Use of Ta_2O_5 as a photocatalyst for degradation of Crystal violet using solar energy

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ABSTRACT

The photocatalytic degradation of Crystal Violet was studied using Ta_2O_5 as semiconductor. Visible light was used as the source of energy. The effect of various parameters like amount of semiconductor, pH, light intensity, dye concentration etc. on the photodegradation were investigated. A tentative mechanism is proposed.

Keywords: Photocatalytic bleaching, Ta_2O_5, crystal violet.

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INTRODUCTION

In recent years, array of industrial activities have been disturbing the water quality by release of various contaminants like dyestuff, heavy metal ions and many other organic substances. Due to the high concentration of organics in the effluents and the higher stability of modern synthetic dyes, the conventional biological methods are ineffective for the complete colour removal and degradation of organics and dyes. Heterogeneous photocatalysis by semiconductor particles is a promising technology for water treatment.

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

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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 solvethis 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]. 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. TiO_2 sol-gel deposited over glass and its application as a effect of TiO_2 acidic pretreatment 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. The Kim *et al.* [15] used ZnO coated TiO_2 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

The stock solution of dye was prepared in doubly distilled water and diluted as required. The pH of the solution was adjusted by adding prestandarized NaOH and HCl solutions and was determined by pH meter (Hena imported pen type).

In photocatalytic experiments, the dye solution and known amount of semiconductor (Ta_2O_5) were taken in a beaker and the beaker was covered with water filter to avoid the thermal reaction. The solution was irradiate by visible tungsten lamp. Dye sample of about 2-3 ml was taken out at a regular time interval from the test solution and optical density (O.D.) was recorded spectrophotometrically (systronics spectrophotometer). Intensity of light was measured by suryamapi (CEL Model SM201).

RESULTS AND DISCUSSION

The plot of 1+log O.D. vs. time was found straight line suggesting that bleaching of dye by Ta_2O_5 follows pseudo first order rate law. Rate constant was calculated by graphs as follows:

$$K_1 = 2.303 \times slope$$

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A typical run is given in Table-1 and Fig.1

Table-1
[Crystal violet] = 1.2 × 10^{-4} M; pH = 8.5, Ta$_2$O$_5$ = 0.08g; Light intensity = 37.0mW cm^{-2}

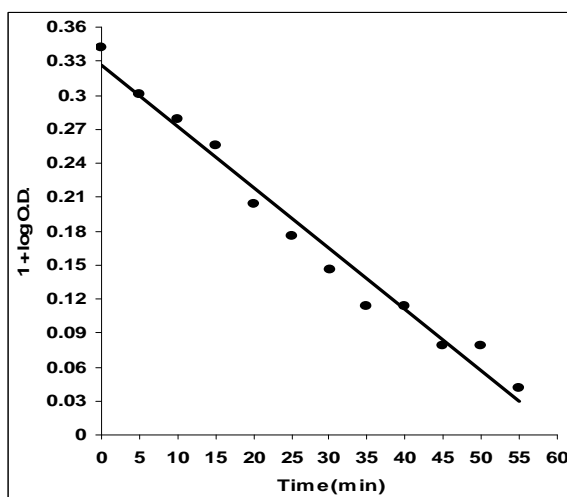| Time(min)	O.D.	1+log O.D.
0	0.22	0.342
5	0.20	0.301
10	0.19	0.279
15	0.18	0.255
20	0.16	0.204
25	0.15	0.176
30	0.14	0.146
35	0.13	0.114
40	0.13	0.114
45	0.12	0.079
50	0.12	0.079
55	0.11	0.041

Fig. 1. A TYPICAL RUN

Effect of pH:
The effect of pH variation on rate of the photodegradation of Crystal Violet is given in Table 2 and Fig.2. It was found that as pH of the reaction mixture is raised, the rate of photocatalytic bleaching increases. It attains maximum value at pH 8.5. After this, if pH is raised further, the rate decreases. The pH affects not only the surface properties of Ta$_2$O$_5$ but also the dissociation of dye molecules and the formation of hydroxyl radicals. Increase in pH will increase the number of OH$^-$ ions. A hole is generated in semiconductor, which abstracts an electron from OH$^-$ ions converting it into OH$^.$ free radical. This free radical is responsible for the bleaching of dye as confirmed by use of scavenger.

