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Photocatalytic degradation of Rose Bengal using semiconducting zinc sulphide as the photocatalyst

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Abstract: Various semiconductors have been used as photocatalysts for the removal of different dyes from their aqueous solutions. Zinc sulphide semiconductor was used in the present investigation as a photocatalyst for the removal of Rose Bengal dye. Effect of different parameters that affect the rate of reaction, such as pH, concentration of dye, amount of semiconductor and light intensity were studied. A mechanism is proposed in which hydroxyl radicals are shown as the active oxidizing species.

Keywords: semiconductor; photocatalyst; Rose Bengal; zinc sulphide; hydroxyl radical.

INTRODUCTION

Today the entire world is facing a major problem of water pollution, which is caused in different manners. Dyes from different textile, dyeing and printing industries are one type of pollutant as these industries discharge their effluent into near-by natural water resources without any treatment. Many researchers have developed different methods to overcome this problem. Photochemistry may play an important role in solving this problem. Its different methods are now proven green and benign in nature. Various semiconductors have been used as photocatalysts for the removal of different dyes from their aqueous solutions. Photocatalytic and oxidative degradation of wastewater pollutants in the presence of TiO_2 was observed by Das *et al.*[1] It was observed that certain organic molecules adsorbed on TiO_2 could be reduced with the concomitant oxidation of water. The photoreduction of CO_2 and water into formaldehyde and methanol in aqueous suspensions of $SrTiO_3$ and TiO_2 was investigated by Blajeni *et al.*[2] Photocatalytic degradation of an H-acid over a novel TiO_2 thin film fixed in a

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reactor was studied by Noorjahan *et al.*[3] Ameta *et al.*[4] performed the photodegradation of Naphthol Green B in the presence of semiconducting antimony trisulphide. The photo-oxidation of oxalate ions in aqueous dispersion of ZnO under UV illumination was investigated by Domenech and Costa[5] in order to determine the efficiency of oxalate ions as hole scavengers. Mansilla and Villasnov[6] investigated the ZnO-catalysed photodegradation of Kraft-black liquor, which is an effluent from the pulp and paper industries. Platinum impregnated ZnO yielded 100 % decolourisation after 60 min.

ZnS was used for the photoreduction of carbon dioxide by Kanemoto *et al.*[7] Anpo *et al.*[8] gave direct evidence for the participation of extrinsic surface sites in the enhancement of the photocatalytic activity of luminescent ZnS catalyst. Boarh *et al.*[9] studied the structural and optical properties of ZnS nanoparticles, while Hu *et al.*[10] studied the mass production and high photocatalytic activity of ZnS nanoporous nanoparticles. ZnS–montmorillonite nanocomposites were used for the degradation of Eosin B by Miao *et al.*[11]

The photocatalytic activity of antimony(III) sulphide in the bleaching of Azure-B was studied by Ameta *et al.*[12] Rufus *et al.*[13] observed the decomposition of aqueous sulphide in presence of CdS with iridium sulphide and platinum sulphate as photocatalysts. Borgarello *et al.*[14] observed the oxidation of H_2S to sulphur at CdS semiconductor surface while the photocatalytic oxidation of propan-2-ol over a zeolite composite and CdS was carried out by Green and Rudham.[15] Kinetic monitoring of the photocatalytic degradation of amaranth by semiconducting ammonium phosphomolybdate was realized by Bansal *et al.*[16] The photocatalytic oxidation of benzydrol over CdS was investigated by Gu *et al.*[17] Chittora *et al.*[18] studied the photoreduction of CO_2 in presence of some photocatalyst such ZnO, Fe_2O_3, *etc*. Darwent and Mills[19] observed the photooxidation of water sensitized by WO_3 powder. The bleaching products of Rose Bengal under reducing condition was studied by Zakrzewski *et al.*[20] On the other hand, Sharma *et al.*[21] used semi-conducting bismuth sulphide as a photocatalyst for degradation of Rose Bengal.

EXPERIMENTAL

A 1.0×10^{-3} M solution of Rose Bengal was prepared as a stock solution, which was diluted further as and when required. The optical density of the Rose Bengal solution was determined using a spectrophotometer (Systronics model 106) at λ_{max} = 550 nm.

