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Ta_2O_5 USED AS PHOTOCATALYST FOR DEGRADATION OF EOSIN USING SOLAR ENERGY

Nikhil Kumar Verma, Jayant Gandhi and Shipra Bhardwaj*
Department of Chemistry, M.P.Govt. P.G. College, Chittorgarh (Rajasthan)
E-mail: sidsidsmart@yahoo.co.in

ABSTRACT

The photocatalytic degradation of Eosin 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: Semiconductor, Sunlight, Pseudo first order rate law, pH, Concentration of dye, bleaching of dye, Eosin, Ta_2O_5 etc.

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.

The removal of dyes from water has drawn the attention of scientists and a lot of work has been carried out in this field. TiO_2 has been frequently used as a semiconductor for this purpose[1-4] . High temperature transport properties of Nb and Ta substituted $CaMnO_3$ system was studied by Xu et al[5]. Ye et al[6] investigated a novel series of water splitting photocatalysts NiM_2O_6 (M-Nb, Ta) under visible light. The oxidative photodegradation of mercurochrome using TiO_2 as a photocatalyst has been observed by tennakone et al[7]. Non linear electrical properties of Ta-doped titania capacitor-varistor ceramics was investigated by Li et al[8]. Modification of TiO_2 ceramic varistor modified with Ta and Ba have been done by Gaikwad et al[9]. New tantalum oxynitride as a photocatalyst has been proposed by Totakenji et al[10]. Ishii et al[11] observed H_2 evolution from an aqueous methanol solution using $SrTiO_3$ photocatalyst co-doped with chromium and tantalum ions under visible light irradiation. Photocatalytic hydrogen and oxygen formation under visible light irradiation with M-doped $InTaO_4$ (M= Mn, Fe, Co, Ni and Cr) catalyst has been studied by Zou et al[12].

The enhanced photocatalytic activities of Ta co-doped TiO_2 thin films under visible light has been reported by Obata et al[13], while Zou et al[14] used visible light sensitive photocatalyst $In_{1-X}M_XTaO_4$. Oxygen evolution on a tantalum oxynitride phtocatalyst under visible light irradiation has been observed by Nakamura et al[15]. They also reported photo-oxidation on a metal oxynitrite surface. A novel preparation of the three dimensionally macroporus M/Ti(M-Zr or Ta) mixed oxide nanoparticles with enhanced photocatalytic activity has been suggested by Wang et al[16].

Use of Ta_2O_5 as semiconductor was not reported yet therefore an attempt has been made to remove these dyes using semiconductor Ta_2O_5 and light. Photocatalytic bleaching is a part of green chemistry where the catalyst utilizes solar energy and convertes harmful dyes into less harmful products. Removeal of toxicity from environment using renewable resource of energy may provide an alternate path to new generation for making their environment clean.

EXPERIMENTAL

The stock solution of dye was prepared in doubly distilled water and diluted as required. The pH of the solution was adjusted by adding prestandardized 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

