Use of semi-conducting lead sulfide for degradation of azure-B: An eco-friendly process

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ABSTRACT

Different methods have been adopted for the removal and degradation of dyes from effluents of textile, dyeing and printing industries. These methods have their own merits and drawbacks. In the present investigation, Lead sulfide has been used as a photocatalyst for the degradation of azure-B. The effect of different parameters like the pH, concentration of dye, amount of semiconductor and light intensity on the rate of reaction has been investigated. The reaction follows pseudo-first order kinetics. The optimum conditions were obtained as: [azure-B] = $3.00 \cdot 10^{-6}$ M; PbS = 0.12 g; pH = 8.0, and light intensity = 37.0 $mW \cdot cm^{-2}$. The rate constant was $2.50 \cdot 10^{-3}$ sec^{-1}. A mechanism has been proposed for the degradation of azure-B involving hydroxyl radicals.

Keywords: semiconductor; azur-B; hydroxyl radical; Lead sulphide; degradation
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INTRODUCTION

The entire world is facing the problem of pollution in its different forms and water pollution is one of the major constituent. In the present time of industrialization, a number of the effluents are discharged in the resources of water without any treatment, which creates water pollution. Different textile, dyeing and printing industries also discharge the coloured water in their nearby water resources without any treatment. This coloured water is quite harmful and also, sometimes, toxic in nature. Different methods are being used for the removal of the coloured dye, but in most of them, the process of adsorption has been used.

Researchers have used different oxides and sulphides-based semiconductors as photocatalyst for destroying dyes for example Photocatalytic activity of antimony (III) sulphide in bleaching of azure-B was carried out by Ameta et al[1]. Sharma et al[2] used BiS as a photocatalyst in photocatalytic degradation of rose Bengal. Sharma and others[3] carried photocatalytic degradation of Azure B by using Bismuth oxide as a Semiconducting Powder while Narahari et al[4] studied the Photocatalytic effect on Azure and Sudan dyes using nano TiO_2 as a photocatalyst.

Photocatalytic degradation of Azure B using $Ni_2P_2O_7$ as photocatalyst was studied by Khant et al[5] where as structural, photophysical and photocatalytic properties of novel Bi_2AlVO_7 was carried out by Luan et al[6]. Sharma and others[7] studied the enhanced photodegradation of Azure-B by co-precipated NiS-ZnS(1:5). Photocatalytic degradation of Methylene Blue and Azure-B over TiO_2 in the presence of inorganic anions, was studied by Kataria et al[8] while Martinez et al[9] investigated enhanced sonochemical degradation of Azure-B by the electro Fenton process.

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Photocatalytic degradation of two commercial dyes in aqueous phase using photo catalyst TiO$_2$ was carried out by Mehra et al[10]. Zhang et al[11] carried out the Photocatalytic removal and recovery of mercury from water using TiO$_2$ modified sewage sludge carbon and Karunakaran et al[12] studied semiconductor catalysis of solar photooxidation,

Gogna et al[13]observed the Biodegradation of rose bengal by Phanerochaete chrysosporium while Photoreduction of Congo red by ascorbic acid and EDTA over cadmium sulphide as photocatalyst was carried out by Kothari et al[14]. Kinetic monitoring of photocatalytic activity of bismuth sulphide for degradation of Malachite green was carried out by Sharma and others[15] where as cadmium sulfide photocatalysed reduction of Malachite green by ascorbic acid and EDTA as reductants was studied by Kothari et al[16] . Photo catalytic degradation of two commercial dyes in aqueous phase using photo catalyst TiO2 was studied by Meeti Mehra & and T. R. Sharma [17], Gandhi et al[18] carried out a comparative study Photocatalytic bleaching of malachite green and brilliant green dyes using ZnS-CdS as semiconductor:.Vinod S. Shrivastava [19] studied the removal of Indigo Caramine dye by using nanosized Semiconducting Photocatalyst in aqueous media , Heterogeneous photocatalytic treatment of textile dye effluent containing Azo Dye: Direct Crysophenine G.was carried out by Preeti Mehta et al[20].

After carrying out a rigorous literature survey, it was found that fewer work if carried out with lead sulphide as a photocatalyst. Thus in the present work a kinetic and mechanistic study of the degradation of azure-B using lead sulfide as a photocatalyst was carried out.

MATERIALS AND METHODS

0.0306 g of Azure-B was dissolved in 100 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. The optical density of this dye solution was determined with the help of a spectrophotometer (Systronics Model 106) at λmax = 650 nm.

