HARVESTING SOLAR ENERGY FOR TREATING DYE STUFF IN INDUSTRIAL EFFLUENTS - ZNS-CDS USED AS PHOTOCATALYST

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ABSTRACT

The removal of Crystal Violet was carried out through semiconductor ZnS-CdS. Visible light was used as the source of energy. Various parameters like amount of semiconductor, pH, light intensity, dye concentration etc. were varied. A tentative mechanism is proposed.

Key Words:*Semiconductor, sun light, pH, concentration of dye, bleaching of dye etc.*

INTRODUCTION

Photo catalysis has received considerable attention in recent years as an alternate for treating water polluted with heavy metal ions, dyes and other pollutants. Dyes are used by industries on a vast scale. These dyes are released in the environment causing severe pollution. Photo catalysis has large capability for the water treatment and so an attempt is made to remove these dyes through photo catalysis.

Hachem et al[1] reported decolonization of textile industry waste water by photo catalytic degradation process where as Saquib et al[2] studied semiconductor mediated photocatalysed degradation of an anthraquinone dye Remazol Brilliant Blue. Zang et al[3] reported photocatalytic reduction of Methyl Yellow on CdS nanoparticles mediated in reverse micelles. N-dealkylation on Rhodamine B and Crystal Violet on CdS was studied by Takizawa[4]. Photo catalytic reaction of environmental pollutants over CdS powder selecting Cr(VI) as a substrate was studied by Wang et al[5]. Several other catalysts like ZnO, PbS, WO_3, TiO_2 etc. are used for this purpose.

Nasr et al[6] studied photocatalytic reduction of azo dyes like Naphthol Blue Black and Disperse Blue 79 while photosensitized approach for the degradation of textile azo dye Acid Orange 7 was made by Vinodgopal et al[7]. Recently nanotechnology is used in visible light photocatalysis via CdS/TiO_2 nanocomposite materials by Sesha et al[8]. Mixed oxide/sulfide systems for photocatalysis were reported by A. Di Paola et al[9].

An attempt is made to remove these dyes using ZnS-CdS in presence of solar energy which may provide an efficient and cheaper way for removal of dyes.

EXPERIMENTAL

The stock solution of dye was prepared in distilled water and diluted as required. The pH of the solutions was attained by adding prestandardized HCl solution and was determined using pH meter (Hena imported pen type). Solution of dye was taken in a beaker; known amount of ZnS-CdS was added and covered with water filter to avoid the heat reaction. The solution was irradiated by visible tungsten lamp and the O.D. was recorded spectrophotometrically (Systronics Spectrophotometer).

The semiconductor was prepared by taking known weight of salts of Zn and Cd and precipitating by passing H_2S. The precipitate was allowed to settle down and further presence of precipitate was checked by passing more H_2S in the supernatant solution. Then the precipitate was washed several times with distilled water and was allowed to dry at room temperature. The yellow powdered solid insoluble in water was used as semiconductor for studies.

RESULT AND DISCUSSION

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

K_1 = 2.303 x Slope

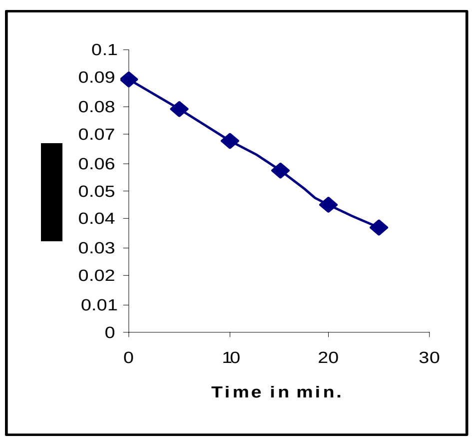
A typical run is given in table 1 and graph 1

Table – 1

[Crystal Violet] = 2.00 x 10^{-5} M, pH = 4.5,
ZnS-CdS = 0.12 g, Intensity = 37.0 mW cm^{-2}

Time in min.	O.D.	1 + Log O.D.
0	0.23	0.0899
5	0.20	0.0791
10	0.17	0.0681
15	0.14	0.0569
20	0.11	0.0453
25	0.09	0.0374

Slope= 3.81 x 10^{-3} Sec^{-1}



Graph 1 – A Typical Run

Effect of pH variation

Effect of variation of pH was studied. The data are recorded in table 2 and graph 2. . It is established that surface properties of semiconductor are responsible for photocatalytic process[10].

