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Photocatalytic degradation of Azure B using Bismuth oxide Semiconducting Powder

Deependra Sharma[1], A. Bansal[2], R. Ameta[3] and H. S. Sharma*

Department of Chemistry, Govt. College, Bundi (Raj.) India.
Email: deependarsharma0@gmail.com

[1]Department of Chemistry, Savita Devi Jaiswal Memorial College , Shamgarh – 458883(MP),India.

[2]CC Plant, DCM, Kota (Raj.) India.

[3]Department of Pure and Applied Chemistry, University of Kota,Kota -324005 (Raj.)India.
Email: rakshit_ameta@yahoo.in

Abstract: Photo catalysis has been predicted as a promising technology for waste water treatment. Bismuth oxide has been used as effective photo catalysts for carrying out number of chemical reactions. The photo catalytic bleaching of azure - B was carried out in the presence of semi conducting Bismuth oxide and the progress of the reaction was observed spectrophotometrically. The effects of various operating variables like pH, concentration of dyes, amount of semiconductor and light intensity on the rate of bleaching was observed. A tentative mechanism has been proposed for the photo catalytic bleaching of dyes.
Key words: - Photocatalytic degradation, Bismuth oxide, Azure – B.

Introduction

Water is basic requirement in all industrial processes, domestic and commercial activities, Industrial textile dyes are present in wastewaters at different concentrations, so the wastewater generated from these various processes contains various contaminants depending upon process, mainly pharmaceutical, textile, acrylic Fiber, pesticides and other organic chemicals manufacturing industries etc. generate waste water containing phenolic compounds and various dyes. These effluents are intensely colored and are contaminated with high concentration of organic compounds such as suspended and dissolved salts and many other recalcitrant compounds. Even small concentration of these compounds present in effluent causes toxicity and foul odors to water. If these effluents are improperly treated, they will pose to serious threat to all species on earth because hydrolysis of the pollutants in waste water can produce a great deal of toxic products. Degradation of these non-biodegradable organic compounds is not possible by conventional biological treatment processes. Lately, there has been a lot of interest in application of the advanced oxidation processes (AOP's) for the removal of these organic compounds. Many processes such as photolysis, photo catalytic oxidation, ozonation, Fenton oxidation, wet air oxidation and membrane separation has been proposed for the degradation of these compounds even at low concentration. The photocatalytic bleaching was found to be the most promising and efficient process in controlling the environmental pollution, waste water treatment etc, in which semiconductor particles act as photocatalysts or short-circuited microelectrodes on excitation. On excitation, semiconductor generates electron-hole pair which may be used either for reduction or oxidation of the dye.

Exhaustive researches in the field of photocatalysis have shown various fascinating applications of photocatalytic reactions based on the use of semiconductors.[1, 2] the photocatalytic degradation of methylene blue, rhodamine-B and methyl orange in presence of CdS as photocatalyst has been reported.[3, 4] Photoreduction of fluorescent dye 2',7'-dichlorofluorescein was reported by Marchesi *et al.*[5] Punjabi *et al.*[6] studied the photoreduction of congo red by ascorbic acid and EDTA as reductants and cadmium sulfide as photocatalyst. Kim *et al.7* used ZnO coated TiO2 nanoparticles for the flexible dye-sensitized solar cells. Use of semiconducting iron (II) oxide in photocatalytic bleaching of some dyes (malachite green, crystal violet and methylene blue) has been reported by Ameta *et al.*[8] Photocatalytic degradation of brilliant red dye and textile waste water has been suggested by Martins *et al.*[9] photocatalytic degradation of acid blue-62 over CuO-SnO2 nanocomposite photocatalyst under simulated sunlight reported by Xia.[10]
Chen *et al.*[11] showed the activities of different metal oxide as photocatalyst on no reduction and cooxidation. The photodegradation of arylmethane and azo dyes over TiO2/In2O3 nano composite films reported Skorb *et al.*[12] Sun *et al.*[13] reported the photocatalytic activity of titanium cobalt oxides in the degradation of methyl orange. Photo induced transformation of some organophosphorous pesticides over TiO2 was investigated by Calza *et al.*[14] Reddy *et al.*[15] showed the photocatalytic activity of Bi2O3 for the treatment of phenolic wastes. Photocatalytic degradation of brilliant red dye and textile waste water has been suggested by Martins *et al.* [16]. The synthesis, characterization and photocatalytic activity of lanthanum cerium oxide (LaCeO3) catalyst was reported by Jose *et al.* [17]. Photocatalytic degradation of cetylpyridinium chloride over TiO_2 has been reported by Singhal *et al.* [18]. Photoreduction of Congo red by ascorbic acid and EDTA over cadmium sulphide as photocatalyst was carried out by Kothari et al. [19]. Photocatalytic activity of antimony (III) sulphide in bleaching of Azure-B was carried out by Ameta et al. [20].

