PHOTOCATALYTIC DEGRADATION OF AZURE B IN AQUEOUS SOLUTION BY CALCIUM OXIDE

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ABSTRACT

Photocatalytic degradation of Azure B has been carried out using calcium oxide semiconductor. Effect of various parameters like pH, concentration of dyes, amount of semiconductor and light intensity has been studied on the rate of reaction. Various control experiments were carried out, which indicated that semiconductor calcium oxide played a key role in photocatalytic degradation of dye. A suitable tentative mechanism has been proposed for photocatalytic degradation of dye.

Key words: Photocatalytic degradation, Azure B, Calcium oxide.

INTRODUCTION

The treatment of dye containing waste water by conventional methods, such as flocculation, activated carbon adsorption and reverse osmosis are quite ineffective in decolourization of wastewater since dye stuffs are recalcitrant and difficult to remove by these processes due to their low molecular weight and high water solubility. Moreover, these methods merely transfer the pollutant from one phase to another phase. Alternative biological treatment is difficult to control in order to achieve the desired degree of removal. Recently, there has been considerable interest in the utilization of advanced oxidation processes for the complete degradation of dyes used in textile industry.

Rao et al.[1] observed the photocatalytic bleaching of Crystal violet in aqueous suspension of zinc oxide. Photocatalytic transformation of Acid orange 20 and Cr (VI) in aqueous TiO_2 suspensions was studied by Papadam et al.[2] Zhao et al.[3] reported enhanced photocatalytic degradation of dye pollutants under visible irradiation on Al (III) modified TiO_2. Cheng et al.[4] reported visible light assisted degradation of dye pollutants over Fe (III) loaded resin in the presence of H_2O_2 at neutral pH values. The sunlight mediated photocatalytic degradation of Rhodamine B dye was studied by Byrappa et al.[5] Chem et al.[6] investigated photodegradation of dye pollutants catalyzed by porous $K_3PW_{12}O_{40}$ under visible irradiation. Mahmoodi et al.[7] used immobilized titanium dioxide nanoparticle for degradation and toxicity reduction of textile wastewater. Photocatalytic degradation of an azo dye Metanil yellow was carried out by Sleiman et al.[8] Photodegradation of squarylium cyanine dye under visible light irradiation was studied by Wu et al.[9]

Commercial textile azo dye were photocatalytically degraded by Mirkhani et al.[10] The photocatalytic degradation of Acid orange 7, a non-biodegradable azo-dye, has been investigated over TiO_2 photocatalysts by Kiriakidou et al.[11] Photocatalytic activity of TiO_2- In_2O_3 powders for the degradation of 2-chlorophenol in water was reported by Shchukin et al.[12] Pare et al.[13] investigated photocatalytic degradation of Methylene violet in aqueous heterogeneous suspension. Photoelectrocatalytic degradation of Rose Bengal has been carried out by Liu et al.[14] Photocatalytic degradation of Amaranth, an alimentary dye, was investigated by Karkmaz et al.[15] in an irradiated titanium dioxide aqueous suspension. Akpan and Hameed[16] studied the effect of operating parameters on the photocatalytic degradation of textile dyes using TiO_2 based photocatalysts. Photocatalytic degradation of azo dyes has been studied by Hustert and Zepp[17]. Zamora et al.[18] compared degradation of reactive dye among ozonation, enzymatic and photochemical process.

EXPERIMENTAL

Azure B dye was used as a model system to investigate the photocatalytic degradation by CaO. Molecular formula of Azure B is $C_{15}H_{16}ClN_3S$, and its molar mass is 305.83 g/mol. 1.0×10^{-3} M solution of Azure B (0.3058 g Azure B in 100.0 mL water) was prepared in volumetric flask with doubly distilled water and stored as a stock solution.
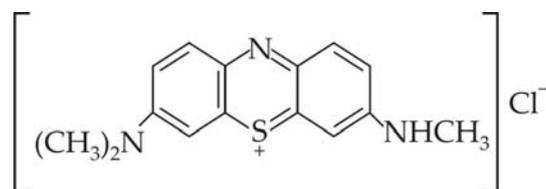
Structure of Azure B

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

(i) The first beaker containing only dye solution was kept in dark.

(ii) The second beaker containing only dye solution was kept in sunlight.

