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PHOTOCATALYTIC DEGRADATION OF AZURE-B IN AQUEOUS SOLUTION USING MANGANESE DIOXIDE AS PHOTOCATALYST

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ABSTRACT

The photocatalytic degradation of aqueous solution of azure-B over manganese dioxide has been carried out. The photocatalytic reaction has been studied spectrophotometrically by observing absorbance at different time intervals. The effect of variation of various parameters such as concentration of azure-B, pH, amount of semiconductor and intensity of light on the rate of reaction has been observed. The photocatalytic degradation of azure-B follows first order kinetics.

A tentative mechanism for the reaction has been proposed.

Key words: Photocatalysis, Photocatalytic degradation, Azure-B, Semiconductor, Manganese dioxide.

INTRODUCTION

One of the most essential parts of life is clean water and addition of any undesired chemical substance to it leads to contamination and as a result, it becomes unfit for the use by human and animal beings. Dye effluents of various textile and paper industries are one of the important pollutants. In this era of rapid industrialization, the problem of degradation of pollutants has become vary serious from ecological point of view. Textiles, tannery, paper, pulp and printing industries are the biggest sources of polluting the environment.[1, 2] the effluents of these industries are highly coloured, toxic and complex in nature. These may have adverse, sometimes irreversible effects on animals and plants, as well.

However, researchers are now directed towards assessing the extent of dye pollution[3-5] and finding some better methods for waste water treatment. The photocatalytic

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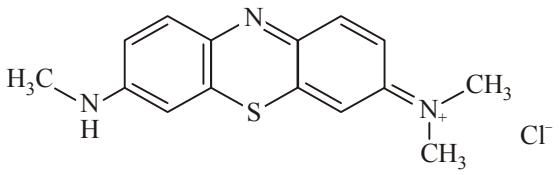
degradation provides a promising solution to this problem.

Number of attempts have been made by various researchers to degrade different dyes photochemiclly. Chen and Chou[6], Sharma et al.[7,8] Papadam et al.[9] and Tang et al.[10] have studied the photocatalytic degradation of dyes using aqueous TiO_2 suspensions.

Azure-B is used as a dye for dyeing wood, silk, paper and in inks. It is also used as a biological stain. This dye is known to be a carcinogen, so removal of azure-B is of great importance. In the present study, photocatalytic degradation of azure-B over MnO_2 semiconductor has been carried out.



EXPERIMENTAL

Azure-B (chroma) and MnO_2 (Merck) were used. The photocatalytic reaction of azure-B was observed by taking 40 mL of dye solution (3.0×10^{-5} M) and 0.1 g of MnO_2 powder. The desired pH of the solution was measured by a digital pH Meter (MAC 552 Model). The desired pH of the solution was adjusted by previously standardized H_2SO_4 (for acidic range) or NaOH (for basic range). The solution was irradiated using a 200 W tungsten lamp (Bajaj). The intensity of light was measured by Suryamapi (CEL Model SM 201). Water filter was used to cut off thermal radiations. The optical density or absorbance was measured by a U.V.Visible spectrophotometer (Systronics Model 106).

RESULTS AND DISCUSSION

The photocatalytic degradation of azure-B was observed spectrophotometrically at λ max = 650 nm. The results for a typical run are given in Table 1 and graphically represented in Fig. 1.

It was observed that absorbance decreases with increasing time of irradiation indicating that azure-B is degraded (bleached) on exposure to light. The rate constant for this reaction was determined using the expression -

Rate constant (k) = 2.303 × Slope …(1)

Table 1: Photocatalytic degradation of azure-B : A typical run

[Azure-B] = 3.0×10^{-5}M Manganese dioxide = 0.13 g
Temperature = 303 K pH = 9.5
Light intensity = 50.0 mWcm^{-2}

Time (sec.)	Optical density	1 + log O. D.
0.0	1.487	1.172
300	1.252	1.097
600	0.968	0.985
900	0.757	0.879
1200	0.625	0.795
1500	0.467	0.669
1800	0.344	0.536
2100	0.267	0.426

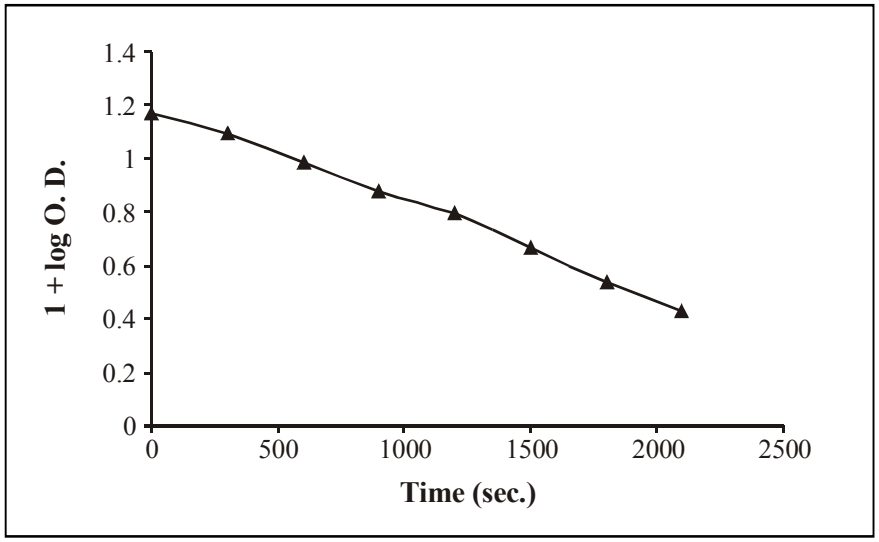


Fig. 1: A typical run

Effect of pH variation

The effect of pH on the rate of photocatalytic reaction was investigated in the pH range 8.0 to 11.5. The results are reported in Table 2.

