

# Photo Catalytic Degradation of Azure B Using Nanoscale ZnO in the Presence of Visible and Solar Light Radiations

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## Abstract

Heterogeneous photocatalytic oxidation is an effective method to remove low concentrations of organic dyes. The present work incorporates the study of efficiency of ZnO for photocatalytic degradation of Azure B dye. The disappearance of the dye has been monitored spectrophotometrically, followed pseudo-first order kinetics, according to Langmuir-Hinshelwood model. Effect of some factors such as catalyst dose, concentration of salt and pH etc., on degradation of the dye was examined. 95% of dye was degraded by the ZnO upon exposure to solar and visible light irradiation for 90 min. The reduction in COD values and increase in CO<sub>2</sub> values indicates the complete mineralization of Azure B dye

**Keywords** — Advanced oxidation technologies (AOTs), Destruction of organic dyes, Hydrogen peroxide and hydroxyl radical

## I. INTRODUCTION

The oxidative decolourization techniques of dye have several limitations, e.g., biological oxidation, oxidation with H<sub>2</sub>O<sub>2</sub> take a long time for the effluent to reach the required standards and produce a large quantity of sludge, which normally cannot be reused and oxidation with ozone is costly [1].

Advanced oxidation processes (AOPs) have been attracting substantial interest due to its effectiveness and sustainability in the long term [2]. Advanced oxidation processes (AOPs) involves the generation of highly reactive hydroxyl radicals (HO•) [3] at near ambient temperature and pressure.

In the phenothiazine class of dyes an atom of sulphur replacing oxygen in the heterocyclic ring. These dyes have phenazonium nucleus as chromophore with amino group's para to the ring nitrogen as auxochromes. They have colour range from green to blue and have been used for colouring paper, tannin mordant cotton and silk. Fastness to light is usually only fair. Azure B is a type of phenothiazine class.

## II. KINETICS OF PHOTOCATALYTIC DEGRADATION OF DYES

Langmuir-Hinshelwood theory is the most commonly used kinetic model for describing photocatalytic behaviours. In Langmuir-

Hinshelwood treatment of heterogeneous surface reactions, the photochemical degradation rate is described by pseudo first order kinetics.

The values of order of reaction and rate constant have been calculated to find the net degradation rate of selected dyes. However, for the simplification of analysis, it is assumed that there is a rate-determining step within all the reactions and k represents the rate constant of this slowest one.

## III. MATERIALS USED

Azure B solution: Stock solution of Azure B  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup> was prepared by dissolving 0.0306 gm of Azure B in 100 ml double distilled water.

Sodium carbonate solution: Stock solution of Na<sub>2</sub>CO<sub>3</sub>  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup> was prepared by dissolving 0.106 g of Na<sub>2</sub>CO<sub>3</sub> in 100 mL distilled water.

Sodium chloride solution: Stock solution of NaCl  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup> was prepared by dissolving 0.058 g of NaCl in 100 mL distilled water.

## IV. PHOTOREACTOR DESIGN FOR EXPERIMENT

The photocatalytic and photolytic experiments were carried out in a slurry type batch reactor. The pyrex glass vessel equipped with magnetic stirrer was surrounded by thermostatic water circulation arrangement to keep temperature in the range of 30±0.3°C. The irradiation was carried out using 500 W halogen lamps (Philips India) surrounded with aluminium reflectors in order to avoid loss of irradiation. Decolourization was studied by spectrophotometrically. Beer's law was valid for the measurement under the experimental conditions considered. No apparent interference from the other reagents, intermediates or products had been noticed. Experiments were performed at room temperature, with a constant lamp power of 500 W and a fixed distance between the photoreactor and the lamp housing (50 cm).

## V. KINETIC ANALYSIS OF AZURE B

The effect of various experimental parameters on the processes of performance has been investigated. Total degradation of the dyes was assessed in terms of chemical oxygen demand (COD), CO<sub>2</sub> and UV-analysis.

Experimental conditions that directly affect the degradation of dyes through photocatalytic oxidation processes include the initial concentration of dyes, light intensity, amount of photocatalyst, effect of NaCl, and Na<sub>2</sub>CO<sub>3</sub> on the rate of reaction, effect of pH and effect of temperature on degradation rate. Standard analytical methods for identification of mineralized products were used.

The photocatalytic degradation of azure B dye followed pseudo first kinetics. The detection was realized at 640 nm. The absorbance of azure B dye decreased with an increase in irradiation time. The plot of log absorbance versus time followed pseudo first order kinetics with correlation co-efficient of 0.96, rate constant of  $3.30 \times 10^{-4} \text{ s}^{-1}$  and half life time of  $2.10 \times 10^3 \text{ s}$  (Fig. 1).

