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SHORT COMMUNICATION

**Photodegradation of Naphthol green B in the presence of
semiconducting antimony trisulphide**

RAKSHIT AMETA¹, PINKI BALA PUNJABI² and SURESH C. AMETA^{2*}

¹Department of Pure & Applied Chemistry, University of Kota, Kota - 324010 (Rajasthan) and

²Department of Chemistry, M. L. Sukhadia University, Udaipur -313002 (Rajasthan) India

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Abstract: Different methods of wastewater treatment are being used for the removal of dyes from their solution, but in most of the cases, either homogeneous catalysts or different adsorbents are used. These methods have their own merits and demerits. In the present work, antimony trisulphide was used as a heterogeneous catalyst. The effects of different parameters on the rate of the reaction were observed, such as pH, concentration of dye, amount of semiconductor and light intensity. A tentative mechanism is proposed in which the role of hydroxyl radical as an active oxidizing species is shown for degradation of Naphthol green B.

Keywords: semiconductor; photocatalyst; Naphthol Green B; hydroxyl radical; antimony trisulphide.

INTRODUCTION

In the entire world, everyone is facing a major problem of water pollution by industrial effluents. Although industries are obliged to make their effluents harmless by different methods, water pollution is continuously increasing. Although researchers are already employing different methods for the removal of dye from wastewater, photochemistry may still play an important role for solving this problem, as sunlight is readily available all over the world. Different heterogeneous catalyst may be used as photocatalysts for the removal of different dyes. Photodegradation of Methylene blue using sunlight and TiO₂ was investigated by Noguerria and Jardin.¹ Mercury(II) ions were photocatalytically eliminated from aqueous solutions in presence of ZnO powder.² Ameta *et al.*³ investigated the effect of surfactants on the photobleaching of Basic Blue-24. Cao and Suils⁴ reported the photo-oxidation of propan-2-ol to acetone using amorphous manga-

*Corresponding author. E-mail: ameta_sc@yahoo.com

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nese oxide as catalyst. Sharma *et al.*⁵ observed the photocatalytic bleaching of Crystal violet in aqueous suspensions of zinc oxides. Fu *et al.*⁶ reported the photoreduction of hexachloroplatinate(IV) on cadmium sulphide while Wang and Zhuang.⁷ performed the photocatalytic reduction of Cr(VI) over CdS powder under visible light. The photochemical reduction of Cr(VI) on CdS was investigated by Domenech and Munoz.⁸

Mansilla and Villasnov⁹ investigated the ZnO-catalysed photodegradation of Kraft-Black liquor, which is an effluent from pulp and paper industries. ZnS was used for the photoreduction of carbon dioxide by Kanemoto *et al.*¹⁰ Ameta *et al.*¹¹ used semiconducting iron(III) oxide as the photocatalyst for the bleaching of Methylene blue, Crystal violet and Malachite green dyes. The photocatalytic reduction of the dye Methylene Blue by Bi₂S₃/CdS nanocomposites was realised by Kobasa and Tarasenko.¹² Biodegradation of Rose Bengal by *Phanerochaete chrysosporium* was performed by Gogna *et al.*¹³ The mechanism of the photoreduction of silver ions over tungsten oxide was reported by Sviridov and Kulak.¹⁴ The photoreduction of carbon dioxide and water into formaldehyde and methanol in aqueous suspensions of WO₃ was studied by Blajeni *et al.*¹⁵

EXPERIMENTAL

Antimony trisulphide was selected as the heterogeneous photocatalyst as it is coloured and thus absorbs a major part of sunlight

A 1.0×10^{-3} M stock solution of Naphthol green B was prepared by dissolving 0.0878 g of the dye in 100.0 mL doubly distilled water. The optical density (O.D.) of this dye solution at $\lambda_{\text{max}} = 635$ nm was determined using a Systronics Model 106 spectrophotometer.

The dye solution was placed in equal amounts into four beakers (50 mL of the dye solution was kept in four beakers):

- i) The first beaker containing Naphthol green B solution was kept in the dark.
- ii) The second beaker containing Naphthol green B solution was exposed to the light of a 200 W tungsten lamp.
- iii) The third beaker containing Naphthol green B solution and 0.10 g antimony trisulphide was kept in dark.
- iv) The fourth beaker containing Naphthol green B solution and 0.10 g antimony trisulphide was exposed to the light of a 200 W tungsten lamp.

