



## USE OF ADVANCED OXIDATION TECHNOLOGY FOR REMOVAL OF AZURE B

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### ABSTRACT

Many of the researchers have used different methods for degradation of organic pollutants from effluents of various industries. Out of which, photocatalysis; a part of advanced oxidation technology is considered as a promising technology for waste water treatment. Azure B dye has been degraded using Well-dowson polyoxometalate, as a photocatalyst. Various rate affecting parameters have been studied. The degradation rate monitored spectrophotometrically, On the basis of observed data, a tentative mechanism has been proposed. The kinetic study of this system shows that this reaction follows pseudo-first order kinetics.

**Key words:** Advanced oxidation technology, Photocatalysis, Well-Dowson polyoxometalate, Azure B.

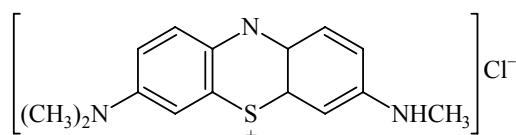
### INTRODUCTION

Water pollution is a major problem faced by everyone all over the globe. There is a pressing demand to search some eco-friendly methods, which may provide a solution to this problem. Although, there are many methods available for removal of various water pollutants, but these are associated with some or the other demerits. One of the most economical and ecofriendly methods is, however, the use of photocatalytic reactions. In last few years, Advanced Oxidation Processes (AOP's) like photocatalysis, photo-Fenton reaction, ozonation, sonolysis etc, have emerged as successful techniques in combating against the problem of environmental pollution. Applications based on AOP's in treatment of water has increased considerably during last twenty five years. The photocatalytic degradation 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. On excitation, semiconductor generates electron-hole pair, which may be used either for reduction or oxidation of the pollutants. Coloured 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 purposes. 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.<sup>1-3</sup> Photocatalytic degradation of cetylpyridinium chloride over TiO<sub>2</sub> has been reported by Singhal et al.<sup>4</sup> Similar photocatalytic reaction of xylydine ponceau and orange-G dyes by ZnO powder has been reported by Sharma et al.<sup>5</sup> Yoneyama et al.<sup>6</sup> studied the photocatalytic reduction of dichromate ions using WO<sub>3</sub> powder in acidic range. Photocatalytic degradation of brilliant red dye and textile waste water has been suggested by Martins et al.<sup>7</sup> Photocatalytic degradation of acid blue-62 over CuO/SnO<sub>2</sub> nanocomposite photocatalyst under simulated sunlight has been reported by Xia et al.<sup>8</sup> Photocatalytic degradation of azo dye acid readily in water using ZnO as photocatalytic has been investigated by Daneshvar et al.<sup>9</sup>

TiO<sub>2</sub> sol-gel deposited over glass and its application on the photocatalytic phenol degradation was reported by Colon et al.<sup>10</sup> whereas photodegradation of lignin from black liquor using a UV/TiO<sub>2</sub> system was investigated by Ksibi et al.<sup>11</sup> Morwetz and Selli<sup>12</sup> investigated the effect of iron species in photocatalytic degradation of azo dye in TiO<sub>2</sub> suspension. Photocatalytic water decontamination has been reported by Gelover et al.<sup>13</sup> Photo-induced transformation of some organophosphorous pesticides over TiO<sub>2</sub> was investigated by Calza et al.<sup>14</sup> Reddy et al.<sup>15</sup> showed the photocatalytic activity of Bi<sub>2</sub>O<sub>3</sub> for the treatment of phenolic wastes. Degradation of some dyes using zirconium phosphate photocatalyst have been studied by Panwar et al.<sup>16</sup> Photoreduction of Congo red by ascorbic acid and EDTA over cadmium sulphide as photocatalyst was carried out by Kothari et al.<sup>17</sup> Sharma et al.<sup>18</sup> used semiconducting bismuth sulfide as a photocatalyst for degradation of rose Bengal.

## EXPERIMENTAL



**Structure of Azure - B**

IUPAC Name : 3H-Phenothiazine, 3-(dimethylamino)-7-(methylimino) hydrochloride

Molecular formula : C<sub>15</sub>H<sub>16</sub>ClN<sub>3</sub>S

Molar mass : 305.83 g/mol

Solubility : Water

$\lambda_{\max}$  : 648-655 (650 nm)

0.3058 g of azure B was dissolved in 100.0 mL of doubly distilled water so that the concentration of dye solution was  $1.0 \times 10^{-3}$  M. It was used as a stock solution. This stock solution was further diluted.

The optical density of azure B solution was determined with the help of a spectrophotometer at  $\lambda_{\max} = 650$  nm. The dye solution was placed in equal amounts in four beakers.

- The first beaker was kept in dark, containing (50 mL) azure B solution.
- The second beaker was kept in light, containing (50 mL) azure B solution.

- The third beaker was kept in dark which contains (50 mL) azure B solution and 0.10 g nickel containing polytungstometalate.
- The fourth beaker was exposed to light, containing (50 mL) azure B solution and 0.10 g Nickel containing polytungstometalate.

