



USE OF COPRECIPITATED ZnS-MnS IN DEGRADATION OF ROSE BENGAL

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ABSTRACT

The photocatalytic degradation of rose bengal has been investigated in presence of coprecipitated ZnS-MnS. The rate of photocatalytic degradation of dye was observed spectrophotometrically. The effect of variation of different parameters like pH, concentration of dye, amount of semiconductor and light intensity on the rate of photobleaching was also observed. A tentative mechanism for the photocatalytic degradation of rose bengal has also been proposed.

Key words: Photocatalytic degradation, Rose bengal, Coprecipitated sulphide.

INTRODUCTION

Our environment is composed of atmosphere, earth, water and space. Under normal circumstances, it remains clean and therefore, enjoyable also. Unfortunately on account of the man made activities, the composition and complex nature of the environment has changed a lot. Rapidly growing industrialization, series of new constructions, many fold increase in transportation, etc. are such anthropogenic activities. Although these are the most desirable activities for human development, but lead to generation and release of objectionable materials into the environment, which makes it polluted.

Various industrial effluents contain a number of chemical pollutants, generally dyes, which are toxic to aquatic life at higher concentrations. Adsorption, osmosis, flocculation and other methods have been used traditionally to remove dyes from water bodies, but all such methods suffer from various drawbacks. The photocatalytic treatment of such effluents

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holds a good promise. Photocatalysis is a phenomenon where an electron-hole pair is generated on exposing semiconducting materials to the light of suitable energy.

Mengyue *et al.*¹ carried out photocatalytic degradation of organophosphorus pesticides using thin films of TiO₂. Kako *et al.*² have suggested some preventive methods against catalytic poisoning of TiO₂ photocatalyst by H₂S. Rao *et al.*³ reported photocatalytic degradation of crystal violet over semiconductor ZnO powder suspended in aqueous solution. Photocatalytic reduction of environmental pollutant Cr (VI) over CdS powder under visible light illumination has been observed by Wang *et al.*⁴

Photoreduction of CO₂ over ZnS to 2- and 4- carbon acids was observed by Eggine *et al.*⁵ Liu *et al.*⁶ studied structural, optical and magnetic properties of Co-doped ZnO films. Kobayashi *et al.*⁷ investigated the photocatalytic properties of alumina supported ZnS-CdS catalyst. Jin *et al.*⁸ synthesized water soluble coprecipitated Cd_xZn_(1-x)S nanoparticles by capping method. Kakuta *et al.*⁹ used coprecipitated ZnS-CdS over SiO₂ for photoassisted catalysis of H₂ production in aqueous sulphite solution.

Roy and De¹⁰ investigated the immobilisation of CdS, ZnS and mixed ZnS-CdS on filter paper and studied the effect of hydrogen production from alkaline Na₂S/Na₂S₂O₃ solution. The surfaces of ZnS and PbS were modified by interfacing PbS on ZnS and ZnS on PbS nanoparticles by Anil and Anshuman.¹¹ This produced coreshell nanocomposites ZnS/PbS and PbS/ZnS with tunable electronic properties.

CdS-ZnS has been used as a photocatalyst for photodehydrodimerisation of 2,5-dihydrofuran by Helderich and Kisch.¹² Poulios *et al.*¹³ observed the photooxidation of eosin Y in the presence of ZnO and TiO₂, where 85% reduction in toxicity of eosin Y solution has been observed.

Mixed WO₃/WS₂ and ZnS/ZnO have been prepared by Paola *et al.*¹⁴ Coupling of two tungsten chalcogenides increases the rate of disappearance of organic substance. Unlike this, zinc chalcogenides exhibit lower photocatalytic activity than pure ZnO. Preparation, characterization and photoactivity of polycrystalline ZnO/TiO₂ system has been reported by Marci *et al.*¹⁵

Yan *et al.*¹⁶ used precipitation method for deposition of ultra small gold nanoparticles over titania modified SBA15. Yin *et al.*¹⁷ reported that photocatalytic chlorination of 1,2,3,4-tetrachlorobenzene using nanosized CdS//TiO₂ hybrid photocatalyst under visible light irradiation was enhanced as compared to that of CdS. The electronic characterization and photocatalytic properties of CdS/TiO₂ semiconductor composite was

studied by Tristao *et al.*¹⁸ Ren *et al.*¹⁹ studied the relationship between the coprecipitation mechanism, doping structure and physical properties of $Zn_{(1-x)}Co_xS$ nanocrystallites.

