

ICGSEE-2013[14th – 16th March 2013]
International Conference on Global Scenario in Environment and Energy

Photodegradation Of Azure B With The Help Of Bismuth Oxide And Bismuth Sulphide Used As Photocatalytic: A Comparative Study

Deependra Kumar Sharma¹, Ashish Bansal², Rakshit Ameta³
and H. S. Sharma*

¹Department of Chemistry, Govt. College Kota (Raj.)

²DCM Shriram Consolidated Ltd., Kota

³ Department of Chemistry, Pacific College of Basic & Applied Sciences,
PAHER University, Udaipur

*Department of Chemistry, Govt. College, Bundi (Raj.) India

Corres.author: deependarsharma0@gmail.com

Abstract: Bi₂O₃ and Bi₂S₃ catalyzed photocatalytic degradation of azure B dye have been investigated. The effect of various parameters, such as the pH, concentration of dyes, effect of amount of semiconductor and effect of light intensity etc. were observed and discussed. The progress of the photochemical oxidation was monitored spectrophotometrically. The optimum reaction conditions were experimentally determined. The photochemical oxidation of dyes follows pseudo – first kinetics. The final products of degradation were characterized and a tentative mechanism was proposed for the photochemical oxidation of dyes.

Key words: Bismuth oxide, Bismuth Sulphide, Azure B, Photocatalysts.

Introduction

There are many methods for eliminating water pollutants like thermal dehydration, adsorption by charcoal *etc.* One of the most economical and ecofriendly methods is, however, the use of photocatalytic reactions. Following is a literature survey on the use of photocatalytic reactions in elimination of water pollutants. As we stepped into the twenty-first century, we are facing the challenge of purification of water and air resources. On one hand, we are enjoying the comforts and benefits that chemistry has provided to us, e.g. from drugs to

dyes, from composites to computer chips, etc. On the other hand, we are facing with the problem of proper disposal of various products and byproducts of dye industries. In spite of many uses, the dyes are toxic and carcinogenic in nature and environmental contamination by these toxic chemicals is emerging as a serious global problem. Colored solution 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 and almost harmless. Secondly, dye containing coloured water 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 purpose. The photocatalytic bleaching seems to be quite promising and can provide a low cost method to solve this problem.

The field of photocatalysis has been excellently reviewed by Ameta *et al.*^{1,2}. Photocatalytic degradation of cetylpyridinium chloride over TiO₂ has been reported by Singhal *et al.*³. Similar photocatalytic reaction of xylydine ponceau and orange-G dyes by ZnO powder has been reported by Sharma *et al.*⁴. Yoneyama *et al.*⁵ studied the photocatalytic reduction of dichromate ions using WO₃ powder in acidic range. Costa *et al.*⁶ proposed the mechanism of gas phase degradation of cyclohexanol and methylcyclohexanol catalyzed by niobium pentoxide and phosphite. Shyama and Arakawa⁷ have used zirconium dioxide as photocatalyst. A composite system of polycrystalline ZnO/TiO₂ and its photocatalytic activity was studied by Marci *et al.*⁸. TiO₂ sol-gel deposited over glass and its application as an effect of TiO₂ acidic pretreatment on the photocatalytic phenol degradation was reported by Colon *et al.*⁹ whereas photodegradation of lignin from black liquor using a UV/TiO₂ system was investigated by Ksibi *et al.*¹⁰. The Photodegradation of Azure B with the help of bismuth oxide and bismuth sulphide used as photocatalytic: A comparative study in the present investigation.

Experimental Procedure

Cationic dyes (Azure B) and semi conducting bismuth oxide or bismuth sulphide powders were used in the present investigation. All the solutions were prepared in doubly distilled water. The photocatalytic degradation of the dyes was observed by taking dye solution and bismuth oxide or bismuth sulphide together. Irradiation was carried out by keeping the whole assembly exposed to a 200W Tungsten lamp (Philips; light intensity = 50.0 mW cm⁻² and 60.0 mW cm⁻² respectively). The intensity of light at various distances from the lamp was measured with the help of a solarimeter. A water filter was used to cut out thermal radiations. The pH of the solutions was measured with the help of digital pH-meter.

