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EFFECT OF SURFACE CHARGE ON PHOTOCATALYTIC REDUCTION OF CATIONIC DYES BY ZINC OXIDE POWDER: A COMPARATIVE STUDY

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ABSTRACT

The field of photocatalysis has opened new avenues of research in chemistry, as many chemical reactions can now be driven photocatalytically, which was not possible by ordinary chemical or photochemical methods. The photoreduction of cationic dyes (Brilliant green and Crystal violet) in presence of ZnO as photocatalyst has been carried out. The rate of this photochemical reaction was observed spectrophotochemically. The effect of different parameters like pH, concentration of dyes, amount of semiconductor and light intensity on the reaction rate was observed . The effect of charge of different cations, anions and ligands on the reaction rate was also studied by taking cations like Na^+, Ba^{2+}, Al^{3+}, anions like Cl^-, SO_4^{2-}, PO_4^{3-} and ligands like EDTA, NTA. Further behavior of photocatalytic bleaching was studied by varying the concentration of cation (Ba^{2+}), anion (PO_4^{3-}) and ligand (EDTA). A tentative mechanism for the photocatalytic degradation of dyes has also been observed.

KEYWORDS: Photodegradation, Photocatalytic bleaching, Zinc oxide, Cationic dyes.

INTRODUCTION

The world is in the cancerous grip of pollution with multidentate kinds of pollution, although a number of waste water treatment processes are available to fight back and restore the clean and green globe, but there is a pressing demand to modify conventional methods of waste water treatment processes. In recent years, Advanced Oxidation Processes (AOP'S) like photocatalysis, photo-Fenton reaction, sonolysis, ozonation, etc. have emerged as successful techniques in combating against the problem of environment pollution. The photocatalytic bleaching was found to be the most promising and efficient process in controlling the environment pollution, waste water treatment, etc., in which semiconductor particles act as photocatalyst or short-circuited microelectrodes. On excitation, semiconductor generates electron-hole pair, which may be used either for reduction or oxidation of the dye. 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 non-toxic and harmless.

Exhaustive researches in the field of photocatalysis have shown various fascinating applications of photocatalytic reactions based on the use of semiconductors (Ameta et al.[1] 2003; Scheavello et al.[10] 1997). The photocatalytic degradation of azo dye acid red was reported in water on ZnO (Daneshvar et al.[2] 2004). ZnO appears to be a suitable alternative to TiO2, since its photodegradation mechanism has been proven to be similar to that of TiO2. (Dindar et al.[3] 2001). The effect of chloride ions was investigated on 4-chlorophenol photodegradation in the absence and presence of titania silicate-2 (Kang et al.[4] 2001). The photooxidation of 2-phenylphenol (Khodja et al.[5] 2001) and photocatalysed oxidation of phenol (Serpone et al.[11] 1995; Marci et al.[7] 2001) has also been investigated. Composite system of polycrystalline ZnO/TiO2 and its photocatalytic activity was studied (Marei *et al.*[6] 2001; Sharma et. al.[12] 1995). The triplet sensitized photobleaching of crystal violet was observed (Najuib *et al.*[8] 1996). The effect of surface charge was observed on reduction rate of methyl orange photosensitized by ZnO (Ran et al.[9] 1995) while photocatalytic degradation of xylidine ponceau and orange-G was reported (Sharma et. al.[13] 1995). Photocatalytic degradation of acid blue-62 over CuO-SnO2 nanocomposite photocatalyst under simulated sunlight was carried out (Xia et al.[14] 2007). ZnO has been reported, sometimes, to be more efficient than TiO2. Its efficiency has been reported to be particularly noticeable in the advanced oxidation of pulp mill bleaching (Yeber et al.[15] 1999). Catalytic activity of iron species in layered clays for photodegradation of organic dyes under visible irradiation (Cheng et. al.[16] 2008).

RESULTS AND DISCUSSION

Photocatalytic degradation of brilliant green and crystal violet was observed at λ_{max} = 620 nm and 590 nm, respectively. The absorbance of the dye solution in presence of ZnO at given time is much lower as compared to samples without ZnO. A plot of log (Absorbance) versus time was linear and hence, the reactions follow pseudo first-order kinetics. The rate constants were determined by varying one parameter at a time, keeping other parameters fixed.