EXPERIMENTAL

Experimental procedure for photocatalytic bleaching of rose bengal

All solutions were prepared in doubly distilled water. Irradiation has been carried out with a 200W tungsten lamp. The light intensity was measured with the help of a solarimeter (CEL, Model SM 201). A water filter has been used to cut off thermal radiations. A digital pH meter (Systronics, Model 335) was used to adjust the pH of the solutions by the addition of previously standardized 0.1N sulfuric acid and 1N sodium hydroxide solutions. The progress of the photocatalytic reaction was observed by measuring the absorbance at regular time intervals using UV-visible spectrophotometer (Systronics Model 106). $ZnSO_4$ (Merck), $MnSO_4$ (Merck) and rose bengal (Himedia) have been used as received. Stock solution of rose bengal (1.0×10^{-3} M) was prepared in doubly distilled water.

Synthesis of semiconductor by coprecipitation

Coprecipitated sulphide was prepared by mixing $ZnSO_4$ (0.5×10^{-3} M) and $MnSO_4$ (0.5×10^{-3} M) in 1 : 1 ratio. Then ammonium chloride and ammonium hydroxide were added and freshly prepared H_2S gas was passed through the mixture. The precipitate obtained was dried and then used as a photocatalyst.

RESULTS AND DISCUSSION

An aliquot of 3.0 mL was taken out from the reaction mixture at regular time intervals and the absorbance was measured at $\lambda_{max} = 550$ nm. It was observed that the absorbance of the solution decreases with increasing time intervals, which indicates that the concentration of rose bengal decreases with increasing time of exposure. A plot of $1 + \log A$ (absorbance) versus time was linear and follows pseudo-first order kinetics. The rate constant was measured using following expression:

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

The data for the typical run are given in Table 1.

Effect of pH

The pH of the solution is likely to affect the photocatalytic bleaching of rose bengal.

The effect of pH on the rate of reaction was investigated in the pH range 5.0 to 8.5 for both ZnS and coprecipitated ZnS-MnS, respectively.

Table 1: Typical run

Time (min.)	[Rose bengal] = 8.0×10^{-6} M pH = 6.0 ZnS = 0.14 g Light intensity = 60.0 mWcm^{-2}		[Rose bengal] = 8.0×10^{-6} M pH = 5.5 ZnS-MnS = 0.12 g Light intensity = 60.0 mWcm^{-2}	
	O.D.	1 + log O.D.	O.D.	1 + log O.D.
0.0	0.848	0.9283	1.258	1.0996
10.0	0.708	0.8500	1.000	1.000
20.0	0.646	0.8100	0.787	0.8960
30.0	0.550	0.7404	0.617	0.7903
40.0	0.479	0.6803	0.501	0.6998
50.0	0.403	0.6030	0.419	0.6222
60.0	0.363	0.5599	0.323	0.5092
70.0	0.309	0.4900	0.248	0.3945
80.0	0.260	0.4150	0.204	0.3096
90.0	0.240	0.3820	0.163	0.2122
		$k = 2.35 \times 10^{-4} \text{ sec}^{-1}$	$k = 3.76 \times 10^{-4} \text{ sec}^{-1}$	

Photocatalytic degradation of rose bengal was observed to be maximum at pH 6.0 for ZnS and 5.5 for coprecipitated ZnS-MnS system. It was observed that the rate of photocatalytic bleaching of rose bengal increases with increase in pH up to 5.5 and on increasing pH further beyond 5.5, the rate of reaction decreases for coprecipitated ZnS-MnS system.

This behaviour may be explained on the basis that as pH was lowered, the protonation of dye molecules will take place as well as the surface of semiconductor will also become positively charged; thereby the dye molecules will experience repulsion from semiconductor. This decreases the rate of reaction. The rate of photocatalytic bleaching of

rose bengal also decreases with increase in pH above 5.5. This may be due to the fact that at higher pH (alkaline), the OH⁻ ions are adsorbed on the surface of the semiconductor making it negatively charged, thereby, the anionic dye will experience repulsion from semiconductor, thus, decreasing the rate of reaction. It means that the rate of photocatalytic bleaching of rose bengal was optimum, when the dye remains almost in its neutral form (approx. pH 6.0). The results of pH variations are summarized in Table 2.

