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# RETARDATION OF PHOTOCATALYTIC ACTIVITY OF ZnS ON COPRECIPITATION WITH CoS : BLEACHING OF ROSE BENGAL

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## ABSTRACT

Photocatalysis has been established as an emerging technology for waste water treatment, since photocatalytic activity of number of semiconducting materials has already been established. Sulphides of different transition metals have been used as photocatalysts. The photocatalytic degradation of rose bengal has been investigated using ZnS and coprecipitated ZnS-CoS. The photocatalytic degradation of dye was monitored 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 retardation in the rate of reaction was observed in case of coprecipitated ZnS-CoS. A tentative mechanism for the photocatalytic degradation of rose bengal has also been proposed.

**Key words**: Photocatalytic degradation, Rose bengal, Coprecipitated sulphides, ZnS, ZnS-CoS.

## INTRODUCTION

The environment, we live in, consists of atmosphere, earth, water and space. On account of anthropogenic activities, the composition of complex nature of the environment is changing regularly. Water is an essential commodity for the life of organisms and it is becoming polluted as a result of multifarious human activities. Various industrial effluents contain a number of pollutants, mainly dyes, which are toxic to aquatic life at higher levels. The photocatalytic treatment of such effluents holds a good promise over the traditional methods. Photocatalysis is a phenomenon, where an electron-hole pair is generated on exposing semiconducting materials to the light of suitable energy and as a result, the organic pollutants undergo mineralization.

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The field of photocatalysis has been extensively reviewed by Steinbach[1], Gratzel[2] and Pelizzette and Serpone[3]. Photoreduction of $CO_2$ over ZnS to 2- and 4-carbon acids was observed by Eggine *et al.*[4] Mengyne *et al.*[5] carried out photocatalytic degradation of organophosphorus pesticides using thin films of $TiO_2$. Rao *et al.*[6] 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.*[7] The use of zirconium and germanium phosphates in heterogeneous photocatalytic oxidation of naphthalene to phthalic anhydride was reported by Monaci *et al.*[8]

Kobayashi *et al.*[9] investigated the photocatalytic properties of alumina supported ZnS-CdS catalyst. Roy and De[10] 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. Jin *et al.*[11] synthesized water soluble coprecipitated $Cd_xZn_{(x-1)}S$ nanoparticles by capping method. Ren *et al.*[12] studied the relationship between the coprecipitation mechanism, doping structure and physical properties of $Zn_{(1-x)}Co_xS$ nanocrystallites. The surfaces of ZnS and PbS were modified by interfacing PbS on ZnS and ZnS on PbS nanoparticles by Anil and Anshuman.[13]

CdS-ZnS has been used as a photocatalyst for photohydrodimerisation of 2,5-dihydrofuran by Helterich and Kisch.[14] Kakuta *et al.*[15] used coprecipitated ZnS-CdS over $SiO_2$ for photoassisted catalysis of $H_2$ production in aqueous sulphite solution. In the present work, coprecipitated sulphide (ZnS-CoS) has been prepared and used as a photocatalyst for the degradation of rose bengal.

## EXPERIMENTAL

### Synthesis of semiconductor by coprecipitation

The semiconductor was prepared by coprecipitation of sulphides from a mixture of aqueous solution of $ZnSO_4$ ($5.0 \times 10^{-4}$ M; Merck) and $CoSO_4$ ($5.0 \times 10^{-4}$ M; Merck) in 1:1 ratio by the addition of ammonium chloride and ammonium hydroxide solution and passing freshly prepared $H_2S$ gas through the mixture. The precipitate obtained was washed, dried and then used as a photocatalyst.

### Experimental procedure of the photocatalytic bleaching of rose bengal

Rose bengal and semiconductors (ZnS and ZnS-CoS) were used in present investigations. The solution of rose bengal (RB) was prepared in doubly distilled water. The photocatalytic bleaching of rose bengal was studied in the presence of semiconducting

coprecipitated sulphides catalyst and light. 0.1050 g of rose bengal was dissolved in 100 mL of double distilled water so that the concentration of dye solution was 1.0 x $10^{-3}$ M. This solution was used as a stock solution. The photocatalytic bleaching of the dye was observed using different concentrations of the dye, amount of semiconductor, pH and light intensities. The irradiation was carried out keeping the whole assembly under light.