[Structure of Azure-B]
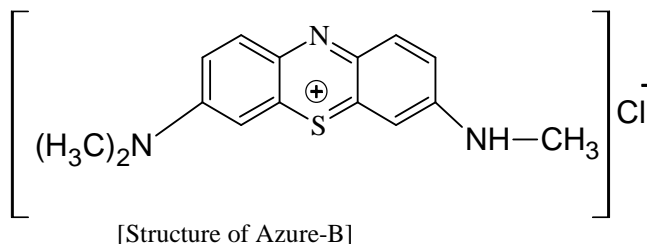
RESULTS AND DISCUSSION

3.1 KINETIC STUDY

A solution of 3.0×10^{-6} M of Azure-B was prepared in doubly distilled water and 0.12g of PbS was added to it .The pH of the reaction mixture was adjust to 8.0 and then the solution was exposed to a 200 W tungsten lamp. An aliquot of 2.0 ml was taken out from the reaction mixture and it optical density was observed at 650 nm at regular time intervals.

It was observed that the concentration of azure-B decreases with increasing time of exposure. A plot of 1 + log O.D. against time was found to be linear. The rate constant was measured with the expression

$$K = 2.303 \text{ x slope}$$

A typical run has been tabulated in table-1 and graphically presented in Figure A.1.

It was observed that the optical density of azure-B solution in presence of semiconductor was much low as compared to sample without semiconductor at the same intervals. It means that the rate of this photocatalytic degradation is favorably affected by a semiconductor in the case of azure-B. The plot of 1+ logO.D. v/s time was linear and hence, this reaction follows pseudo first order kinetics.
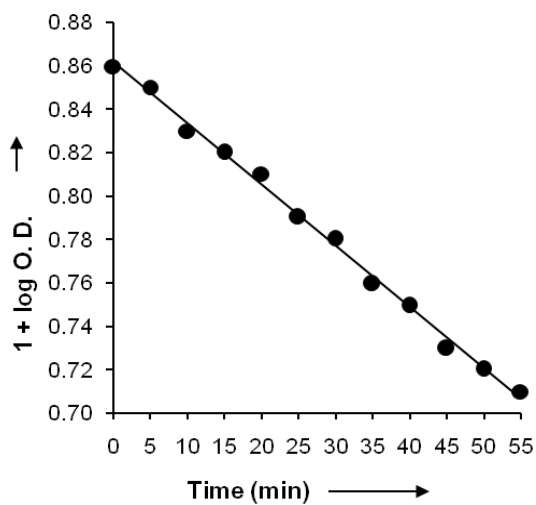
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Fig. A.1 A TYPICAL RUN

TABLE-1
A Typical Run

[Azure-B] = 3.0 × 10⁻⁶ M, pH = 8.0,
Light intensity = 37.0 mWcm⁻², Lead sulphide = 0.12 g

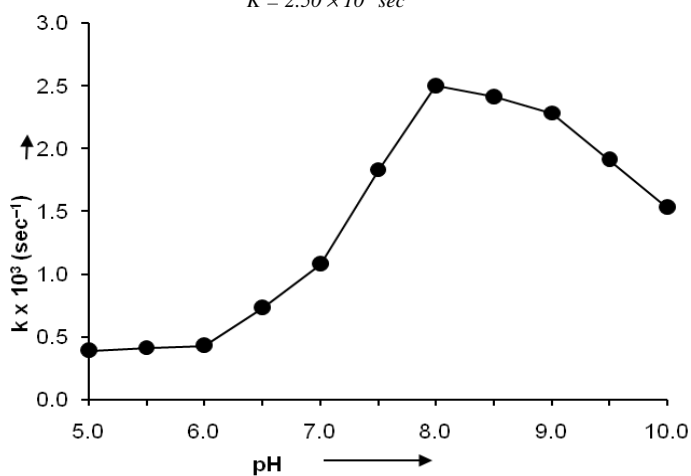| Time (min.)	Optical density (O.D.)	1 + log O.D.
0.0	0.724	0.8597
5.0	0.708	0.8500
10.0	0.676	0.8299
15.0	0.661	0.8202
20.0	0.646	0.8102
25.0	0.617	0.7903
30.0	0.603	0.7803
35.0	0.575	0.7597
40.0	0.562	0.7497
45.0	0.537	0.7298
50.0	0.525	0.7202
55.0	0.513	0.7101