The hole generated by semiconductor creates H^+ ions in the solution from water .These protons are utilized by dissolved oxygen in solution.

$$2h^+ + H_2O \rightarrow 1/2O_2 + 2H^+ \quad \text{--------------------- (i)}$$

$$2H^+ + O_2 + 2e^- \rightarrow H_2O_2 \quad \text{---------------------- (ii)}$$

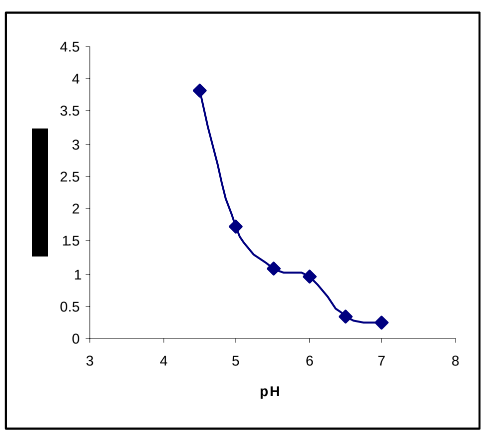
These two reactions counter balance each other to a particular extent. The surface charge on the semiconductor-electrolyte interface will play a major role in deciding the fate of this photocatalytic reaction. The surface charge on semiconductor favors the reaction when it is positive. This surface charge depends on the pH of the solution being positive in acidic media and negative in alkaline media. After a particular pH net charge on semiconductor surface becomes zero and is called point of zero discharge (PZC) [11].

Table – 2

[Crystal Violet] = 2.00 x 10^{-5} M,

Intensity = 37.0 mW cm^{-2}, ZnS-CdS = 0.12 g

pH	**K_1 x 10^3 (S^{-1})**
4.5	**3.81**
5.0	1.72
5.5	1.07
6.0	0.97
6.5	0.33
7.0	0.25



Graph 2 - Effect of Variation of pH

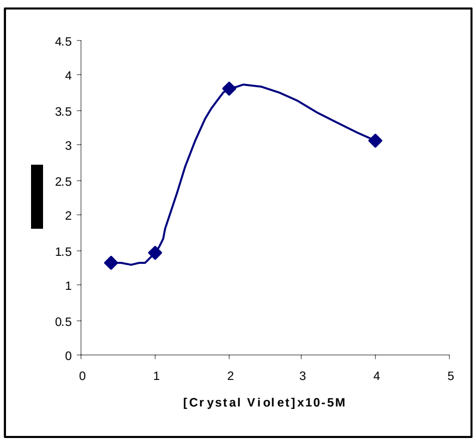
Effect of concentration of Crystal Violet

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 and graph 3. The rate of photo catalytic bleaching was found to increase with increase in the concentration of Crystal Violet (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 Crystal Violet (Concentration 2.00 x 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 Crystal Violet decreases.