0.3058 g of azure 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 stock solution was further diluted as and when required. The absorbance of these dye solutions were determined with the help of a spectrophotometer at $\lambda_{\max} = 650$ nm for azure B. The solutions of the dyes were divided into four parts; the first beaker containing only dye solution was

kept in dark; the second beaker containing only dye solution was kept in light; in the third beaker dye solution and 0.10 g and 0.12 g of semiconductor bismuth oxide and bismuth sulphide respectively was kept in dark and in the fourth beaker dye solution with 0.10 g and 0.12 g of semiconductor bismuth oxide and bismuth sulphide respectively was exposed to light.

These beakers were kept for 4 hours and then the absorbance of solution in each beaker was measured. It was observed that the solutions in the first three beakers had the almost same initial absorbance while the solution in the fourth beaker had a decrease in its initial value of absorbance. Thus, by performing blank experiment it was confirmed that the reaction between azure B and semiconductor powder is neither thermal nor photochemical but it is a photocatalytic reaction. The progress of the reaction was monitored spectrophotometrically by taking absorbance of the reaction mixture at different time interval. From these results, it is clear that reaction requires both light and semiconductor to degrade dye, hence showing the photocatalytic nature of the reaction.

Results And Discussion

Photocatalytic degradation of azure b observed at $\lambda_{\max} = 650$ nm. Degradation of the dyes in absence of semiconductor (Bi₂O₃ or Bi₂S₃) is negligible. Thus, photocatalytic degradation is favorably affected by semiconductor. A plot of optical density ($2 + \log OD$) versus time is linear and hence, the reactions follow pseudo first-order kinetics (Table 1 and Figure 1). The rate constants are determined with the help of the curves.

Effect Of pH

The pH of the solution is likely to affect the bleaching of the azure b. The effect of pH on the rate of bleaching of azure b was investigated in the pH range 7.00-10.0. The results are reported in Table 2 and Figure 2. It is evident from the observed data that the rate of photocatalytic degradation of azure b are optimum at pH 9.50 and 9.00 respectively and after that the rate constant decreases on further increasing the pH of the solutions. The increase in the rate of photocatalytic bleaching with increase in pH may be due to more generations of $\cdot OH$ radicals, which are produced from the interaction of OH⁻ and hole (h⁺) of the semiconductor. These $\cdot OH$ oxidize the dye molecules in their leuco forms, which ultimately degrade in the non-hazardous products. But after pH 9.50 and 9.00 for azure b, the dye molecules becomes neutral and feel less attraction to $\cdot OH$ and hence the rate of the reaction decreases on further increasing pH of the solutions.

Table 1 A Typical Run

Time (min.)	Bismuth oxide	Bismuth sulphide
	2 + log O. D.	2 + log O. D.
0	1.7202	1.7619
20	1.6304	1.7076
40	1.5441	1.6609
60	1.4713	1.6201
80	1.3787	1.5809
100	1.2923	1.5403
120	1.1761	1.5011
140	1.1303	1.4624
160	1.0414	1.4150
180	0.9590	1.3711
200	0.8828	1.3304
220	0.8062	1.2878
240	0.7160	1.2480
260	-	1.2041
280	-	1.1614
300	-	1.1206
320	-	1.0755
340	-	1.0334
360	-	0.9868