K = 2.50 × 10⁻³ sec⁻¹

Fig. A.2 EFFECT OF pH
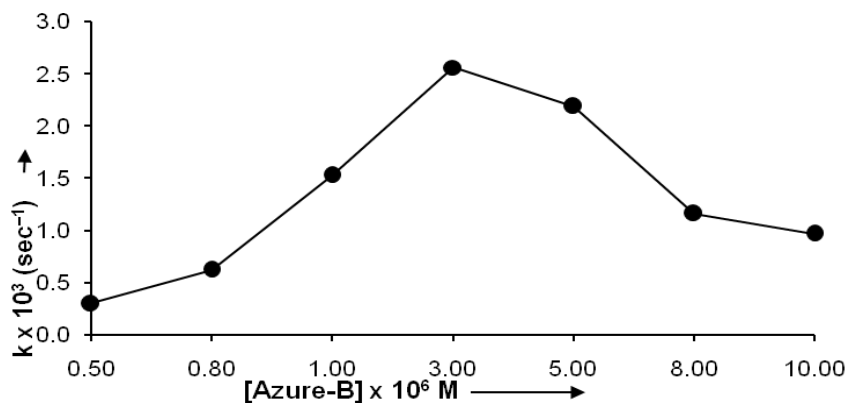
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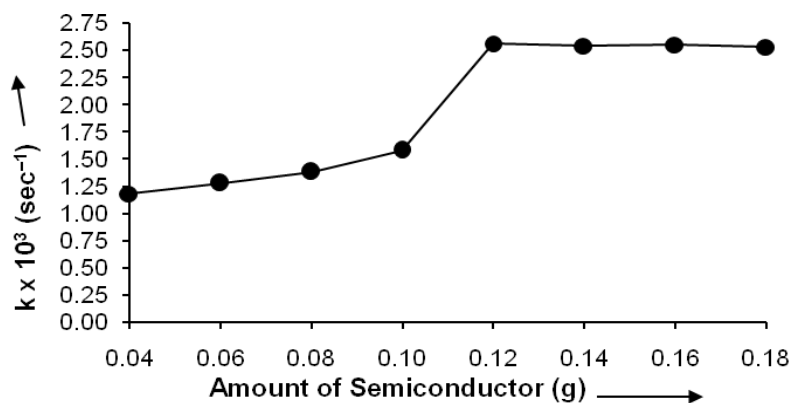**Fig. A.3 EFFECT OF DYE CONCENTRATION**

**Fig. A.4 EFFECT OF AMOUNT OF
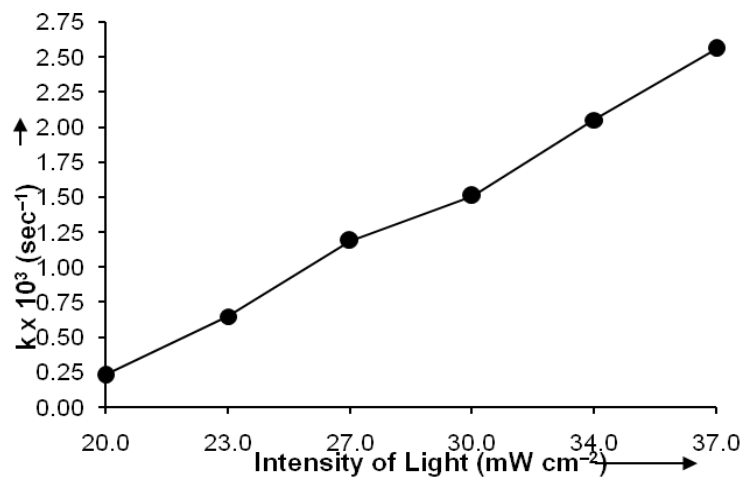SEMICONDUCTOR**

Fig. A.5 EFFECT OF LIGHT INTENSITY

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3.2 EFFECT OF pH
The pH of the solution is likely to affect the bleaching of the dye. The effect of pH on the rate of bleaching of dye solution was investigated in the pH range (5.0 – 10.0). The results are graphically presented in Figure A.2.

