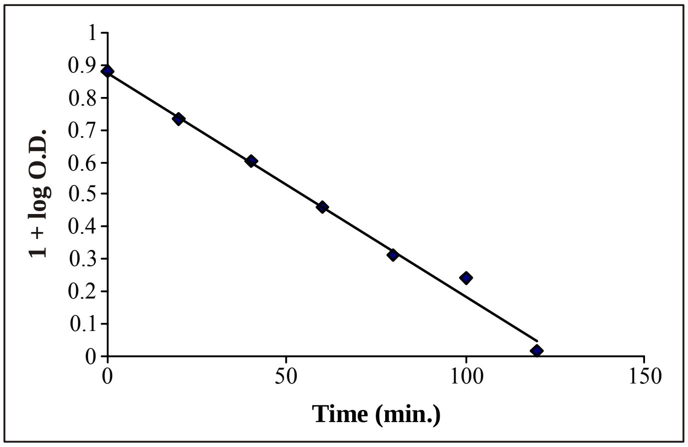


Fig. 1: A typical run

Effect of pH

The pH of solution is likely to affect the photocatalytic degradation of the dye and hence, the effect of pH on the rate of dye solution was investigated in the pH range (9.5 to 13). The results are represented in the Table 2 and graphically presented in Fig. 2.

Table 2: Effect of pH

[Azure B] = 1.2×10^{-5} M
Copper hexacyanoferrate (II) = 0.05 g Light intensity = 51.0 mWcm^{-2}

pH	k × 10^4 (sec^{-1})
09.5	1.38
10.0	1.50
10.5	1.98
11.0	2.64
11.5	1.89
12.0	1.74
12.5	1.53
13.0	1.38

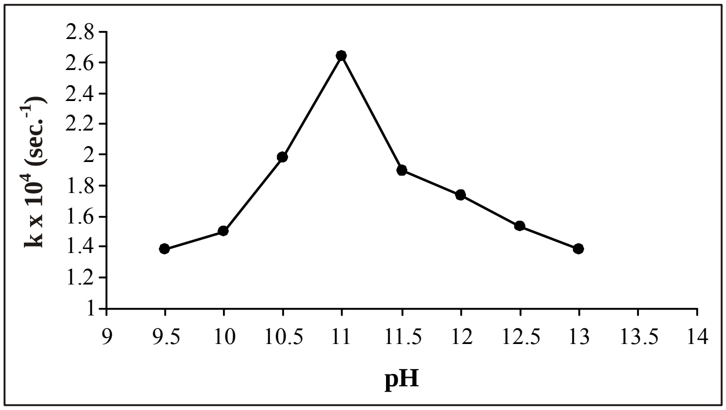


Fig. 2: Effect of pH

It has been observed that the photocatalytic degradation of azure B increases with increase in pH upto pH = 11.0. It is due to more availability of the OH^- ion at higher pH values. These OH^- ions combine with the hole to form $^{\bullet}OH$ radicals, thus more OH^- will generate more $^{\bullet}OH$ radicals. These hydroxyl free radicals are responsible for this photocatalytic degradation. On increasing the pH above pH = 11.0, rate of degradation of dye decreases, as the pH of the solution is increased, more OH^- ion will be available and these ions are absorbed on the surface of semiconductor making it negatively charged and as a consequence of repulsive force between two negatively charged species (OH^- ion and electron rich dye), the approach of electron rich dye to the semiconductor surface will be retarded. This will result into decrease in the rate of photocatalytic degradation of azure B.

Effect of azure B concentration

The effect of variation of azure B concentration on the rate of reaction was observed by using different concentrations of azure B. The results are reported in Table 3 and graphically presented in Fig. 3.

