

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

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The Photocatalytic degradation of Azure-B has been investigated using Zinc hexacyanoferrate (II) as semiconductor. Zinc hexacyanoferrate (II) was prepared from co-precipitation process. The effect of operational parameters, *i.e.* pH of solution, amount of semiconductor, concentration of dye solution and effect of light intensities on the rate of photocatalytic process has been examined. A tentative mechanism for the photocatalytic degradation of Azure B has also been proposed.

Keywords: Azure B (Az-B); Optical density (OD); Photocatalyst; Semiconductor (SC); Zinc hexacyanoferrate (II).

Introduction

Different dyes, which are used in various industries like textile, paper, leather, wool, pulp etc. ultimately enter into near aquatic system. Dyes exert various biological effects on plants as well as on animals. These toxic effluents may even destroyed the life of plants and animal in water. Ever increasing industrialization has caused a serious environmental problem of water pollution. Therefore, there is an utmost need to search for effective route to treat the polluted water to make it almost free from contaminants.

Due to the high concentration of organics and synthetic dyes, the conventional biological methods are ineffective for the complete colour removal and degradation of organics and dyes. Photocatalysis by semiconductor particles is a promising technology for water treatment. Photocatalytic bleaching is a part of green chemistry, where the catalyst utilizes visible light and convert harmful dyes into less harmful products. TiO_2 has been frequently used as a semiconductor for this purpose¹. Various semiconductors like oxides², *e.g.* Bi_2O_3 , sulphides^{3,4}, *e.g.* CdS and ZnS ion are used as photocatalyst in degradation of organic pollutant or dyes. Now combination of sulphides of two metals, oxides of two metals are taken as photocatalyst. Sharma *et al.*^{5,6} used coprecipitation of NiS-ZnS (1: 5) as semiconductor in photocatalytic degradation of Azure B and Alizarin red, respectively. Nanoparticles of TiO_2 are used as photocatalyst in UV light induced photodegradation of malachite green⁷. Sadik⁸ studied the

effect of inorganic oxidant in photodecolourization an azo dye acid orange-7. Other oxides⁹ like TiO_2/ZnO , MnO_2 ^{10,11} are also used as photocatalyst.

Presently, different transition metal complexes play an important role in photocatalytic degradation of different dyes. Copper hexacyanoferrate (II) is used in photocatalytic degradation of Rose Bengal¹² and Bismark brown¹³. Amidoblack-10B is also photodecoloured using copper hexacyanoferrate¹⁴ (II) and nickel hexacyanoferrate (II) as photocatalyst¹⁵. The Nickel hexacyanoferrate¹⁶ (II) is used as a semiconductor for photobleaching of benzyl alcohol. From the literature survey, it is apparent that very little attention has been paid on Zinc hexacyanoferrate (II) as semiconductor for photocatalytic bleaching of dyes.

In present study Zinc hexacyanoferrate (II) was used as a semiconductor for photocatalytic bleaching of Azure B dye. Zinc hexacyanoferrate (II) is white coloured and insoluble in water. It absorbs visible radiation. Azure B is called methylene Azure B trimethyl thionine chloride, a dye used in biological stain.

Material and Method

Azure B and Zinc hexacyanoferrate (II)

Apparatus - Spectrophotometer (Systronics - 104), Solarimeter (Surya mapi CEL Model 201) and digital pH meter (Systronics, Model 335) were used for the measurement of absorbance, light intensity and pH, respectively. Centrifuging machine (Remi, Model 1258) was used to remove SC for every measurement of OD. 200 W tungsten lamp (Philips) was used for irradiation. *Photocatalytic degradation of Azure B*-The stock solution

Table 1. A typical run [Azure B] = 1.6×10^{-5} M. Light intensity = 51.0 m W cm^{-2} ; Zinc hexacyanoferrate (II) = 0.075 gm . pH = 10^{-5}

Time (min.)	Optical density	1 + log O.D.
0	0.957	0.981
20	0.632	0.801
40	0.446	0.650
60	0.301	0.479
80	0.223	0.350
100	0.158	0.199
120	0.102	0.010

$$k = 3.03 \times 10^{-4} \text{ sec}^{-1}$$

Table 3. Effect of Azure B concentration
Zinc hexacyanoferrate (II) = 0.075 gm .
Light intensity = 51.0 m W cm^{-2} pH = 10.5

[Azure B] $\times 10^3 \text{ M}$	$k \times 10^4 (\text{Sec}^{-1})$
0.8	2.32
1.2	2.80
1.6	3.03
2.0	2.83
2.4	2.54
2.8	2.40
3.2	2.20

