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Photocatalytic Degradation of Azure-B by Using Zinc Oxide as Photocatalyst

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Abstract: The photocatalytic degradation of Azure-B over zinc oxide suspended in aqueous solution has been carried out. The progress of reaction was observed by measuring optical density of the reaction mixture, containing dye and zinc oxide at different time intervals with the help of UV Spectro photometer.
A decrease in the optical density indicates that the dye was bleaching during the photochemical process. Effect of various parameters like pH, concentration of dye, amount of semi-conductor and light intensity on the reaction rate has been investigated and tentative mechanism has been proposed.
Keywords: Photocatalytic degradation, Azure-B, Zinc oxide, Semiconductor, Light intensity.

I. INTRODUCTION

Nature now a days is suffering from a serious problem of environmental pollution. Large amount of chemicals are produced in different industries, some of which are toxic for human life. Dying, printing and textile industries throw a lot of chemicals in the water resources around, thus causing water pollution[1]. The colored and polluted water can neither be used for irrigation purpose nor for any domestic use.
Popular treatment methods for eliminating dyes from the waste water stream, suffer from many drawbacks. Photocatalytic degradation is found to be a very efficient process for mineralization of organic pollutants where semi- conductor acts as a photocatalyst[2]. In the present work the photocatalytic degradation of Azure-B on zinc oxide powder in aqueous suspension under light has been studied. The choice of zinc oxide as a catalyst for this purpose is based on its higher photoactivity shown in several photo electrochemical process[3].
Therefore, it is important to remove this dye from water resources.

II. MATERIALS&METHODS

Azure-B (Schmid), zinc oxide (CDH) were used in the present investigation. The dye solution of Azure-B was prepared in doubly distilled water.
The photocatalytic degradation of Azure-B was studied in the presence of semi-conductor Zinc oxide and Light. 0.0305 g of Azure - B was dissolved in 100.0 ml doubly distilled water hence the concentration of dye solution remains 1.0×10^{-3} M. It was used as a stock solution.
The photocatalytic degradation of Azure-B was observed taking 200.0 ml of dye solution ($1{\cdot}0 \times 10^{-5}$M) and 0.10 gm of zinc oxide semiconductor.
A 200W tungsten lamp (Light intensity 40.0mW cm^{-2}) was used for irradiating the reaction mixture in the visible range. The intensity of light at various distances from the lamp was measured with the help of a solarimeter (Surya Mapi Model CEL 201). A water filter was used to cut off the thermal radiations. The pH of the solution was measured by a digital pH meter (Hanna instruments ISO-9001).
The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solution. A UV spectrophotometer (Systronics Model 108) was used for measuring absorption maximum and optical density (OD) at different time intervals[4].

III. RESULTS AND DISCUSSION

The photocatalytic degradation of Azure-B was observed at λ_{max} 650nm[5]. The result for a typical run is given in Table 1 and graphically presented in Figure 1

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A. A typical run

TABLE I: A typical run

[Azure-B] = 4.0 x 10-5 M pH=9.5
Light Intensity = 40.0 mW cm^{-2} Zinc oxide = 0.10 g

S.No.	TIME (min.)	Optical Density (O.D)	1 + log O.D.
1	0.0	0.516	0.712
2	30.0	0.425	0.628
3	60.0	0.354	0.549
4	90.0	0.294	0.468
5	120.0	0.242	0.383
6	150.0	0.205	0.311
7	180.0	0.171	0.232
8	210.0	0.142	0.152