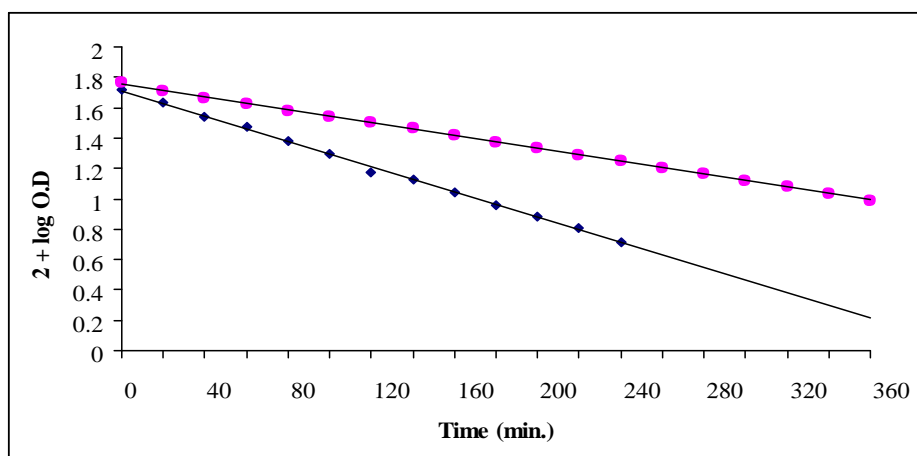


Figure: - 1. A Typical Run (♦ - [Azure B] = 1.8×10^{-5} M, Bi_2O_3 = 0.10g, pH = 9.5, Light Intensity = 50.0 mW cm^{-2} , $k = 1.62 \times 10^{-4} \text{ sec}^{-1}$ and • [Azure B] = 2.0×10^{-5} M, Bi_2S_3 = 0.12g, Light Intensity = 60.0 mW cm^{-2} , pH = 9.00, $k = 8.62 \times 10^{-5} \text{ sec}^{-1}$)

Table 2 Effect OF pH

pH	Bismuth oxide	Bismuth sulphide
	$k \times 10^5 (\text{sec}^{-1})$	$k \times 10^5 (\text{sec}^{-1})$
7.00	4.16	2.55
7.25	4.46	2.74
7.50	5.11	3.19
7.75	7.67	3.83
8.00	8.63	4.51
8.25	9.59	5.48
8.50	10.83	6.39
8.75	11.23	7.67
9.00	13.20	8.62
9.25	15.83	8.46
9.50	16.16	8.44
9.75	16.00	8.22
10.00	15.70	7.94

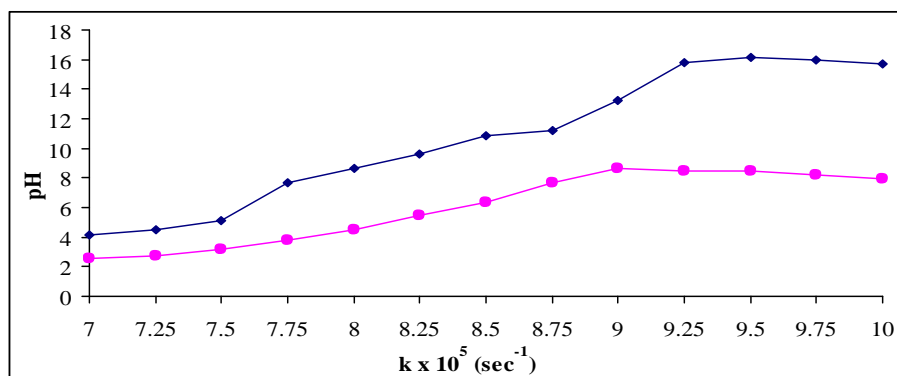


Figure- 2. Effect of pH (♦ - [Azure B] = 1.8×10^{-5} M, Bi_2O_3 = 0.10g, Light Intensity = 50.0 mW cm^{-2} and • [Azure B] = 2.0×10^{-5} M, Bi_2S_3 = 0.12g, Light Intensity = 60.0 mW cm^{-2})

Effect Of Dye Concentration

Effect of concentration of azure b was studied by taking different concentrations of this dye. The results are tabulated in Table 3 and Figure 3. It was observed that the rate of photocatalytic bleaching increases with an increase in the concentration of the dyes.