Zinc sulphide (Reidel), 8.0 μm with a band gap is 3.5 eV, was used as a photocatalyst in the present investigation. Its dispersion was quite stable during illumination, the ZnS powder neither degrading nor dissolving under the employed experimental conditions.

First, the feasibility of using the semiconductor zinc sulphide as a photocatalyst was confirmed. Thus, four sample solutions were made. using 50 mL of 1.20×10^{-5} M Rose Bengal in four beaker.s The first and second solutions contained only Rose Bengal; the first solution was kept in the dark while the second was exposed to light. The third and fourth samples contained in addition to Rose Bengal, 0.10 g zinc sulphide; the third sample was kept in dark, while the fourth was exposed to light.

After 4 h, the optical densities of the four solutions were measured using a spectrophotometer. It was found that the optical densities of solutions 1–3 remained almost constant, while that of the fourth solution had decreased from its initial value. From these observations, it was clear that this reaction requires presence of both light and zinc sulphide, *i.e.*, it was a photocatalytic reaction.

A solution of 1.20×10^{-5} M of R. Bengal was prepared in doubly distilled water and 0.10 g of zinc sulphide was added to it. The pH of the reaction mixture was adjusted to 8.5 with previously standardized sodium hydroxide and sulphuric acid solutions. Then the solution was exposed to a 200 W tungsten lamp. An aliquot of 2.0 mL was taken out from the reaction mixture and its optical density was observed at 550 nm at regular time intervals.

It was observed that the optical density of R. Bengal solution decreased with increasing time of exposure and that the degradation of R. Bengal was almost completed after 8 h of illumination. This was confirmed experimentally in additional experiments.

A plot of log *OD* against time was found to be linear. The rate constant was determined as $k = 2.303\times\text{slope}$). A typical run is presented in Table I.

TABLE I. A typical run; [Rose Bengal] = 1.20×10^{-5} M, m(ZnS) = 0.10 g, light intensity = = 70.0 mW cm^{-2}, pH 8.5. Rate constant, $k = 4.51\times10^{-5}$ s^{-1}

Time, min	Optical density (*OD*)	1 + log *OD*
0.0	0.361	0.5575
15.0	0.345	0.5378
30.0	0.335	0.5250
45.0	0.322	0.5078
60.0	0.304	0.4829
75.0	0.288	0.4594
90.0	0.282	0.4502
105.0	0.266	0.4249
120.0	0.258	0.4116
135.0	0.250	0.3979
150.0	0.237	0.3747
165.0	0.230	0.3617
180.0	0.220	0.3424

RESULTS AND DISCUSSION

In the present investigation, four rate affecting factors. *i.e.*, pH, concentration of dye, amount of semiconductor and light intensity were studied.

Effect of pH

The pH of the solution is likely to affect the degradation of Rose Bengal and hence, the effect of pH on the rate of degradation of Rose Bengal was investigated in the pH range 5.0–10.0, as the degradation was found to be reasonably fast in this range. The results are reported in Table II.

It is evident from these data that the rate of photocatalytic degradation of Rose Bengal increased with increasing pH. The increase in the rate of photocatalytic degradation may be due to greater availability of OH^- at higher pH values. The OH^- will generate more OH radicals by combining with the photogenerated holes in the semiconductor and these hydroxyl radicals are considered responsible for this photocatalytic degradation.

TABLE II. Effect of pH; [Rose Bengal] = 1.20×10^{-5} M, m(ZnS) = 0.10 g, light intensity = = 70.0 mW cm^{-2}

pH	$k\times10^5$ / s^{-1}
5.0	2.57
5.5	2.85
6.0	3.16
6.5	3.41
7.0	3.78
7.5	4.00
8.0	4.26
8.5	4.51
9.0	4.16
9.5	3.89
10.0	3.54

However, after a certain pH value, *i.e.*, 8.5, a further increase in pH of the medium decreased the rate of photocatalytic degradation. This may be due to the fact that Rose Bengal does not remain in its cationic form because of the larger concentration of OH^- and, as such, the force of attraction between the dye and negatively charged semiconductor surface decreases. As a consequence, the reaction rate decreases. It means that for an efficient photocatalytic degradation of Rose Bengal, it should remain either in its neutral form or partially in cationic form.