k=10.23 x 10^{-5} sec^{-1}

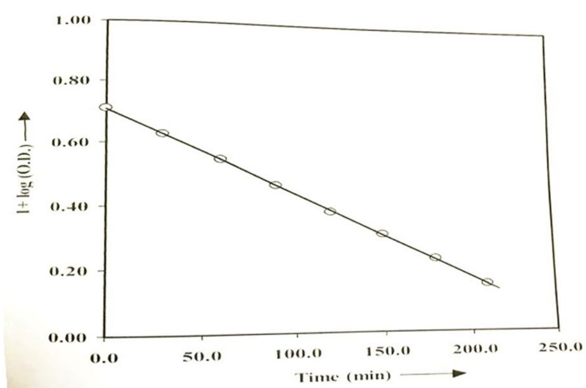

Fig 1 A typical run

It was observed that the optical density of Azure-B solution in presence of semiconductor was much low as compared to the sample without semiconductor at the same time 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 log OD vs time was linear and hence this reaction follows pseudo-first order kinetics.

B. Effect Of pH Variation

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 (7.0 - 10.5)[6]. The results are reported in Table 2 and graphically presented in Figure 2.

TABLE II : Effect of pH

[Azure-B] = 4.0 x 10-5M Zinc oxide = 0.10 g
Light Intensity = 40.0 mW cm^{-2}

S. No	pH	k x 10^5 (sec^{-1})
1	7.0	4.36
2	7.5	5.38
3	8.0	5.86
4	8.5	6.88
5	9.0	7.82
6	9.5	10.23
7	10.0	20.50
8	10.5	23.17

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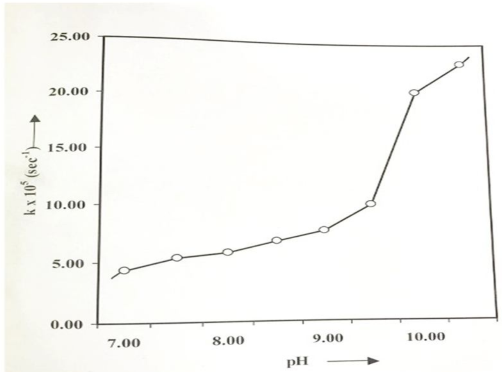

Fig 2 Effect of pH

It has been observed that the rate of photocatalytic bleaching of dye increases on increasing the pH. This can be explained on the basis that as the pH of the medium was increased, there is a corresponding increase in the concentration of hydroxyl ions. These hydroxyl ions get adsorbed on the semiconductor surface making it negatively charged. Thus, there will be a coulombic attraction between semiconductor surface and cationic dye. This has been reflected by the increase in the rate of photobleaching of the dye on increasing pH.

C. Effect Of Azure-B Concentration

Effect of variation of dye concentration was also studied by taking different concentrations of Azure-B[7]. The results are tabulated in Table III and graphically represented in Figure 3.

TABLE III: Effect Of Azure-B Concentration

pH=9.5 Zinc oxide = 0.10 g

Light Intensity = 40.0 mW cm

S.No.	[Azure-B] x 10^5M	K x 10^5 (sec^{-1})
1	3.5	5.42
2	4.0	10.23
3	4.5	7.48
4	5.0	6.96
5	5.5	6.48
6	6.0	5.65

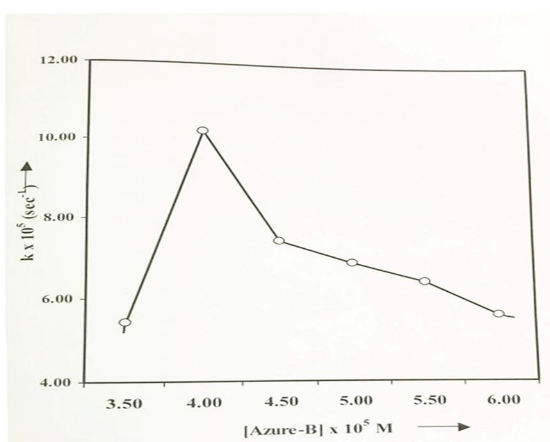

Fig3 Effect Of Azure-B Concentration

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It has been observed that the rate of photocatalytic bleaching increases with an increase in the concentration of the dye. 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 an increase in the concentration of the dye further. 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 light intensity to reach the semiconductor particles, thus, decreasing the rate of photocatalytic bleaching of Azure-B.