Table 2: Effect of pH

pH	[Rose bengal] = 8.0 x 10 ⁻⁶ M ZnS = 0.14 g Light intensity = 60.0 mWcm ⁻²	[Rose bengal] = 8.0 x 10 ⁻⁶ M ZnS-MnS = 0.12 g Light intensity = 60.0 mWcm ⁻²
	k x 10 ⁴ (s ⁻¹)	k x 10 ⁴ (s ⁻¹)
5.0	0.89	1.73
5.5	1.82	3.76
6.0	2.35	1.71
6.5	1.99	1.05
7.0	1.61	0.75
7.5	1.23	0.69
8.0	1.06	0.63
8.5	0.64	0.59

Effect of concentration of rose bengal

The effect of variation of rose bengal concentration on the degradation was also observed and the results are summarized in Table 3.

The rate of photocatalytic degradation was found to increase with increase in the concentration of rose bengal upto 8.0 x 10⁻⁶ M, for both ZnS and coprecipitated ZnS-MnS. Further increase in the concentration beyond this limit results in decrease in the rate of degradation. The increase in rate may be due to the fact that as the concentration of rose bengal is increased, more dye molecules are available for excitation and energy transfer and hence, an increase in the rate has been observed. The rate of dye bleaching was found to

decrease with a further increase in the concentration above 8.0×10^{-6} M. This may be attributed to the fact that the dye will start acting as a filter for the incident light and it will not permit the desired light intensity to reach the semiconductor particles and thus, a decrease in the rate of photocatalytic degradation of rose bengal has been observed.

Table 3: Effect of dye concentration

[Rose bengal] x 10^5 M	pH = 6.0 ZnS = 0.14 g Light intensity = 60.0 mWcm ⁻²	pH = 5.5 ZnS-MnS = 0.12 g Light intensity = 60.0 mWcm ⁻²
	k x 10 ⁴ (s ⁻¹)	k x 10 ⁴ (s ⁻¹)
0.2	1.24	1.29
0.3	1.43	1.70
0.4	1.93	2.19
0.6	2.20	2.26
0.8	2.35	3.76
1.0	1.72	2.25
1.2	1.29	1.88
1.4	0.96	1.41
1.6	0.32	0.83

Effect of amount of semiconductor

The effect of the amount of semiconductor on the rate of photocatalytic degradation of rose bengal was observed by keeping all other factors identical. The results are reported in Table 4.

The rate of degradation was found to increase with increasing amount of semiconductor in both the cases and ultimately, it becomes almost constant after a certain amount of semiconductor. The rate was found to be maximum for 0.14 g and 0.12 g for ZnS and coprecipitated ZnS-MnS, respectively. This may be explained on the basis that as the amount of semiconductor was increased, the exposed surface area of semiconductor also increases, but after a certain limit, if the amount of semiconductor was further increased,

then there will be no increase in the exposed surface area of the photocatalyst. It may be considered like a saturation point above which any increase in the amount of semiconductor has negligible effect on the rate of photocatalytic bleaching of rose bengal, because any increase in the amount of semiconductor after this saturation point will only increase the thickness of the layer at the bottom of the reaction vessel.

Table 4: Effect of amount of semiconductor

Semi-conductor (g)	pH = 6.0 [Rose bengal] = 8.0×10^{-6} M Light intensity = 60.0 mWcm^{-2}	pH = 5.5 [Rose bengal] = 8.0×10^{-6} M Light intensity = 60.0 mWcm^{-2}
	$k \times 10^4 \text{ (s}^{-1}\text{)}$	$k \times 10^4 \text{ (s}^{-1}\text{)}$
0.02	0.39	1.01
0.04	0.54	1.42
0.06	0.63	1.81
0.08	0.78	2.19
0.10	1.09	2.60
0.12	2.11	3.76
0.14	2.35	3.72
0.16	2.34	3.77
0.18	2.35	3.76

Effect of light intensity

The effect of light intensity on the photocatalytic degradation of rose bengal was also investigated. The results are reported in Table 5.

