MEASUREMENT OF KINETIC PARAMETERS: USE OF NOVEL NANO SIZED PHOTOCATALYST BAWO$_4$ FOR DEGRADATION OF AZURE B

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ABSTRACT:
A study on photocatalytic degradation of azure B in aqueous solution has been carried out in presence of barium tungsten oxide as semiconductor. The extent of bleaching was monitored spectrophotometrically by measuring the absorbance at λmax = 648 nm. The effect of various parameters such as the pH, concentration of dye, amount of semiconductor and light intensity on the degradation rates was observed. The rate of bleaching of azure B was found to follow pseudo-first order kinetic. A tentative mechanism is proposed.
Keywords: photocatalysis, pseudo first order rate, scavenger

INTRODUCTION

Organic dyes are one of the major causes of pollution of wastewaters which are produced through various industrial processes[1–3]. Over 15% of these used textile dyes are excreted in wastewater stream during dyeing operation. If water is to be reused, it should be purified. There are several treatments for the degradation and removal of dyes from effluents like coagulation, flocculation, ion–exchange, activated carbon absorption, oxidation, reduction, biological methods etc. In recent years, studies have been focused on the photocatalytic degradation of organic compounds mediated by semiconductor particles acting as photocatalysts[4-6].The removal of color from waste effluents becomes of fundamental importance to the environment[7,8]. Few dyes like methylene blue[9-11,26], violet GL2B[12], amido black 10B[13], indigo caramine[14], methyl orange[15,24], basic violet 2[16], naphtol blue black and disperse blue 97[17], coralene dark red 2B azo dye[18], coralene red F3BS[19], malachite green[25] etc. have been degraded photocatalytically. Lot of work has been carried out in this field using TiO$_2$[6,14-16,20-22,25], ZnO[19,23], CdS[15], ZnS[3], WO$_3$[4,24]etc. Recently search of novel nano sized photocatalysts has drawn the attention of scientists and so the selection of barium tungsten oxide as a semiconductor came in existence. Barium tungsten oxide serves as an excellent candidate as a photocatalyst, because of its optical properties, which include a high refractive index, chemical stability, low cost, greater efficiency, recovery with ease, selectivity

and convenient way of treating several undesirable chemicals.

MATERIALS AND METHODS

Stock solutions of Azure B dye (0.030583g/100 ml=1x10^{-3}M) was prepared in doubly distilled water and diluted as required. The optical density (O.D.) of the solution at λmax = 648 nm was determined using a spectrophotometer (Systronics Model 106). The pH of the solution was varied by prestandardized NaOH and HCl solutions and was determined by pH meter (Hena pen type). To 50 ml of the solution, 0.18 g of the photocatalyst (Barium tungstate) was added and it was exposed to a 200 watt tungsten lamp (Philips). The O.D. of the solution was recorded at different time intervals and graph was plotted between time and 1+log O.D. It was found to be a straight line suggesting the reaction to follow pseudo first order kinetics. The rate constant was determined by –

$$K = 2.303 \times slope$$

A water filter was used to cut off the heat reaction. Use of scavenger suggested the participation of OH˙ free radical in the reaction. This free radical is found to be strong enough to break the different bond of dye (C=N, C-N, C=C, C-C, C-S etc). Controlled experiments proved the reaction neither photo degradation nor catalytic degradation rather it was a photo catalytic degrading process.
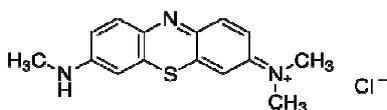
Fig. 1: Structure of Azure B

RESULTS AND DISCUSSION

Effect of irradiation time

The solution was irradiated and the decrease in optical density (O.D.) was recorded in table-1 and figure-2. The degradation was found to obey a pseudo first order kinetics rule.

Table-1: A typical run
[Azure B] = 4x10^{-6} M, amount of semiconductor = 0.18g, pH = 7.3, intensity = 37mW/cm^2.

Time (min.)	O.D.	1+log O.D.
00.0	0.265	0.4232
15.0	0.249	0.3961
30.0	0.238	0.3765
45.0	0.236	0.3729
60.0	0.227	0.3560
75.0	0.221	0.3443
90.0	0.219	0.3404
105.0	0.209	0.3201
120.0	0.173	0.2380
135.0	0.169	0.2278

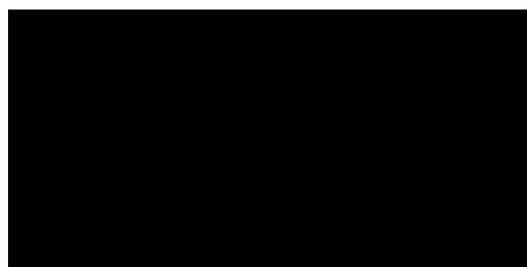$$K = 4.94 \times 10^{-5} \text{ Sec}^{-1}$$

Figure-2: A typical run (Time v/s 1+ log O.D.)

