Photocatalytic bleaching of malachite green and brilliant green dyes using ZnS-CdS as semiconductor: A comparative study

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ABSTRACT

ZnS-CdS catalysed photocatalytic bleaching of malachite green and brilliant green dyes has been investigated. The effect of various parameters, such as the pH, concentration of dyes, effect of amount of semiconductor and effect of light intensity etc. were observed and discussed. The progress of the photochemical oxidation was monitored spectrophotometrically. The optimum reaction conditions were experimentally determined. The photochemical oxidation of dyes follows pseudo – first kinetics. The final products of degradation were characterized and a tentative mechanism was proposed for the photochemical oxidation of dyes.

Key words: Photocatalytic bleaching, ZnS-CdS, malachite green and brilliant green
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INTRODUCTION

As we stepped into the twenty-first century, we are facing the challenge of purification of water and air resources. On one hand, we are enjoying the comforts and benefits that chemistry has provided to us, e.g. from drugs to dyes, from composites to computer chips, etc. On the other hand, we are facing with the problem of proper disposal of various products and byproducts of dye industries.Inspite of many uses, the dyes are toxic and carcinogenic in nature and environmental contamination by these toxic chemicals is emerging as a serious global problem. 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 purpose. The photocatalytic bleaching seems to be quite promising and can provide a low cost method to solve

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this problem. The field of photocatalysis has been excellently reviewed by Ameta *et al.*[1, 2]. Photocatalytic degradation of cetylpyridinium chloride over TiO_2 has been reported by Singhal *et al.*[3]. Similar photocatalytic reaction of xylidine ponceau and orange-G dyes by ZnO powder has been reported by Sharma *et al.*[4]. Yoneyama *et al.*[5] studied the photocatalytic reduction of dichromate ions using WO_3 powder in acidic range. Costa *et al.*[6] proposed the mechanism of gas phase degradation of cyclohexanol and methylcyclohexanol catalyzed by niobyum pentaoxide and phosphite. Shyama and Arakawa[7] have used zirconium dioxide as photocatalyst. A composite system of polycrystalline ZnO/TiO_2 and its photocatalytic activity was studied by Marci *et al.*[8]. TiO2 sol-gel deposited over glass and its application as a effect of TiO_2 acidic pre-treatment on the photocatalytic phenol degradation was reported by Colon *et al.*[11] whereas photodegradation of lignin from black liquor using a UV/TiO_2 system was investigated by Ksibi *et al.*[12]. Enhanced efficiency of unsymmetrical versus symmetrical squaraine dyes sensitized nanocrystalline TiO_2 was reported by Alex *et al.*[13]. Morwetz and Selli[14] investigated the effect of iron species in photocatalytic degradation of azo dye in TiO_2 suspension. photocatalyst for water decontamination has been reported by Gelover *et al.*[9]. Kako *et al.*[10] suggested some preventive methods against catalytic poisoning of TiO_2 photocatalyst by H_2S. The Kim *et al.*[15] used ZnO coated TiO2 nanoparticles for the flexible dye-sensitized solar cells. Photocatalytic degradation of brilliant red dye and textile waste water has been suggested by Martins *et al.*[16]. Photocatalytic degradation of acid blue-62 over $CuO-SnO_2$ nanocomposite photocatalyst under simulated sunlight has been reported by Xia *et al.*[17]. Bleaching of some dyes using zirconium phosphate photocatalyst have been studied by Panwar *et al.*[18].The photocatalytic bleaching of malachite green and brilliant green dyes in presence of ZnS-CdS photocatalyst is being reported in the present investigation.

MATERIALS AND METHODS

Malachite green (Hi media) and Brilliant (Hi media), ZnS-CdS were used in the present investigations. The dyes solution of malachite green and brilliant green were prepared in doubly distilled water. The photocatalysed oxidation of dyes were studied in the presence of ZnS-CdS, 2.0×10^{-3} M and 1.0×10^{-3} M, respectively for azure-B and erythrosine solutions were prepared by dissolving 0.0456g and 0.120 g, respectively of the dyes in 250.0 ml of doubly distilled water. The absorption maximum of the dye was determined with the help of a spectrophotometer (Systronics type). It was found to be 620 nm and 625 nm, respectively for malachite green and brilliant green

Photochemical degradation of malachite green was studied by taking 50.0 mL reaction mixture which contains 4.0×10^{-6} M of malachite green and 0.12 g of ZnS-CdS. It was exposed to light of 37.0 mWcm^{-2} intensity. The pH was maintained at 4.0.

Similarly, photochemical degradation of brilliant green was studied by taking 50.0 mL reaction mixture which contains 2.0×10^{-6} M of azure–B, 0.06 g of ZnS-CdS. It was exposed to light of 37.0 mWcm ^{2} intensity. The pH was maintained at 4.0.

A 200 W tungsten lamp (Philips) was used for irradiation purpose. The intensity of light was measured by Suryamapi (CEL Model 201). A water filter was used to cut off thermal radiation. The pH of the solution was measured by a digital pH meter (Systronics Model). The desired pH

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of the solution was adjusted by the addition of previously standardized sulphuric and sodium hydroxide solutions.