Alkaline conditions provide more OH^- and, as a consequence, more hydroxyl radicals were generated and therefore the reaction proceeded more smoothly in alkaline medium. Moreover, the formation of hydroxyl radicals may be efficient on the surface of metal oxides or sulphides.

Effect of dye concentration

Effect of variation of dye concentration was studied by taking different concentrations of Rose Bengal. The results are tabulated in Table III.

It was observed that the rate of photocatalytic degradation first increased with increasing concentration of Rose Bengal. This 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 was observed. However, on further increase in the dye concentration, the rate of photocatalytic degradation decreased. This may be attributed to the fact that the dye started acting as a filter for the incident light that did not permit the desired light intensity to reach the semiconductor particles; thus, the rate of photocatalytic degradation of Rose Bengal decreased.

TABLE III. Effect of Rose Bengal concentration; light intensity = 70.0 mW cm^{-2}, m(ZnS) = = 0.10 g, pH 8.5

[Rose Bengal]×10^5 M	k×10^5 / s^{-1}
0.4	2.20
0.6	2.78
0.8	3.29
1.0	4.02
1.2	4.51
1.4	4.22
1.6	3.97
1.8	3.66
2.0	3.28

Effect of amount of semiconductor

The amount of semiconductor is also likely to affect the process of dye degradation and hence, different amounts of photocatalyst were used. The results are reported in Table IV.

TABLE IV. Effect of amount of semiconductor; [Rose Bengal] = 1.20×10^{-5} M, pH 8.5, light intensity = 70.0 mW cm^{-2}

Zinc sulphide amount, g	k×10^5 / s^{-1}
0.02	2.44
0.04	2.81
0.06	3.20
0.08	3.84
0.10	4.51
0.12	4.52
0.14	4.51
0.16	4.50

It has been observed that the rate of photodegradation of Rose Bengal initially increased with increasing amount of semiconductor but ultimately, it becomes almost constant after a certain amount. This may be attributed to the fact that as the amount of semiconductor was increased, the amount of exposed surface area also increases, but after a certain limit, *i.e.*, 0.10 g, if the amount of semiconductor was further increased, there would be no increase in the exposed surface area of the photocatalyst. This may be considered like a saturation point; above which, any increase in the amount of semiconductor had negligible or no effect on the rate of photocatalytic degradation of Rose Bengal, as any increase in the amount of semiconductor after this saturation point would only increase the thickness of the layer at the bottom of the reaction vessel. This was confirmed by taking reaction vessels of different dimensions. The saturation point shifted to higher range for larger vessels, while the reverse was true for smaller vessels.

Effect of light intensity

To investigate the effect of light intensity on the photocatalytic degradation of Rose Bengal, the distance between the light source and the exposed surface area was varied. The intensity of light at each distance was measured by Suryamapi (CEL Model SM201). The results are summarized in Table V.

TABLE V. Effect of light intensity; [Rose Bengal] = 1.20×10^{-5} M, m(ZnS) = 0.08 g, pH 8.5

Intensity of light, mW cm^{-2}	$k\times10^5$ / s^{-1}
10.0	1.12
20.0	1.76
30.0	2.50
40.0	3.11
50.0	3.62
60.0	4.05
70.0	4.51
80.0	4.06

The results indicate that degradation of Rose Bengal was accelerated as the intensity of light was increased, because any increase in the light intensity will increase the number of photons striking per unit area of semiconductor powder. An almost linear behaviour between light intensity and rate of reaction was observed. However, on increasing the intensity above 70.0 mW cm^{-2}, there was a decrease in the rate. This may be due to some side reactions.

The effect of different parameters on rate constant was studied and it was observed that it was changed from 4.51×10^{-5} to 2.57×10^{-5} s^{-1} (in case of pH), to 2.20×10^{-5} (in case of dye concentration), to 2.44×10^{-5} s^{-1} (in case of amount of semiconductor) and to 1.12×10^{-5} s^{-1} (in case of light intensity). *i.e.*, by 1.75; 2.05; 1.85 and 4.02 times, respectively, that is approximately 100–200 % increases. This amount of change is significant as far as the rate is concerned.