A 200 watt tungsten lamp (Philips) was used for irradiation purpose. The intensity of light at various distances was measured by Suryamapi (CEL model SM 201). A water filter was used to cut off thermal radiations. The pH of the solution was measured by a digital pH meter (Systronics Model 324). The desired pH of the solution was adjusted by the addition of previously standardized 0.1N sulphuric acid and 0.1N sodium hydroxide solutions. The necessary condition for the correct measurement of optical density is that the solution must be free from semiconductor particles and other impurities. Therefore, a G-3 sintered glass crucible was used for filtration to obtain the desired accuracy in measurement of absorbance (optical density) of the dye solution. A U.V. spectrophotometer (Systronics Model 106) was used for measuring absorbance at different time intervals.

## 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 on increasing time intervals, which indicates that the concentration of rose bengal decreases with increasing time of exposure. A plot of 1 + log O. D. (absorbance) versus time was linear (Fig. 1) and follows pseudo-first order kinetics. The rate constant was measured using following expression:

$k = 2.303 \times slope$

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

**Table 1: A typical run**

| **Time (min.)** | **[Rose bengal] = 8.0 x $10^{-6}$ M<br>pH = 6.0<br>ZnS = 0.14 g<br>Light intensity = 60.0 mWcm$^{-2}$** | | **[Rose bengal] = 8.0 x $10^{-6}$ M<br>pH = 5.5<br>ZnS-CoS = 0.14 g<br>Light intensity = 70.0 mWcm$^{-2}$** | |
|---|---|---|---|---|
| | **O.D.** | **1 + log O.D.** | **O.D.** | **1 + log O.D.** |
| 0.0 | 0.848 | 0.9283 | 0.869 | 0.9390 |

Cont…

| Time (min.) | [Rose bengal] = $8.0 \times 10^{-6}$ M<br>pH = 6.0<br>ZnS = 0.14 g<br>Light intensity = 60.0 mWcm$^{-2}$ | | [Rose bengal] = $8.0 \times 10^{-6}$ M<br>pH = 5.5<br>ZnS-CoS = 0.14 g<br>Light intensity = 70.0 mWcm$^{-2}$ | |
|---|---|---|---|---|
| | **O.D.** | **1 + log O.D.** | **O.D.** | **1 + log O.D.** |
| 10.0 | 0.781 | 0.8926 | 0.812 | 0.9100 |
| 20.0 | 0.645 | 0.8095 | 0.762 | 0.8819 |
| 30.0 | 0.610 | 0.7853 | 0.693 | 0.8407 |
| 40.0 | 0.480 | 0.6816 | 0.680 | 0.8325 |
| 50.0 | 0.460 | 0.6627 | 0.565 | 0.7524 |
| 60.0 | 0.298 | 0.4742 | 0.540 | 0.7323 |
| 70.0 | 0.226 | 0.3541 | 0.441 | 0.6444 |
| 80.0 | 0.219 | 0.3404 | 0.408 | 0.6106 |
| 90.0 | 0.188 | 0.2741 | 0.382 | 0.5820 |
| | $k = 1.68 \times 10^{-4}$ sec$^{-1}$ | | $k = 0.92 \times 10^{-4}$ sec$^{-1}$ | |

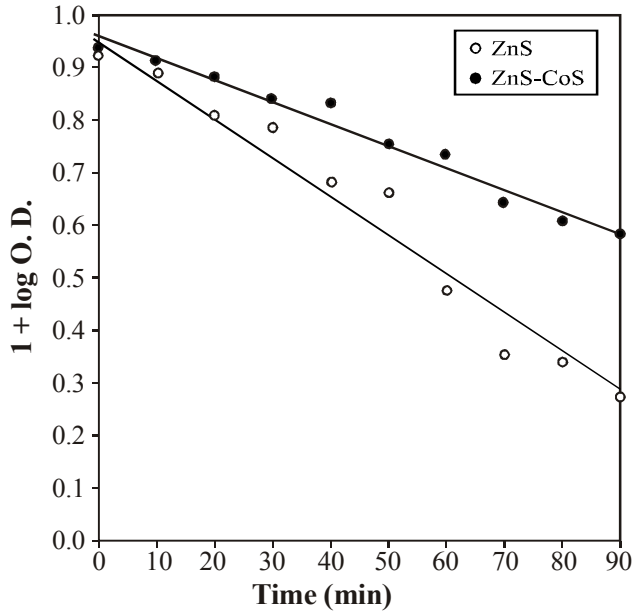


**Fig. 1: A typical run**

## 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 5.5-9.0 and 5.0-7.0 for ZnS and ZnS-CoS system, respectively (Table 2).

