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ROLE OF COPRECIPITATED NiS-ZnS IN PHOTOCATALYTIC DEGRADATION OF ALIZARIN RED S

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ABSTRACT

NiS-ZnS in molar ratio 1 : 2 was prepared using coprecipitation method. It photocatalytic activity was evaluated using alizarin red S as a model dye. The dependence of the rate of degradation on the amount of catalyst, pH, concentration of dye and light intensity has been studied. A comparative study on the photocatalytic activities of NiS-ZnS with pure ZnS was also made. A tentative mechanism for the photocatalytic degradation of alizarin red S has also been proposed.

Key words: NiS-ZnS, Photocatalytic activity, Alizarin red S, Coprecipitation.

INTRODUCTION

In recent years, the scientific community has shown a great concern for the possible adverse effects that the presence of pollutants in water and food may have on human health and the equilibrium of the ecosystem, such as carcinogenesis, neurotoxicity, effects on reproduction and cell development effects ; particularly in the early stages of life.

Heterogeneous photocatalytic destruction of organic pollutants in waste water by using sun light or visible light as the excitation energy is an appealing field. Widely used semiconductor photocatalysts, such as anatase TiO_2 and ZnS; showed very low photoactivity under visible light excitation. Therefore, several attempts have been made to produce new and efficient photocatalytic materials.

Paola et al.[1] studied photocatalytic degradation of organic compounds in aqueous systems by transition metal doped polycrystalline TiO_2. Hong et al.[2] reported the synthesis of nanosized TiO_2/SiO_2 particles in the micro-emulsion and their photocatalytic activity on the

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decomposition of p-nitrophenol. In order to extend the effective wavelength of TiO_2 particulate photocatalyst into visible region, Ru-doped TiO_2 particles were prepared and their properties as the photocatalyst were investigated by Ohno et al.[3] using Fe (III) ions as an electron acceptor. Gou et al.[4] reported the preparation and photocatalytic characterization of conjugated polymer/ZnS complex. It had extremely high photocatalytic activity for degradation of dyes.

Roy and De[5] investigated the immobilization of CdS, ZnS and mixed ZnS-CdS on filter paper and studied the effect of hydrogen production from alkaline $Na_2S/Na_2S_2O_3$ solution. Photoreduction of CO_2 over ZnS to 2-and 4-carbon acids was observed by Eggine et al.[6] Kobayashi et al.[7] investigated the photocatalytic properties of alumina supported ZnS-CdS catalyst. Ren et al.[8] studied the relationship between the coprecipitation mechanism, doping structure and physical properties of $Zn_{(1-x)}Co_xS$ nanocrystallites. Kakuta et al.[9] used coprecipitated ZnS-CdS over SiO_2 for photoassisted catalysis of H_2 production in aqueous sulphite solution.

In the present work, coprecipitation method has been used for preparing NiS-ZnS and used for photobleaching of alizarin red S.

EXPERIMENTAL

Synthesis of semiconductor by coprecipitation

NiS-ZnS (1 : 2) photocatalyst was prepared by mixing equal amounts of $ZnSO_4$ (M/2 : Merck) and $NiSO_4$ solutions (M/4 : Merck). To the above solution, solid NH_4Cl and aqueous solution of NH_4OH were added and freshly prepared H_2S gas was slowly passed through the mixture for 2 hours. Precipitates were washed with distilled water and dried at room temperature.

Photocatalytic bleaching of alizarin red S

Solution of dye was prepared in double distilled water. The photocatalytic bleaching was observed in presence of NiS-ZnS using different concentrations of the dye, amount of semiconductor, pH and light intensities.

Irradiation was carried out with 200 W tungsten lamp (visible light, Philips; light intensity = 50.0 $mWcm^{-2}$). The light intensities at various distances from the lamp were measured with the help of solarimeter (CEL, India; Model SM 201). A water filter was used

to cut thermal radiations. A digital pH meter (Eutech WP-2) was used to adjust the pH of the solution by the addition of previously standardized 0.1N sulphuric acid (Rankem) and 0.1N NaOH solution (Rankem). For correct measurement of optical activity, the solution must be free from semiconductor particles and solid impurities; thus, a centrifuge (Remi, Model 1258) was used for removing suspended particles. The progress of the photocatalytic reaction was observed by measuring the absorbance of solution at regular time intervals using UV visible spectrophotometer (Systronics Model 106).

