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A COMPARATIVE STUDY OF ZnS AND CoS-ZnS (1 : 2) IN PHOTOCATALYTIC DEGRADATION OF AZURE B

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ABSTRACT

A mixed semiconductor CoS-ZnS (in 1 : 2 mole ratios) was prepared through coprecipitation and used as photocatalyst in the photodegradation of azure B. 1 : 2 CoS-ZnS was found superior in degradation of azure B under visible light irradiation as compared to ZnS. Various parameters like amount of semiconductor, pH, light intensity, dye concentration etc. were varied and their effect on rate of degradation was observed. A tentative mechanism has been proposed.

Key words: CoS-ZnS, Photodegradation, Azure B, Coprecipitation.

INTRODUCTION

Elimination of dyes and other commercial colorants from waste water effluents of textile and paper mills and other colorant manufactures is now the subject of considerable concern from environmental point of view. Recently, a lot of studies have been concentrated on the degradation using toxic organic compounds in waste water via photocatalysis using various semiconductors like oxides and sulphides of metal ions.

Hetterich and Kisch[1] studied the photocatalytic activity of ZnS where as Paola et al.[2] worked on mixed WO_3/WS_2 and ZnO/ZnS systems. Pouretedal et al.[3] used doped ZnS with manganese, nickel and copper as nanophotocatalyst where as Dangi et al.[4] worked on ZnS-CdS in photocatalytic degradation of dyes. Use of coprecipitated oxides CeO_2-ZrO_2 in bleaching of dyes was made by Letichevsky et al.[5] Cun et al.[6] carried out photocatalytic bleaching of methyl orange in presence of nanosized ZnO/SnO_2 coupled photocatalyst where as Aguedach et al.[7] worked on photocatalytic degradation of dyes in water over a newly deposited titanium dioxide. Photocatalytic degradation of 2-chlorophenol by Co-doped TiO_2

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nanoparticles has been reported by Barakat et al.[8] Wu et al.[9] reported enhancement of the photocatalytic performance of TiO_2 catalyst via transition metal modifications.

Oxides and sulphides of metal ions like TiO_2, ZnO, ZnS, etc. can barely absorb visible light due to their wide band gap energies. ZnS is off-white in color and it does not absorb a major portion in the visible region. In an effort to synthesize a visible light driven photocatalyst, a mixed semiconductor 1 : 2 CoS-ZnS was prepared through coprecipitation, which proves to be more efficient photocatalyst than ZnS.

EXPERIMENTAL

Degradation of azure B

The stock solution of dye (1.0×10^{-3}M) was prepared in distilled water and diluted as and when required. The pH of the solutions was adjusted by NaOH and H_2SO_4 and determined by a digital pH meter (Eutech WP-2). Solution of dye was taken in beaker and known amount of 1 : 2 CoS-ZnS was added. The beaker was covered with water filter to avoid the thermal degradation. The solution was irradiated by a 200W tungsten lamp. The light intensity was measured with the help of a solarimeter (CEL, Model SM 201) and the optical density was recorded at regular time intervals using UV – visible spectrophotometer (Systronics Model 106).

Preparation of 1 : 2 CoS-ZnS by coprecipitation

The 1 : 2 CoS-ZnS semiconductor was prepared by mixing clear solutions of $ZnSO_4$ (M/2 molar) and $CoSO_4$ (M/4 molar) in water. After mixing equal volumes of these two solutions, it was made alkaline by adding NH_4Cl and NH_4OH solutions. It was then precipitated by passing H_2S gas and precipitates were filtered. Wet cake obtained was washed with distilled water several times and it was allowed to dry at room temperature. Grey crystals obtained were crushed to get uniform particle size, which was used as 1 : 2 CoS-ZnS in further experiments.