The dependence of the pseudo first order rate constant (k) for the photocatalytic degradation of brilliant green and crystal violet on various parameters are reported in Table 1 and 2, respectively.

Effect of pH

The pH of the solution is likely to affect the bleaching of the dye. The effect of pH on the rate of bleaching of the dye solution was investigated in the pH range (5.5-9.5). The results are reported in table 1 & table 2.

The rate of photo catalytic bleaching of dye increases on increasing the pH. As the pH of the medium was increased, there is a corresponding increase in the concentration of hydroxyl ions. These hydroxyl ions will adsorb on the semiconductor surface, making it negatively charged. Thus there will be a coulombic attraction between semiconductor surface and cationic dye. This has reflected in the increase of rate of photobleaching of the dye on increasing pH.

Effect of dye concentration

Effect of varitation of dye concentrations was also studied by taking different concentrations of both dyes. The results are tabulated in table1 & table 2. It has been observed that the rate of photocatalytic bleaching increase with the increase in the concentration of dyes. As the concentration of dyes was increased, more dye molecules were available for excitation and electron transfer from semiconductor and hence, an increase in the rate was observed. After a certain limit, [Brilliant green] = 1.85×10^{-5} M and [Crystal violet] = 1.00×10^{-5} M, a decrease in the rate of reaction was observed with the increase in the concentration of dye solution. A increase in the dye concentration beyond a certain limit will not permit the desired light intensity to reach the semiconductor surface or in other words, one can say that dye itself acts as filter, hence, a decrease in the rate of reaction has been observed beyond a particular dye concentration.

Effect of amount of semiconductor

Amount of semiconductor is also likely to affect the process of dye bleaching. Different amounts of photocatalyst were used and the results are reported in the table1 & table 2.

It has been observed that the rate constants for photobleaching of both dyes increase with an increase in the amount of semiconductor but ultimately, it becomes almost constant after a certain amount. As the amount of semiconductor was increased, the exposed surface areas also increase but after the certain limit, if the amount of semiconductor was further increased, there will be no increase in the exposed surface area of the photocatalyst. It may be considered like a saturation point. Above which, any increase in the amount of semiconductor has negligible or no effect on the rate of photocatalytic bleaching of crystal violet. As any increase in the amount of semiconductor after this saturation point will only increase the thickness of the layer at the bottom of the vessel; once, the complete bottom of the reaction vessel is covered by the photocatalyst.

Effect of light intensity

To observe the effect of intensity of light on the photocatalytic bleaching of both the dyes, the light intensity was varied. The intensity of light at each distance was measured by surymapi (CEL model SM 201) the results are reported in Table1 & table 2.

Results given indicate that bleaching action 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 the semiconductor powder. Further increase in the intensity of light will increase the temperature of the dye solution and, thermal reactions may occur in place of photocatalytic reactions and therefore, higher intensities were avoided. A linear relationship between light and rate of reaction was observed up to 60.0 $mWcm^{-2}$; therefore a slight decrease in the rate of reaction was observed with increasing intensity of light. This may be due to some side thermal reactions.

Effect of Cation

Effect of variation of charge of cation and its concentration on rate of bleaching was also studied by taking different cations like Na+, Ba2+ and Al3+ ions. The results are tabulated in Table 3 & 3.1

It was observed that the charge of cation adversely affect the rate of photocatalytic bleaching of brilliant green and crystal violet. Both dyes are cationic dyes and they will face more electrostatic repulsion with cations adsorbed on the semiconductor surface, as the charges on these ions are more. Secondly, a similar effect has been observed, when the concentration of this cation (Ba2+ in this case) was increased, where larger concentrations of cation will reduce the rate of this reaction.

Effect of anion

Effect of variation of charge of anion and its concentration on photocatalytic bleaching of brilliant green and crystal violet was also studied by taking different anions like Cl^-, SO_4^{2-}, and PO_4^{3-}.The results are tabulated in Table 4 and 4.1.