Table 3: Effect of azure B concentration

Copper hexacyanoferrate (II) = 0.05 g

Light intensity = 51.0 $mWcm^{-2}$ pH = 11.0

[Azure B] × 10^5 M	k × 10^4 (sec^{-1})
0.4	1.83
0.8	2.19
1.2	2.64
1.6	2.35
2.0	1.67
2.4	1.46
2.8	1.31

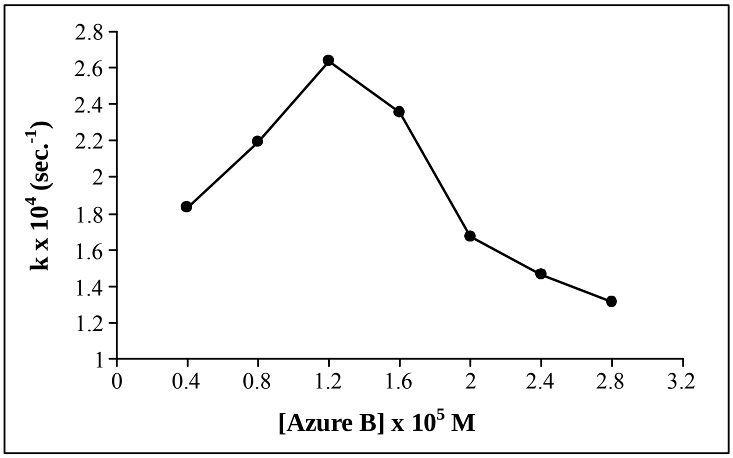


Fig. 3: Effect of dye concentration

It has been observed that the rate of photocatalytic degradation increases with an increase in the dye up 1.2×10^{-5} M. Further increase in concentration of dye resulted into decrease in the rate of photocatalytic degradation. It may be explained on the basis of the fact as the concentration of azure B was increased, more dye molecules will be available excitation and for consecutive energy transfer, hence, increase in the rate of photocatalytic degradation is observed. But when the concentration of azure B is increased above 1.2×10^{-5} M, the dye itself will start acting as a filter for incident light. It does not permit the desired light intensity to reach the semiconductor surface; Thus, decreasing the rate of photocatalytic degradation of azure B.

Effect of amount of semiconductor

The effect of amount of copper hexacyanoferrate (II) powder on the rate of photocatalytic degradation of azure B was observed. The results are reported in Table 4 and graphically presented in Fig. 4.

Table 4: Effect of amount of semiconductor

[Azure B] = 1.2×10^{-5} M

Light intensity = 51.0 mWcm^{-2} pH = 11.0

Amount of copper hexacyanoferrate (II) (g)	$k \times 10^4$ (sec^{-1})
0.025	1.83
0.050	2.64
0.075	2.64
0.100	2.64
0.125	2.64
0.150	2.62
0.175	2.61

As indicated from the data, it was observed that rate of photocatalytic degradation of dye increases with increase in the amount of copper hexacyanoferrate (II) up to 0.05 g. but beyond 0.05 g, the rate reaction becomes virtually constant. This can be explained on the fact that, as the amount of semiconductor is increased, exposed surface area of semiconductor will also increase, thus, an increase in the rate of reaction is observed. But, after certain limiting amount of semiconductor (0.05 g), if the amount of semiconductor was further increased, it will not contribute to an increase in the exposed surface area. This was also confirmed by using reaction vessels of different dimensions. Thus, after certain amount of semiconductor, the saturation point reached.

