Nb_2O_5 Used as Photocatalyst for Degradation of Eosin-Y Using Solar Energy

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The photocatalytic degradation of eosin-Y was studied using Nb_2O_5 as semiconductor. Visible light is used as the source of energy. The effect of various parameters like amount of semiconductor, pH, light intensity, dye concentration, *etc.* on the photodegradation are investigated. A tentative mechanism is proposed.

Key Words: Semiconductor, Sunlight, Pseudo first order, Nb_2O_5.

INTRODUCTION

High temperature properties of niobium and tantalum substituted $CaMnO_3$ system was studied by Xu *et al.*[1]. Ye *et al.*[2] 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.*[3]. Non-linear electrical properties of tantalum doped titania capacitor varistor ceramics was investigated by Li *et al.*[4]. Modification of TiO_2 ceramic varistor modified with tantalum and barium has been done by Gaikwad *et al.*[5]. New tantalum oxynitride as a photocatalyst has been proposed by Totakenji *et al.*[6]. Ishii *et al.*[7] observed hydrogen evolution from an aqueous methanol solution of $SrTiO_3$ photocatalysts co-doped with chromium and tantalum ions under visible light irradiation while M-doped $InTaO_4$ (M = Mn, Te Co, Ni and Cr) catalyst has been studied by Zou *et al.*[8]. Ibhadon *et al.*[9] studied the photocatalytic activity of TiO_2 foam and surface modified binary oxide titania nanoparticles. Novel Ag_2ZnGeO_4 photocatalyst was used for dye degradation under visible light irradiation by Xiukai Li *et al.*[10]. An attempt in present work has been made to remove these dyes using semiconductor Nb_2O_5 and light.

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 pre-standarized 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 (Nb_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 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 (Table-1) was found straight line suggesting that bleaching of dye by Nb_2O_5 follows pseudo first order rate law. Rate constant was calculated by graphs as follows

$$K_1 = 2.303 \times slope$$

TABLE-1
[Eosin-Y] = 1.0×10^{-6} M; Nb_2O_5 = 0.10 g; pH = 7.5; Intensity = 37.0 mW cm^{-2}

Time (min)	Optical density (O.D.)	1 + log O.D.	Time (min)	Optical density (O.D.)	1 + log O.D.
0	0.27	0.4314	50	0.24	0.3802
10	0.28	0.4472	60	0.22	0.3424
20	0.28	0.4472	70	0.22	0.3424
30	0.27	0.4314	80	0.20	0.3010
40	0.26	0.4150	90	0.19	0.2788

Effect of pH: The effect of pH variation on rate of the photodegradation of eosin yellowish is given in Table-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 7.5. After this, if pH is raised further, the rate decreases. The pH affects not only the surface properties of Nb_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 $OH^{\bullet}$. 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 (1.0×10^{-6} 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 $OH^{\bullet}$ 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.

Effect of amount of Nb_2O_5: Experiments were carried out by taking different amount of Nb_2O_5 and keeping other factors constant. It was found that up to a particular amount (0.10 g), the rate of photocatalytic bleaching increases. It may

TABLE-2
[Eosin-Y] = 1.0×10^{-6} M; Nb_2O_5 = 0.10 g; Intensity= 37.0 mW cm^{-2}

pH	$K_1 \times 10^5$ (S^{-1})
7.0	4.3
7.5	**7.5**
8.0	5.4
8.5	4.8
9.0	4

TABLE-3
pH = 7.5; Intensity = 37.0 mW cm^{-2}; Nb_2O_5 = 0.10g

[Eosin-Y] $\times 10^{-6}$ M	$K_1 \times 10^5$ (S^{-1})
0.6	6.4
1.0	**7.5**
1.4	5.9
1.8	4.7
2.2	2.4

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.

Effect of light intensity: The effect of intensity of light on rate of bleaching was studied and the data are given in Table-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 Nb_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.

TABLE-4
[Eosin-Y] = 1.0×10^{-6} M; pH = 7.5; Intensity = 37.0 mW cm^{-2}

Amount of semiconductor (g)	$K_1 \times 10^5$ (S^{-1})
0.04	3.5
0.06	3.9
0.08	4.3
0.10	**7.5**
0.12	4.1
0.14	3.8
0.16	3.0

TABLE-5
[Eosin-Y] = 1.0×10^{-6} M; pH = 7.5; Nb_2O_5 = 0.10 g

Intensity (mW cm^{-2})	$K_1 \times 10^5$ (S^{-1})
23	0.9
27	1.1
30	2.3
37	**7.5**

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

$^3Dye_1 + OH^\bullet \rightarrow$ 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^- ion generating $OH^•$ free radical. The dye is now being bleached by this free radical. The participation of $OH^•$ radical was confirmed by using scavenger, which almost stops the bleaching reaction.

Conclusion

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

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