It may be due to the fact that as the concentration of dye increases more dye molecules are available for excitation and energy transfer and hence, an increase in the rate of photocatalytic degradation of the dyes were observed. The rate of photocatalytic degradation was found to decrease with further increase in the concentration of the dyes i.e. above 1.8×10^{-5} M and 2.0×10^{-5} M for azure b. This may be attributed to the fact that after certain concentration, the dye itself will start acting as a filter for the incident light and it will not permit the desired light intensity to reach the semiconductor particles; thus, decreasing the rate of photocatalytic degradation of dye.

Effect Of Amount Of Semiconductor

The amount of semiconductor is also likely to affect the rate of photocatalytic bleaching of azure b hence; different amounts of photocatalyst were used. The results are reported in Table 4 and Figure

4. It was observed that the rate of photocatalytic degradation of azure b increases with an increase in the amount of semiconductor but ultimately, it became almost constant after a certain amount i.e. 0.10 g a for bismuth oxide and 0.12 g of bismuth sulphide.

This may be attributed to the fact that as the amount of semiconductor was increased, the exposed surface area increased, which absorb more number of photons and as a result the rate of photocatalytic degradation of the dyes increased, but after a certain limit, if the amount of semiconductor was further increased, then there will be 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 has negligible or no effect on the rate of photocatalytic degradation of the dyes, as any increase in the amount of semiconductor after this saturation point will only increase the thickness of the layer at the bottom of the reaction vessel. This was confirmed by taking reaction vessels of different dimensions. The saturation point shifts to higher range for larger vessels, while reverse was true for smaller vessels.

Table 3 Effect Of Dye Concentration

[Azure B] x 10^5 M	Bismuth oxide $k \times 10^5$ (sec ⁻¹)	Bismuth sulphide $k \times 10^5$ (sec ⁻¹)
0.8	14.2	5.46
1.00	14.7	6.49
1.20	15.2	6.82
1.40	15.8	7.27
1.60	16.0	7.58
1.80	16.2	8.22
2.00	15.1	8.62
2.20	14.4	8.37
2.40	14.0	7.90
2.60	13.9	7.67

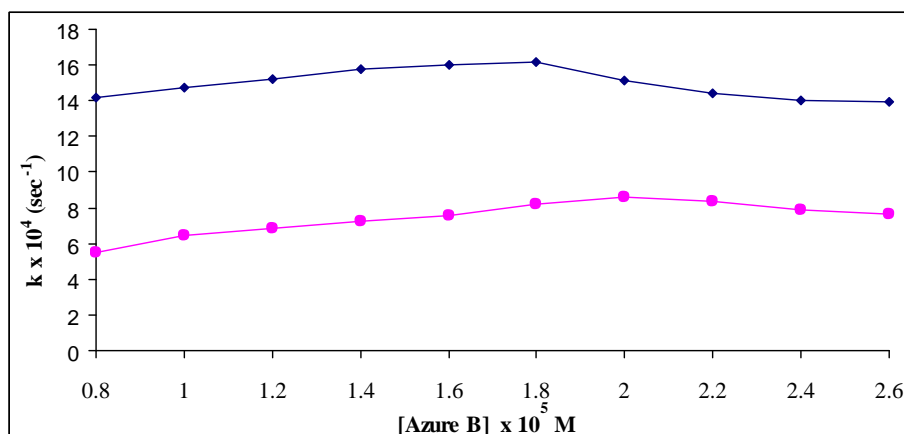


Figure: - 3. Effect of dye concentrations (♦ - Bi₂O₃ = 0.10g, pH = 9.5, Light Intensity = 50.0 mW cm⁻² and • Bi₂S₃ = 0.12g, Light Intensity = 60.0 mWcm⁻², pH = 9.00)