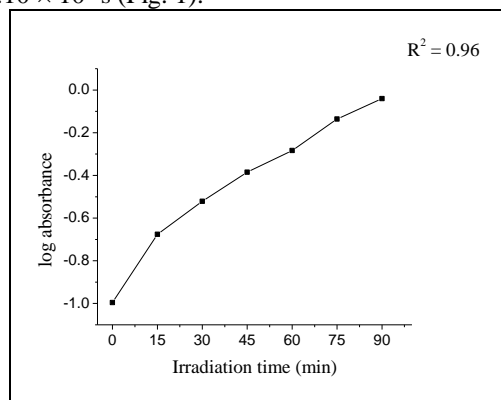


Fig 1: Pseudo first order kinetics:  
 [Azure B] =  $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ , pH = 8.0  
 ZnO = 250 mg/100 mL,  
 Light intensity =  $27 \times 10^3 \text{ lux}$   
 Temperature =  $30 \pm 0.3 \text{ }^\circ\text{C}$ .

## VI. RESULT AND DISCUSSION

### A. Effect of Catalyst loading

The amount of catalyst is one of the main parameters for the degradation studies from economical point of view. In order to avoid the use of excess catalyst it is necessary to find out the optimum loading for efficient removal of dye. The increase in the rate of decolourization may be attributed to increase in the exposed surface area of semiconductor [4]. But after a certain limit, other factors affect the decolourization of dyes (Table I).

Table 1: Effect of catalyst loading

[Azure B] =  $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ , pH = 8.0

Light intensity =  $27 \times 10^3 \text{ lux}$ , Temp. =  $30 \pm 0.3 \text{ }^\circ\text{C}$ .

ZnO mg/100mL	$k \times 10^{-4} \text{ s}^{-1}$	$t_{1/2} \times 10^3 \text{ s}$
100	2.4	2.88
150	2.6	2.66
200	3.1	2.23
250	3.3	2.10
300	2.6	2.66
350	1.5	4.62
400	1.2	5.77

At high concentrations, particles aggregate which in turn reduced the interfacial area between the reaction solution and the photocatalyst. Thus, the number of active sites on the catalyst surface was decreased. The increase in opacity and light scattering by the particle might be the other reasons for the decrease in the decolourization rate at higher catalyst concentration [5],[6].

### B. Effect of substrate concentration

The rate constant (k) for the degradation of azure B first increased with the increase in substrate concentration and reached to highest efficiency at the concentration of  $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ . This could be explained on the basis of the fact that the reaction rates increased as more molecules of dye were available for oxidation [7]. On further increase in the dye concentration beyond of  $5.0 \times 10^{-5} \text{ mol dm}^{-3}$  the degradation rate was found to be decreased (Table 2).

Table 2: Effect of dye concentration: ZnO = 250

mg/100 mL, pH = 8.0, Light intensity =  $27 \times 10^3 \text{ lux}$ ,

Temperature =  $30 \pm 0.3 \text{ }^\circ\text{C}$ .

[Azure B] $\times 10^{-5} \text{ mol dm}^{-3}$	$k \times 10^{-4} \text{ s}^{-1}$	$t_{1/2} \times 10^3 \text{ s}$
1.0	1.95	3.55
2.0	2.07	3.34
3.0	2.49	2.78
4.0	2.80	2.47
5.0	3.30	2.09
6.0	2.45	2.82
7.0	1.95	3.55

This phenomenon is characterised in case of heterogeneous systems. This decrease in degradation rate may be attributed to following reason; (i) As dye concentration increases, number of photons reaching to catalyst surface decreases resulting less number of catalyst molecules to undergo excitation and hence rate of formation of holes, hydroxyl radicals and supraoxide ( $O^{\cdot-}$ ) ions decreased thus decreasing the rate of degradation; (ii) Since catalyst surface area is fixed, so as the concentration of dye increases rate of degradation decreases because limited number of dye molecules attach to active site of catalyst. (iii) At higher concentration, numbers of dye molecules are also high so there will be more competition for attachment to active site of catalyst between dye molecules, resulting in reduction of the rate of degradation [8].

### C. Role of pH

In accordance with Nernst's law, varying the solution pH would shift the energy of the valence and conduction band edges, by 0.059 per pH unit. This results in the valence band electron becoming more effective and the conduction band holes less effective at higher pH [9].