The results indicate that an increase in the light intensity increases the rate of reaction and maxima were found to be for 60.0 mWcm^{-2} for both ZnS and coprecipitated ZnS-MnS system. It may be explained on the basis that as the light intensity was increased, the number of photons striking per unit area also increase, resulting into a higher rate of degradation. Higher intensities of light were not used just to avoid any thermal side reactions.

Table 5: Effect of light intensity

Light intensity (mWcm ⁻²)	pH = 6.0 [Rose bengal] = 8.0 x 10 ⁻⁶ M ZnS = 0.14 g	pH = 5.5 [Rose bengal] = 8.0 x 10 ⁻⁶ M Zns-MnS = 0.12 g
	k x 10 ⁴ (s ⁻¹)	k x 10 ⁴ (s ⁻¹)
10.0	1.10	0.78
20.0	1.29	1.03
30.0	1.49	1.36
40.0	1.92	1.49
50.0	2.14	2.55
60.0	2.35	3.76

MECHANISM

On the basis of the experimental observations and corroborating the existing literature, a tentative mechanism has been proposed for the degradation of rose bengal by ZnS and coprecipitated ZnS-MnS system.



When the solution of the dye was exposed to light in the presence of a semiconductor, the rose bengal molecules are excited to their first singlet state. These excited molecules are converted to their triplet state through inter system crossing (ISC). The semiconductor uses the light energy to excite its electron from valence band to conduction band; thus, leaving behind a hole (h⁺). The hole abstracts an electron from OH⁻

ion to generate OH radical ($\cdot\text{OH}$) which will ultimately degrade the dye to the products via its leuco form. The participation of OH radical as an active oxidizing species was confirmed by using hydroxyl radical scavengers like 2-propanol, where the reaction rate is drastically reduced.

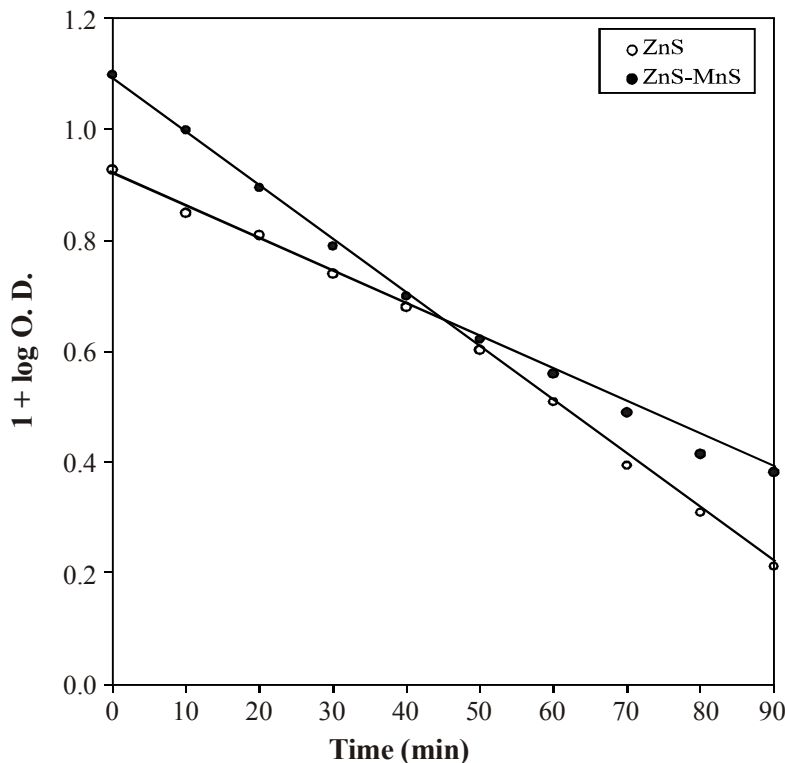


Fig. 1: A typical run

CONCLUSION

The rate of photocatalytic degradation of rose bengal is enhanced by coprecipitating ZnS with MnS as compared to pure ZnS. The order of rate of degradation of rose bengal is -



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