Table 4 Effect Of Amount Of Semiconductor

Semiconductor amount (g)	Bismuth oxide k x 10 ⁵ (sec ⁻¹)	Bismuth sulphide k x 10 ⁵ (sec ⁻¹)
0.02	10.5	4.72
0.04	10.8	5.11
0.06	13.8	5.28
0.08	15.2	6.39
0.10	16.2	7.19
0.12	16.0	8.62
0.14	15.8	8.52

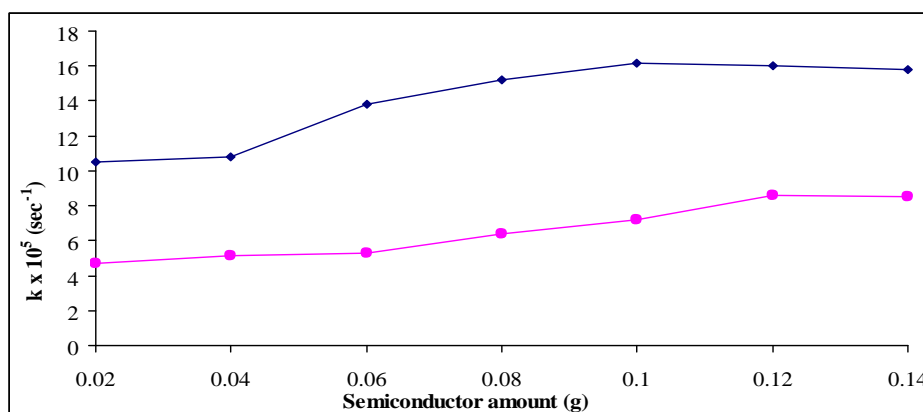


Figure: - 4. Effect of amount of semiconductor (♦ - [Azure B] = 1.8 x 10⁻⁵ M, pH = 9.5, Light Intensity = 50.0 mW cm⁻², and • [Azure B] = 2.0 x 10⁻⁵ M, Light Intensity = 60.0 mWcm⁻², pH = 9.00)

Effect Of Light Intensity

To observe the effect of intensity of light on the photocatalytic degradation of the dyes, the light intensity was varied. The results obtained are reported in Table 5 and Figure 5.

The data indicate that an increase in the light intensity increases the rate of reaction and the optimum values were found at 50 mW cm⁻² for

bismuth oxide and 60 mW cm⁻² for bismuth sulphide semiconductors. 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 of degradation. Further increase in the intensity beyond the maximum limits result in decrease in the rate of reaction. It may be probably due to thermal side reactions.

Table 5. Effect Of Light Intensity

Intensity of Light (mWcm^{-2})	Bismuth oxide	Bismuth sulphide
	$k \times 10^5 (\text{sec}^{-1})$	$k \times 10^5 (\text{sec}^{-1})$
10.0	9.44	5.32
20.0	10.86	5.96
30.0	15.15	6.72
40.0	16.05	7.42
50.0	16.16	7.99
60.0		8.62

