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USE OF ZIRCONIUM DIOXIDE PARTICULATE SYSTEM AS A PHOTOCATALYST : PHOTOBLEACHING OF ERYTHROSINE–B AND EOSIN –Y

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ABSTRACT

Photocatalytic bleaching of Erythrosine–B (EB) and Eosin–Y (EY) on zirconium dioxide powder were carried out in presence of light. The effects of variation of different parameters, like concentration of dye, pH, amount of semiconductor and light intensity on the rate of bleaching were observed. A tentative mechanism for the photocatalytic bleaching of EB and EY has been proposed.

Key words : Zirconium dioxide, Photocatalyst, Erythrosine–B, Eosin–Y, Photocatalytic bleaching.

INTRODUCTION

There are many environmental issues growing in size and complexity at present. Water pollution is one of them. The effluent from dyeing, textile and chemical industries pollute the water. Inspite of many uses, the dyes are toxic and carcinogenic in nature. Coloured solution containing dyes may cause skin cancer, and photodynamic action. On the contrary, bleached dye solution is less toxic and almost harmless. If coloured solution is bleached to give colourless water, then it may be used for washing, cleaning, irrigation and some other domestic purposes. In this context, photocatalytic bleaching provides a promising and low cost method to solve this problem.

Ameta *et al.*[1] reported photobleaching of basic blue–24 over zinc oxide particulate system. Photocatalytic bleaching of methyl orange in aqueous solution with titanium dioxide was reported by Chen and Chou[2]. Photodegradation of sodium lauryl sulphate in presence of titanium dioxide has been reported by Ameta *et al.*[3] Lou *et al.*[4] reported the titanium dioxide assisted photodegradation of a squarylium dye in aqueous dispersion under visible light irradiation. Photoassisted degradation of dyes in presence of Fe^{3+} and H_2O_2 under visible irradiation was investigated by Xie *et al.*[5] Chen *et al.*[6] studied visible light assisted photodegradation of sulphorhodamine–B dye in aqueous titanium dioxide dispersion.

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Neppolian *et al*[7] reported solar/U.V. induced photocatalytic degradation of three commercial textile dyes. Photobleaching of rose bengal over zinc oxide particulate system was reported by Ameta *et al.*[8]

Photocatalytic mineralisation of methylene blue using buoyant titanium dioxide coated polystyrene beads has been investigated by Febiyi and Skelton[9]. Zang *et al.*[10] studied the effect of surface charge on reduction rate of methyl orange photocatalysed by zinc sulphide solution. Gopidas and Kamat[11] reported the photoreduction of phenosafranine dye in colloidal titanium dioxide and cadmium sulphide suspensions. Photocatalytic degradation of methylene blue in presence of niobium pentoxide was reported by Artemev *et al.*[12] Takizawa *et al.*[13] reported mild oxidation of methylene blue by photogenerated holes on cadmium sulphide particles. Photobleaching of methylene blue sensitized by titanium dioxide was reported by Mills and Wang[14]. Photoreduction of thiazine dye over titanium dioxide colloid was investigated by Kamat[15]. No work has yet been reported on photocatalytic bleaching of Erythrosine–B and Eosin–Y over zirconium dioxide particulate system. This was the motivation behind the work.

EXPERIMENTAL

Erythrosine–B (BDH), Eosin–Y (LC) and zirconium dioxide (BDH) were used in present investigations. The photocatalytic bleaching of EB and EY was studied in the presence of semiconducting zirconium dioxide. Stock solution of EB and EY (concentration = 1.0×10^{-3}M) were prepared in doubly distilled water. The photocatalytic bleaching of EB and EY was observed by taking dye solution and 0.10 g of zirconium dioxide. Irradiation was carried out keeping the whole assembly exposed to a tungsten lamp (light intensity = 40.0 $mWcm^{-2}$). The intensity of light at various distances from the lamp was measured with the help of a solarimeter (Surya Mapi Model CEL 201). A water filter was used to cut out thermal radiations. The pH of the solution was measured by a digital pH meter (Hanna Instrument ISO 9001). The desired pH of the solution was adjusted by addition of previously standardized sulphuric acid or sodium hydroxide solution. The progress of the photocatalytic reaction was observed by taking optical density at regular time intervals using spectrophotometer (Systronic Model 106).