Effect of concentration of dye:
Experiments were carried out by keeping the pH constant and it was found that up to an optimum concentration (1.2x10^{-4} M); the rate of photocatalytic bleaching increases as the rate of reaction

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is directly proportional to the molar concentration of reacting species. After this limit, if more concentration of dye is taken, it imparts a dark colour to the solution so it may act as filter to the incident light reaching to the semiconductor surface. Thereby only fewer photons reach the catalyst surface and therefore, generation of OH· free radical on the catalyst surface is reduced since the active site of semiconductor gets covered by dye ions. This results in the decrease of the rate of bleaching. The data are given in Table-3 and Fig.3.

Effect of amount of Ta_2O_5:
Experiments were carried out by taking different amount of Ta_2O_5 and keeping other factors constant. It was found that up to a particular amount (0.08g), the rate of photocatalytic bleaching increases. It may due to the increase in the active site available on the catalyst surface for the reaction; which in turn increases the rate of radical formation. After this, the rate of bleaching decreases when the catalyst amount is increased. With a higher catalyst loading the deactivation of activated molecules by collision with ground state molecules dominates, thus reducing the rate of reaction. The data are summarized in Table-4 and Fig.4

Table-2
[Dye]=1.2x10^{-4} M; Intensity=37.0 mW cm^{-2}; Ta_2O_5=0.08g

pH	$K \times 10^4 (S^{-1})$
6.0	0.72
6.5	0.76
7.0	0.88
7.5	1.11
8.0	1.45
8.5	**2.07**
9.0	1.97
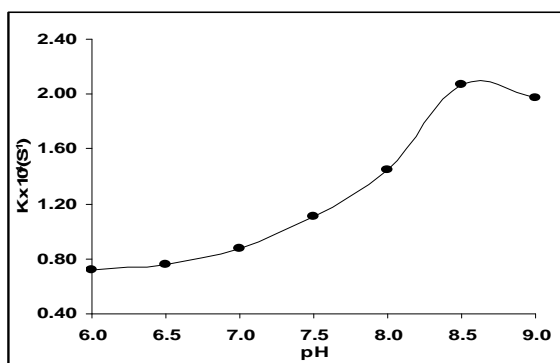
Fig.2. EFFECT OF pH

Table-3
pH=8.5; Ta_2O_5=0.08g; Intensity= 37.0 mW cm^{-2}

[Dye]x10^{-4} M	$Kx10^4 (S^{-1})$
0.6	1.04
0.8	1.19
1.0	1.97
1.2	**2.07**
1.4	1.90
1.6	1.50

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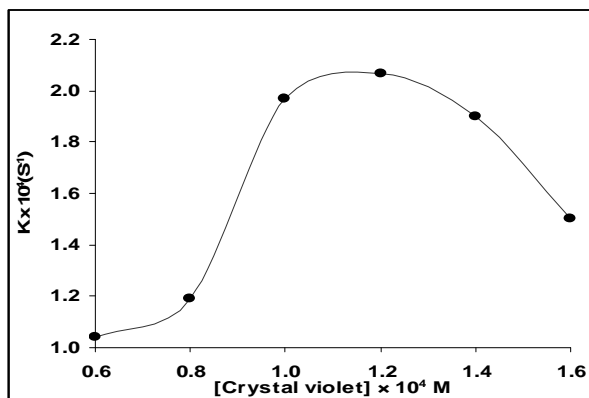
Fig. 3. EFFECT OF DYE CONCENTRATION