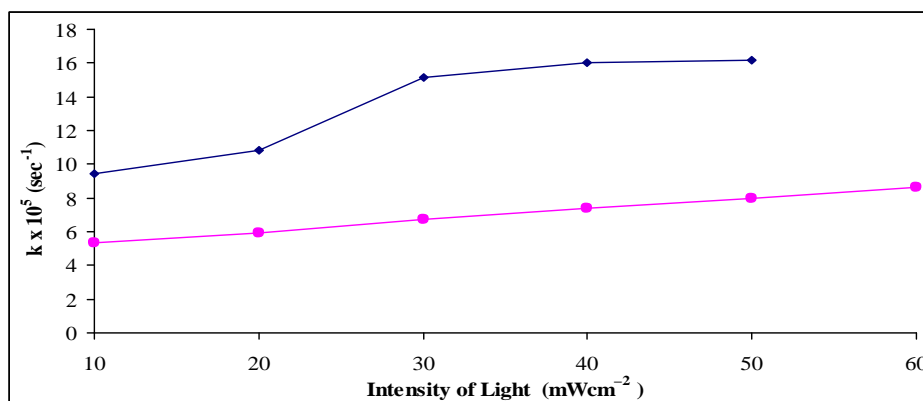
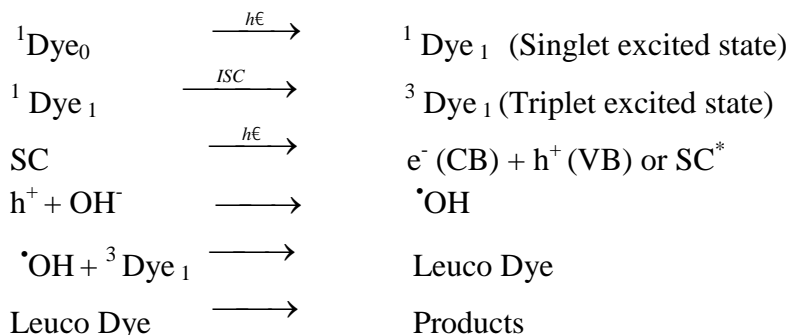


Figure: - 5. Effect of light intensity (\blacklozenge - [Azure B] = 1.8×10^{-5} M, Bi_2O_3 = 0.10g, pH = 9.5, and \bullet [Azure B] = 2.0×10^{-5} M, Bi_2S_3 = 0.12g pH = 9.00)

Mechanism:-



Azure B absorbs radiations of suitable wavelength and gives rise to its excited singlet state. Then it undergoes intersystem crossing (ISC) to give the triplet state of the dyes. The involvement of triplet state was confirmed by using triplet state scavengers, where the reaction rate was almost negligible. On the other hand, the semi-conducting bismuth oxide (SC) also utilizes the radiant energy to excite its electron from valence band to the

conduction band; thus, leaving behind a hole. This hole abstracts an electron from OH^- ions to generate $\cdot\text{OH}$ radicals. These radicals will oxidize the dye to its leuco form, which may ultimately degrade to products. The participation of $\cdot\text{OH}$ radicals as an active oxidizing species was confirmed by using hydroxyl radical scavenger isopropanol, where the rate of bleaching was drastically reduced.

References

1. Sahasi S, Jain N K, Dak M, Bala M, Ameta S C, *Asian J Chem Rev*, 1991, 2, 90 .
2. Ali Z, Ameta R, Vardia J, Ameta R, Ameta S C, *J India Chem Soc*, 1999, 78, 281.
3. Singhal B, Porwal A, Sharma A, Ameta R, Ameta S C, . *Photochem Photobiol A*, 1997, 108, 85.
4. Sharma A, Rao P, Mathur R P, Ameta S C, *J Photchem Photobiol A*, 1995, 86, 197.
5. Yoneyama H, Yamashita Y, Tamura H, *Nature*, 1979, 282, 817.
6. Costa M C C, Hodson L F, Johnstone R A W, Liu J Y, *J Mol Catl A*, 1999, 142, 349.
7. Sayama K, Arakawa H, *J Phys Chem*, 1993, 97, 531.
8. Marci G, Augughiaro V, Tilley R J D, Lopez M J- Munoz, Martin C, Palmisano I L, Rives V, Schiavello M S, *J Phys Chem B*, 2001, 105, 1026 .
9. Colon G, Sanchez J M-Espana, Hidalgo M C, Navio J A, *J Photochem Photobiol A*, 2006, 179, 20 .
10. Ksibi M, Ben S-Amor, Cherif S, Elaouim E, Houas A, Elaloui M, *J Photochem Photobiol A*, 2003, 154, 211.
11. Alex S, Santosh U, Das D, *J Photochem Photobiol A*, 2005, 172, 63.