Table 5. Effect of light intensity

[Azure B] = $1.6 \times 10^{-5} \text{ M}$

Zinc hexacyanoferrate (II) pH = 10.5

Light intensity in m W cm^{-2}	$k \times 10^4 (\text{sec}^{-1})$
35	2.52
38	2.56
41	2.61
44	2.72
47	2.83
50	2.91
51	3.03

($1.0 \times 10^{-3} \text{ M}$) of Azure B was prepared in double distilled water (500 ml) and diluted as and when required. The desired pH of the solution was adjusted by addition previously standardised H_2SO_4 and NaOH solution and measured by digital pH meter. 0.075 g of Zinc hexacyanoferrate (II) was added to 50.0 ml for $1.6 \times 10^{-5} \text{ M}$ Azure B solution. The solution was irradiated by a 200 W tungsten lamp (Philips). The intensity of light was measured by a solarimeter. A water filter was used to

Table 2. Effect of pH [Azure B] = $1.6 \times 10^{-5} \text{ M}$
Zinc hexacyanoferrate (II) = 0.075 g
Light intensity = 51.0 m W cm^{-2}

pH	$k \times 10^4 (\text{sec}^{-1})$
9.5	2.16
10.0	2.45
10.5	3.03
11.0	2.49
11.5	2.17
12.0	1.73
12.5	1.44
13.0	1.20

Table 4. Effect of amount of semiconductor
[Azure B] = $1.6 \times 10^{-5} \text{ M}$
Light intensity = 51.0 m W cm^{-2} pH = 10.5

Amount of Zinc hexacyanoferrate (II) (g)	$k \times 10^4 (\text{Sec}^{-1})$
0.025	1.91
0.050	2.62
0.075	3.03
0.100	3.03
0.125	3.02
0.150	3.01
0.175	3.01

remove thermal degradation. The optical density of solution was recorded at regular time interval by using Spectrophotometer. Before measuring OD, Zinc hexacyanoferrate (II) was removed with the help of centrifuging machine.

Results and Discussion

Photocatalytic degradation of Azure B was observed at $\lambda_{\text{max}} = 640 \text{ nm}$. A graph plotted between exposure time and 1+ log OD, was obtained as a straight line, which indicated that photocatalytic degradation of Azure B follow pseudo first order kinetics. The rate constant k for the reaction was determined by using the expression-

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

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

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 from 9.5 to 13. The results are presented in the Table 2 and graphically presented in Fig. 2.