Charge of anions affects the rate of photodegradation of both dyes favorably. This may be attributed to the increase in columbic attraction between negatively charged semiconductor surface due to absorbed anions and cationic dyes. The increase in concentration of anion (PO_4^{3-} in this case) will also increase the rate of photo bleaching of dye as the charge on the semiconductor will be more for larger concentration of anions .

Effect of ligands

Effect of variation of ligands like NTA and EDTA and its concentration on the rate of the reaction was also studied. The results are tabulated in Table 5 and 5.1

The presence of ligands also affects the rate of photocatalytic bleaching of brilliant green and crystal violet favorably as the ligands are electron rich species and these will make semiconducting surface more electron rich; thus pulling more molecules of cationic dyes. Increase in concentration of ligand (EDTA in this case) will increase rate of this reaction; however, the order of effectiveness of the two ligands was quite surprising.
NTA > EDTA

It seems that geometry of the ligand on the semiconductor surface does not permit more electron rich sites of EDTA to be exposed outside to pull cationic dyes as compared to NTA molecules.

MECHANISM

On the basis of the experimental observations, tentative mechanism for photocatalytic bleaching of both dyes may be proposed as [Figure 5] -

$$^{1}\text{Dye}_0 \xrightarrow{h\nu} {}^{1}\text{Dye}_1$$

$$^{1}\text{Dye}_1 \xrightarrow{\text{ISC}} {}^{3}\text{Dye}_1$$

$$^{3}\text{Dye}_1 + \text{ZnO} \longrightarrow \text{Dye+ +ZnO (e-)}$$

$$\text{ZnO (e-) + O2} \longrightarrow \text{ZnO + O2-}$$

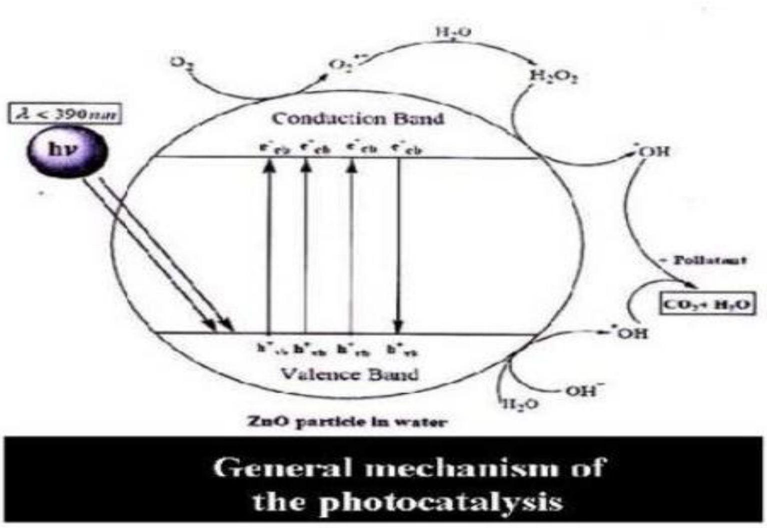
$$\text{Dye + OH-} \longrightarrow \text{Dye +OH-}$$

$$\text{Dye + OH-} \longrightarrow \text{Products}$$

When the solution of the dye was exposed to light in presence of semiconductor; initially, dye molecules are excited to first exited single state. Then these excited singlet molecules are transferred to the triplet state through intersystem crossing (ISC). The triplet dye may donate its electrons to the semiconductor and the dye (Brilliant green and Crystal violet) become positively charged. The dissolved oxygen of the solution will pull an electron from the conduction band of semiconductor; thus, regenerating the semiconductor. The positively charged molecules of dye will immediately react with hydroxyl ions to form $^{\cdot}$OH radicals and these $^{\cdot}$OH radicals will oxidize the dye molecules into products, which are colorless. The participation of .OH radicals as an active oxidizing species was confirmed by carrying out the reaction in presence of hydroxyl scavenger eg. 2-propanol; when the reaction rate was retarded to a large extent.

