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Photocatalytic reactions of bromocresol purple on semiconductor zinc oxide powder

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Abstract
The photo catalytic reaction of bromo cresol purple on zinc oxide powder was carried out. Photocatalytic bleaching of the dye was observed spectrophotometrically. The effects of the variation of various parameter such as the concentration of bromocresol purple, pH, amount and particle size of semiconductor and light intensity on the rate of photocatalytic bleaching were observed. A tentative mechanism for the reaction has been proposed.

Keywords: Photocatalytic reactions, bromocresol purple, semiconductor, zinc oxide

Introduction
Dyes are commercially important chemicals and frequently used in dying, printing, textile, photography, food and cosmetic industries [1-3]. Some of these dyes are toxic and contamination of aquatic environment by these dyes is a serious problem. Photocatalysis can also provide a promising solution to this problem. A number of attempts have been made by Brown and Darwent [4] Chen and Chao [5] and Sharma *et al.* [6] to degrade a few dyes photocatalytically. Rao *et al.* [7] reported photo catalytic degradation of crystal violet, a triphenylmethane dye over semiconductor zinc oxide powder suspended in aqueous solution. Feng *et al.* [8] applied semiconductor photocatalysis for removal of dyes from aqueous solution. The photo catalytic reactions of dyes have been used in laser passive Q- switches [9-12].

Experimental Detail
Reagents of analytical grade were used without further purification. 0.0562 gram of bromocresol purple was dissolved in 1000 ml of double distilled water, to get a solution of 1.0×10^{-4} M. It was used as a stock solution
Photocatalytic bleaching of bromo cresol purple was studied by taking 100 ml of solution and 0.50 gram of ZnO powder as semiconductor. The reaction mixture was exposed to light. (Light intensity=40mW cm). A water filter was used to cut off thermal radiations. The optical density was measured by a UV visible spectrophotometer (sytronics model 108). The necessary condition for the correct measurement of the optical density is that the solution must be free from semiconductor particles. A G-3 sintered glass crucible was used for filtration to obtain the desired accuracy in the measurement of the absorbance of the dye solution, and absorption maximum of the dye was determined by a UV-visible recording spectrophotometer.

Results and Discussion
The photo catalytic bleaching of bromo cresol purple was observed spectrophotometrically at absorption maxima 585 n. m. The results for typical run are given in Table 1

Table 1: A Typical Run

Time (minutes)	Optical Density (O. D.)	2+log O. D.
0.0	0.490	1.6902
30.0	0.470	1.6721
60.0	0.445	1.6483
90.0	0.425	1.6284
120.0	0.410	1.6120
150.0	0.385	1.5854
180.0	0.370	1.5682

[Bromocresol purple] = 2.0 x 10^{-5} M Light Intesity = 40 mW cm^{-2}
Temperature = 303K pH = 7.0 Zinc oxide =0.50g

It was observed that optical density decreases with time of irradiation indicating that bromocresol purple is degraded on exposure to light. The rate constant for this reaction was determined using the expression,

Rate constant (k) = 2.303 × slop

Effect of [bromocresol purple] variation

Effect of variation of bromocresol purple concentration on the rate of its photo catalytic bleaching was studied by taking different concentration of bromocresol purple. The results obtained are represented in Table 2

Table 2: Effect of [bromocresol purple] variation

[bromocresol purple] x 10^5M	Rate constant k x 10^5 (sec^{-1})	6 + log k (sec^{-1})
1.00	3.85	1.5854
1.5	3.20	1.5051
2.0	2.70	1.4313
2.5	2.25	1.3521
3.0	1.85	1.2671
3.5	1.60	1.2071
4.0	1.35	1.1303

Light Intesity = 40 mW cm^{-2} pH = 7.0 Temperature = 303K Zinc oxide =0.50g

It is evident from the Table 2 that as the concentration of bromocresol purple increases, rate of photocatalytic bleaching of the dye decreases. It can be explained on the basis of results obtained that as the concentration of dye was increased it will start acting like a filter for the incident light and its larger concentration will not permit the desired light to reach the zinc oxide particles and the results into a decrease in the rate of photo catalytic bleaching of bromocresol purple.

Effect of variation of pH

The effect of pH on the rate of photo catalytic reaction was investigated in pH range 6.5 to 10.0. The value of pH was varied by the addition of HCl(for acidic range) and NaOH (for basic range) to the dye solution. Results are presented in Table 3.