D. Effect Of Amount Of Semiconductor

The amount of semiconductor is also likely to affect the process of dye bleaching[8]. Different amounts of photocatalysts were used and the results are reported in Table IV and graphically represented in Figure 4

TABLE-IV Effect Of Amount Of Semiconductor

[Azure-B]=4.0 x 10^{-5}M pH = 9.5

Light Intensity = 40.0 mW cm^{-2}

S.No.	Amount of Semiconductor (g)	k x 10^5 (sec^{-1})
1	0.02	5.72
2	0.04	7.02
3	0.06	8.12
4	0.08	9.20
5	0.10	10.23
6	0.12	10.26
7	0.14	10.22

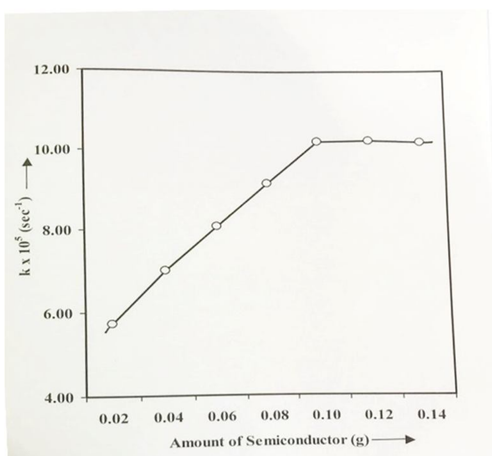

Fig 4 Effect of Amount of Semiconductor

It has been observed that the rate of photobleaching of Azure-B increases with an increase in the amount of semiconductor but ultimately it becomes almost constant after a certain amount. 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 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 bleaching of Azure-B. 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 vessel, once the complete bottom of the reaction vessel is covered by the photocatalyst. It may also be confirmed on the basis of geometry of the reaction vessel. This was observed 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[9].

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E. Effect Of Light Intensity

To observe the effect of intensity of light on the photocatalytic bleaching of Azure-B, light sources of different wattage were used or the distance between the light source and the exposed surface area was varied. The intensity of light at each distance was measured by Suryamapi (CEL Model SM 201)[10]. The results obtained are reported in Table V and graphically represented in Figure 5.

TABLE -V Effect Of Light Intensity

[Azure B]=4.0 x 10^{-5} M Zinc oxide = 0.10 g

pH = 9.5

S.No.	Intensity of Light (mW cm^{-2})	k x 10^5 (sec^{-1})
1	20.0	8.16
2	30.0	9.38
3	40.0	10.23
4	50.0	11.22
5	60.0	12.20
6	70.0	13.24

The results given in Table V indicate that 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.