EXPERIMENTAL PROCEDURE

For the photodegradation of brilliant green and crystal violet (Table 1), a solution containing known concentration of dye was taken. 0.1 g ZnO was added and it was allowed to equilibrate for 30 min in the darkness, and then 50 mL of the prepared suspension was transferred to a 100 mL pyrex reactor. The pH values were adjusted at desired level using dilute NaOH and H2SO4. The pH values were measured with pH meter (Systronics , Model 335). After this the solution was irradiated by a lamp. The light intensities at various distances from the lamp were measured with the help of a solarimeter (CEL, India; Model SM 201). For correct measurment of optical activity, the solution free from semiconductor particles and solid impurities is required; A centrifuge (Remi, India; Model 1258) was used for removal of such particles. The concentration of dye was determined with a UV-visible spectrophotometer (JASCO 7800).



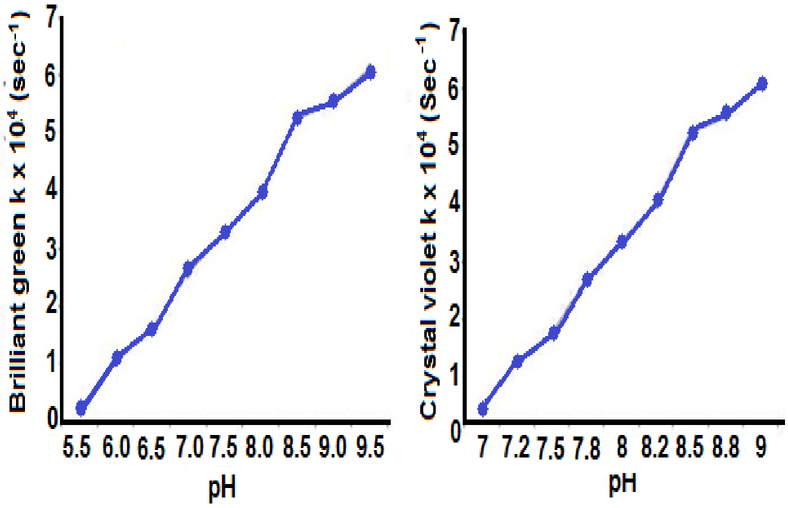


Figure 2

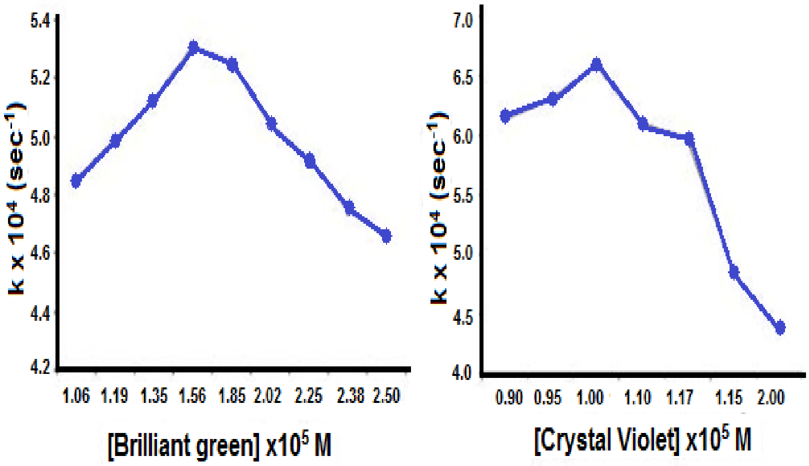