RESULTS AND DISCUSSION

Pure ZnS and 1 : 2 CoS-ZnS both were used as photocatalysts in the photodegradation of azure B. The experimental results indicated that pure ZnS could not degrade azure B dye but when 1 : 2 CoS-ZnS catalyst was used in place of pure ZnS, a fast rate of degradation was observed. The results of typical run are reported in Table 1 and graphically represented in Fig. 1. The plot of 1 + log O.D. versus time indicates that degradation of dye by pure ZnS is negligible but in case of 1 : 2 CoS-ZnS, the rate of

degradation of dye was relatively faster. The plot was found to be a straight line suggesting that degradation of dye by 1 : 2 CoS-ZnS follows pseudo-first order rate law. The rate constant for this reaction was determined using the expression -

$$k = 2.303 \times \text{slope}$$

Table 1: A typical run

Time (min.)	**[Azure B] = 4.0×10^{-5} M 1 : 2 CoS-ZnS = 0.25 g Light Intensity = 60.0 m Wcm^{-2} pH = 7.00**		**[Azure B] = 4.0×10^{-5} M ZnS = 0.20 g Light Intensity = 60.0 m Wcm^{-2} pH = 7.00**	
	Optical density	**1 + log O.D.**	**Optical density**	**1 + log O.D.**
0	0.977	0.989	0.921	0.9642
15	0.895	0.951	0.918	0.9628
30	0.787	0.895	0.916	0.9619
45	0.684	0.835	0.919	0.9633
60	0.602	0.779	0.915	0.9614
75	0.530	0.724	0.910	0.9590
90	0.468	0.670	0.905	0.9566
105	0.413	0.615	0.901	0.9547
-	**$k = 1.42 \times 10^{-4}$ (sec^{-1})**		**$k = 3.40 \times 10^{-6}$ (sec^{-1})**	

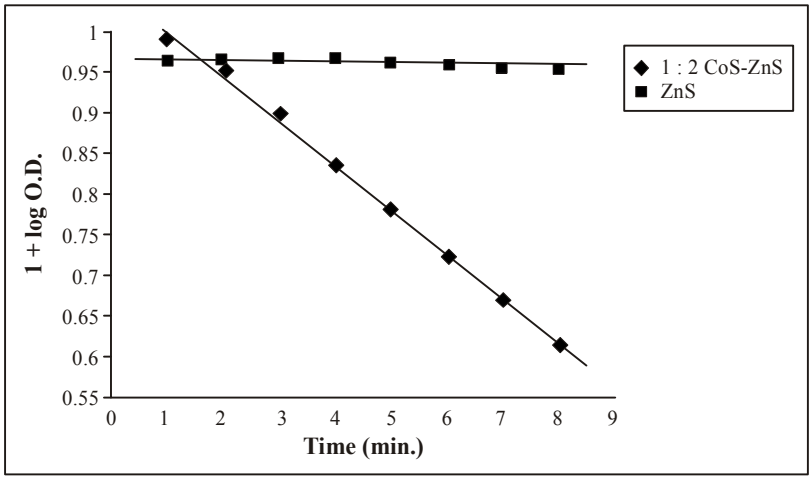

Fig. 1: A typical run

Effect of pH

To study the effect of pH on the decolorization efficiency, experiments were carried out at various pH values without changing other parameters. The reaction rates were determined in the pH range 6.0–9.0. It has been observed that with an increase in pH, the rate of photocatalytic degradation of dye increases from 6.0 to 7.0. A further increase in pH resulted into a decrease in the rate of photocatalytic bleaching. At pH 7.0, maximum degradation rate was observed. The effect of pH variation on the rate is given in Table 2.

Table 2: Effect of pH

pH	**[Azure B] = 4.0 × 10^{-5} M 1 : 2 CoS-ZnS = 0.25 g Light Intensity = 60.0 mWcm^{-2}**
	k x 10^4 (sec^{-1})
6.0	0.90
6.5	1.10
7.0	1.42
7.5	1.30
8.0	1.20
8.5	0.97
9.0	1.08

This can be explained on the basis that as the pH of medium was decreased below 7.0, then the surface of semiconductor remains positively charged due to adsorption of H^+ ions and the dye also loses its anionic behavior and hence, there is a corresponding decrease in the rate of bleaching due to coulombic repulsion between positively charged semiconductor surface and protonated dye molecules. Above pH 7.0, more OH^- ions are in the solution and these OH^- ions will adsorb on the semiconductor surface making it negatively charged. Thus, there will be a coulombic repulsion between negatively charged semiconductor surface and anionic dye, which resulted into a decrease in the rate of photocatalytic bleaching of the dye azure B.