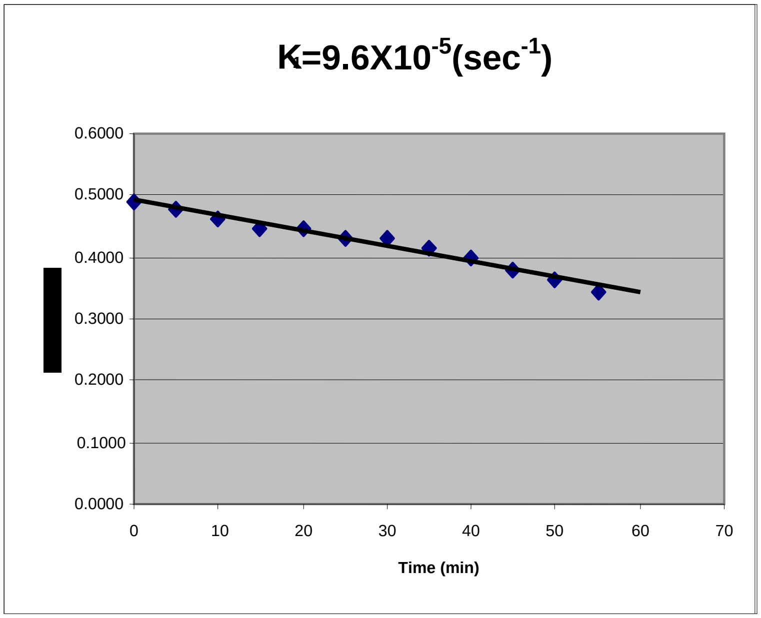
$$K_1 = 2.303 \text{ x slope}$$

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

Table-1 and Fig.1

[Dye]= $1x10^{-5}$ M; Ta_2O_5=0.10g;
pH=8.0; Intensity= 37.0 mW cm^{-2}

Time(min)	O.D.	1+log O.D.
0	0.31	1.3100
5	0.30	1.3000
10	0.29	1.2900
15	0.28	1.2800
20	0.28	1.2800
25	0.27	1.2700
30	0.27	1.2700
35	0.26	1.2600
40	0.25	1.2500
45	0.24	1.2400
50	0.23	1.2300
55	0.22	1.2200
60	0.21	1.2100



A typical run

Effect of pH:

The effect of pH variation on rate of the photodegradation of eosin is given in Table 1 and Fig.1. It was found that as pH of the reaction mixture is raised, the rate of photocatalytic bleaching increases. It attains maximum value at pH 8.0. After this, if pH is raised further, the rate decreases. The pH affects not only the surface properties of Ta_2O_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 $OH^\cdot$ free Radical. This free radical is responsible for the bleaching of dye as confirmed by use of scavenger.

Table-2 and Fig.2
[Dye]=1.0x10^{-5} M; Intensity=37.0 mW cm^{-2};
Ta_2O_5=0.10g
Effect of pH variation

pH	**K_1 x 10^5 (S^{-1})**
6.0	5.0
6.5	7.3
7.0	7.9
7.5	8.4
8.0	**9.6**
8.5	8.5
9.0	6.2

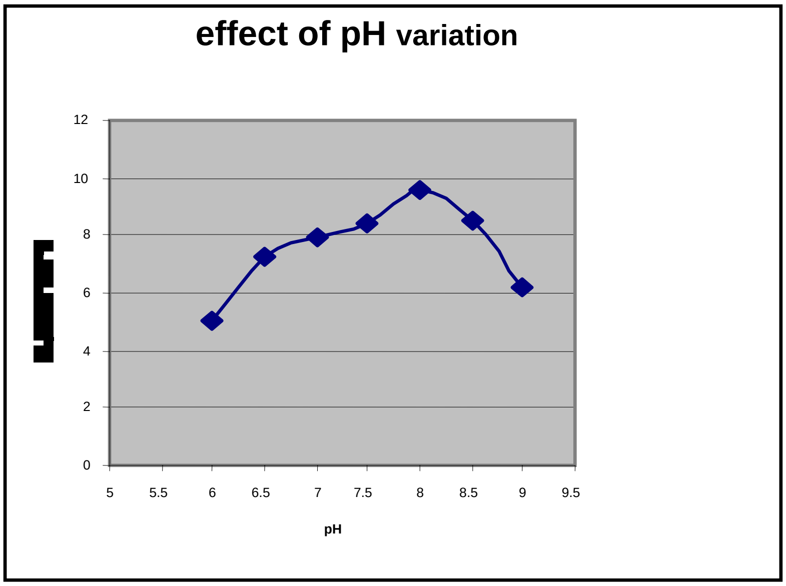


Table-3 and Fig. 3
pH=8.0; Ta_2O_5=0.1g;
Intensity= 37.0 mW cm^{-2}

Effect of concentration variation

[Dye]x10^{-5} M	**K_1x10^5 (S^{-1})**
0.6	5.8
0.8	8.3
1.0	**9.6**
1.2	5.9
1.4	5.1