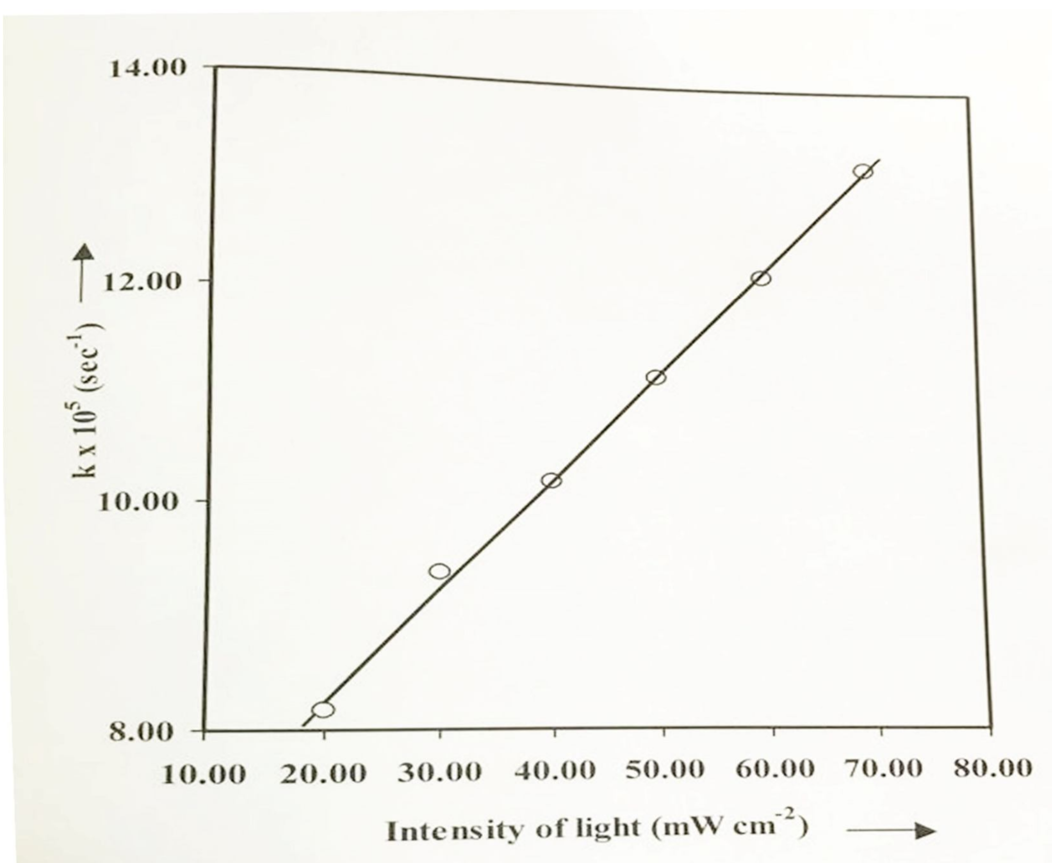

Fig 5 *Effect Of Light Intensity*

IV. MECHANISM

On the basis of the experimental observations, a tentative mechanism for photocatalytic bleaching of Azure-B may be proposed:

$$^1AB_0 \xrightarrow{h\nu} {}^1AB_1 \quad \ldots(1.1)$$

$$^1AB_1 \xrightarrow{ISC} {}^3AB_1 \quad \ldots(1.2)$$

$$^3AB_1 + ZnO \longrightarrow AB^+ + ZnO\ (e^-) \quad \ldots(1.3)$$

$$ZnO(e^-) + O_2 \longrightarrow ZnO\ (e^-) + O_2^{\bullet -} \quad \ldots(1.4)$$

$$AB^+ + OH^- \longrightarrow AB + OH^\bullet \quad \ldots(1.5)$$

$$AB + OH^\bullet \longrightarrow Products \quad \ldots(1.6)$$

When the solution of the dye was exposed to light in presence of a semiconductor, initially the Azure-B molecules are excited to first excited singlet state. Then these excited singlet molecules are transferred to the triplet state through inter system crossing (ISC). The triplet state may donate its electrons to the semiconductor and the Azure-B becomes positively charged. The dissolved oxygen of the solution may pull an electron from the conduction band of semiconductor thus, regenerating the semiconductor. The positively charged molecules of Azure-B will immediately react with hydroxyl ions to form OH^* radicals and these OH^* radicals will oxidize the azure-B molecules into colorless products. The participation of OH^* radicals as an active oxidizing species was confirmed by carrying out the reaction in presence of hydroxyl ion scavenger e.g. 2-propanol; where the reaction rate was drastically retarded[11].

V. CONCLUSION

A. The rate of Photocatalytic degradation of Azure-B increases with increase in pH.
B. A optimum rate of photocatalytic degradation was observed at concentration $4.0X10^{-5}$ml.
C. The increase in the amount of semiconductor increases the rate of photocatalytic degradation of Azure-B.
D. A linear behavior between light intensity and the rate of photocatalytic degradation was observed.