Effect of concentration of azure B

The effect of azure B concentration on the photocatalytic degradation was also investigated and the results are summarized in Table 3.

It was observed that as the concentration of dye was increased up to 4.0 x 10^{-5} M, the degradation rate increases. On increasing concentration further, the rate of degradation of dye decreases. As the concentration of azure B was increased, more dye molecules were available for excitation and hence, an increase in the rate of reaction was observed. A decrease in the rate at higher concentration of dye may be attributed to the fact that the dye will start acting as a filter for the incident light and it will not allow the desired light intensity to reach the semiconductor particles and thus, decreasing the rate of photocatalytic beaching.

Table 3: Effect of dye concentration

[Azure B] x 10^5M	**1 : 2 CoS-ZnS = 0.25 g Light Intensity = 60.0 mWcm^{-2} pH = 7.0**
	k x 10^4 (sec^{-1})
2.0	1.30
4.0	1.42
6.0	1.22
8.0	0.99
10.0	0.78
12.0	0.70

Effect of amount of 1 : 2 CoS-ZnS

The effect of amount of semiconductor on the degradation of azure B was observed and the results are summarized in Table 4.

The quantity of 1 : 2 CoS-ZnS was varied keeping all remaining parameters same and its effect on degradation rate was studied. From the experimental data, it was found that up to 0.25 g, the rate of degradation increases. After a limit, it remains virtually constant or rather decreases slightly. This may be explained on the basis that as the amount of semiconductor was increased, the exposed surface area also increases, but after a certain limit, there will be no increase in the exposed surface area of photocatalyst, because particle settled in a layered form so that upper layer is only excited and participate in a degradation process. It may be considered like a saturation point above which any increase in the amount of semiconductor has negligible or no effect on the rate of photocatalytic bleaching of dyes

as any increase in the amount of semiconductor after this saturation point will only increase the thickness of the layer at the bottom of the vessel.

Table 4: Effect of amount of semiconductor

Semiconductor (g)	[Azure B] = 4.0×10^{-5} M Light Intensity = 60.0 mWcm^{-2} pH = 7.0
	k x 10^4 (sec^{-1})
0.15	0.96
0.20	1.16
0.25	1.42
0.30	1.35
0.35	1.30
0.40	1.31

Effect of light intensity

The effect of light intensity on the degradation of azure B was also studied and the results are summarized in Table 5.

Table 5: Effect of light intensity

Light intensity (mWcm^{-2})	[Azure B] = 4.0×10^{-5} M 1 : 2 CoS-ZnS = 0.25 g pH = 7.0
	k x 10^4 (sec^{-1})
30.0	1.28
40.0	1.38
50.0	1.40
60.0	1.42
70.0	1.70

The rate of photocatalytic degradation increases with increasing light intensity. It can be explained on the basis of excited molecules. As light intensity was increased, more number of catalyst molecules get excited, which in turn degrade more dye molecules. As a result, dye degradation increases with increase in intensity of light.

MECHANISM

On the basis of experimental observations, a tentative mechanism has been proposed.

$$^{1}Dye_0 \longrightarrow {}^{1}Dye_1 \text{ (Singlet excited state)} \quad ...(1)$$

$$^{1}Dye_1 \longrightarrow {}^{3}Dye_1 \text{ (Triplet excited state)} \quad ...(2)$$

$$SC \longrightarrow e^- + h^+ \text{ or } SC^+ \quad ...(3)$$

$$h^+ + H_2O \text{ (from base)} \longrightarrow H^+ + {}^{\bullet}OH \quad ...(4)$$

$$^{3}Dye_1 + {}^{\bullet}OH \longrightarrow \text{Products} \quad ...(5)$$

When the solution of dye was exposed to light in the presence of semiconductor, dye molecule absorbs the light and gets excited to 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 the hole. The hole abstracts an electron from OH^- ions generating $^{\bullet}OH$ free radicals. The dye is being bleached by this free radical.

CONCLUSION

The rate of photocatalytic bleaching of azure B is enhanced by coprecipitated CoS-ZnS as compared to pure ZnS. The order of degradation is -

CoS - ZnS > ZnS

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