Experimental Procedure

Cationic dye (azure - B) and semiconducting bismuth oxide powder 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 together. Irradiation was carried out by keeping the whole assembly exposed to a 200W Tungsten lamp (Philips; light intensity = 50.0 mW cm^{-2}). 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.

0.0305 g of malachite green was dissolved in 100.0 mL of doubly distilled water to prepare their 1.0×10^{-3} M solutions, which were used as stock solutions. The stock solutions were further diluted as and when required. The absorbance of these dye solutions were determined with the help of a spectrophotometer at λ_{max} = 610 nm for malachite green. 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 of semiconductor bismuth oxide was kept in dark and in the fourth beaker dye solution with 0.10 g of semiconductor bismuth oxide 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 malachite green 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 malachite green is observed at λ_{max} = 610 nm. Degradation of the dyes in absence of semiconductor (Bi_2O_3) 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.

Table -1: Typical Run

Time(min)	Malachite green	
	Optical Density (OD)	2 + log O.D.
0	0.508	1.7059
10	0.447	1.6503
20	0.400	1.6021
30	0.355	1.5502
40	0.318	1.5024
50	0.282	1.4502
60	0.253	1.4031
70	0.224	1.3502
80	0.205	1.3118
90	0.181	1.2577
100	0.162	1.2095
110	0.144	1.1584
120	0.135	1.1303
130	0.120	1.0792
140	0.107	1.0294
150	0.094	0.9731
160	0.086	0.9345
170	0.077	0.8865
180	0.067	0.8261
190	0.061	0.7853
200	0.053	0.7243
210	0.046	0.6628
220	0.041	0.6128
230	0.036	0.5563
240	0.033	0.5185

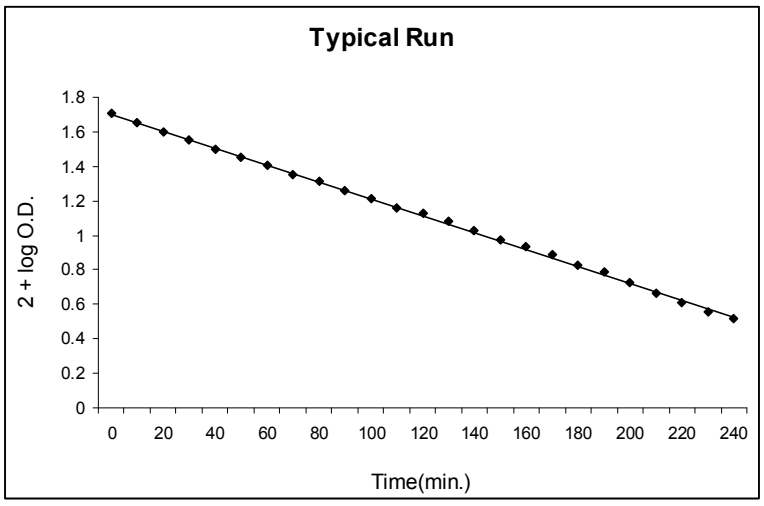

Figure: - 1. A Typical Run (◆ - Bi_2O_3 = 0.10g, [Azure B] x 10^{-5} = 1.80 x 10^{-5} M, pH = 9.50, k = 16.16 x 10^{-5} s^{-1}, light intensity 50 $mWcm^{-2}$)

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 – 10.00. The results are reported in Figure 2. It is evident from the observed data that the rate of photocatalytic degradation of azure B are optimum at pH 9.50 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 $^{\bullet}OH$ radicals, which are produced from the interaction of OH^- and hole (h^+) of the semiconductor. These $^{\bullet}OH$ oxidize the dye molecules

in their leuco forms, which ultimately degrade in the non-hazardous products. But after pH 9.50 for azure B, the dye molecules becomes neutral and feel less attraction to OH^- and hence the rate of the reaction decreases on further increasing pH of the solutions.