**Table 2: Effect of pH**

| pH | **[Rose bengal] = 8.0 x $10^{-6}$ M<br>ZnS = 0.14 g<br>Light intensity = 60.0 mWcm$^{-2}$** | **[Rose bengal] = 8.0 x $10^{-6}$ M<br>ZnS-CoS = 0.14 g<br>Light intensity = 70.0 mWcm$^{-2}$** |
|---|---|---|
| | **k x $10^4$ ($s^{-1}$)** | **k x $10^4$ ($s^{-1}$)** |
| 5.0 | 0.64 | 0.65 |
| 5.5 | 1.30 | 0.92 |
| 6.0 | 1.68 | 0.40 |
| 6.5 | 1.42 | 0.20 |
| 7.0 | 1.15 | 0.13 |
| 7.5 | 0.88 | 0.09 |
| 8.0 | 0.76 | 0.05 |
| 8.5 | 0.46 | 0.02 |
| 9.0 | 0.29 | 0.01 |

Photocatalytic degradation of rose bengal was observed to be maximum at pH 6.0 and 5.5 for ZnS and ZnS-CoS system, respectively. It was observed that in both the systems, the rate of photocatalytic bleaching of rose bengal increases with increase in pH and on increasing pH beyond an optimum limit, the rate of reaction decreases.

This behaviour may be explained on the basis that as the pH was lowered (more acidic), the protonation of dye molecules will take place as well as the surface of the semiconductor will also become positively charged; thereby the dye molecules will experience a force of repulsion. This will decrease the rate of reaction. On the other hand, the rate of photocatalytic bleaching of rose bengal also decreased with increase in the pH above the optimum value. 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 and as a result, the anionic dye will be repelled, causing a decrease in 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.

## Effect of concentration of rose bengal

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

**Table 3: Effect of dye concentration**

| **[Rose bengal] x $10^5$M** | **pH = 6.0<br>ZnS = 0.14 g<br>Light intensity = 60.0 mWcm$^{-2}$** | **pH = 5.5<br>ZnS-CoS = 0.14 g<br>Light intensity = 70.0 mWcm$^{-2}$** |
|---|---|---|
| | **k x $10^4$ ($s^{-1}$)** | **k x $10^4$ ($s^{-1}$)** |
| 0.4 | 1.38 | 0.60 |
| 0.6 | 1.57 | 0.78 |
| 0.8 | 1.68 | 0.92 |
| 1.0 | 1.23 | 0.74 |
| 1.2 | 0.92 | 0.49 |
| 1.4 | 0.69 | 0.31 |
| 1.6 | 0.23 | 0.19 |

The rate of photocatalytic degradation was found to increase with increase in the concentration of rose bengal up to 8.0 x $10^{-6}$ M for both; ZnS and coprecipitated ZnS-CoS systems. Further increase in the concentration beyond this limit results in a decrease in the rate of degradation. The increase in rate may be due to the fact that as the concentration of rose bengal was increased, more dye molecules were available for excitation and energy transfer and hence, an increase in the rate of the reaction was observed. The rate of dye bleaching was found to decrease with a further increase in the concentration above 8.0 x $10^{-6}$ 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, decreasing the rate of photocatalytic degradation.

## Effect of amount of semiconductor

The effect of 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.

**Table 4: Effect of amount of semiconductor**

| Semi-conductor (g) | pH = 6.0<br>[Rose bengal] = $8.0 \times 10^{-6}$ M<br>Light intensity = 60.0 mWcm$^{-2}$ | pH = 5.5<br>[Rose bengal] = $8.0 \times 10^{-6}$ M<br>Light intensity = 70.0 mWcm$^{-2}$ |
|---|---|---|
| | $k \times 10^4$ ($s^{-1}$) | $k \times 10^4$ ($s^{-1}$) |
| 0.04 | 0.39 | 0.96 |
| 0.06 | 0.45 | 1.84 |
| 0.08 | 0.56 | 3.68 |
| 0.10 | 0.78 | 4.14 |
| 0.12 | 1.51 | 6.44 |
| 0.14 | 1.68 | 9.21 |
| 0.16 | 1.67 | 3.68 |
| 0.18 | 1.68 | 1.92 |

The rate of degradation was found to increase with increasing concentration of semiconductor in both cases and then ultimately, it becomes almost constant after a certain amount of semiconductor. The rate is maximum at 0.14 g for both; ZnS and coprecipitated ZnS-CoS systems. This may be explained on the basis that as the amount of semiconductor was increased, the exposed surface area also increased, 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 this point, semiconductor has no or 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 and not the exposed surface area.

