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Photocatalytic reactions of xylidine ponceau on semiconducting zinc oxide powder

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Abstract

The photocatalytic reaction of xylidine ponceau on zinc oxide power was carried out. Photocatalytic bleaching of the dye was observed spectrophotometrically. The effects of the variation of various parameters, such as the concentration of xylidine ponceau, pH, amount and particle size of the semiconductor and light intensity, on the rate of photocatalytic bleaching were observed. A tentative mechanism for the photocatalytic bleaching of xylidine ponceau is proposed.

Keywords: Photocatalytic reactions; Photocatalytic bleaching

1. Introduction

The photocatalytic reactions of dyes have been used in laser passive Q-switches [1–4], oxygen evolving systems for astronautical craft [5], liquid lasers [6–9], chemical dosimetry systems [9–12], the provision of flash blindness protection or memory in computers [13,14], the basis of a new kind of photography [15], photochemically regenerative electrochemical systems [16], fuel cell cathodes [17–19], gas detectors [20], light-sensitive targets in vidicon camera tubes for television [21] and automatic variable density light filters. However, the dyes are toxic and may be carcinogenic. Environmental contamination by these toxic chemicals is a serious global problem. Coloured solutions containing dyes (from industrial effluents of textile, dyeing and printing industries) may cause skin cancer due to photosensitization and photodynamic damage. In contrast, bleached dye solutions are non-toxic and harmless. In addition, coloured water containing dyes is of almost no use, but if it is bleached to give colourless water, it may be used for washing, cooling, irrigation and cleaning purposes. Photocatalytic bleaching may provide a low cost method to solve this problem.

Oster [22] has investigated the photoreduction of methylene blue (a phenothiazine dye) in the presence of acidified stannous chloride, and the photoreduction of thiazine dyes over TiO_2 colloid has been reported by Kamat [23]. It was found by Oster and Oster [24] that methylene blue, which is normally reduced in the presence of a reducing agent and visible light, can be photoreduced without any agent in aqueous solution using far-UV light ($\lambda < 250$ nm). Recently, Chen and Chou [25] have reported the photobleaching of methyl orange (an azo dye) in an aqueous solution of suspended titanium dioxide, and Sharma et al. [26] have investigated the photocatalytic bleaching of bromopyrogallol red (a triphenylmethane dye) in aqueous zinc oxide solution. No work has been reported on the photocatalytic bleaching of xylidine ponceau (an azo dye), although it is used extensively in dyeing and printing industries. In this study, we investigate the photocatalytic reactions of this dye on zinc oxide powder.

2. Experimental details

Xylidine ponceau (XP) (SdS) and zinc oxide (Merck) were used in the investigations. The photocatalytic bleaching of XP was studied in the presence of semiconducting zinc oxide and light. XP (0.0048 g) was dissolved in 100 ml of doubly distilled water to give a concentration of 1.0×10^{-4} M. This was used as stock solution. The photocatalytic bleaching of XP was observed by taking 200 ml of a dye solution (1.0×10^{-5} M) and 0.50 g of zinc oxide semiconductor. Irradiation was carried out with magnetic stirring keeping the whole assembly exposed to the light source (intensity, 26 mW cm^{-2}). A 200 W tungsten lamp (Sylvania Laxman) was used for irradiation. Sunlight was used for higher in-

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tensity light. The intensity of light at various distances from the lamp was measured using a Suryamapi apparatus (CEL model SM 201). A water filter was used to cut out thermal radiation. 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 sulphuric acid and sodium hydroxide solutions. The necessary condition for the correct measurement of the optical density is that the solution must be free from semiconductor particles and other impurities; a centrifuge (Remi-1258) and Whatman filter paper were used to remove these species, but proved to be unsuitable. Thus a G-3 sintered glass crucible was used for filtration to obtain the desired accuracy in the measurement of the absorbance (optical density) of the dye solutions. A UV spectrophotometer (Systronics model 108) was used to measure the optical density at different time intervals; λ_{max} for the dye was determined using a UV–visible recording spectrophotometer (Shimadzu UV-240).