Table-2: Effect of pH

pH	Malachite green
	$k \times 10^5$ (sec^{-1})
7.00	11.51
7.25	15.84
7.50	19.19
7.75	18.10
8.00	17.27
8.25	17.13
8.50	17.05
8.75	16.83
9.00	16.50
9.25	16.22
9.50	15.99
9.75	15.70
10.00	15.46

Effect of Dye Concentration:-

Effect of concentration of malachite green was studied by taking different concentrations of these dyes. The results are reported in 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 1.80×10^{-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 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 for azure B.

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.

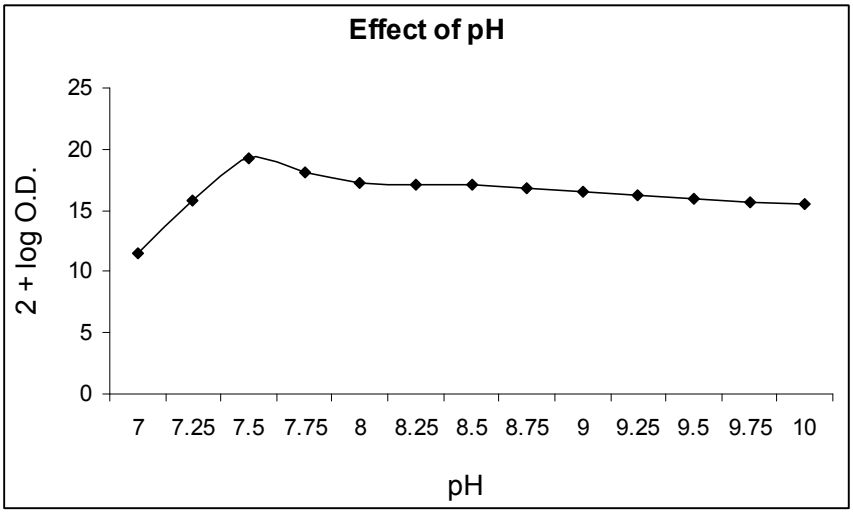

Figure: - 2 Effect of pH

Table – 3: Effect of Dyes Concentration

Dye × 10^5 (sec^{-1})	Malachite green
	k × 10^5 (sec^{-1})
1.00	14.58
1.20	15.30
1.40	15.86
1.60	16.74
1.80	17.90
2.00	19.19
2.20	18.30
2.40	17.60
2.60	16.76

Table – 4: Effect of Amount of Semiconductor

Amount of Semiconductor	Malachite green
	k × 10^5 (sec^{-1})
0.02	16.20
0.04	17.29
0.06	17.44
0.08	18.31
0.10	19.19
0.12	19.19
0.14	19.02
0.16	18.81
0.18	18.74