RESULTS AND DISCUSSION

An aliquot of 2.0 mL was taken out from the reaction mixture at regular time intervals and absorbance was measured spectrophotometrically at $\lambda_{max} = 620$ nm and 625 nm, respectively. It was observed that the absorbance of the solution decreases with increasing time intervals showing thereby that the concentration of the dyes decreases with increasing time of exposure. A plot of 1 + log A versus time was linear and follows pseudo-first order kinetics. The rate constant was measured by following expression:

$$k = 2.303 \times \text{Slope}$$

The results for typical run are given in Table I.

Table – I: A Typical Run

| Malachite green [Malachite green] = 4.0 x 10^{-6} M Light intensity = 37.0 mW cm^{-2} pH = 4.0 ZnS-CdS= 0.12 g		Brilliant green [Brilliant green] = 2.0 x 10^{-6} M Light intensity = 37.0 mW cm^{-2} pH = 4.0 ZnS-CdS= 0.06 g	
Time (min.)	**1 + log A**	**Time (min.)**	**1 + log A**
0.0	0.500	0.0	0.441
10.0	0.472	30.0	0.431
20.0	0.451	60.0	0.420
30.0	0.426	90.0	0.412
40.0	0.404	120.0	0.402
50.0	0.380	150.0	0.392
60.0	0.355	180.0	0.385
70.0	0.321	_	_
80.0	0.315	_	_
	k = 9.96 x 10^{-5} s^{-1}		**k = 1.10 x 10^{-5} s^{-1}**

Table – II: Effect of pH

Malachite green [Malachite green] = 4.0 x 10^{-6} M Light intensity = 37.0 mW cm^{-2} ZnS-CdS = 0.12		Brilliant green [Brilliant green] = 2.0 x 10^{-6} M Light intensity = 37.0 mW cm^{-2} ZnS-CdS= 0.06 g	
pH	**k x 10^5 s^{-1}**	**pH**	**k x 10^5 s^{-1}**
3.5	8.42	3.0	0.06
4.0	**9.96**	3.5	0.91
4.5	8.21	**4.0**	**1.10**
5.0	7.32	4.5	0.91
5.5	7.01	5.0	0.81
6.0	6.83	5.5	0.52
_	_	6.0	0.13

Effect of pH: The pH of the solution is likely to affect the degradation of malachite green and brilliant green and hence, the effect of pH on the rates of degradation of these dyes was

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investigated in the pH range 3.5 to 6.0 and 3.0 to 6.0, respectively. The results are reported in Table II.

It has been observed that the rate of bleaching increases with increase in pH of the solutions upto 4.0 for both the dyes i.e. malachite green and brilliant green. The effect of pH on rate is that at a higher (pH = > 4.0) the semiconductor surface is slightly negatively charged and so the anionic dye molecule will experience a force of repulsion causing a decrease in the rate of the reaction. On the other hand at lower pH (4.0) the surface of the semiconductor becomes slightly positively charged and the dye molecules may become protonated causing a force of repulsion between the surface of semiconductor and the protonated dye molecules. This will also retard the rate of the reaction.

It is established that surface properties of semiconductor are responsible for photocatalytic process. The hole generated by semiconductor creates H^+ ions in the solution from water. These protons are utilized by dissolved oxygen in solution.

$$2h^+ + H_2O \longrightarrow \frac{1}{2}O_2 + 2H^+$$

$$2H^+ + O_2 + 2e^- \longrightarrow H_2O_2$$
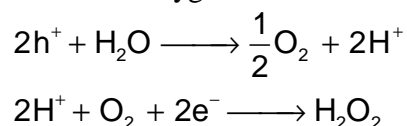
These two reactions counter balance each other to a particular extent. The surface charge on the semiconductor-electrolyte interface will plays a major role in deciding the fate of this photocatalytic reaction. The surface charge on semiconductor favours the reaction when it is positive. The surface charge depends on the pH of the solution being positive in acidic media and negative in alkaline media. After a particular pH net charge on semiconductor surface becomes zero and is called point of zero discharge (pzc).

Effect of dye concentration: The effect of dye concentration on the rate of the reaction of photochemical bleaching was studied by taking different concentration of dyes. The results are reported in Table III.

Table – III: Effect of dye concentration

Malachite green pH = 4.0 Light intensity = 37.0 mW cm^{-2} ZnS-CdS= 0.12 g		Brilliant green pH = 4.0 Light intensity = 37.0 mW cm^{-2} ZnS-CdS= 0.06 g	
[Malachite green] $\times 10^6$ M	k x 10^5 s^{-1}	[Brilliant green] $\times 10^6$ M	k x 10^5 s^{-1}
0.8	7.82	1.0	0.43
1.0	8.11	**2.0**	**1.10**
2.0	8.42	4.0	0.53
4.0	**9.96**	6.0	0.42
6.0	8.02	8.0	0.47
8.0	7.88	10.0	0.41

It has been observed that the rate of bleaching increases with the increase in concentration of the dye upto 4.0×10^{-6} M and 2.0×10^{-6} M for malachite green and brilliant green, respectively. On the further increase in the concentration of dyes, the rate of photochemical bleaching decreases.