Effect of pH

The pH of the solution is one of the major factors affecting the degradation of Azure B. The effect was investigated in the pH range 5.3–8.6. The results are reported in table-2 and figure 3.

Table 2: Effect of variation of pH
[AzureB]=4x10^{-6}M, amount of semiconductor=0.18g, intensity = 37mW/cm^2.

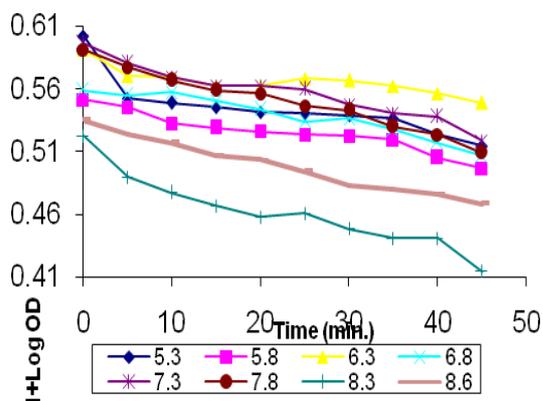| pH	K×10^{-5} sec^{-1}
5.3	3.12
5.8	3.24
6.3	1.43
6.8	3.24
7.3	**4.94**
7.8	4.26
8.3	3.84
8.6	3.71

Fig. 3: Effect of pH

On increasing the pH of the reaction medium, the rate of degradation increases. It is due to the fact that more number of OH$^-$ ions is generated. These ions loose an electron to the hole generated at semiconductor surface forming OH* free radicals. These free radicals abstract an electron from weaker site of the dye which results in its degradation. Above a maxima (pH 7.3), the rate decreases with increase in pH. It is because the semiconductor surface becomes covered with adsorbed hydroxyl ions, making it negatively charged. This negatively charged surface will not permit a close approach of dye molecules near the semiconductor surface as the dyes are also negatively charged and therefore caused repulsion reduces the reaction rate.

Effect of dye concentration
The effect of variation of the dye concentration was studied by taking different concentrations of azure B. The data are given in table-3 and figure-4.

Table-3 Effect of dye concentration
Amount of semiconductor =0.18g, pH = 7.3, intensity = 37mW/cm^2.

Dye concentration $\times 10^{-6}$ M	$K \times 10^{-5}$ sec^{-1}
3.0	4.28
4.0	**4.94**
5.0	3.71

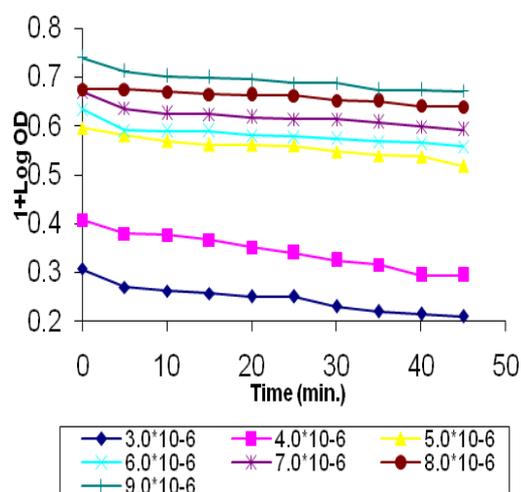|	
6.0	2.57
7.0	2.35
8.0	1.93
9.0	1.71

Fig.4: Effect of dye concentration in mole/litre

The rate of photocatalytic degradation of dye increased with increasing dye concentration up to a certain value (5×10^{-6} M). Beyond this concentration, the rate of photocatalytic degradation decreases. This may be explained by the fact that as the concentration of dye was increased, more dye molecules were available for excitation and consecutive energy transfer and as a result, an increase in the rate was observed. A decrease in rate was observed with further increase in the dye concentration, which may be attributed to the fact that the dye starts acting as an internal filter for the incident light and do not permit the desired light intensity to reach the semiconductor particles. Thus, a corresponding decrease in the rate was observed.

Effect of catalyst dose
The amount of semiconductor is also likely to affect the process of dye degradation and hence,

different amounts of photocatalyst were used. The results are reported in table-4 and Figure 5.

Table-4: Variation of amount of semiconductor
[Azure B]=$4x10^{-6}$M, pH=7.3, intensity = 37mW/cm^2.