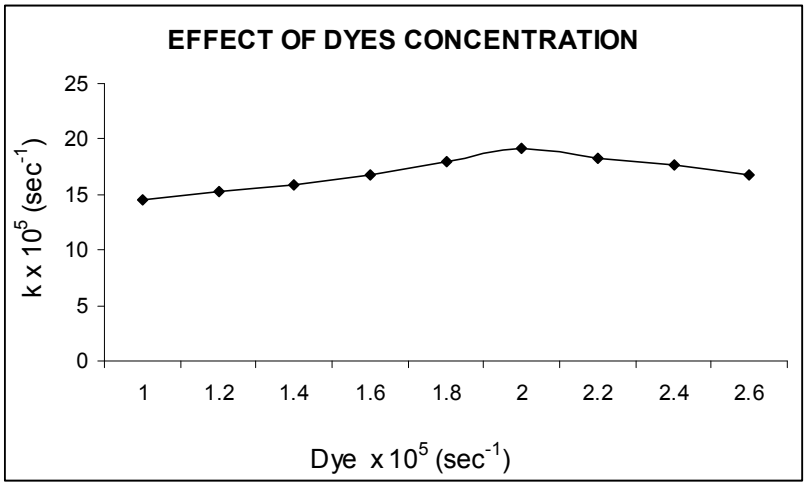

Figure: - 3 Effect of dyes concentration

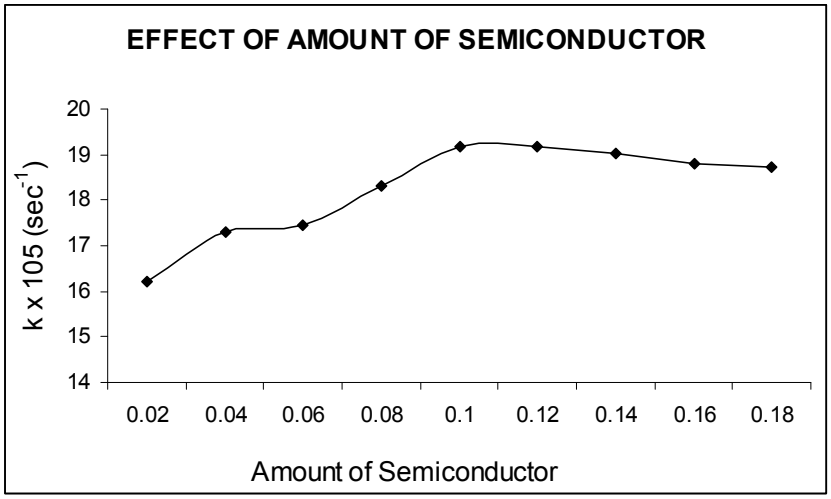

Figure: - 4 Effect of Amount of semiconductor

Table-5: Effect of Light Intensity

Intensity of Light (mW cm^2)	Malachite green
	$k \times 10^5$ (sec^{-1})
10	15.99
20	16.65
30	17.33
40	18.82
50	19.19
60	18.88
70	18.35

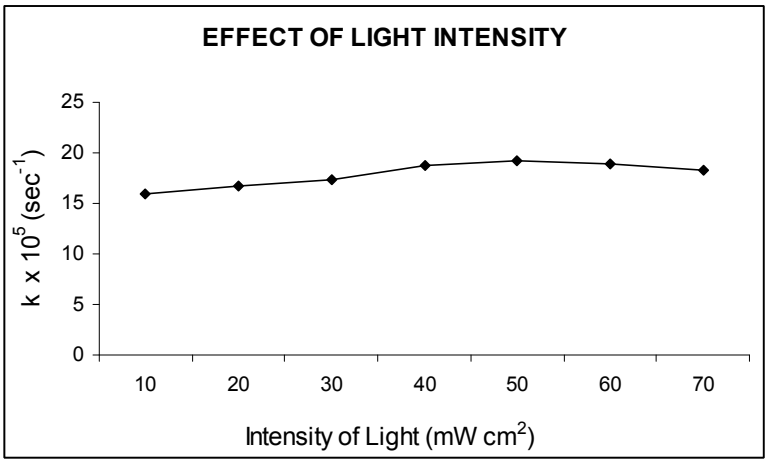

Figure: - 5 Effect of Light intensity

Effect of Light intensity:-

To observe the effect of intensity of light on the photocatalytic degradation of the dye, the light intensity was varied. The results obtained are reported in 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 the malachite green dye.

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.

Mechanism:-

$^1Dye_0 \rightarrow {}^1Dye_1$ (Singlet excited state)

$^1Dye_1 \rightarrow {}^3Dye_1$ (Triplet excited state)

$SC \rightarrow e^-(CB) + h^+(VB)$ or SC^+

$h^+ + OH^- \longrightarrow {}^\bullet OH$

$HO^\cdot + {}^3Dye_1 \rightarrow$ Leuco dye

Leuco dye → Product

Malachite green 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 $^\bullet OH$ radicals. These radicals will oxidize the dye to its leuco form, which may ultimately degrade to products. The participation of $^\bullet OH$ radicals as an active oxidizing species was confirmed by using hydroxyl radical scavenger isopropanol, where the rate of bleaching was drastically reduced.

Conclusions:-

Thus, azure B dye can be degraded photocatalytically by using Bi_2O_3 as visible light photocatalyst.

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