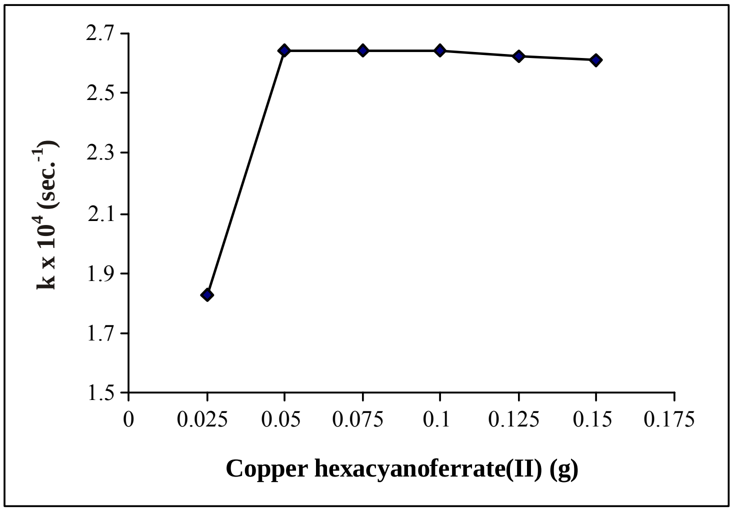


Fig. 4: Effect of amount of semiconductor

Effect of intensity of light

The effect of variation of light intensity on the rate of photocatalytic degradation of azure B was also observed. The results are reported in Table 5 and graphically presented Fig. 5.

Table 5: Effect of light intensity

[Azure B] = 1.2×10^{-5} M

Copper hexacyanoferrate (II) = 0.05 g pH = 11.0

Light intensity (mWcm^{-2})	k × 10^4 (sec^{-1})
35	2.09
38	2.11
41	2.21
44	2.32
47	2.41
50	2.54
51	2.64

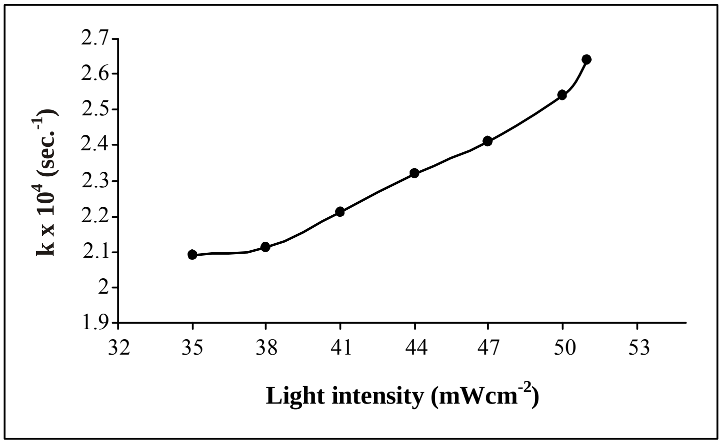


Fig. 5: Effect of light intensity

As indicated from data, it was observed that rate of photocatalytic degradation of azure B increases on the increasing the intensity of light from 35.0 mW cm^{-2} to 51.0 mW cm^{-2}. It may be explained on the basis that as the light intensity is increased, the number of photon striking per unit area of semiconductor also increases. Thus, increase in the rate of photocatalytic reaction is observed and an almost linear behaviour light between intensity and rate of reaction is observed. However, higher intensities are avoided due to thermal effect.

Mechanism

On the basis of experimental observation a tentative mechanism has been proposed for degradation of azure B by copper hexacyanoferrate (II).

$^1\text{Dye}_0 + h\nu \longrightarrow {}^1\text{Dye}_1$ (Singlet excited state) ...(1)

$^1\text{Dye}_1 \xrightarrow{\text{ISC}} {}^3\text{Dye}_1$ (triplet excited state) …(2)

$\text{SC} + h\nu \longrightarrow e^- + h^+$ or SC* …(3)

$h^+ + \text{OH}^-$ (from base) $\longrightarrow {}^{\bullet}\text{OH}$ …(4)

$^3\text{Dye}_1 + {}^{\bullet}\text{OH} \longrightarrow$ Products …(5)

When solution of dye was exposed to light in presence of semiconductor (SC); initially, the dye molecules were excited first to their excited singlet state. These excited state molecules were converted to the triplet state through inter system crossing (ISC). Semiconductor also utilize radiant energy to excite its electron from valence band to conduction band; thus, living behind a hole. This hole abstracts an electron from OH^- ions generating $^{\bullet}OH$ free radical. The dye is bleached by this $^{\bullet}OH$ radical.

CONCLUSION

Azure B dye can be successfully degraded using copper hexacyanoferrate (II) semiconductor under visible light irradiation. Thus, copper hexacyanoferrate (II) may act as a photocatalyst quite effectively to photodegrade different dye molecules to colourless less toxic products.

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