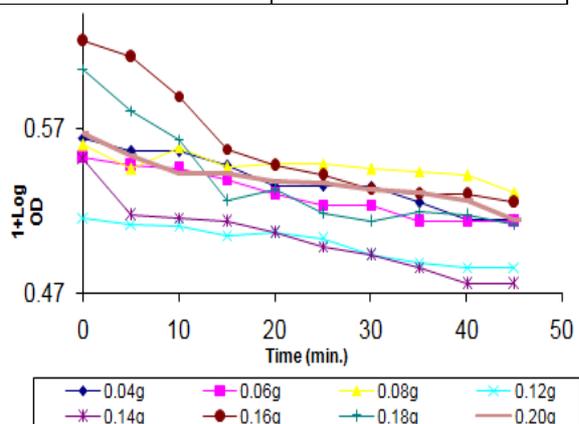| Amount of semiconductor (g)	$K \times 10^{-5}$ sec^{-1}
0.04	1.83
0.06	1.58
0.08	1.27
0.12	1..15
0.14	2.23
0.16	2.46
0.18	**4.94**
0.20	1.52

Fig.5: Effect of amount of semiconductor

The rate constants for the photo degradation of the dye initially increased with increasing amount of semiconductor but after reaching a certain amount (0.18g), the rate decreases. This may be because as the amount of semiconductor increases, the exposed area for capturing the photons increases and as a result, the rate of the reaction increased. After a certain limit (0.18 g), if the amount of semiconductor was further increased, the rate was found to decrease. Increase in the amount of the semiconductor after this particular amount would only increase the thickness of the layer. This multilayer structure will generate more number of holes and electrons and this crowd forces the

recombination of the two causing reduction of the rate of the reaction.

Effect of light intensity
To investigate the effect of the light intensity on the photocatalytic degradation of Azure B, the distance between the light source and the exposed surface area was varied. The results are reported in table-5 and Figure 6.

Table-5: Variation of intensity of light
[Azure B] = $4x10^{-6}$M, pH = 7.3, amount of semiconductor = 0.18g.

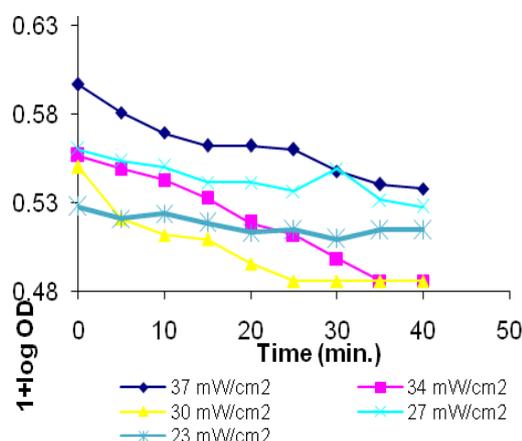| Intensity of light (mW/cm^{-2})	$K \times 10^{-5}$ sec^{-1}
37	**4.94**
34	3.28
30	2.99
27	1.22
23	0.84

Fig. 6: Effect of light intensity

The rate of photocatalytic degradation of the dye was found to increase with increasing light intensity. An increase in the intensity of light increases the number of photons striking the semiconductor particles per unit area per unit time. As a result, more electron–hole pairs are generated, which results in an overall increase in the rate of
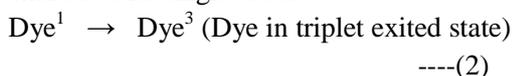
the reaction. However, at higher light intensities, some thermal side reactions may commence and so further studies at higher intensities were not carried out.

CONCLUSION

It is concluded here by that dyes are being degraded, with the help of photocatalyst and in presence of visible light, into fragments and no harmful products are formed. The proposed mechanism is

$$h\nu + Dye \rightarrow \quad Dye^1 \text{ (Dye in singlet exited state)} \quad ----(1)$$
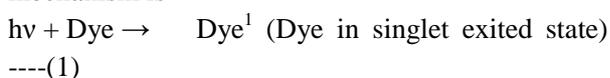
Dye absorbs photons from sun light and gets excited to its singlet state.

$$Dye^1 \rightarrow Dye^3 \text{ (Dye in triplet exited state)} \quad ----(2)$$

The dye in next step, gets converted to triplet state by losing some energy through inter system crossing (ISC).

$$h\nu + SC \rightarrow h^+ + e^- \quad ----(3)$$

On the other hand, semiconductor absorbs photons and an electron from valence band gets excited to conduction band generating hole (h^+) and electron (e^-) pair. This electron is responsible for reduction and the hole for oxidation of any organic pollutant.

$$h^+ + OH^- \rightarrow h + OH^* \quad ----(4)$$

Now the generated hole abstracts an electron from base i.e. OH^- ion and OH* free radical is generated.

$$OH^* + Dye^3 \rightarrow \text{Leuco form of dye} \rightarrow CO_2, H_2O, NH_4^+, SO_4^-, Cl^- \text{ etc.} \quad ----(5)$$
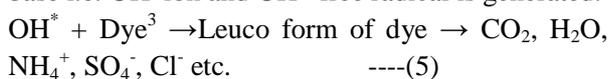
The OH* free radical abstracts an electron from weaker site of the dye causing break down of conjugation in the dye which slowly degrades into harmless fragments like CO_2, H_2O, NH_4^+, SO_4^-, Cl^- etc. ions.

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