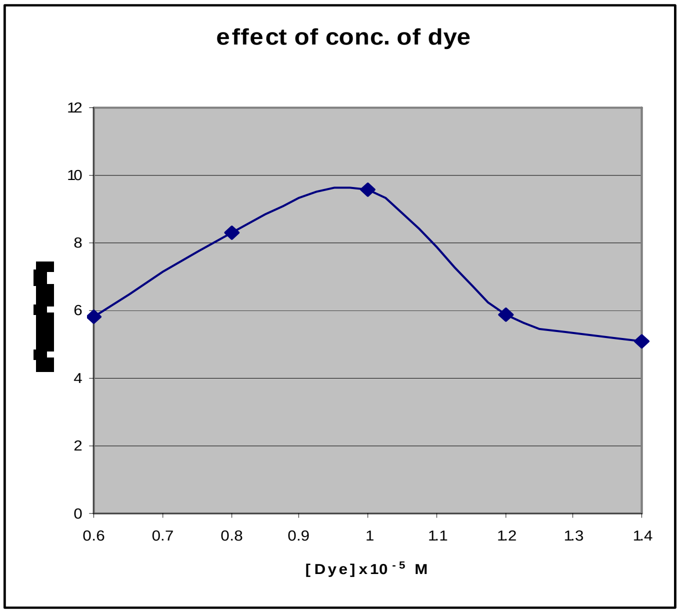


Table-4 and Fig. 4
[Dye]=1.0×10^{-5} M; pH=8.0;
Intensity= 37.0 mW cm^{-2}

Effect of semiconductor variation

Amount of Semiconductor(g)	**$K_1 x 10^5$ (S^{-1})**
0.06	2.2
0.08	6.6
0.10	**9.6**
0.12	5.0
0.14	3.0

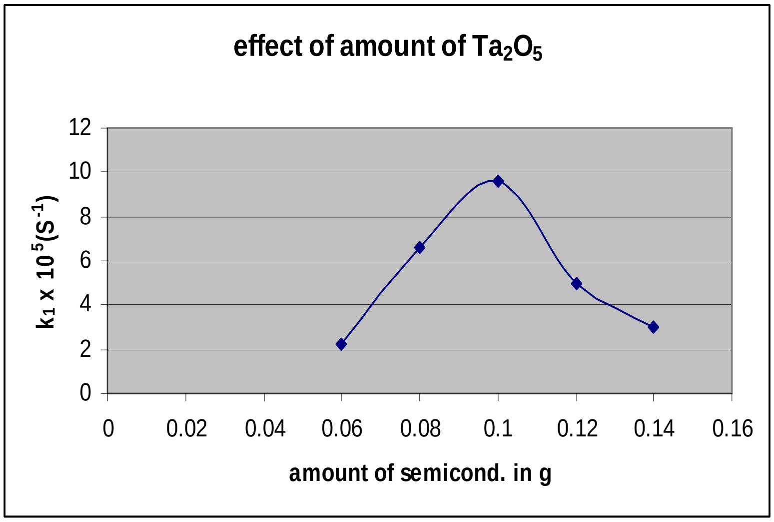
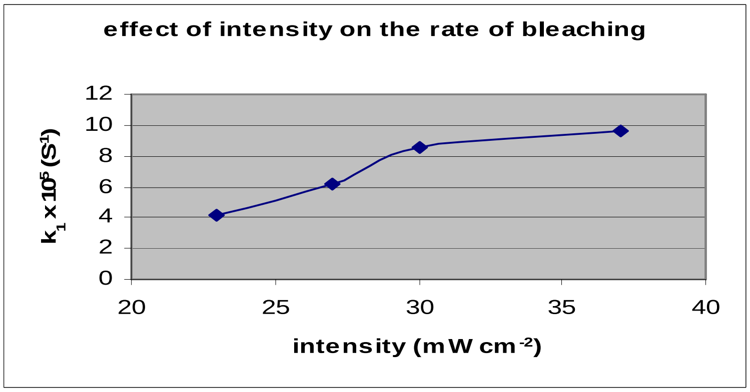


Table-5 and Fig.5
[Dye]=1.0×10^{-5} M; pH=8.0;
Ta_2O_5=0.10g

Intensity(mW cm^{-2})	**$K_1 x 10^5$ (S^{-1})**
23	4.2
27	6.2
30	8.5
37	**9.6**

[redacted]



Effect of concentration of dye:
Experiments were carried out by keeping all other factors constant and it was found that up to an optimum concentration (1.0×10^{-5} M); the rate of photocatalytic bleaching increases as the rate of reaction 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 $OH^{\cdot}$ free radical on the catalyst surface is reduced since the active site of semiconductor gets covered by dye molecules. 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 (0.10g), 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

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.

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

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

CONCLUSIONS

The photocatalytic degradation of eosin 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 Red-orange to colourless is irreversible and degradation rate of the dye follows the pseudo-first order kinetics.

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