(iii) 0.30 g of semiconductor calcium oxide was added to the third beaker containing dye solution and was kept in dark, and

(iv) 0.30 g of semiconductor calcium oxide was added to the fourth beaker containing dye solution and was exposed to sunlight.

After 4 hours, the optical density of the solution in each beaker was measured with the help of a spectrophotometer. It was observed 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. The above experiments confirms that the reaction between Azure B and semiconductor powder is neither thermal nor photochemical but it is a photocatalytic reaction. The data for a typical run are presented in Table 1 and graphically presented in Fig. 1.

The photocatalytic degradation of Azure B was observed by taking dye solution of 2.5×10^{-5} M and 0.30 g of CaO. Irradiation was carried out keeping the whole assembly exposed to a 200 W tungsten lamp at 70.0 $mWcm^{-2}$. A decrease in optical density of Azure B solution was observed with increasing time of exposure. A plot of 2 + log O.D. against time was found to be linear. The rate constant was measured with the following expression k = 2.303 × slope.

Table 1: A typical run

pH = 6   [Azure B] = 2.50×10^{-5} M
Semiconductor = 0.30 g   Light intensity = 70.0 mWcm^{-2}
                                                                  Temperature = 298 K

Time (min.)	Optical density (O. D.)	2 + log O. D.
0.0	0.742	1.8704
10.0	0.536	1.7292
20.0	0.356	1.5514
30.0	0.248	1.3945
40.0	0.172	1.2355
50.0	0.120	1.0792
60.0	0.082	0.9138
70.0	0.057	0.7559

Rate constant (k) = 6.14×10^{-4} sec^{-1}
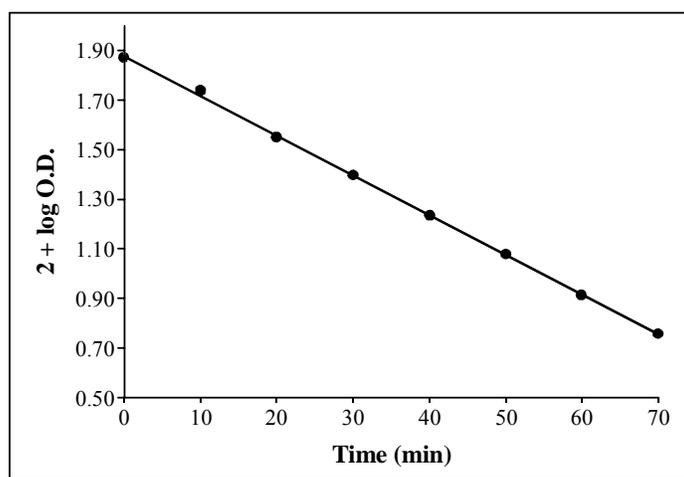
Fig. 1: A typical run

Effect of pH

The effect of pH on photocatalytic degradation was investigated in the range 3.0-8.0. The results are reported in Table 2.

Table 2: Effect of pH

[Azure B] = 2.0×10^{-5} M   Light intensity = 70.0 mWcm^{-2}
CaO = 0.30 g   Temp. = 298 K

pH	k × 10^4 (sec^{-1})
3.0	3.76
4.0	4.27
5.0	4.59
5.5	4.59

pH	$k \times 10^4$ (sec^{-1})
6.0	**6.14**
6.5	4.86
7.0	4.59
8.0	4.17

It is evident from the data that the degradation rate of Azure B increases with increasing pH of solution upto 6.0 and above this value of pH the rate of photocatalytic degradation of Azure B starts decreasing. It may be explained on the basis that at low pH, the anionic dye was attracted by positively charged surface of photocatalyst, but further increase in pH above 6.0, a decrease in the rate of photocatalytic degradation of the dye may be due to the fact that Azure B does not remain in its cationic form and will not experience a force of attraction with negatively charged surface of the semiconductor due to adsorption of more OH$^-$ ions on the surface of photocatalyst.
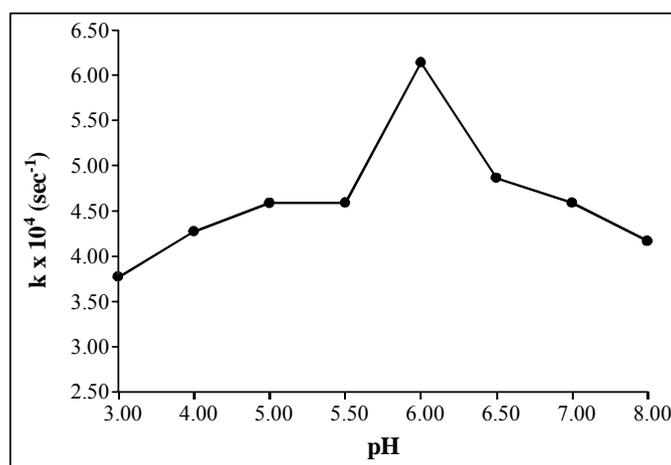
Fig. 2: Effect of pH