Table – 3

ZnS-CdS = 0.12 g, pH = 4.5, Intensity = 37.0 mW cm^{-2}

[Crystal Violet] x 10^{-5} M	**K_1 x 10^3 (S^{-1})**
0.4	1.33
1.0	1.47
2.0	**3.81**
4.0	3.07



Graph 3 - Effect of concentration of Crystal Violet

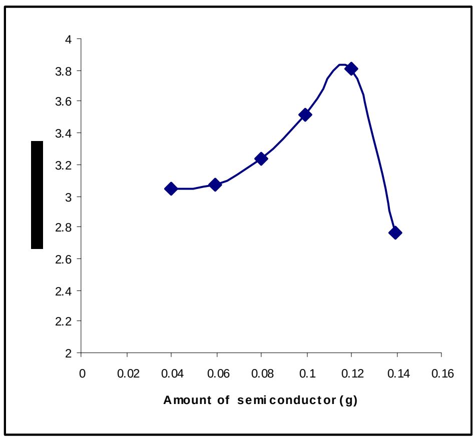
Effect of Amount of ZnS-CdS

The weight of ZnS-CdS was varied and its effect on bleaching was studied whose results are summarised in table 4 and graph 4. It was found that up to a limited weight, the rate of photo-bleaching increases. 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 ZnS-CdS. The abundance of molecules interferes in the pathway of other molecules gaining the excited state, thus resulting decrease in bleaching.

Table – 4

[Crystal Violet] = 2.00 x 10^{-5} M, pH =4.5,
Intensity = 37.0 mW cm^{-2}

Amount of semiconductor (g)	**K_1 x 10^3 (S^{-1})**
0.04	3.05
0.06	3.07
0.08	3.24
0.10	3.52
0.12	**3.81**
0.14	2.77



Graph 4 - Variation of Amount of ZnS-CdS

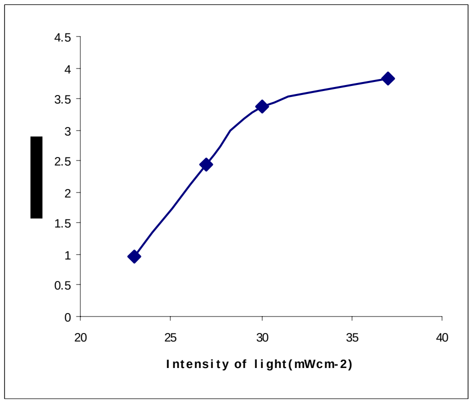
Effect of intensity on rate of bleaching

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 and graph 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 ZnS-CdS 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 – 5

[Crystal Violet] = 2.00 x 10^{-5} M, pH = 4.5,
ZnS-CdS = 0.12 g

Intensity (mW cm^{-2})	**K_1 x 10^3 (S^{-1})**
23.0	0.98
27.0	2.44
30.0	3.38
37.0	**3.81**



Graph 5-Effect of intensity on the rate of bleaching

On the basis of above studies carried out, mechanism is proposed of bleaching of the dye as follows -

$$^{1}\mathbf{Dye}_0 \longrightarrow {}^{1}\mathbf{Dye}_1 \text{ (Singlet excited state)}$$

$$^{1}\mathbf{Dye}_1 \xrightarrow{\mathbf{ICS}} {}^{3}\mathbf{Dye}_1 \text{ (Triplet excited state)}$$

$$\mathbf{Sc} \longrightarrow \mathbf{e^-(CB) + h^+(VB) \text{ or } Sc^+}$$

$$\mathbf{e^- + O_2} \longrightarrow \mathbf{O_2^{-\cdot}}$$

$$\mathbf{O_2^{-\cdot} + H^+} \longrightarrow \mathbf{HO_2^{\cdot}}$$

$$\mathbf{HO_2^{\cdot}} + {}^{3}\mathbf{Dye}_1 \longrightarrow \textbf{Leuco dye}$$

$$\textbf{Leuco dye} \longrightarrow \textbf{Product}$$

Dye absorbs the light and gets excited to singlet state and through intersystem crossing gets converted to triplet state. On the other hand the semiconductor absorbs light and an electron is excited from valance band to conduction band leaving behind a hole. The generated electron then reacts with dissolved oxygen to generate an anion free radical. This on reaction with H^+ ion of acid yield HO_2 free radical. The dye is now being bleached from this free radical producing luco dye and this then converts into product. The participation of $HO_2^{\cdot}$ radical is confirmed by the use of scavenger, which stops the bleaching reaction completely.

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