After keeping these beakers for a few hours, the optical density of the solution in each beaker was measured (visible light spectrum). It was found that the solutions of the first three beakers had almost the same optical density as their initial value while the solution of the fourth beaker had decreased. From this observation, it becomes clear that this reaction required the presence of both light and the semiconductor antimony trisulphide. Hence, this reaction is photocatalytic in nature.

In further experiments, the pH of the dye solution, the concentration of Naphthol green B, the amount of antimony trichloride, and the light intensity were varied.

RESULTS AND DISCUSSION

An aliquot of 2.0 mL was taken out from the reaction mixture and its optical density was observed at 635 nm at regular time intervals. It was observed that the amount of Naphthol green B decreased with increasing light exposure time.

A plot of $\log O.D.$ against time was found to be linear. The rate constant was calculated from the expression:

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

The data from a typical run are given in Table I.

TABLE I. The results of a typical photodegradation experiment. [Naphthol green B] = 1.50×10^{-5} M; antimony trisulphide amount = 0.18 g in 50 mL; light intensity = 50.0 mW cm^{-2} ; pH 8.0; rate constant, $k = 8.95 \times 10^{-4} \text{ s}^{-1}$

Time, min	Optical density (O.D.)	2+ $\log O.D.$
0.0	0.407	1.6096
5.0	0.245	1.5092
10.0	0.245	1.3892
15.0	0.188	1.2553
20.0	0.132	1.1206
25.0	0.100	1.0000
30.0	0.076	0.8808
35.0	0.058	0.7634
40.0	0.044	0.6434
45.0	0.033	0.5185
50.0	0.025	0.3979
55.0	0.019	0.2787
60.0	0.014	0.1461

Effect of pH

The pH of the solution is likely to affect the degradation of Naphthol green B. The effect of pH on the rate of degradation of Naphthol green B was investigated in the pH range 5.0–10.0. The results are reported in Table II.

On increasing the pH of the reaction medium above its optimum value (pH 8.0), the semiconductor surface becomes covered with adsorbed hydroxyl ions, making it negatively charged. This negatively charged surface will not permit a close approach of dye molecules near the semiconductor surface and therefore the reaction rate is retarded.

Effect of dye concentration

The effect of variation of the dye concentration was studied by taking different concentrations of Naphthol green B. The obtained results are tabulated in Table III.

The rate of photocatalytic degradation of dye increased with increasing dye concentration up to a certain value. Beyond this concentration, the rate of photo-

catalytic degradation started to decrease. This may be explained by the fact that as the concentration of dye was increased, more dye molecules were available for excitation and consecutive energy transfer and as a result, an increase in the rate was observed. A decrease in rate of photocatalytic degradation was observed with further increase in the dye concentration, which may be attributed to the fact that the dye started acting as an internal filter for the incident light and hence did not permit the desired light intensity to reach and excite a large number of the semiconductor particles. Thus, a corresponding decrease in the rate of photocatalytic degradation of the dye was observed.

TABLE II. Effect of pH on the rate of the photodegradation of the dye. [Naphthol green B] = 1.50×10^{-5} M; antimony trisulphide amount = 0.18 g in 50 mL; light intensity = 50.0 mW cm^{-2}

pH	$k / 10^{-4} \text{ s}^{-1}$
5.0	5.28
5.5	5.63
6.0	6.57
6.5	6.77
7.0	6.99
7.5	7.97
8.0	8.95
8.5	6.67
9.0	6.07
9.5	5.33
10.0	4.60

TABLE III. Effect of Naphthol green B concentration on the rate of its photodegradation. Light Intensity = 50.0 mW cm^{-2} ; antimony trisulphide amount = 0.18 g in 50 mL; pH 8.0

[Naphthol green B] $\times 10^5$, M	$k / 10^{-4} \text{ s}^{-1}$
0.4	1.01
0.6	2.10
0.8	4.24
1.0	6.41
1.5	8.95
2.0	8.39
2.5	7.63
3.0	7.10
3.5	6.71
4.0	5.47
4.5	3.10

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 the amount of semiconductor on the rate of photodegradation of the dye. [Naphthol green B] = 1.50×10^{-5} M; pH 8.0; light intensity = 50.0 mW cm^{-2}

Antimony trisulphide amount (in 50 mL solution, g)	$k / 10^{-4} \text{ s}^{-1}$
0.04	0.94
0.06	1.86
0.08	2.48
0.10	4.10
0.12	5.59
0.14	6.99
0.16	8.24
0.18	8.95
0.20	8.92
0.22	8.94
0.24	8.96