RESULTS AND DISCUSSION

The photocatalytic bleaching of Erythrosine–B and Eosin–Y were monitored at λ_{max} = 520 nm and 517 nm, respectively. The results for typical run are graphically represented in Figure 1.

The optical density of EB and EY were found to decrease with the increase in the time of irradiation, thus indicating that the dye was consumed on irradiation.

Effect of pH

The effect of variation of pH on the rate of bleaching of Erythrosine–B and Eosin–Y were investigated by determining the rate at different pH values. The semiconductor may dissolve in

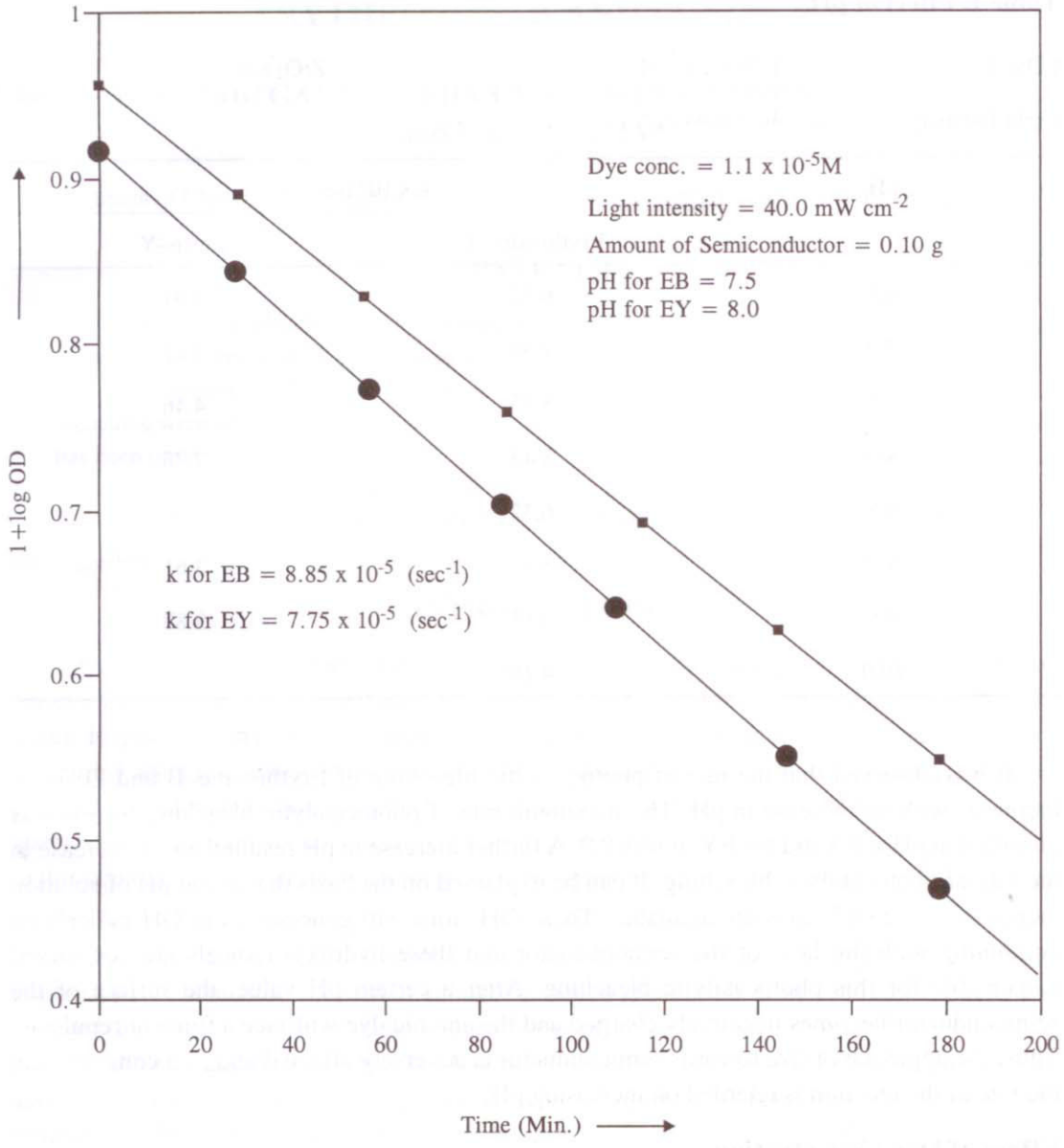

Fig. 1. A TYPICAL RUN

highly acidic media and therefore, photocatalytic bleaching could not be investigated in lower pH range. The results are reported in Table 1.