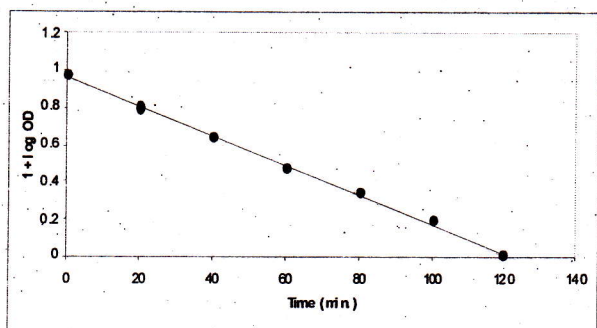


Fig.1. A typical run

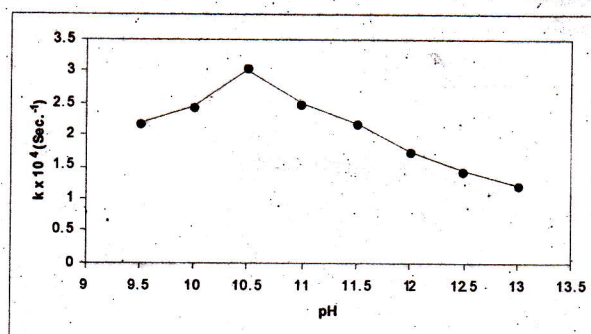


Fig.2. Effect of pH

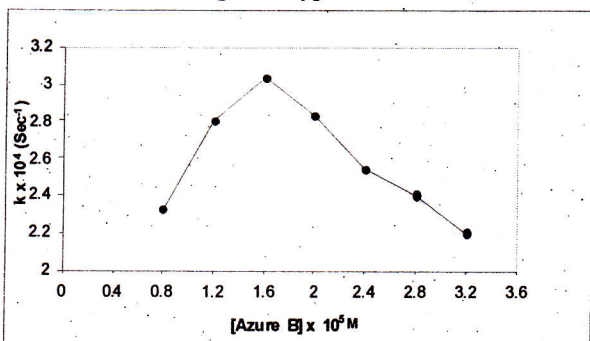


Fig.3. Effect dye concentration

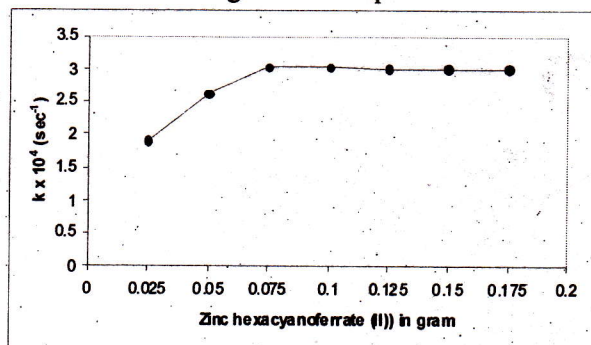


Fig.4. Effect of amount of semiconductor

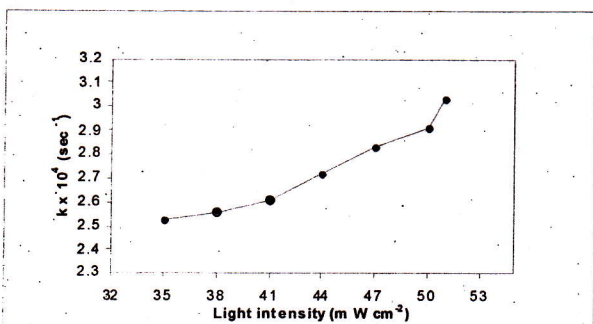


Fig.5. Effect of light intensity

It was observed that the photocatalytic degradation of Azure B increased with the increase in pH up to 10.5. It was due to availability of more OH⁻ ions at higher pH values. These OH⁻ ions combine with the hole to form [•]OH radicals, thus more OH⁻ will generate more [•]OH radicals. These hydroxyl free radicals are responsible for this photocatalytic degradation. On increasing the pH, above 10.5, the 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 in the decreased rate of photocatalytic degradation of Azure B.

Effect of Azure B concentration-The effect of different concentrations of Azure B on the rate of reaction was observed and the results are reported in Table 3 and graphically presented in Fig. 3.

It was observed that the rate of photocatalytic degradation increased with an increase in the concentration of dye up to 1.6×10^{-5} M. Further increase in concentration of dye resulted in the reduced rate of photocatalytic degradation. It might be explained on the basis of the fact that as the concentration of Azure B was increased, more dye molecules would be available for excitation and for consecutive energy transfer, hence increase in the rate of photocatalytic degradation was observed. But when the concentration of Azure B was increased above 1.6×10^{-5} M, the dye itself would have started acting as a filter for incident light. It did not permit the desired light intensity to reach the semiconductor surface. Thus, decrease in the rate of photocatalytic degradation of Azure B was observed.

Effect of amount of semiconductor-The effect of amount of Zinc hexacyanoferrate (II) powder on the rate of photocatalytic degradation of Azure B was observed. The results are reported in Table 4 and graphically

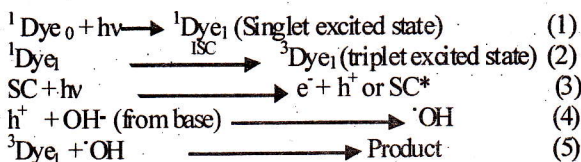
presented in Fig.4.

It was observed that rate of photocatalytic degradation of dye increased with the increase in amount of Zinc hexacyanoferrate (II) up to 0.075 gm, but beyond that, the rate of reaction became virtually constant (Table 4). This can be explained on the basis of the fact that, as the amount of semiconductor was increased the exposed surface area of SC would also be increased, thus an increase in the rate of reaction was observed. But, after a certain limiting amount of SC (0.075g), if the amount of SC was further increased, it did not contribute to an increase in the exposed surface area. This will also be confirmed by using reaction vessels of different dimensions. Thus, after certain amount of SC, the saturation point was achieved.

Effect of intensity-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 in Fig.5.

As indicated from the data, it was observed that rate of photocatalytic degradation of Azure B increased on increasing the intensity of light from 35 m W cm⁻² to 51 m W cm⁻². As the light intensity was increased, the number of photon striking per unit area of SC were also increased. Thus, increase in the rate of photocatalytic reaction and a linear behaviour between light intensity and rate of reaction was observed.

Mechanism-On the basis of experimental observation, a tentative mechanism has been proposed for degradation of Azure B by Zinc hexacyanoferrate (II).