The optimum rate of photocatalytic bleaching of azure B was observed at pH = 8.0. Below and above this pH, the rate of reaction was found to decrease. This behavior may be explained on the basis that at low pH (pH < 8.0), the surface of semiconductor is positively charged and therefore, due to coulombic repulsion between the surface of semiconductor and the cationic dye, decrease in the rate of the reaction is observed. Whereas at higher pH (pH > 8.0), the surface of the semiconductor become negatively charged and dye molecules become neutral causing almost no attraction between the negative surface and neutral dye molecules. This will also result into a decrease in the rate of reaction.

3.3 EFFECT OF CONCENTRATION OF DYE
Effect of variation of dye concentration was also studied by taking different concentration of azure-B. The results are graphically presented in Figure A.3. It has been observed that the rate of photocatalytic bleaching increases with an increase in the concentration of the dye ($3*10^{-6}$ M). It may be due to the fact that as the concentration of azure-B was increased, more dye molecules were available for excitation and energy transfer and hence, an increase in the rate was observed. The rate of photocatalytic bleaching was found to decrease with further increase in the concentration of the dye. This may be attributed to the fact that the dye will start acting as a filter for the incident light and it will not permit the desired photons to reach the semiconductor particle; thus, decreasing the rate of photocatalytic bleaching of azure-B.

3.4 EFFECT OF AMOUNT OF SEMICONDUCTOR
The amount of semiconductor is also likely to affect the bleaching of azure-B dye. Different amount of photocatalyst were used and the results are reported graphically in Figure A.4. It has been observed that the rate of photo-bleaching of azure-B increases with an increase in the amount of semiconductor but ultimately, it becomes almost constant after a certain amount (0.12g). This may be due to the fact that as the amount of semiconductor was increased, the exposed surface area also increases, but after a certain limit, if the amount of semiconductor was further increased, then there is no increase in the exposed surface area of the photocatalyst. It may be considered like a saturation point; above which, any increase in the amount of semiconductor will have negligible effect on the rate of photocatalytic bleaching of azure-B. Further increase in the amount of semiconductor will only increase the thickness of the layer at the bottom of the vessel, once the bottom of the reaction vessel is completely covered by the photocatalyst.
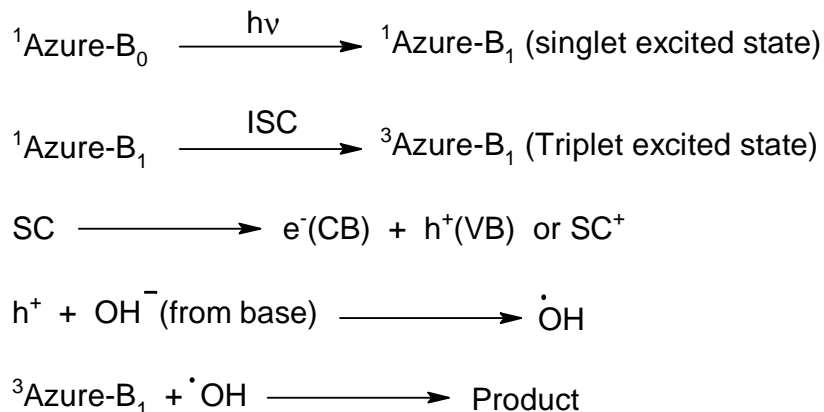
It was also confirmed by taking reaction vessels of different dimensions. The point of saturation was shifted to higher value when vessels of larger capacities were used. A reverse trend was observed when vessels of smaller capacities were used.

3.5 EFFECT OF INTENSITY OF LIGHT
To observe the effect of intensity of light on the photocatalytic bleaching of azure-B, light sources of different intensities can be used or the distance between light source and the bottom of vessels may be varied. The intensity of light at each distance was measured by Suryamapi (CEL model SM 201). The results obtained are graphically presented in Fig. A.5. The result given indicates that the bleaching action was accelerated as the intensity of light was increased, because any increase in the light intensity will increase the number of photons striking per unit area of semiconductor powder. A linear behavior between light intensity and rate of reaction was observed.