3. Results and discussion

The photocatalytic bleaching of XP was observed at $\lambda_{max} = 507$ nm; the results for a typical run are given in Table 1 and represented graphically in Fig. 1. The optical density of the XP solution decreases with increasing time of irradiation, indicating that XP is consumed on irradiation.

3.1. Effect of pH variation

The effect of pH on the rate of bleaching of XP was investigated in the pH range 6.0–10.0. The semiconductor zinc oxide dissolves in the presence of highly acidic media and therefore photocatalytic bleaching could not be investigated in the lower pH range. The rate constants for this reaction were determined using the expression

Table 1
Photocatalytic bleaching of XP: a typical run ($[XP] = 1.0 \times 10^{-5}$ M; pH 7.4; light intensity, 26.0 mW cm^{-2}; zinc oxide, 0.50 g; temperature, 308 K)

Time (min)	Optical density (OD)	2 + log OD
0.0	0.282	1.450
15.0	0.189	1.276
30.0	0.129	1.110
45.0	0.088	0.944
60.0	0.060	0.778
75.0	0.041	0.612
90.0	0.028	0.447
105.0	0.019	0.278
120.0	0.013	0.113
130.0	0.010	0.000

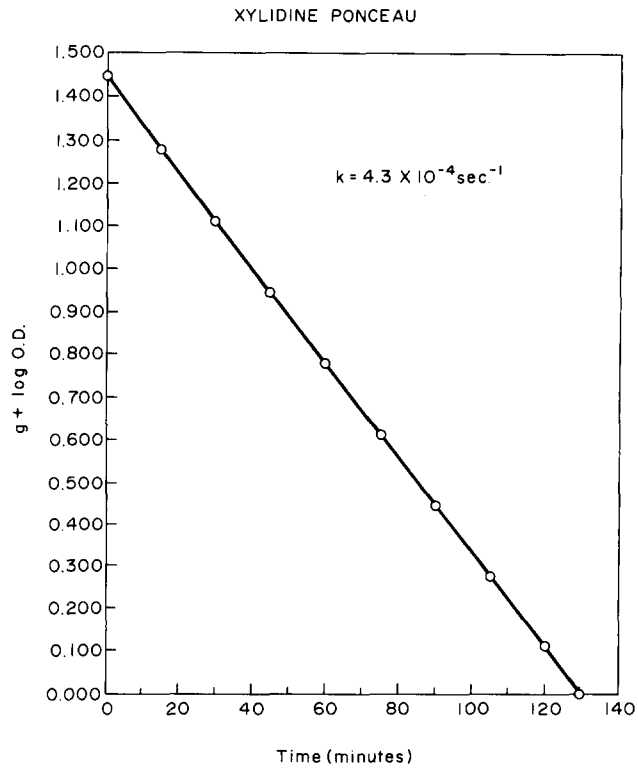

Fig. 1. Photocatalytic bleaching of XP: a typical run.

Table 2
Effect of pH variation $[XP] = 1.0 \times 10^{-5}$ M; zinc oxide, 0.50 g; light intensity, 26.0 mW cm^{-2}; temperature, 308 K)

pH	Rate constant $10^4 \times k$ (s^{-1})
6.0	1.7
6.5	2.6
7.0	3.5
7.5	4.3
8.0	5.3
8.5	6.2
9.0	7.1
9.5	8.0
10.0	9.0

rate constant $(k) = 2.303 \times$ slope

The results are reported in Table 2. It is observed that the rate of bleaching of XP increases with increasing pH value of the medium. This observation is similar to that of Domenech and Peral [27], Mehta [28] and Porwal [29].