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This is probably due to the fact that after certain limits of dye concentration, the dye molecules present in the upper layer of the solution will absorb a major portion of light. This will prevent the incident light to reach the dye molecule in the bulk of the solution. The high concentration of dye will act as a filter for the incident light and hence, at higher concentration of the dyes, the rate of bleaching decrease.

Effect of amount of ZnS-CdS: The amount of ZnS-CdS is also likely to affect the rate of photochemical degradation of dyes and therefore, different amount of ZnS-CdS were used. The results are reported in Table IV.

Table – IV: Effect of amount of ZnS-CdS

Malachite green [Malachite green] = 4.0×10^{-6} M Light intensity = 37.0 mW cm^{-2} pH = 4.0		Brilliant green [Brilliant green] = 4.0×10^{-6} M Light intensity = 37.0 mW cm^{-2} pH = 4.0	
ZnS-CdS (g)	**k x 10^5 s^{-1}**	**ZnS-CdS (g)**	**k x 10^5 s^{-1}**
0.06	8.00	0.04	1.04
0.08	8.61	**0.06**	**1.10**
0.10	9.22	0.08	0.56
0.12	**9.96**	0.10	0.59
0.14	9.52	0.12	0.51
0.16	9.01	0.14	0.59

It has been observed that on increasing the amount of ZnS-CdS upto 0.12 g and 0.06 g for malachite green and brilliant green, respectively; the bleaching of malachite green and brilliant green also increases. Increase in bleaching rate with increase in amount of semiconductor is due to more surface area available of semiconductor to catch hold the light and generate the excited states. On the further increase in amount, a reverse trend was obtained. It is due to the interference of molecules of ZnS-CdS. The abundance of molecules interferes in the pathway of other molecules gaining the excited state thus resulting decrease in bleaching.

Effect of light intensity: The effect of light intensity on the rate of the reaction was also observed and the observations are summarized in Table V.
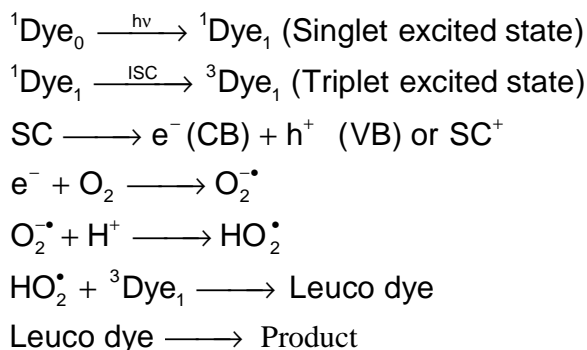
Table – V: Effect of light intensity

Malachite green [Malachite green] = 4.0×10^{-6} M pH = 4.0 ZnS-CdS= 0.12 g		Brilliant green [Brilliant green] = 4.0×10^{-6} M pH = 4.0 ZnS-CdS= 0.06 g	
Light Intensity (mW cm^{-2})	**k x 10^5 s^{-1}**	**k x 10^5 s^{-1}**	
22.0	8.02	0.716	
27.0	8.55	0.766	
32.0	9.12	0.866	
37.0	**9.96**	**1.10**	

It has been observed that on increasing the intensity of light, the rate of reaction also increases because on increasing the intensity, the number of photons striking per unit area of reaction

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mixture will also increase. This will result in a corresponding increase in the rate of bleaching of malachite green and brilliant green.

Mechanism

On the basis of above studies carried out, the mechanism is proposed of bleaching of the dye as follows –

$$^1Dye_0 \xrightarrow{h\nu} {}^1Dye_1 \text{ (Singlet excited state)}$$

$$^1Dye_1 \xrightarrow{ISC} {}^3Dye_1 \text{ (Triplet excited state)}$$

$$SC \longrightarrow e^- (CB) + h^+ \ (VB) \text{ or } SC^+$$

$$e^- + O_2 \longrightarrow O_2^{-\bullet}$$

$$O_2^{-\bullet} + H^+ \longrightarrow HO_2^{\bullet}$$

$$HO_2^{\bullet} + {}^3Dye_1 \longrightarrow \text{Leuco dye}$$

$$\text{Leuco dye} \longrightarrow \text{Product}$$

Dye absorbs the light and get excited to singlet state and through intersystem crossing gets converted to triplet state. On the other hand the semiconductor absorbs light and an electron is excited from valence band to conduction band leaving behind a hole. The generated electron then reacts with dissolved oxygen to generate an anion free radical. This on reaction with H^+ ion of acid yield HO_2^* free radical. The dye is now being bleached from this free radical producing leuco dye and this then converts into product. The participation of $HO_2^{\bullet}$ radical is confirmed by the use of scavenger, which stops the bleaching reaction completely.

Acknowledgement

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