When the solution of dye was exposed to light in presence of semiconductor; 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 leaving behind a hole. This hole abstracts an electron form OH⁻ ions generating $\cdot\text{OH}$ free radical. The dye is bleached by this $\cdot\text{OH}$ radical.

The photodegradation of Azure B in aqueous solution was observed by using manganese dioxide, bismuth oxide, coprecipitation of NiS-ZnS (1:5) and CoS-

ZnS (1:2) in earlier report⁶. The rate of degradation of Azure B by using these semiconductors was very slow while the reaction rate of degradation of Azure B was found very high ($k = 3.03 \times 10^{-4} \text{ sec}^{-1}$) by using Zinc hexacyanoferrate (II). After irradiation for 2 hours, 89.34% of Azure B dye was degraded with addition of 0.075g/50ml Zinc hexacyanoferrate (II) to solution containing $1.6 \times 10^{-5} \text{ M}$ of Azure B

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

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References

1. Robert D, Dongui B and Weber J V 2003, Ta₂O₅ used as photocatalytic for degradation of Eosin using solar energy. *J. Photochem. Photobiol.* 156A 195.
2. Sharma D, Bansal A, Ameta R and Sharma H S 2011, Photocatalytic degradation of Azure B using Bismuth oxide semiconductor powder. *Int. J. Chem. Tech. Research* 3 1008-1014.
3. Mills A and Williams G 1987, Methyl orange as a probe of the semiconductor - Electrolyte Interface in CdS Suspension. *J. Chem. Soc. Faraday Trans 1* 83(8) 2647.
4. Vaya D, Vyas R, Ameta R and Sharma V K 2008, Use of modified ZnS in presence of Eosin-Y. *J. Ind. Chem. Soc.* 85 1266.
5. Sharma V, Gandhi N, Khant A and Khandelwal R C 2010, Enhanced photodegradation of Azure B by coprecipitated. *Int. J. Chem. Sci.* 8(3) 1965-1972.
6. Sharma V, Gandhi N, Khant A and Khandelwal R C 2010, Role of coprecipitated NiS-ZnS in photocatalytic degradation of Alizarin red S. *Int. J. Chem. Sci.* 8(2) 961-968.
7. Chen C, Lu C S, Chung Y C and Jan J L 2007, UV light induced photodegradation of malachite green on TiO₂ nanoparticle. *J. Hazardous Materials* 141 520-528.
8. Sadik W A 2007, Effect of inorganic oxidants in photodecolourization of an Azo dye. *J. Photochem. Photobiol.* 191A 132-137.
9. Liao D C, Badour C A and Liao B Q 2008, Preparation

- of nanosized TiO₂/ZnO composite catalysis and its photocatalytic activity for degradation of methyl orange. *J. Photochem. Photobiol.* 194A 11-19.
10. Chaturvedi N, Sharma S, Sharma M and Sharma R K 2010, Decolorization of safranin O in aqueous solution employing manganese dioxide semiconductor. *J. Indus. Pollution control* 26(2) 161-164.
 11. Ameta K L, Malkani R K and Ameta S C 2010, Use of semiconducting manganese(IV) oxide particulate system as a photocatalyst: Photoassisted bleaching of some dyes. *J. Chem. Sci.* 8(3) 1658.
 12. Tak P, Ameta R, Sharma J C, Jhala Y and Panjabi P B 2009, Use of Copper hexacyanoferrate (II) as a photocatalyst for photodegradation of Rose Bengal dye. *Int. J. Chem. Sci.* 7(4) 2736.
 13. Tak P, Ameta A, Ameta R, Sharma V K and Punjabi P B 2010, Photodegradation of Bismark brown in presence of copper hexacyanoferrate (II). *J. Chem. Sci.* 8(1) 351.
 14. Sharma O P, Sharma M and Sharma M K 2012, Photocatalytic degradation of Amido black-10B using copper hexacyanoferrate (II) as semiconductor. *Int. J. Chem. Sci.* 10 (2) 956.
 15. Sharma O P, Sharma M, Upadhyay D P and Sharma M K 2012, Photocatalytic degradation of Amido black-10B using copperhexacyanoferrate (II) as semiconductor. *J. Industrial Pollu. Cont.* 28(2) 171.
 16. Ali S R, Chandra P, Latwal M, Jain S K, Bansal V K and Singh S P 2011, Synthesis of Nickel hexacyanoferrate nanoferrates and their potential as heterogeneous catalysis for the solvent free oxidation of benzyl alcohol. *Chin. Jr. Catal.* 32(12) 1-6.