3.2. Effect of [XP] variation

The effect of the variation of dye concentration was also studied by using different concentrations of XP solution. The results are given in Table 3. It can be seen that, as the concentration of XP increases, the reaction rate decreases. This can be explained by the

Table 3
Effect of XP concentration (zinc oxide, 0.50 g; pH 7.4; light intensity, 26.0 mW cm^{-2}; temperature, 308 K)

[XP] (10^{-5} M)	Rate constant $10^4 \times k$ (s^{-1})
1.10	12.6
1.25	9.5
1.50	6.5
1.75	5.3
1.00	4.3
1.25	3.5
1.50	2.9
1.75	2.3
2.00	2.1

Table 4
Effect of the amount of zinc oxide ([XP] = 1.0×10^{-5} M; pH 7.4; light intensity, 26.0 mW cm^{-2}; temperature, 308 K)

Amount of ZnO (g)	Rate constant $10^4 \times k$ (s^{-1})
0.10	1.4
0.20	2.1
0.30	2.8
0.40	3.5
0.50	4.3
0.60	5.0
0.70	5.5
0.80	5.5
0.90	5.5

fact that, as the concentration of XP is increased, it starts to act as a filter for the incident light, and at high concentrations does not permit the light to reach the zinc oxide particles; thus a decrease in the rate of photocatalytic bleaching of XP is observed.

3.3. Effect of the amount of zinc oxide

The amount of semiconductor zinc oxide powder may also affect the rate of bleaching of XP, and therefore different amounts of photocatalyst were used. The results are reported in Table 4. It can be seen that k increases with an increase in the amount of zinc oxide, and the time taken for bleaching of the XP solution decreases with an increase in the amount of semiconductor zinc oxide. This increase in the rate of bleaching may be attributed to an increase in the exposed surface area of the semiconductor. However, after a certain limit (0.70 g) has been reached, if the amount of zinc oxide is increased further, there is no increase in the exposed surface area of the photocatalyst. This is the saturation point, above which an increase in the amount of semiconductor has no effect on the rate of photocatalytic bleaching of XP.

The geometry of the reaction vessel also has an effect. This was confirmed by taking reaction vessels of different geometry. It was observed that the point of saturation was shifted to a higher value when beakers of larger capacity were used. On the other hand, the plateau was observed earlier when smaller beakers were used.

3.4. Effect of light intensity variation

An effect of the light intensity on the photocatalytic bleaching of XP was also observed. The results obtained are reported in Table 5. It can be seen that bleaching action is accelerated as the light intensity is increased. A large increase in the light intensity will increase the temperature of the dye solution; thus thermal reactions may occur instead of photocatalytic reactions; therefore, very high intensities were avoided.

3.5. Effect of the particle size of zinc oxide

The effect of the particle size on the rate of bleaching of XP was also investigated by taking zinc oxide particles of different sizes. The results are summarized in Table 6. It can be seen that, as the particle size of the semiconductor is increased, there is a corresponding decrease in the reaction rate. This may be due to the fact that, on increasing the particle size (keeping the amount constant) of the photocatalyst, the overall surface area of the semiconductor will decrease, thus resulting in a decrease in the rate of bleaching of XP.

3.6. Mechanism

On the basis of the observed data, the following tentative mechanism may be proposed for the pho-

Table 5
Effect of light intensity ([XP] = 1.0×10^{-5} M; pH 7.47; zinc oxide, 0.50 g; temperature, 308 K)

Intensity of light (mW cm^{-2}	Rate constant $10^4 \times k$ (s^{-1})
11.0	0.8
15.0	1.9
18.0	2.6
26.0	4.3
40.0	5.2
60.0	6.5

Table 6
Effect of particle size ([XP] = 1.0×10^{-5} M; pH 7.4; light intensity, 26.0 mW cm^{-2}; zinc oxide, 0.50 g; temperature, 308 K)

Particle size (μm)	Rate constant $10^4 \times k$ (s^{-1})
0.80	4.3
1.60	3.5
2.40	2.7
3.20	1.9
4.00	1.5

tocatalytic bleaching of XP. The semiconductor (SC) will be excited on exposure to give (SC*). This excited state will provide an electron (e^-) in the conduction band and a hole (h^+) in the valence band. The electron in the conduction band may be utilized to reduce [XP] to its leuco form.

$$SC \xrightarrow{h\nu} SC^* \quad (1)$$

$$SC^* \longrightarrow SC^+ \text{ (or } h^+) + e^- \quad (2)$$

$$e^- + [XP] \longrightarrow \text{leuco [XP]} \quad (3)$$

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