Figure 3

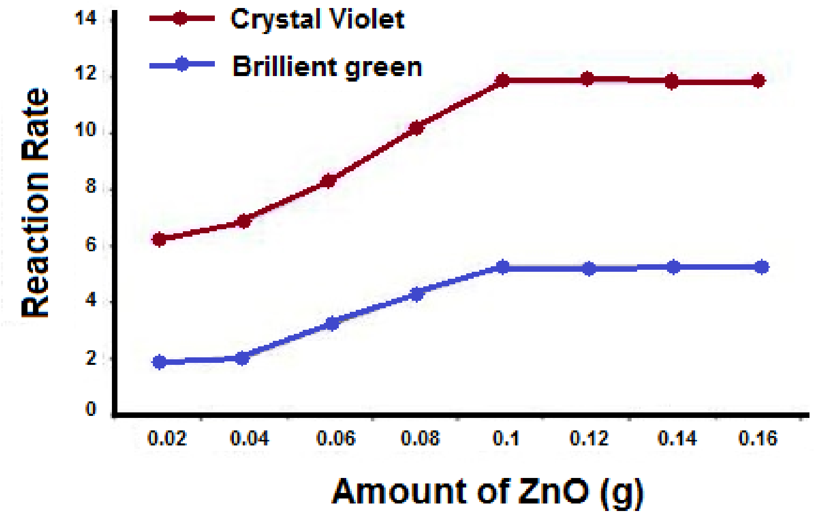


Figure 4

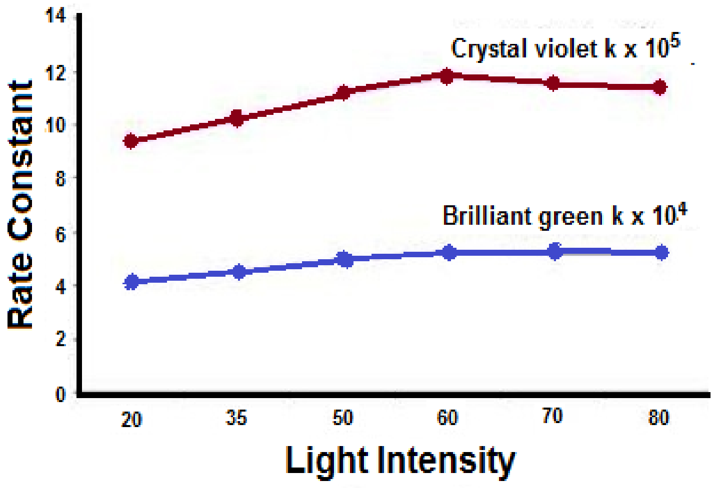


Figure 5

Table 1 Dyes used

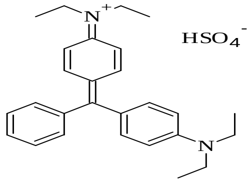
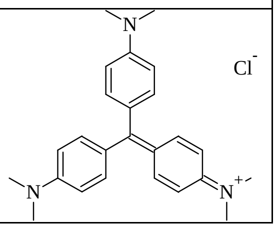
Name	Molecular formula	Molecular weight	Colour index	λ_{max} (nm)	Structure
Brilliant green	$C_{27}H_{33}N_2HO_4S$	482.65	42040	620	
Crystal violet	$C_{25}H_{30}ClN_3$	407.98	42535	590	

Table 2

pH	**Brilliant green k x 10^4 (sec^{-1})**	**[Brilliant green] x 10^5**	**K x 10^4 (sec^{-1})**	**ZnO (g)**	**Brilliant green k x 10^4 (sec^{-1})**	**Light Intensity ($mWcm^{-2}$)**	**k x 10^4 (sec^{-1})**
5.5	0.23	1.06	4.85	0.02	1.88	20.0	4.10
6.0	1.07	1.19	4.99	0.04	2.04	35.0	4.50
6.5	1.60	1.35	5.12	0.06	3.16	50.0	4.94
7.0	2.57	1.56	5.31	0.08	4.29	60.0	5.25
7.5	3.26	1.85	5.25	0.10	5.25	70.0	5.20
8.0	3.96	2.02	5.04	0.12	5.23	80.0	5.17
8.5	5.25	2.25	4.92	0.14	5.24		
9.0	5.54	2.38	4.75	0.10			
9.5	6.11	2.50	4.66				

[Brilliant green] = 1.85 x 10^{-5} M, ZnO = 0.10 g, Light intensity = 60.0 $mWcm^{-2}$, pH = 8.5