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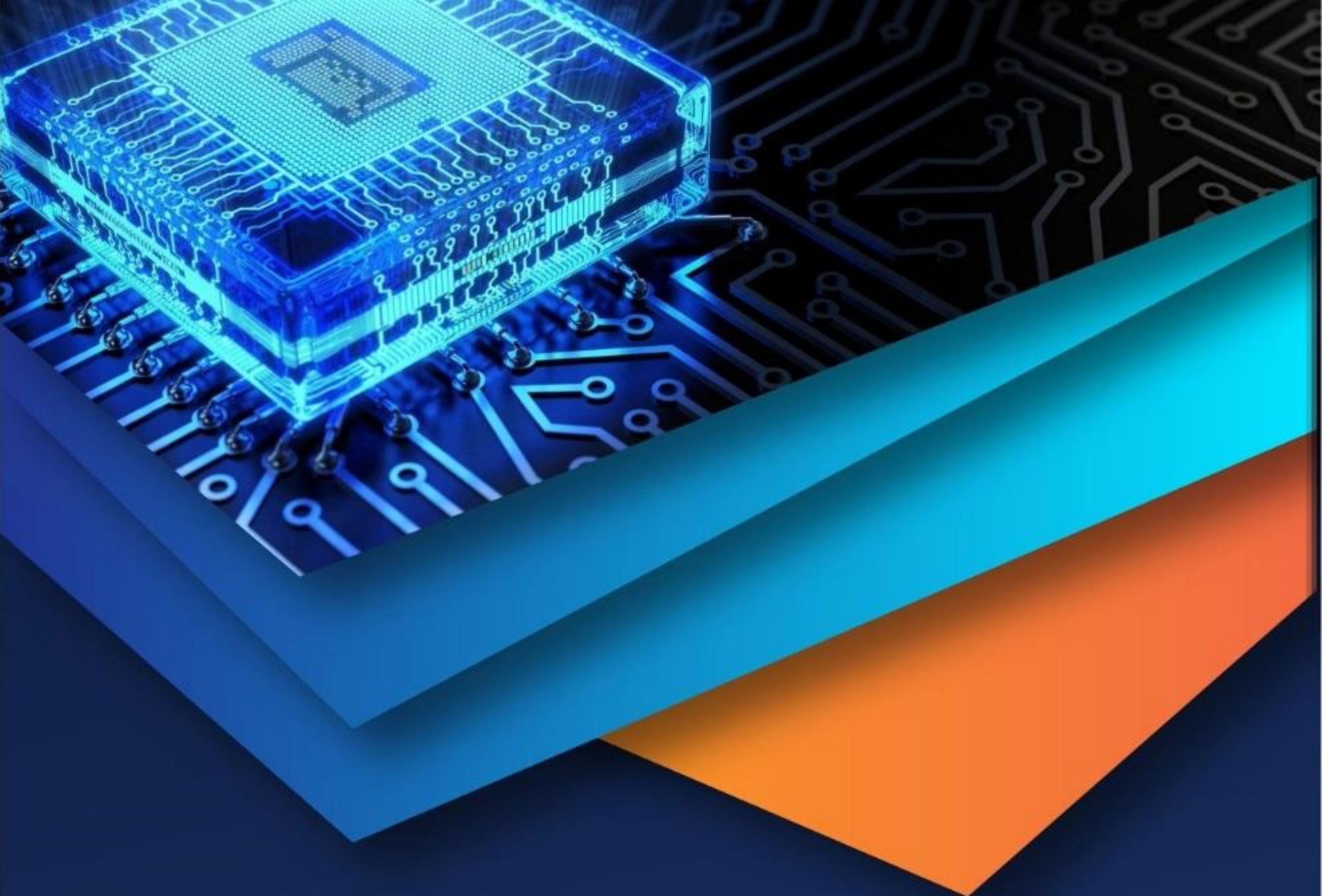

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