Table-4
[Dye]=1.2x10^{-4} M; pH=8.5; Intensity= 37.0 mW cm^{-2}

Amount of Semiconductor(g)	Kx10^4 (S^{-1})
0.06	1.73
0.08	**2.07**
0.10	1.96
0.12	1.77
0.14	1.46
0.16	1.19
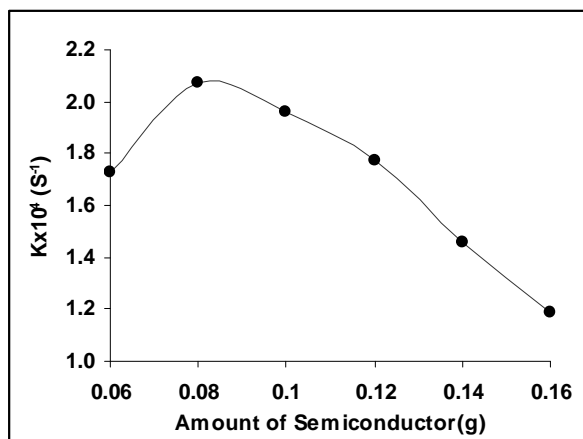
Fig. 4. EFFECT OF AMOUNT OF SEMICONDUCTOR

Table-5
[Dye]=1.2x10^{-4} M; pH=8.5; Ta$_2$O$_5$=0.08g

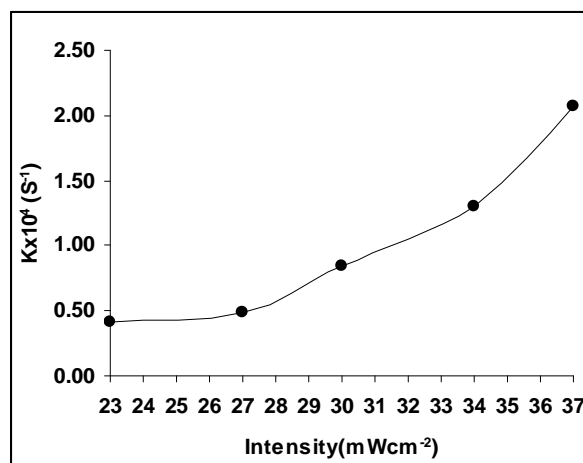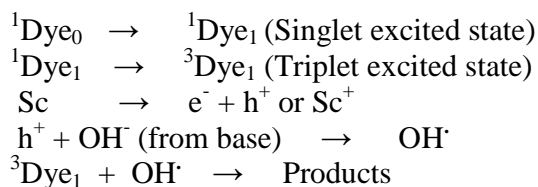| Intensity(mWcm^{-2})	Kx10^4 (S^{-1})
23	0.42
27	0.49
30	0.84
34	1.30
37	**2.07**

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Fig. 5. EFFECT OF LIGHT INTENSITY

Effect of light intensity:

The effect of intensity of light on rate of bleaching was studied and the data are given in Table-5 and Fig.5. The rate of photocatalytic bleaching increases as the light intensity was increased. It may be explained on the basis of number of excited molecules. As more intensity of light falls on Ta_2O_5 molecules, more number of molecules get excited which in turn may bleach more dye molecules and thus the rate of bleaching was found to increase with increase in intensity of light.

MECHANISM

On the basis of above studies, a tentative mechanism has been proposed for the bleaching of dye by Ta_2O_5 particles.

$$^1Dye_0 \quad \rightarrow \quad ^1Dye_1 \text{ (Singlet excited state)}$$
$$^1Dye_1 \quad \rightarrow \quad ^3Dye_1 \text{ (Triplet excited state)}$$
$$Sc \quad \rightarrow \quad e^- + h^+ \text{ or } Sc^+$$
$$h^+ + OH^- \text{ (from base)} \quad \rightarrow \quad OH^\cdot$$
$$^3Dye_1 + OH^\cdot \quad \rightarrow \quad Products$$

Dye absorbs the light and gets excited to its first singlet state. This gets converted to triplet state through intersystem crossing. On the other hand, the semiconductor gets excited by absorbing light and an electron is excited from its valence band to conduction band leaving behind a hole. This hole abstracts an electron from OH^- ion generating $OH^\cdot$ free radical. The dye is now being bleached by this free radical. The participation of $OH^\cdot$ radical was confirmed by using scavenger, which almost stops the bleaching reaction. The dye gets decomposed completely and various gaseous products like NO_2, SO_2, CO_2, H_2O etc. are formed.

CONCLUSION

The photocatalytic degradation of Crystal Violet dye was found to be dependent on various Kinetic parameters like concentration of dye, pH, amount of semiconductor, intensity of light etc. Colour change from Blue to colourless is irreversible and degradation rate of the dye follows the pseudo-first order kinetics.

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