Effect of dye concentration

The effect of dye concentration on the rate of reaction was also observed by using different concentration of the Azure B solution. The results are given in Table 3.

Table 3: Effect of dye concentration

pH = 6	Light Intensity = 70.0 mWcm^{-2}
Semiconductor = 0.30 g	Temp. = 298 K

[Azure B] x 10^5 M	$k \times 10^4$ (sec^{-1})
0.50	2.98
1.00	3.67
1.50	4.68
2.00	5.31
2.50	**6.14**
3.00	5.69
3.50	4.29
4.00	4.24

It was observed that the rate of photocatalytic degradation increase in the concentration of the dye upto 2.5×10^{-5} M. It may be due to fact that as the dye was increased, more dye molecules were available for excitation and consecutive degradation. Hence, an increase in the rate was observed. The rate of photocatalytic degradation was found to decrease with further increase in the concentration of dye. This may be attributed to the fact that the dye started acting as a filter for the incident light and it does not permit the desired light intensity to reach the photocatalyst surface; thus, a decrease in the rate of photocatalytic degradation was observed.
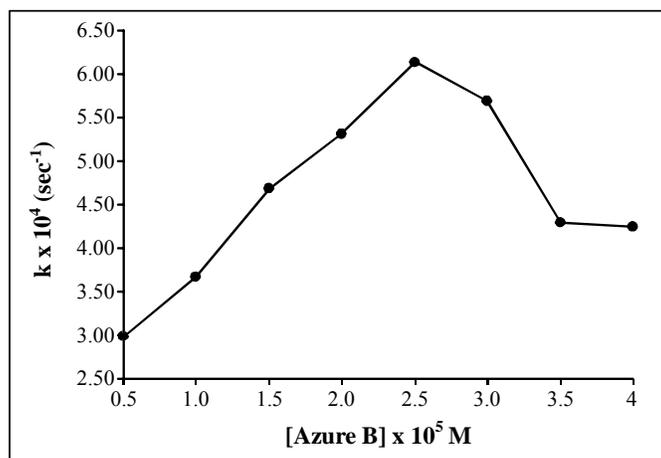
Fig. 3: Effect of dye concentration

Effect of amount of semiconductor

The effect of amount of semiconductor on the rate of photocatalytic degradation of Azure B was also observed. The results are reported in Table 4.

Table 4: Effect of amount of semiconductor

[Azure B] = 2.50×10^{-5} M   pH = 6.0
Light intensity = 70.0 mWcm^{-2} Temp. = 298 K

Amount of semiconductor (g)	$k \times 10^4$ (sec^{-1})
0.10	3.57
0.20	5.45
0.30	**6.14**
0.40	5.62
0.50	5.41
0.60	5.41
0.70	5.28
0.80	5.28

It was observed that the rate of reaction increases with increase in the amount of semiconductor upto 0.30 g and beyond 0.30 g, the rate of reaction becomes almost constant; however, there is a slight decrease. This may be due to the fact that as the amount of semiconductor was increased in the initial state, the exposed surface area of the semiconductor also increases but after this limiting value (0.30 g) any increase in the amount of semiconductor will not increase the exposed surface area but only the thickness of the semiconductor layer. This was also confirmed by using reaction vessels of different dimensions.
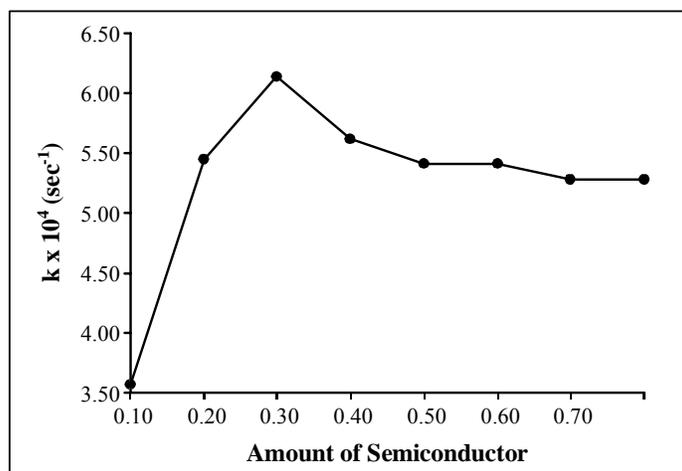
Fig. 4: Effect of amount of semiconductor

