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Removal of Dye Stuff from Industrial Effluents Using $MnWO_4$ as Semiconductor

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The bleaching of Eosin-Y was carried out in presence of semiconductor $MnWO_4$. The source used for energy was visible light. Various parameters like amount of semiconductor, pH, light intensity, dye concentration, *etc.* were varied. A tentative mechanism is proposed.

Key Words: Semiconductor, Sun light, Pseudo first order rate law, pH, Concentration of dye, Bleaching of dye.

INTRODUCTION

Spectrophotometric study of adsorption of bromo thymol blue on charcoal and phosphates of Fe^{3+}, Al^{3+}, Cr^{3+} and Zn^{2+} was carried out by Budhraja *et al.*[1]. Modification of photo catalytic activity of SbS_3 in presence of $NaHCO_3$ was reported by Ameta *et al.*[2]. Mills *et al.*[3] reported photo oxidation of water using WO_3 powder in presence of Fe^{3+} ions. Sharma *et al.*[4] observed the catalytic activity of transition metal oxides and mixed metal oxides. Adsorption of triphenyl methane dyes on to jackfruit peel carbon was reported by Inbaraj *et al.*[5]. The kinetics of photo bleaching of Aber Chrome 540 in various solvents was carried out by Rappon and Syitski[6]. The chemistry of NO_2 and SO_2, Zn and ZnO powder has been reported by Rodrigenez *et al.*[7].

An attempt is made to remove these dyes semiconductor $MnWO_4$ and light which may provide an alternative cheaper path.

EXPERIMENTAL

The stock solution of dye was prepared in distilled water and diluted as required. The pH of the solutions was determined using pH meter (Hena imported pen type). Solution of dye was taken in a beaker and a known amount of $MnWO_4$ was added and covered with water filter to avoid the heat reaction. The solution was irradiated by visible tungsten lamp and the optical density (OD) was recorded spectrophotometrically. Intensity of light was measured by Suryamapi (CEL Model SM 201).

RESULTS AND DISCUSSION

The plot of 1 + log OD was found straight line suggesting that bleaching of dye by $MnWO_4$ follows pseudo first order rate law. Rate constant were calculated by graphs as follows:

$$K_1 = 2.303 \times \text{Slope}$$

A typical run is given in Table-1.

TABLE-1
[Eosine-Y] = 7.00×10^{-5} M, pH = 7.5, $MnWO_4$ = 0.10 g,
Intensity = 37.0 mW cm^{-2}

Time (min)	OD	1 + log OD
0	0.3310	0.5198
20	0.3100	0.4914
40	0.2910	0.4639
60	0.2710	0.4330
80	0.2530	0.4031
100	0.2370	0.3747
120	0.2220	0.3464
140	0.2070	0.5775

Effect of pH variation: The effect of variation of pH was studied. It was found that as pH of the reaction mixture is raised, the rate of photo catalytic bleaching increases. It attains a maximum value. After it, if pH is raised, the rate of reaction decreases. Increase in pH increases the number of OH^- ions. When a hole is generated by semiconductor, an electron is abstracted from OH^- ion converting it into $OH^\bullet$ free radical. This free radical is responsible for the bleaching of dye as proved by use of scavenger. The effect of pH variation is given in Table-2.

Effect of concentration of Eosine-Y: Keeping all other factors constant, the concentration of dye was changed and its effect on rate of bleaching was studied. The data are summarized in Table-3. The rate of photo catalytic bleaching was found to increase with increase in the concentration of Eosine-Y (Table-3). This may be explained that rate of reaction is directly proportional to the molar concentration of reacting species and it will be up to optimum concentration of Eosine-Y (Concentration 7.00×10^{-5} M). If more concentration of dye is taken, it imparts a darker colour to the solution and it may act as filter to the incident light reaching the semiconductor surface. As a consequence, the rate of photo catalytic bleaching of Eosine-Y decreases.

Effect of amount of $MnWO_4$: The weight of $MnWO_4$ was varied and its effect on bleaching was studied whose results are summarized in Table-4. It was found that up to a limited weight, the rate of photo-bleaching increases.

TABLE-2
[Eosine-Y] = 7.00 × 10^{-5} M, Intensity = 37.0 mW $cm^{-2,}$ $MnWO_4$ = 0.10 g

pH	$K_1 \times 10^5$ (S^{-1})
6.0	1.11
6.5	1.92
7.0	3.00
7.5	5.53
8.0	2.85
8.5	2.29
9.0	1.32

TABLE-3
$MnWO_4$ = 0.10 g, pH = 7.5, Intensity = 37.0 mW cm^{-2}

[Eosine-Y] × 10^{-5} M	$K_1 \times 10^5$ (s^{-1})
2	1.66
3	2.98
4	3.25
5	4.18
6	4.59
7	5.53
8	4.13
9	3.35

It may be due to more surface area available of semiconductor to catch hold the light and generate the excited states. After a limit, rate of bleaching may decrease due to the interference of molecules of $MnWO_4$. The abundance of molecules interferes in the pathway of other molecules gaining the excited state, thus resulting decrease in bleaching.

Effect of intensity on rate of bleaching: The effect of intensity of light on rate of bleaching was studied by keeping the reaction mixture at different places below the lamp. The data are given in Table-5. The rate of photo catalytic bleaching increases as the intensity increases. It may be explained on basis of number of excited molecules. As more intensity of light falls on $MnWO_4$ molecules, more number of molecules get excited which in turn may bleach more dye molecules, thus the rate of bleaching was found increasing with increase in intensity of light.

TABLE-4
[Eosine-Y] = 7.00 × 10^{-5} M, pH = 7.5, Intensity = 37.0 mW cm^{-2}

Amount of semiconductor (g)	$K_1 \times 10^5$ (s^{-1})
0.04	1.04
0.06	1.56
0.08	2.78
0.10	5.53
0.12	4.51
0.14	2.97
0.16	1.82

TABLE-5
[Eosine-Y] = 7.00 × 10^{-5} M, pH = 7.5, $MnWO_4$ = 0.10 g

Intensity (mW cm^{-2})	$K_1 \times 10^5$ (s^{-1})
23.0	0.94
27.0	1.16
30.0	1.64
37.0	5.53

On the basis of above studies carried out, mechanism is proposed of bleaching of the dye.

$$^{1}\mathrm{Dye}_0 \longrightarrow {}^{1}\mathrm{Dye}_1 \text{ (Singlet excited state)}$$
$$^{1}\mathrm{Dye}_1 \longrightarrow {}^{3}\mathrm{Dye}_1 \text{ (Triplet excited state)}$$
$$\mathrm{Sc} \longrightarrow e^- + h^+ \text{ or } \mathrm{Sc}^+$$
$$h^+ + \mathrm{OH}^- \text{ (from base)} \longrightarrow {}^{\bullet}\mathrm{OH}$$
$$^{3}\mathrm{Dye}_1 + {}^{\bullet}\mathrm{OH} \longrightarrow \text{Products}$$

Dye absorbs the light and gets excited to singlet state. This through intersystem crossing gets converted to triplet state. On the other hand the semiconductor gets excited by absorbing light and an electron is excited from valance band to conduction band leaving behind a hole. The hole abstracts an electron from OH^- ions generating $^{\bullet}\mathrm{OH}$ free radical. This dye is now being bleached from this free radical producing lucobase. The participation of $^{\bullet}\mathrm{OH}$ radical is confirmed by the use of scavenger, which stops the bleaching reaction completely.

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