Table 1. Effect of pH

[Dye] = 1.10×10^{-5} M $ZrO_2 = 0.10$ g

Light Intensity = 40.0 $mWcm^{-2}$

pH	k x 10^5 (sec^{-1})	
	Erythrosine–B	Eosin–Y
6.5	6.32	2.91
7.0	7.38	3.95
7.5	8.85	4.46
8.0	8.43	7.78
8.5	6.32	6.32
9.0	5.75	3.61
9.5	4.88	2.87
10.0	4.16	–

It was observed that the rate of photocatalytic bleaching of Erythrosine–B and Eosin–Y increases with an increase in pH. The maximum rate of photocatalytic bleaching for EB was observed at pH = 7.5 and for EY, it was 8.0. A further increase in pH resulted into a decrease in the rate of photocatalytic bleaching. It can be explained on the basis that as the pH of solution increases, more OH^- ions are available. These OH^- ions will generate more OH radicals by combining with the hole of the semiconductor and these hydroxyl radicals are considered responsible for this photocatalytic bleaching. After a certain pH value, the surface of the semiconductor becomes negatively charged and the anionic dye will face a force of repulsion. Thus, the approach of dye towards semiconductor is adversely affected and as a consequence, the rate of the reaction is retarded on increasing pH.

Effect of Dye Concetration

The effect of concentration variation of dye on the rate of its photocatalytic degradation was also observed by taking different concentrations of dye. The result are given in Table 2.

Table 2. Effect of dye concentration

ZrO_2 = 0.10 g Light Intensity = 40.0 $mWcm^{-2}$

[Dye] x 10^5 M	k x 10^5 (sec^{-1})	
	Erythrosine–B (pH = 7.5)	Eosin–Y (pH = 8.0)
0.83	12.51	14.20
0.90	11.57	11.64
1.00	9.26	9.31
1.11	8.85	7.78
1.25	7.31	6.65
1.42	6.17	5.58
1.66	4.87	–

It was observed that as the concentration of dye was increased, the rate of photocatalytic bleaching was decreased. This can be explained by the fact that as the concentration of dye was increased, it will act like a filter for incident light and it will not permit the desired light intensity to reach the semiconductor (ZrO_2) particles and as a result, a decrease in the rate of photocatalytic degradation was observed.

Effect of Amount of Semiconductor

The effect of variation of amount of semiconductor on the rate of bleaching of dye was also investigated. The results are reported in Table 3

Table 3. Effect of amount of semiconductor

[Dye] = 1.10 x 10^{-5} M Light Intensity = 40.0 $mWcm^{-2}$

Amount of Semiconductor (g)	k x 10^5 (sec^{-1})	
	Erythrosine–B (pH = 7.5)	Eosin–Y (pH = 8.0)
0.025	7.42	3.89
0.050	7.86	5.13
0.075	8.85	6.22
0.100	8.85	7.78
0.125	8.95	7.78
0.150	8.85	7.82
0.175	–	7.78

As indicated from the data, the increase in amount of semiconductor (ZrO_2) increases the rate of photocatalytic bleaching of dye, but after a certain limiting amount of semiconductor, the rate of photocatalytic reaction becomes almost constant. This may be explained on the fact that as the amount of semiconductor was increased, the exposed surface area also increases, but after a certain limit, if the amount of semiconductor is further increased, there will be no increase in the exposed surface area of semiconductor. It may be considered as a saturation point, above which, any increase in the amount of semiconductor has negligible or no effect on the rate of photocatalytic bleaching of dye. This is due to the fact that extra amount will increase only the thickness of semiconductor layer at the bottom of the reaction vessel, once the saturation point is reached.