Effect of light intensity

The effect of light intensity on the rate of Azure B was also observed. The results are reported in Table 5.

Table 5: Effect of light intensity

[Azure B] = 2.50×10^{-5} M	pH = 6.0
Semiconductor = 0.30 g	Temp. = 298 K

Light intensity (mWcm^{-2})	$k \times 10^4$ (sec^{-1})
20.0	3.50
30.0	3.94
40.0	4.67
50.0	5.70
60.0	5.84
70.0	**6.14**
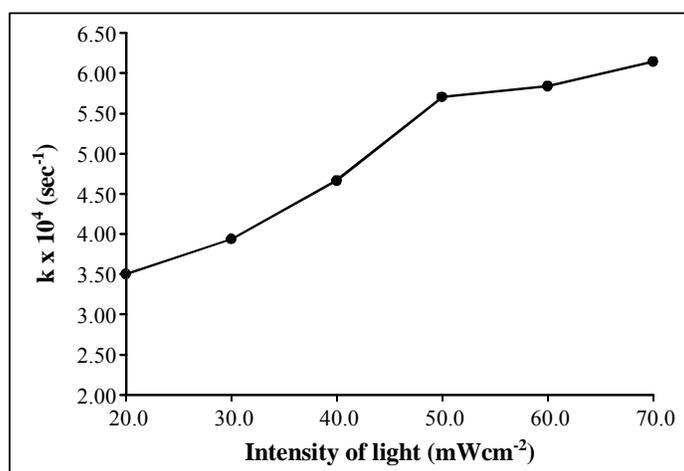
Fig. 5: Effect of light intensity

The data indicate that the degradation action was accelerated as the intensity of light was increased, because any increase in the light intensity increases the number of photons striking per unit time per unit area of the photocatalyst powder. An almost linear behaviour between light intensity and the rate of reaction was observed. However, higher intensities were avoided due to thermal effects.

Tentative mechanism of Azure B photodegradation

On the basis of our experimental observations, a tentative mechanism for photocatalytic degradation of Azure B may be proposed as -

$$^1Dye_0 \xrightarrow{\ h\nu\ } \ ^1Dye_1^* \qquad\qquad ....(1)$$

$$^1Dye_1^* \xrightarrow{\ ISC\ } \ ^3Dye_1^* \qquad\qquad ....(2)$$

$$CaO \xrightarrow{\ h\nu\ } CaO\,[h^+\,(VB) + e^-\,(CB)] \qquad\qquad ....(3)$$

$$OH^- + CaO\,(h^+) \longrightarrow \ ^\bullet OH + CaO \qquad\qquad ....(4)$$

$$^3Dye_1 + \ ^\bullet OH \longrightarrow Products \qquad\qquad ....(5)$$
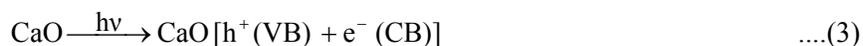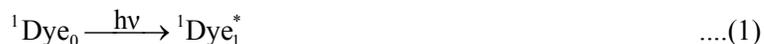
When the solution of the dye was exposed to light in presence of CaO, the $^1Dye_0$ molecules are excited to first excited singlet state ($^1Dye_1^*$). Then these excited molecules are transferred to the triplet state through intersystem crossing (ISC). On the other hand, the semiconductor CaO also absorbs photons and as a result electron-hole pair is generated. The OH^- will react with hole of the semiconductor to generate $^\bullet OH$ radicals and these radicals will convert the dye molecules into products, which are colourless. The participation of $^\bullet OH$ radicals as an active oxidizing species was confirmed by carrying out the reaction in presence of some hydroxyl radical scavengers like 2-propanol, where the rate of degradation was drastically reduced.

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