## 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.

**Table 5: Effect of light intensity**

| Light intensity ($mWcm^{-2}$) | pH = 6.0<br>[Rose bengal] = $8.0 \times 10^{-6}$ M<br>Zns = 0.14 g | pH = 5.5<br>[Rose bengal] = $8.0 \times 10^{-6}$ M<br>Zns-CoS = 0.14 g |
|---|---|---|
| | $k \times 10^4$ ($s^{-1}$) | $k \times 10^4$ ($s^{-1}$) |
| 10 | 0.79 | 0.11 |
| 20 | 0.92 | 0.20 |
| 30 | 1.07 | 0.32 |
| 40 | 1.37 | 0.52 |
| 50 | 1.53 | 0.57 |
| 60 | 1.68 | 0.86 |
| 70 | -- | 0.92 |

The data indicate that an increase in the light intensity increases the rate of reaction and maxima were obtained at 60.0 $mWcm^{-2}$ and 70.0 $mWcm^{-2}$ for ZnS and coprecipitated ZnS-CoS system, respectively. It may be explained on the basis that as the light intensity was increased, the number of photons striking per unit area also increases, resulting into a higher rate of degradation. Further increase in the intensity beyond the maximum limits may result in decrease in the rate of reaction probably due to thermal side reactions and hence, higher intensities were avoided.

## Mechanism

On the basis of the observed data, the following tentative mechanism may be proposed for the photocatalytic bleaching of rose bengal (RB).

$$^1RB_0 \xrightarrow{h\nu} {}^1RB_1 \quad \ldots(1)$$

$$^1RB_1 \xrightarrow{ISC} {}^3RB_1 \quad \ldots(2)$$

$$SC \xrightarrow{h\nu} SC\,[h^+ (VB) + e^- (CB)] \quad \ldots(3)$$

$$SC\,[h^+ (VB) + e^- (CB)] + O_2 \longrightarrow SC\,[h^+ (VB)] + O_2^{-\bullet} \quad \ldots(4)$$

$$SC\,[h^+ (CB)] + OH^- \longrightarrow {}^{\bullet}OH + SC \quad \ldots(5)$$

$$^3RB_1 + {}^{\bullet}OH \longrightarrow \text{Leuco RB} \quad \ldots(6)$$

$$\text{Leuco RB} \longrightarrow \text{Products} \quad \ldots(7)$$

When the solution of the dye was exposed to light in the presence of semiconductor, the rose bengal molecules are excited to their singlet states. These excited singlet molecules are converted to the triplet state through intersystem crossing (ISC). On the other hand, the semiconductors (ZnS and ZnS-CoS) also utilize the radiant energy to excite their electron from valence band to the conduction band; thus, leaving behind a hole. The dissolved oxygen may pull an electron from the conduction band forming the superoxide anion radical. The hole abstracts an electron from $OH^-$ ions to generate $^{\bullet}OH$ radicals. These radicals will oxidize the dye to its leuco form, which may ultimately degrade to products. The participation of $^{\bullet}OH$ radicals as an active oxidizing species was confirmed by using hydroxyl radical scavengers like 2-propanol, where the reaction rate was drastically reduced.

## CONCLUSION

The order of rate of photocatalytic degradation of rose bengal is:

$$ZnS > ZnS\text{-}CoS$$

It shows that the rate of photocatalytic degradation of rose bengal is retarded by using ZnS-CoS than only ZnS. This may be attributed to the fact that cobalt ions ($Co^{2+}$) can trap a hole to give $Co^{3+}$, while it can revert back to $Co^{2+}$ by utilizing an electron. In that case, electrons and holes are used up and are not available for photocatalytic degradation of rose bengal. It results in retarding the rate of reaction.

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