Mechanism

Based on these observations, a tentative mechanism for the photocatalytic degradation of Rose Bengal (RB) is proposed:

$$^1\mathrm{RB_o} \xrightarrow{h\nu} {}^1\mathrm{RB_1} \qquad (1)$$

$$^1\mathrm{RB_1} \xrightarrow{\mathrm{ISC}} {}^3\mathrm{RB_1} \qquad (2)$$

$$\mathrm{SC} \xrightarrow{h\nu} e^-(\mathrm{CB}) + h^+(\mathrm{VB}) \qquad (3)$$

$$h^+ + \mathrm{OH}^- \longrightarrow {}^\bullet\mathrm{OH} \qquad (4)$$

$$^3RB_1 + {}^\bullet OH \longrightarrow \text{Leuco RB} \quad (5)$$

$$\text{Leuco RB} \longrightarrow \text{Products} \quad (6)$$

A molecule of Rose Bengal absorbs radiations of a suitable wavelength giving gives rise to its excited singlet state, which then undergoes intersystem crossing (ISC) to give the triplet state of the dye. On the other hand, the semiconducting zinc sulphide (SC) also utilizes the radiant energy to excite its electron from the valence band to the conduction band; thus, leaving behind a hole. This hole abstracts an electron from OH^- to generate OH radicals. These radicals oxidize the dye to its leuco form, which may ultimately degrade to harmless products.

The proposed mechanism involves the oxidation of Rose Bengal to smaller fragments involving hydroxyl radicals which was confirmed by using a hydroxyl radical scavenger. *i.e.*, 2-propanol, when the rate of degradation was drastically reduced in presence of the scavenger. Secondly, the degradation of Rose Bengal to less toxic or harmless products is a green chemical approach to waste water treatment (Advanced Oxidation Processes).

CONCLUSION

Photocatalytic degradation of Rose Bengal was performed in the presence of the semiconductor zinc sulphide. The degradation rate increased with increasing pH because more hydroxyl ions were present (generating more hydroxyl radicals). It attains maximum rate at pH 8.5; a further increase in pH above 8.5 results in a decrease in the rate of the reaction, because of decreasing attraction between the neutral form of the dye and the negatively charged semiconductor surface. Increasing the concentration of Rose Bengal also increased the rate up to a certain value due to the increase in the number of dye molecules, but it shows a declining behaviour on further increase of the concentration of dye. This decrease may be attributed to the fact that at higher concentration, the dye may acts as an internal filter for the incident radiations, which decreases the intensity of the incident radiation on the semiconductor particles.

The results indicate that initially the rate increases with increasing amount of semiconductor but after 0.10 g, the rate becomes virtually constant (saturation behaviour). This may be due to the complete coverage of the bottom of the reaction vessel by the semiconductor. Any further increase will not add to an increase in the exposed surface area but only increases the thickness of the layer. An increase in the light intensity will increase the number of photons striking semiconductor zinc sulphide powder per unit area per second and as a consequence, the reaction rate increases almost linearly with the increase in light intensity. The optimum reaction conditions were obtained as: pH = 8.5; [Rose Bengal] = = 1.20×10^{-5} M; ZnS = 0.10 g; light intensity = 70.0 mW cm^{-2}.

Scavengers trap the active species by reducing their activity in the solution and as a result reaction rate becomes quite low or reaction almost stops. Here, the participation of $^{\bullet}$OH as an active oxidizing species was confirmed by using 1 mL of M/10 2-propanol, which is a specific scavenger of $^{\bullet}$OH. It was observed that the rate of dye degradation was reduced drastically from 4.51×10^{-5} to 2.05×10^{-7} s^{-1}.

ИЗВОД

ФОТОКАТАЛИТИЧКА РАЗГРАДЊА БОЈЕ *ROSE BENGAL* ПОМОЋУ ПОЛУПРОВОДНОГ ЦИНК ОКСИДА КАО ФОТОКАТАЛИЗАТОРА

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Различити полупроводници се користе као фотокатализатори у поступцима уклањања боја из водених раствора. Плупроводни цинк-оксид је у овом истраживању коришћен као фотокатализатор за процес разградње боје *Rose Bengal.* Анализирани су утицаји различитих параметара који могу утицати на брзину реакциије, као што су pH, концентрација боје, количина фотокатализатора и интензитет светла. Предложен је механизам реакције, који показује да је хидроксилни радикал активна оксидујућа врста.

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