Effect of Light Intensity

The effect of light intensity on the rate of photocatalytic bleaching of dye was also observed. The results obtained are reported in Table 4

Table 4. Effect of light intensity

[Dye] = 1.10×10^{-5} M $ZrO_2 = 0.10$ g

Light Intensity ($mWcm^{-2}$)	k x 10^5 (sec^{-1})	
	Erythrosine–B (pH = 7.5)	Eosin–Y (pH = 8.0)
20.0	4.95	3.57
30.0	6.98	5.60
40.0	8.85	7.78
50.0	11.41	9.33
60.0	14.22	10.27
70.0	16.84	14.22

The results obtained above indicate that the rate of photocatalytic degradation of dye increases as the intensity of light was increased. This can be explained on the basis that more photons will be available for excitation on increasing the intensity of light and therefore, more electrons–hole pairs will be generated in the semiconductor resulting in enhanced rate of photocatalytic reaction. Further increase in the light intensity will increase the temperature of dye solution and thermal reaction may occur in place of photocatalytic reaction and therefore, higher intensities of light were avoided.

MECHANISM

On the basis of observed data, a tentative mechanism for photocatalytic bleaching of dye has been proposed as–

$$\text{Dye} \xrightarrow{h\nu} \text{Dye}^* \quad \text{....(1)}$$

$$\text{SC} \xrightarrow{h\nu} e^-(\text{CB}) + h^+(\text{VB}) \text{ or } \text{SC}^+ \quad \text{....(2)}$$

$$h^+ + OH^- \longrightarrow OH^\bullet \quad \text{.....(3)}$$

$$\text{Dye}^* + OH^\bullet \longrightarrow \text{Leuco [Dye]} \quad \text{....(4)}$$

$$\text{Leuco [Dye]} \longrightarrow \text{Products} \quad \text{....(5)}$$

Erythrosine–B (EB) or Eosin–Y (EY) absorbs radiations of suitable wavelength and is excited to its higher energy state. On the other hand, the semiconducting zirconium dioxide also utilizes the radiant energy to excite its electron from valence band to the conduction band, thus leaving behind a hole. This hole will abstract an electron from OH^- ion to generate OH radicals. These radicals will oxidize the dye to its leuco form, which may ultimately degrade to products. The participation of OH radical as an active oxidizing species was also confirmed using hydroxyl radical scavengers, where the bleaching was retarded to a great extent.

REFERENCES

1. R. Ameta, C. Kumari, C. V. Bhatt and Suresh C. Ameta, Ind. Quims., **333**, 36 (1998).
2. L. C. Chen and T. C. Chou, J. Mol. Catal., **85A**, 201 (1993)
3. Suresh C. Ameta, P. B. Punjabi, Pratibha Rao and Bhawana Singhal, J. Indian Chem. Soc.,**77**, 157 (2000)
4. T. Lou, T. Lin, J. Ncatizhao, H. Hidara and N. Serpone, Environ. Sci. Technol., **33**, 1379 (1999)
5. Y. D. Xie, F. Chen and J. C. Jhao, J. Photochem. Photobiol., **136A**, 235 (2000)
6. C. Chen, W. Zhao , J. Li, J. Zhao, H. Hidaka and N. Serpone, Environ. Sci. Technol. **36**, 3604 (2002).
7. B. Neppolian, H. C. Choi, S. Sakthivel, Bannumathi, R. Arabindoo and V. Murugesan, J. Hazardous Mater. , **89**, 303 (2002).
8. A. Sharma, R. Sharma, S. Rathore and Suresh C. Ameta, J. Indian Chem. Soc., **79,** 929 (2002)
9. M. E. Febiyi and R. L. Skelton , J. Photochem. Photobiol., **132A**, 121 (2000)

10. L. Zang, Chun–xan Liu and Xin–Min Ren, J. Photochem. Photobiol., **85A**, 239 (1995)
11. K. R. Gopidas and P. V. Kamat, Langmuir , **5** , 22 (1989).
12. J. M. Artemev, S. M. Artemeva, M. G. Vinogradov and T. L. Llika, Russ. J. Chem., **67**, 1354 (1995).
13. T. Takizawa, T. Watanabe and K. Honda, J. Phys. Chem., **82**, 1391 (1978).
14. A. Mills and J. Wang, Photochem. Photobiol., **127A**, 123 (1999).
15. P. V. Kamat, Langmuir, **1**, 608 (1985).

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