The rate constants for the photodegradation of the dye initially increased with increasing amount of antimony trisulphide but after reaching a certain fixed value of the semiconductor, they became virtually constant. This may be because as the amount of semiconductor was increased, the exposed surface area increased and as a result, the rate of the reaction increased. However, after a certain limit, if the amount of semiconductor was further increased, there would be no corresponding increase in the exposed surface area of the photocatalyst. Furthermore, any increase in the amount of the semiconductor after this particular amount would only increase the thickness of the layer at the bottom of the vessel, once the bottom of the reaction vessel was completely covered by the semiconductor. This multilayer structure would not permit all the semiconductor particles to be exposed to light and as such, the rate of the reaction became almost constant. Thus, saturation like behaviour was observed. This was further confirmed by stirring the reaction mixture, whereby the rate again increased. This point of saturation depends on the dimensions of the vessel. It was shifted to higher values when large vessels were used and to the lower ones with smaller vessels.

Effect of light intensity

To investigate the effect of the light intensity on the photocatalytic degradation of Naphthol green B, the distance between the light source and the exposed surface area was varied. The intensity of light at each distance was measured using a Suryamapi (CEL Model SM 201). The results are summarized in Table V.

The rate of photocatalytic degradation of the dye was found to increase with increasing light intensity, but after a certain limit, the rate decreased with further increasing light intensity. An increase in the intensity of light increases the number of photons striking the semiconductor particles per unit area per unit time. As a result, more electron-hole pairs are generated, which results in an

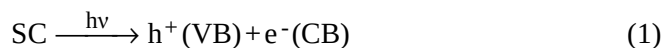
overall increase in the rate of the reaction. However, at higher light intensities, some thermal side reactions may also commence and hence, the rate of photocatalytic degradation decreases on increasing the light intensity.

TABLE V. Effect of the light intensity on the rate of photodegradation of the dye. [Naphthol green B] = 1.50×10^{-5} M; antimony trisulphide amount = 0.18 g in 50 mL; pH 8.0

Light intensity ^a , mW cm ⁻²	$k / 10^{-4} \text{ s}^{-1}$
20.0	5.11
30.0	5.97
40.0	6.25
50.0	8.95
60.0	8.52
70.0	8.06
80.0	7.90

^a60 % of light was absorbed by the system; the results are given only for the incident light

It has been observed that the rate of photocatalytic degradation of the dye increased on increasing the pH of the reaction medium (pH 8.0; Table II). The optimum was observed in alkaline medium. This indicates that hydroxyl radicals were the reactive species in the photocatalytic degradation of the dye, as the hydroxyl ions would be converted to hydroxyl radicals by the photogenerated holes:



The participation of $\cdot\text{OH}$ radicals as the active oxidizing species in the photocatalytic bleaching of the dye was confirmed by performing the studied reaction in presence of an $\cdot\text{OH}$ radical scavenger, *i.e.*, propan-2-ol, whereby the rate of the reaction was drastically reduced.

CONCLUSIONS

The Naphthol green B in the solution was degraded using the semiconducting antimony trisulphide as a photocatalyst. The role of $\cdot\text{OH}$ radicals, which is responsible for degradation of the dye, was confirmed by performing the reaction in the presence of an $\cdot\text{OH}$ radical scavenger.

ИЗВОД

ФОТОДЕГРАДАЦИЈА НАФТОЛ ЗЕЛЕНОГ Б У ПРИСУСТВУ ПОЛУПРОВОДНИКА
АНТИМОН-ТРИСУЛФИДАRAKSHIT AMETA¹, P. B. PUNJABI² и SURESH C. AMETA²¹Department of Pure & Applied Chemistry, University of Kota, Kota - 324010 (Rajasthan) и ²Department of Chemistry, M. L. Sukhadia University, Udaipur -313002 (Rajasthan) India

Разне методе се тренутно користе за уклањање боја из раствора, али у већини случајева се користе или хомогени катализатори или адсорбенти. Ове методе имају својих предности и недостатака. У изложеном раду је коришћен антимоно-трисулфид као хетерогени катализатор. Испитивано је неколико параметара који утичу на брзину реакције, као што су рН, концентрација боје, количина полупроводника и интензитет светла. На крају је изложен претпостављени механизам у којем је приказана улога хидроксил радикала у деградацији нафтола зеленог Б.

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