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CONCLUSION

On the basis of above studies a tentative mechanism is proposed for the photo catalytic degradation of Azure-B as :-

$$^1\text{Azure-B}_0 \xrightarrow{\ h\nu\ } {}^1\text{Azure-B}_1 \text{ (singlet excited state)}$$

$$^1\text{Azure-B}_1 \xrightarrow{\ \text{ISC}\ } {}^3\text{Azure-B}_1 \text{ (Triplet excited state)}$$

$$\text{SC} \longrightarrow e^-(\text{CB}) + h^+(\text{VB}) \text{ or SC}^+$$

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

$$^3\text{Azure-B}_1 + {}^{\bullet}\text{OH} \longrightarrow \text{Product}$$

Azure-B absorbs light radiation of suitable wavelength and it goes to excited singlet state and then undergoes intersystem crossing (ISC) to give the triplet state of the dye. On the other hand, the semiconducting lead sulphide also utilizes the radiant energy to excite its electron from valence band to the conduction band, thus leaving behind a hole (h^+). The hole abstracts an electron form OH^- ions generating $^{\bullet}OH$ radical. Now the excited dye is oxidized by $^{\bullet}OH$ free radicals to give the product. It was observed that dye degrades completely and no harmful by-products are formed. The participation of $^{\bullet}OH$ radical was confirmed by the use of scavanger, where the rate of reaction was drastically reduced.

Lead sulfide can be successfully used for the photocatalytic degradation of Azure-B aqueous solution. The decolorized water can be used for some useful purposes like cleaning, cooling, irrigation etc. The photocatalysis is a promising technology for the treatment of waste water and time is not far off, when this technology will be firmly established as an advanced oxidation process. It is also an eco-friendly technique to combat the problem of colored water effluents released by different textile, printing and dye industries.

REFERENCES

[1] R. Ameta, A. Pandey, P.B. Punjabi and S.C. Ameta, *Chem. Environ. Res.,* **2005,** 14, 255.
[2] Shweta Sharma, Rakshit Ameta, R. K. Malkani and Suresh C. Ameta, *Macedonian Journal of Chemistry and Chemical Engineering*, **2011** ,30, 229.
[3] Deependra Sharma, A. Bansal, R. Ameta and H. S. Sharma, *Journal of Chem. Tech. research*, **2011**,3, 1008.
[4}T.Arthi, Prashanthi Narahari and Gridhar Madras, *Journal of hazardous materials*, **2007**,149,725.
[5] Ankur Khant, Neelam Gandhi, Vijaya Sharma and R C Khandelwal, *Bulletin of the catalysis society of india*, **2010**, 9, 51.
[6] Jingfei Luan, Wei Zhao, Jingwei Feng, Hongling Cai, Zheng Zheng, Bingcai Pan, Xiaoshan Wu and Zhingang Zou, *Materials*,**2009**,164,781.
[7] Vijay Sharma ,Neelam Gandhi, Ankur Khant and R C Khandelwal, *International Journal of chemical science*, **2010**,8,1965.
[8]Paridhi b Kataria, Abhilasha Jain, Rakshit Ameta, V K Singh and P B Panjabi, *international journal of pure and applied chemistry,***2008**,2 ,10.
[9] Susana Silva Martinez, Edgar Velasco Urib, *Ultrasonic sonochemistry*, **2012**, 19,174.
[10] Meeti Mehra and T R Sharma , *Advances in Applied Science Research* (Pelagia Research Library), **2012**, 3, 849.
[11] *F.S.* Zhang, J. Nriagm and H. Itoh, *J. Photochem. Photobiol*., **2004**, 167A,223.
[12] C. Karunakaran and S. Senthilvelan, *Curr. Sci.* , **2005,** 18, 962.
[13] E. Gogna, R. Vohra and P. Sharma, *Lett. Appl. Microbiol*., **2008** ,14,58.
[14] S. Kothari, R. Vyas, R. Ameta and P. B. Punjabi, *Indian J. Chem.,* **2005,** 44A, 2266.

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[15]Deependra Kumar Sharma, Ashish Bansal, Rakshit Ameta and H. S. Sharma , *Der Chemica Sinica*, **2012**, 3, 1163..

[16] Shilpa Kothari, Anil Kumar, Ritu Vyas, Rakshit Ameta and Pinki B. Punjabi, *J. Braz. Chem. Soc*., **2009,** 20, 10.

[17] Meeti Mehra & and T. R. Sharma*, Adv. Appl. Sci. Res*., **2012**, 3, 849.

[18] Jayant Gandhi, Rajesh Dangi, Jagdish Chandra Sharma, Nikhil Verma and Shipra Bhardwaj *Der Chemica Sinica,* **2010**, 1 ,77.

[19] Vinod S. Shrivastava *Adv. Appl. Sci. Res*., **2011**, 2, 280.

[20] Preeti Mehta,Menka Surana, Rajeev Mehta and B.V. Kabra G, *Der Chemica Sinica*, **2011**, 2 ,37.