After 3-4 hours, the optical density of the solution in each beaker was measured with the help of a spectrophotometer. It was noticed that the optical density of solutions of first three beakers remained almost same, while the solution of fourth beaker had a decrease in initial value of optical density. From this result, it is clear that this reaction requires presence of both; the light as well as semiconductor nickel containing polytungstometalate. Hence, this reaction is a photocatalytic reaction.

A solution of  $1.60 \times 10^{-5}$  M azure B was prepared in doubly distilled water and 0.10 g of nickel containing polytungstometalate was added to it. The pH of the reaction mixture was settled to 7.5 and then this solution was exposed to a 200 W tungsten lamp at  $50.0 \text{ mWcm}^{-2}$ . A decrease in optical density of azure B solution was observed with increasing time of exposure. A plot of  $1 + \log \text{O.D.}$  against time was found to be linear. The rate constant was measured with the following expression –

$$k = 2.303 \times \text{slope} \quad \dots(1)$$

A typical run has been presented in Table 1.

**Table 1: Typical run**

[Azure B] = $1.60 \times 10^{-4}$ M		
Semiconductor = 0.10 g		
Light Intensity = $50.0 \text{ mWcm}^{-2}$		
pH = 6.5		
Time (min.)	Optical Density (O. D.)	1 + log O. D.
0.0	0.333	0.5224
20.0	0.427	0.4698
40.0	0.350	0.3692
60.0	0.296	0.2872
80.0	0.239	0.2095
100.0	0.196	0.1271
120.0	0.169	0.1106
140.0	0.135	0.0755
160.0	0.110	0.0453
$k = 1.53 \times 10^{-4} \text{ sec}^{-1}$		

### Effect of pH

The pH of the solution may affect degradation rate of azure B and hence, the reaction rates were determined in the pH range 5.0-10.5. The results are reported in Table 2.

**Table 2: Effect of pH**[Azure B] =  $1.60 \times 10^{-5}$  M

Semiconductor = 0.10 g

Light Intensity =  $50.0 \text{ mWcm}^{-2}$ 

pH	$k \times 10^{-4} (\text{sec}^{-1})$
5.0	0.39
5.5	0.51
6.0	0.77
<b>6.5</b>	<b>1.53</b>
7.0	0.92
7.5	0.77
8.0	0.56
8.5	0.0
9.0	0.0
9.5	0.639
10.0	0.3838
10.5	0.38

It has been observed that the rate of photocatalytic degradation of azure B increases with increase in pH up to 6.5. On further increase in the pH resulted into a decrease in the rate of photocatalytic degradation.

An increase in the rate of photocatalytic degradation of azure B with increase in pH may be due to generation of more  $\cdot\text{OH}$  radicals, which are produced from the reaction between  $\text{OH}^-$  ions and hole ( $\text{h}^+$ ) of the semiconductor. On further increase in pH above 6.5, a decrease in the rate of photocatalytic bleaching of the dye may be due to the fact that azure B does not remain in its cationic form, and will not feel experience a force of attraction with negatively charged surface of the semiconductor (due to adsorption of more  $\text{OH}^-$  ions on the surface of photocatalyst) rather a repulsion.

### Effect of dye concentration

Effect of variation of dye concentration was also observed by taking different concentrations of azure B. The results are tabulated in Table 3.

**Table 3: Effect of azure b concentration**

pH = 6.5

Semiconductor = 0.10 g

Light Intensity =  $50.0 \text{ mWcm}^{-2}$ 

[Azure B] $\times 10^5$ M	$k \times 10^4 (\text{sec}^{-1})$
1.0	0.90
1.2	0.96
1.4	1.20
<b>1.6</b>	<b>1.53</b>



Semiconductor amount (g)	k x 10 <sup>4</sup> (sec <sup>-1</sup> )
0.14	1.50
0.16	1.53
0.18	0.52

### Effect of light intensity

To investigate the effect of light intensity on the photocatalytic bleaching of azure B, 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 201). The results are summarized in Table 5.

**Table 5: Effect of light intensity**

pH = 6.5

[Azure B] = 1.60 x 10<sup>-5</sup> M

Semiconductor = 0.10 g

Intensity of light (mWcm <sup>-2</sup> )	k x 10 <sup>4</sup> (sec <sup>-1</sup> )
20.0	0.39
30.0	0.64
40.0	0.77
<b>50.0</b>	<b>1.53</b>
60.0	1.47
70.0	1.42

The results indicate that degradation 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 per unit time. However, on increasing the intensity above 50.0 mWcm<sup>-2</sup>, there was a decrease in the rate. This may be due to some side reactions.

### Mechanism

On the basis of these observations, a tentative mechanism for photocatalytic degradation of azure B may be proposed as –



Azure B (AB) 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 dye. The involvement of triplet state was confirmed by using triplet state scavengers, where the reaction rate was almost negligible. On the other hand, the semiconducting nickel containing polytungstometalate (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<sup>-</sup> ions to generate •OH radicals. These radicals will oxidize the dye to its leuco form, which may ultimately degrade to products. The participation of •OH radicals as an active oxidizing species was confirmed by using hydroxyl radical scavenger isopropanol, where the rate of degradation was drastically reduced.

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