Table 3

pH	**Crystal violet k x 10^5 (sec^{-1})**	**[Crystal Violet] x 10^5**	**M k x 10^5 (sec^{-1})**	**ZnO (g)**	**Crystal violet k x 10^5 (sec^{-1})**	**Light Intensity ($mWcm^{-2}$)**	**k x 10^5 (sec^{-1})**
5.5	-	0.90	6.15	0.02	4.31	20.0	5.24
6.0	-	0.95	6.30	0.04	4.78	35.0	5.68
6.5	-	1.00	6.59	0.06	5.14	50.0	6.20
7.0	0.23	1.10	6.10	0.08	5.86	60.0	6.59
7.5	1.60	1.17	5.98	0.10	6.59	70.0	6.31
8.0	3.26	1.15	4.85	0.12	6.60	80.0	6.19
8.5	5.25	2.00	4.37	0.14	6.59		
9.0	6.11	-	-	0.10	6.60		

[Crystal violet] = 1.00 x 10^{-5}M, ZnO = 0.10 g, Light intensity = 60.0 $mWcm^{-2}$, pH = 8.5

Table 4

Cation	**k x 10^4(sec^{-1}) (for brilliant green)**	**k x 10^5(sec^{-1}) (for crystal violet)**
-	5.25	6.59
Na+	4.70	6.10
Ba2+	4.41	5.71
Al3+	3.36	3.76

[Brilliant green] = 1.85 x 10^5 M pH = 8.5

[Crystal violet] = 1.00 x 10^5 M ZnO = 0.10 g

[Cation] = 5.0 x 10^{-4} M Light intensity = 60.0 mW cm^{-2}

Table 4.1

$[Ba^{2+}]$ x 10^4 M	**k x 10^4(sec^{-1}) (for brilliant green)**	**k x 10^5 (sec^{-1}) (for crystal violet)**
0.5	4.89	6.22
1.0	4.72	6.10
2.0	4.56	5.8
5.0	4.41	5.71
7.5	4.00	5.18
10.0	3.89	5.03

[Brilliant green] =1.85 x 10^{-5} M pH =8.5
[Crystal violet] =1.00 x 10^{-5} M ZnO =0.10 g
Light intensity = 60.0 mW cm^{-2}

Table 5

Anion	**k x10^4 (sec^{-1}) (for brilliant green)**	**k x10^5 (sec^{-1}) (for crystal violet)**
-	5.25	6.59
Cl^-	4.70	6.10
SO_4^{2-}	5.72	6.92
PO_4^{3}	6.79	7.87

[Brilliant green] = 1.85 x 10^{-5}M pH = 8.5
[Crystal violet] = 1.00 x 10^{-5}M ZnO = 0.10 g
Light intensity = 60.0 $mWcm^2$
[Anion] = 5.0 x 10^{-4}M

Table 5.1

$[PO_4^{3-}]$ x 10^4M	**k x 10^4(sec^{-1}) (for brilliant green)**	**k x 10^5(sec^{-1}) (for crystal violet)**
0.5	5.96	6.88
1.0	6.21	7.12
2.0	6.52	7.50
5.0	6.79	7.87
7.5	7.23	8.19
10.0	7.66	8.87

[Brilliant green] = 1.85 x 10^{-5}M pH = 8.5
[Crystal violet] = 1.00 x 10^{-5}M ZnO = 0.10 g
Light intensity = 60.0 $mWcm^2$

Table 6

Ligands	**k x 10^4(sec^{-1}) (for brilliant green)**	**k x 10^5(sec^{-1}) (for crystal violet)**
-	5.25	0.59
NTA	7.64	9.42
EDTA	7.35	7.81

[Brilliant green] = 1.85 x 10^{-5}M pH = 8.5
[Crystal violet] = 1.00 x 10^{-5} M ZnO = 0.10 g
Light intensity = 60.0 $mWcm^{-2}$
[Ligand] = 5.0 x 10^{-4} M

Table 6.1

[EDTA] x 10^4M	**k x 10^4 (sec^{-1}) (for brilliant green)**	**k x 10^5 (sec^{-1}) (for crystal violet)**
0.5	6.07	6.31
1.0	6.48	6.82
2.0	6.92	7.2
5.0	7.35	7.81
7.5	7.90	8.33
10.0	8.32	8.84

[Brilliant green] = 1.85 x 10^{-5} M pH = 8.5

[Crystal violet] = 1.00 x 10^{-5} M ZnO = 0.10 g

Light intensity = 60.0 $mWcm^{-2}$

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