**Table 3: Effect of pH: [Azure B] =  $5.0 \times 10^{-5}$  mol dm<sup>-3</sup>, ZnO = 250 mg/100 mL  
Light intensity =  $27 \times 10^3$  lux,  
Temperature =  $30 \pm 0.3$  °C.**

pH	$k \times 10^{-4} \text{ s}^{-1}$	$t_{1/2} \times 10^3 \text{ s}$
4	2.11	3.28
5	2.37	2.92
6	2.64	2.62
7	2.99	2.31
8	3.30	2.06
9	2.76	2.51
10	2.64	2.62
11	1.88	3.68
12	1.45	4.77

Rate of degradation was very low on high acidic pH. When pH of the reaction slurry was increased, rate of degradation also increased from  $2.11 \times 10^{-4} \text{ s}^{-1}$  to  $3.30 \times 10^{-4} \text{ s}^{-1}$  till at pH reached to 8.0. On further increasing the pH value the rate of degradation started decreasing. On increasing the pH from 4 onwards the reaction rate increased may be due to the preferential adsorption of  $H^+$  ions on the photocatalyst surface as compared to the cationic dye molecule. In the basic medium rate of degradation found to be decreased due to the competition between  $OH^-$  groups to attach to the active site of catalyst, so rate of attachment of  $OH^-$  groups decreases and the resultant formation of  $OH^{\cdot}$  free radicals decreased

[10]. The effect of pH on the degradation has been shown in Table 3.

### D. Effect of NaCl and Na<sub>2</sub>CO<sub>3</sub>

Dyeing is normally carried out in a neutral or slightly alkaline dye bath at or near boiling point with addition of either sodium chloride or sodium carbonate.

$Na_2CO_3$  is mainly used in the dyeing bath in order to adjust the pH of the bath as it plays an important role in the fixing of the dye on the fabrics and in the fastness of the colour and NaCl usually comes out in effluent along with sectional wastes in textile mills. The effect of presence of NaCl and  $Na_2CO_3$  is shown in Table 4. The photocatalytic degradation rate decreased with the increase in  $Cl^-$  and  $CO_3^{2-}$  ions concentration from  $1.0 \times 10^{-5}$  mol dm<sup>-3</sup> to  $7.0 \times 10^{-5}$  mol dm<sup>-3</sup>. The cause of inhibition is due to the ability of these ions to act as hydroxyl radical ( $OH^{\cdot}$ ) scavengers.

**Table 4: Effect of salt: [Azure B] =  $5.0 \times 10^{-5}$  mol dm<sup>-3</sup>, ZnO = 250 mg/100 mL, Lght intensity =  $27 \times 10^3$  lux, pH = 8.0, Temperature =  $30 \pm 0.3$  °C.**

[Salt] $\times 10^{-5}$ mol dm <sup>-3</sup>	$Na_2CO_3$		NaCl	
	$k \times 10^{-4} \text{ s}^{-1}$	$t_{1/2} \times 10^3 \text{ s}$	$k \times 10^{-4} \text{ s}^{-1}$	$t_{1/2} \times 10^3 \text{ s}$
0.0	3.30	2.1	3.3	2.1
1.0	2.72	2.54	2.57	2.69
2.0	2.14	3.23	2.34	2.96
3.0	2.03	3.41	2.03	3.41
4.0	1.68	4.12	1.45	4.77
5.0	1.49	4.65	1.39	4.98
6.0	1.34	5.17	1.18	5.87
7.0	1.01	6.86	1.11	6.24

### E. Effect of light intensity

The rate constant values found to be increased from  $1.53 \times 10^{-4} \text{ s}^{-1}$  to  $4.84 \times 10^{-4} \text{ s}^{-1}$  on increasing light intensity from  $10 \times 10^3$  lux to  $36 \times 10^3$  lux. This was because at higher intensity electron hole separation competes with electron hole recombination and resulted high reaction rate [11, 12]. The effect of light intensity and rate constant on photo catalytic degradation is showed in Table 5.

**Table 5: Effect of light intensity: [Azure B] =  $5.0 \times 10^{-5}$  mol dm<sup>-3</sup>, pH = 8.0, ZnO = 250 mg/100 mL, Temperature =  $30 \pm 0.3$  °C.**

Light intensity $\times 10^3$ lux	$k \times 10^{-4} s^{-1}$	$t_{1/2} \times 10^3$ s
13	1.53	4.51
21	2.78	2.49
27	3.30	2.10
34	3.42	2.0
55	3.50	1.98
70	3.80	1.59

The effect of light intensity on the kinetics of the photocatalytic degradation of dye as follows:(i) At low light intensities (0–20 mW/cm<sup>2</sup>), the rate of photocatalytic degradation is proportional directly with light intensity (first order).(ii) At high light intensities (25 mW/cm<sup>2</sup>), the rate of photocatalytic degradation is proportional directly with the square root of the light intensity (half order) (iii) At high light intensities the rate of photocatalytic degradation is independent of light intensity (zero order) [13].