RESULTS AND DISCUSSION

Photocatalytic degradation of alizarin red S was observed at λ_{max} 525. An aqueous dispersion (25 mL; 1.2 x 10^{-4} M) of the dye containing NiS-ZnS or ZnS was observed for 210 min. A plot of 1 + log O.D. versus time was linear and follows pseudo-first order kinetics. The rate constants were measured using following expression -

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

Table 1: A typical run

Time (min.)	**[Alizarin red S] = 1.2 × 10^{-4} M NiS-ZnS (1 : 2)= 0.30 g Light Intensity = 50.0 mWcm^{-2} pH = 8.0**		**[Alizarin red S] = 1.6 × 10^{-4} M ZnS = 0.15 g Light Intensity = 50.0 mWcm^{-2} pH = 7.5**	
	Optical density	**1 + log O.D.**	**Optical density**	**1 + log O.D.**
0	0.540	0.732	0.511	0.708
30	0.475	0.676	0.467	0.669
60	0.418	0.621	0.412	0.614
90	0.358	0.553	0.388	0.588
120	0.316	0.499	0.348	0.541
150	0.272	0.434	0.326	0.513
180	0.236	0.372	0.301	0.478
210	0.211	0.324	0.272	0.434
-	$k = 8.44 \times 10^{-5}$ (s^{-1})		$k = 4.88 \times 10^{-5}$ (s^{-1})	

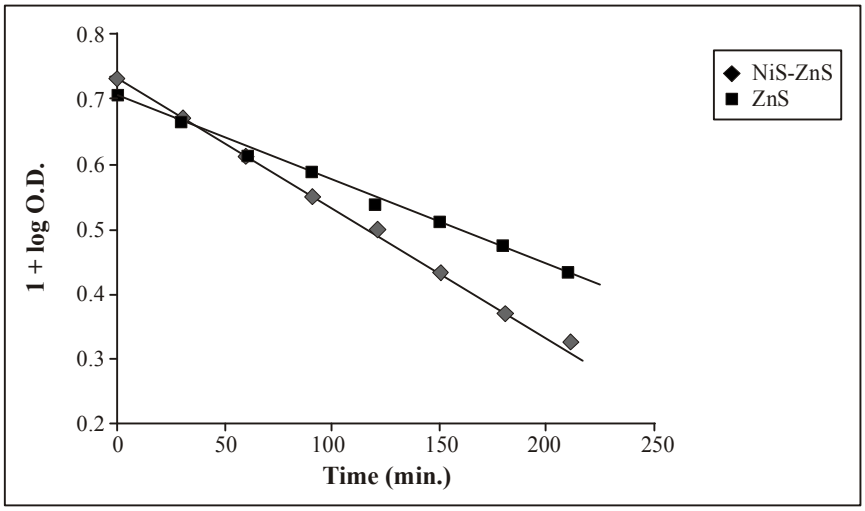

Fig. 1: A typical run

Effect of pH

The reaction rates were determined in the pH range 6.5-9.0 (Table 2). Photocatalytic bleaching of alizarin red S by NiS-ZnS and pure ZnS were maximum at pH 8.0 and 7.5, respectively. At low pH, the dye was in it protonated form or neutral and semiconductor surface is positively charged due to adsorption of H^+ ions. Thus, the dye molecules were repelled from the surface of semiconductor and therefore, the rate of photobleaching was low at lower pH of the medium. Above the respective maximum pH, a further increase in pH

Table 2: Effect of pH

pH	[Alizarin red S] = 1.2×10^{-4} M NiS-ZnS (1 : 2) = 0.30 g Light Intensity = 50.0 mWcm^{-2}	[Alizarin red S] = 1.2×10^{-4} M ZnS = 0.15 g Light Intensity = 50.0 mWcm^{-2}
	$k_1 \times 10^5$ (sec^{-1})	$k_1 \times 10^5$ (sec^{-1})
6.5	7.03	3.04
7.0	6.39	3.44
7.5	8.17	4.88
8.0	8.44	4.25
8.5	6.77	4.03
9.0	6.39	3.50

will result in a negatively charged semiconductor surface due to adsorption of OH^- ions and the anionic dye molecules will face electrostatically repulsion. As a consequence, the rate of reaction decreases on increasing pH of the solution.

Effect of concentration of alizarin red S

The effect of the variation of alizarin red S concentration was observed and results are presented in Table 3.

Table 3: Effect of dye concentration

[Alizarin red S] x 10^4M	**NiS-ZnS (1 : 2) = 0.30 g Light Intensity = 50.0 mWcm^{-2} pH = 8.0**	**ZnS = 0.15 g Light Intensity = 50.0 mWcm^{-2} pH = 7.5**
	k_1 x 10^5 (sec^{-1})	**k_1 x 10^5 (sec^{-1})**
0.8	6.76	4.14
1.2	8.44	4.31
1.6	8.01	4.88
2.0	7.53	4.49
2.4	6.59	3.16
2.8	6.46	2.67

As the concentration of dye was increased, the rate of photocatalytic bleaching also increases up to a certain value i.e. 1.2 x 10^{-4}M and 1.6 x 10^{-4} M; above which the rate decreases on increasing the concentration further; because the dye starts acting as a filter for the incident light and it will not permit the desired light intensity to reach the semiconductor particles.

Effect of amount of NiS-ZnS

The effect of amount of semiconductor on the rate of degradation of dye was also observed and the results are summarized in Table 4.