Table 2: Effect of variation of pH

[Azure-B] = 3.0×10^{-5}M	Manganese dioxide = 0.13 g
Temperature = 303 K	Light intensity = 50.0 mWcm^{-2}
pH	**Rate constant k x 10^4 (sec^{-1})**
8.0	3.90
8.5	4.55
9.0	5.42
9.5	6.52
10.0	6.12
10.5	5.74
11.0	4.90
11.5	3.75

It is evident from the data that the rate of photocatalytic degradation of azure-B increases with increase in pH. This increase in rate of reaction may be due to the more availability of OH^- ions at higher pH values. These OH^- ions will generate more $^{\bullet}OH$ radicals by combining with holes. These hydroxide radicals are responsible for photocatalytic degradation,. But after a certain value of pH (pH = 9.5), a further increase in the pH of medium, decreases the rate of photocatalytic degradation. It may be due to the fact that the dye does not remain in its cationic form due to greater concentration of OH^- ion and as such, the reaction rate decreases.

Azure-b concentration

Effect of variation of azure-B concentration on the rate of its photocatalytic degradation was studied by taking different concentration of azure-B. The results are reported in Table 3.

It was observed that as the concentration of azure-B was increased, the rate of reaction increases and at high concentrations, a decrease in rate of reaction was observed.

This can be explained by the fact that at larger concentrations of dye will start acting like a filter for incident light and at higher concentrations, it will not permit the desired light intensity to reach the manganese dioxide particles.

Table 3: Effect of azure – B concentration

Manganese dioxide = 0.13 Temperature = 303 K	pH = 9.5 Light Intensity = 50.0 $mWcm^{-2}$
[Azure-B] $\times 10^5$M	**Rate constant k x 10^4 (sec^{-1})**
2.00	4.91
2.25	4.91
2.50	5.24
2.75	5.70
3.00	6.52
3.25	6.21
3.50	5.93
3.75	5.02

Effect of amount of semiconductor

Keeping all the factors identical, the effect of amount of semiconductor on the rate of photocatalytic reaction was observed and the results are reported in Table 4.

Table 4: Effect of amount of semiconductor

[Azure-B] = 3.0×10^{-5}M Temperature = 303 K	pH = 9.5 Light Intensity = 50.0 $mWcm^{-2}$
Amount of semiconductor (g)	**Rate constant k x 10^4 (sec^{-1})**
0.10	4.90
0.11	4.98
0.12	5.21
0.13	6.52

Cont..

Amount of semiconductor (g)	Rate constant k x 10^4 (sec^{-1})
0.14	6.43
0.15	5.94
0.16	5.23
0.17	4.92

As indicated from the above data, with an increase in the amount of semiconductor, the rate of photocatalytic reaction increases to a certain amount of semiconductor i.e. saturation point. This can be explained on the basis that with the increase in the amount of semiconductor, the exposed surface area of semiconductor will increase and hence, the rise in rate of reaction has been observed. But after a certain limiting amount of semiconductor, if the amount of semiconductor was further increased, it will increase only the thickness of the layer of semiconductor powder at the bottom of the reaction vessel and thus, saturation point is reached.

Table 5: Effect of light intensity

The effect of light intensity on the rate of photocatalytic reaction of dye was also observed and the results are reported in Table 5.

[Azure-B] = 3.0×10^{-5}M Manganese dioxide = 0.13 g
Temperature = 303 K pH = 9.5

Light intensity ($mWcm^{-2}$)	Rate constant k x 10^4 (sec^{-1})
10.0	2.31
20.0	3.20
30.0	4.47
40.0	5.59
50.0	6.52
60.0	6.13

The results indicate that the rate of photocatalytic degradation of azure-B increases as the intensity of light was increased. This can be explained on the basis that more photons will be available for excitation on increasing the intensity of light and therefore, more

electron-hole pairs will be generated in the semiconductor, resulting in an increase in the rate of reaction.

MECHANISM

On the basis of the observed data, the following tentative mechanism has been proposed for photocatalytic bleaching of azure-B.

$$(Dye)_0 \xrightarrow{h\nu} {}^1(Dye) \quad \text{Singlet excited state} \qquad \ldots(2)$$

$${}^1(Dye) \xrightarrow{ISC} {}^3(Dye) \quad \text{Triplet excited state} \qquad \ldots(3)$$

$$SC \longrightarrow e^- (CB) + h^+ (VB) \qquad \ldots(4)$$

$$h^+ + OH^- \longrightarrow {}^\bullet OH \qquad \ldots(5)$$

$${}^3(Dye) + {}^\bullet OH \longrightarrow \text{Products.} \qquad \ldots(6)$$

Dyes absorb light radiation of suitable wave length and goes to excited singlet state. It then undergoes inter system crossing (ISC) to give the triplet state of dye. The semiconducting manganese dioxide also utilises the radiant energy to excite its electron from valence band to conduction band; thus, leaving behind a hole.

The hole abstracts an electron from OH^- ion generating $^\bullet OH$ radical. Now the excited dyes are oxidised by $^\bullet OH$ free radicals to give the product. The participation of $^\bullet OH$ radical was confirmed by use of scavenger isopropanol, which stops the bleaching reaction almost completely.

CONCLUSION

Manganese dioxide can be used as an effective semiconductor for photodegradation of azure-B dye.

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