Table 3: Effect of variation of pH

pH	Rate constant k x 10^5 (sec^{-1})	5 + log k (sec^{-1})
6.5	3.09	0.4900
7.0	2.70	0.4313
7.5	2.40	0.3802
8.0	2.14	0.3304
8.5	1.91	0.2810
9.0	1.63	0.2122
9.5	1.45	0.1614
10.0	1.30	0.1139

[bromocresol purple] = 2.0 x 10^{-5} M Light Intesity = 40 mW cm^{-2}
Temperature = 303K Zinc oxide =0.50g

It has been observed that rate of photo catalytic bleaching of bromocresol purple decreases on increasing pH above 6.0. This observation can be better explained on the basis that on increasing pH beyond 7.0, the concentration of OH^- ions will also increase. The nature of dye being anionic, there is less probability of the interaction between $OH^-$and the dye due to electrostatic force of repulsion. This force of repulsion will not permit the dye molecule to come in close contact of semiconductor surface which is negatively charged in solutions having pH greater than 7.0 as a consequence the rate of bleaching decreases at higher pH.

Effect of variation of amount of semiconductor

Keeping all the other factors identical the effect of amount of semiconductor was observed. Results are tabulated in Table 4.

Table 4: Effect of variation of amount of semiconductor

Amount of semiconductor (g)	Rate constant k x 10^4 (sec^{-1})
0.1	0.90
0.2	1.40
0.3	1.91
0.4	2.30
0.5	2.70
0.6	3.15
0.7	3.35
0.8	3.35
0.9	3.35

[bromocresol purple] = 2.0 x 10^{-5} M Light Intesity = 40 mW cm^{-2}
Temperature = 303K pH = 7.0

Rate of photo catalytic bleaching of bromocresol purple increases with increase in the amount of semiconductor, but after a certain amount rate becomes almost constant,it may be considered like a saturation point. This may be attributed to the exposed surface area of the semiconductor initially the increase in the amount of semiconductor will increase the surface area but after saturation point any further addition will not increase surface area rather it will increase only the thickness of the layer of the semiconductor at the bottom of reaction vessel.

Effect of variation of light intensity

To observe the effect of light intensity on the photo catalytic reaction of bromocresol purple, light sources of different wattage were used, and the distance between the light source and exposed surface was also varied. The results obtained are shown in Table 5.

Table 5: Effect of variation of light intensity

Light Intesity (mW cm^{-2})	Rate constant k x 10^5 (sec^{-1})
10.0	0.65
20.0	1.35
30.0	2.10
40.0	2.70
50.0	3.02
60.0	3.19

[bromocresol purple] = 2.0 x 10^{-5} M pH = 7.0
Temperature = 303K Zinc oxide =0.50g

The results indicate that bleaching action is accelerated as the intensity of light was increased. This maybe explain 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 thus resulting into enhanced rate of reaction.

Effect of nature of semiconductor

The photo catalytic bleaching of bromocresol purple has been carried out with semiconductors of different band gapes which is Fe_2O_3, CdS, WO_3 and ZnO The results are reported in table 6.

Table 6: Effect of nature of semiconductor

Semiconductor	Band gap	Rate constant k x 10^5 (sec^{-1})
Fe_2O_3	2.2	0
CdS	2.4	0
WO_3	2.6	10.30
ZnO	3.2	2.70

[Bromocresol purple] = 2.0 x 10^{-5} M Light Intesity = 40 mW cm^{-2}
Temperature = 303K pH = 7.0 Zinc oxide =0.50g

It has been observed that rate of photocatalytic bleaching of bromo cresol purple follows the following order.

Fe_2O_3 = CdS< WO_3 >ZnO

There is no photo catalytic bleaching of bromo cresol purple was observed in presence of Fe_2O_3, and CdS. It means band gap is not the only factor deciding photo catalytic bleaching

Mechanism

On the basis of observed data the following tentative mechanism may be proposed as follows.

In the initial step the semiconductor SC will be excited to give SC*, which will provide the electron –hole pair. The electron present in the conduction band will be utilised for reducing the dye to its leuco form. This leuco form may further degrade to volatile or gaseous products.

SC----------→ SC*
SC* --------→ SC(h+) + e-
e- + bromocresol purple ----→ Leuco [bromocresol purple]
Leuco [bromocresol purple] ---→ Products

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