The rate of photobleaching also increases with increasing amount of photocatalyst

but above a certain amount (0.30 g in case of NiS-ZnS and 0.15 g in case of pure ZnS), no increase was observed in these cases. 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. Using vessels of different dimensions, the saturation point was shifted to higher values for larger vessels, and downward for smaller vessels, which clearly confirms that it has a saturation like behaviour.

Table 4: Effect of amount of semiconductor

Semiconductor (g)	[Alizarin red S] = 1.2×10^{-4} M Light Intensity = 50.0 mWcm^{-2} pH = 8.0	[Alizarin red S] = 1.6×10^{-4} M Light Intensity = 50.0 mWcm^{-2} pH = 7.5
	$k_1 \times 10^5$ (sec^{-1})	$k_1 \times 10^5$ (sec^{-1})
0.05	-	3.55
0.10	-	3.91
0.15	5.75	4.88
0.20	6.90	4.84
0.25	7.08	4.84
0.30	8.44	4.83
0.35	8.40	-
0.40	8.43	-

Effect of light intensity

The effect of light intensity on the rate of degradation of alizarin red S was also studied and the results are summarized in Table 5.

With an increase in light intensity, the rate of reaction also increases for both NiS-ZnS and pure ZnS. It may be explained on the basis that as the light intensity was increased, the number of collisions of photons with semiconductor particles also increases per unit area per unit time.

Table 5: Effect of light intensity

Light intensity ($mWcm^{-2}$)	[Alizarin red S] = 1.2×10^{-4} M NiS-ZnS (1 : 2) = 0.30 g pH = 8.0	[Alizarin red S] = 1.6×10^{-4} M ZnS = 0.15 g pH = 7.5
	$k_1 \times 10^5$ (sec^{-1})	$k_1 \times 10^5$ (sec^{-1})
10	5.25	3.16
20	5.43	3.42
30	5.80	3.91
40	6.27	4.57
50	8.44	4.88
60	9.59	5.38

MECHANISM

On the basis of the experimental observations, a tentative mechanism for photocatalytic bleaching of alizarin red S may be proposed as:

$$^1AR_0 \longrightarrow {}^1AR_1 \text{ (Singlet excited state)}$$

$$^1AR_1 \longrightarrow {}^3AR_1 \text{ (Triplet excited state)}$$

$$SC \longrightarrow e^- + h^+ \text{ or } SC^+$$

$$h^+ + H_2O \longrightarrow H^+ + {}^{\bullet}OH$$

$$^3AR_1 + {}^{\bullet}OH \longrightarrow \text{Products}$$

When the solution of dye was exposed to light in the presence of semiconductor, initially the dye molecules are excited to first singlet state. Then these singlet molecules are transfered to the triplet state through intersystem crossing (ISC). The triplet state may donate an electron to semiconductor. On the other hand, the semiconductor also gets excited by absorbing light and an electron is excited from its valence band to conduction band leaving behind a hole. The hole abstracts an electron from OH^- ions generating $^{\bullet}OH$ free radicals. These $^{\bullet}OH$ radicals will oxidize the dye molecules into colourless products. The participation

of $^{\cdot}OH$ radicals as an active oxidizing species was confirmed by using hydroxyl radical scavengers like 2-propanol, where the reaction rate was drastically reduced.

CONCLUSION

Coprecipitated NiS-ZnS exhibits higher photocatalytic activity than pure ZnS. The increase in photocatalytic activity of NiS-ZnS may be explained on the basis that in NiS-ZnS, NiS acts as an impurity and increases the photocatalytic activity of ZnS virtually two folds.

REFERENCES

1. A. D. Paola, M. Addamo and L. Plamisano, J. Chem. Intermed., **29**, 467 (2003).
2. S. S. Hong, M. S. Lee, S. S. Park and G. D. Lee, Catal. Today, **87**, 99 (2003).
3. T. Ohno, F. Tanigawa, K. Fujihara, S. Izumi and M. Matsumura, J. Photochem. Photobiol., **127A**, 107 (1999).
4. Y. Gou, Z. Su and Z. Xue, Mater. Res. Bull., **39**, 144 (2006).
5. A. M. Roy and G. C. De, J. Photochem. Photobiol., **157**A, 1 (2003).
6. B. R. Eggine, P. K. J. Robertson, J. H. Stewart and E. Woods, J. Chem. Soc., 349 (1993).
7. K. Kobayashi, K. Kitaguchi, H. Tanaka, H. Tsniki and A. Venu, J. Chem. Soc. Faraday Trans. I, **63,** 1395 (1987).
8. G. Ren, Z. Lin, C. Wang, W. Liu, J. Zhang, F. Huang and J. Liang, J. Nanotechnol, **18(3)**, 35705 (2007).
9. N. Kakuta, K. H. Park, M. Finlayson, A. Veno, A. J. Bard, A. Campion, M. A. Fox, S. E. Webber and J. M. White, J. Phys. Chem., **89,** 732 (1985).

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