**F. Effect of temperature**

The photocatalytic systems have been studied due to their ability to photosensitize the complete mineralization of a wide range of organic substrates at ambient temperatures and pressures, without the production of harmful by-products [14].

**Table 6. Effect of temperature: [Azure B] =  $5.0 \times 10^{-5}$  mol dm<sup>-3</sup>, pH = 8.0, ZnO = 250 mg/ 100 mL, Light intensity =  $27 \times 10^3$  lux.**

Temperature (°C)	$k \times 10^{-4} s^{-1}$	$t_{1/2} \times 10^3$ s
30	3.30	2.10
35	3.39	2.04
40	3.44	2.01
45	3.23	2.14
50	2.77	2.50
65	2.34	2.96

It was observed that the effect of temperature on the photocatalytic degradation is insignificant in the range of 30–65 °C [15]. The influence of temperature

has been studied in the range 30 °C to 65 °C (Table 6). Rate constant increased from  $3.30 \times 10^{-4} s^{-1}$  to  $3.44 \times 10^{-4} s^{-1}$  with increase in temperature from 30–40 °C. High temperatures may have a negative impact on the concentration of dissolved oxygen in the solution and consequently, the recombination of holes and electrons increases at the surface of photocatalyst. However, already reported that raising the temperature of reaction enhances the rate of photocatalytic degradation significantly [16].

**G. Chemical oxygen demand (COD) and free CO<sub>2</sub> measurement during photo degradation process**

The efficiency of photocatalytic treatment to mineralize the dyes was investigated. The kinetics of COD removal has been followed as a function of irradiation time (Table 7).

**Table 7: COD and CO<sub>2</sub> measurement during photodegradation process: [Azure B] =  $5 \times 10^{-5}$  mol dm<sup>-3</sup>, ZnO = 250 mg/100 mL, pH = 8.0, Light Intensity =  $27 \times 10^3$  lux, Temperature =  $30 \pm 0.3$  °C.**

Ti m e (h)	CO D (m g/L )	CO <sub>2</sub> (mg/ L)	Ef fic ie nc y ( % )	NO <sub>3</sub> <sup>-</sup> (mg/ L)	SO <sub>4</sub> <sup>2-</sup> (mg/ L)	pH	Cond uctivi ty (mS/c m)
0	340	3.9	0	0	0	8.0	0.120
1	260	8.8	23	3	4.5	7.3	0.211
2	180	26.4	47	5.2	6	7.0	0.321
3	24	35.2	92	9.4	8.2	5.9	0.399
4	18	44	94	11	10	5.1	0.489
5	6	61.6	98	13.5	11.7	4.2	0.587

It is interesting to remark that the COD decreased slower than the discoloration of the solution. This result would be explained by the fact that the dyes are not directly mineralized, but transformed in intermediate photoproducts. These generated

photoproducts may submit other cycles of degradation to complete total mineralization.

The photodegradation is precursor to the mineralization in most of the AOPs. COD and free CO<sub>2</sub> measurement were carried out to record the extent of mineralization of the organic molecule under consideration over ZnO suspension, COD test allowed the measurements of waste in terms of the total quantity of oxygen required for the degradation of organic matter to CO<sub>2</sub> and inorganic ions. After 5 hours of irradiation, COD values decreased from 340 mg/L to 6 mg/L, while there was an increase in CO<sub>2</sub> values and inorganic ions. A decrease in pH and increase in conductivity of solution was observed with increase in the extent of degradation.

## VII. CONCLUSION

The organic dye degradation kinetics by ZnO suspension was experimentally studied. The study of results of the photodegradation rate of dyes under investigation revealed that the degradation rate was function of pH of the system. The degradation is much faster at alkaline pH. The lowering of the degradation rate at high pH levels can be explained by the adsorption-desorption effect. It is also evident that the effect of photodegradation efficiency and decolourization reaction became faster when increased with an increase in the amount of photo catalyst was increased and the results indicated that initial rate of photodegradation increased with increase in catalyst dose up to an optimum loading, when the ZnO dosage was further increased, a shielding effect of excess particles occurred and resulted in a reduced performance. The enhancement of degradation efficiency of dyes with increasing light intensity was attributed to there being more light energy to be used for the photo catalytic degradation. The reduction in COD values and increase in CO<sub>2</sub> values indicates the photodegradation of treated dye solution. The reduction in the estimated COD value and increase in CO<sub>2</sub> value indicated the photodegradation of treated dye solution. A decrease in pH value and increase in conductivity of solution was observed with increase in the extent of mineralization. This has been concluded that heterogeneous photocatalysis can be used as an efficient and environmental friendly technique for effluent treatment of industrial wastewater containing organic compounds and dyes from textile industry.

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