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ORIGINAL ARTICLE

Enhancing photocatalytic activity of zinc oxide by coating with some natural pigments

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Abstract An attempt has been made to enhance the photocatalytic activity of zinc oxide semiconductor by coating it with extracts of natural pigments, chlorophyll and anthocyanin. Coated photocatalyst has been used for the photobleaching of rose bengal dye. Progress of the reaction has been monitored spectrophotometrically by measuring absorbance of the reaction mixture at definite time intervals. The effect of variation of different parameters such as pH, concentration of dye, amount of semiconductor and light intensity on the rate of photobleaching was also observed. A tentative mechanism for the reaction has been proposed.

1. Introduction

Water, an essential commodity for the life of organisms, is becoming polluted as a result of multifarious human activities. Chemical, food and beverage, textile and apparel, pesticide and insecticide, dyeing and printing industries are among those causing water pollution. Polluted water may have detrimental effects on animals, plant life and human themselves. Principal sources of water pollution are dye-based industries where waste water is coloured due to dye components. This polluted water cannot be used either for irrigation or for domestic purposes.

As we have stepped into the 21st century, we have faced the challenges of purification of our water and air resources. Popular treatment methods for eliminating dyes from the waste water stream suffer from one or another drawback. Photocatalytic degradation using semiconductor as a photocatalyst is found to be a very efficient process for mineralization of organic pollutants. Photocatalysis is a phenomenon where an electron hole pair is generated on exposing semiconducting materials to light of suitable energy.

Chen and Chou (1993) reported photobleaching of methyl orange in aqueous solution with suspended titanium dioxide as photocatalyst. Photocatalytic degradation of cetyl pyridinium chloride over TiO_2 has been reported by Singal et al. (1997). Photocatalytic degradation of xylidine ponceau and orange-G dyes by zinc oxide powder as photocatalyst has been reported by Sharma et al. (1995). Xie et al. (2000) observed

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photoassisted degradation of dyes in the presence of Fe^{3+} and H_2O_2 under visible light. Photocatalytic mineralization of methylene blue using buoyant TiO_2-coated polystyrene beads has been studied by Fabiyi andShelton (2000). Photooxidation of alizirin red in TiO_2 dispersions under visible illumination was carried out by Liu et al. (2000). Kim and Yoom (2001) prepared a new photocatalyst for the photoreduction of methyl orange in aqueous medium by encapsulating TiO_2/Y-zeolite. Photocatalytic degradation of brilliant green and crystal violet over zinc oxide has been investigated by Ameta et al. (1997). Ramazol red was degraded in the presence of zinc oxide photocatalyst by Sivakumar et al. (1999).

Neppolian et al. (1999) reported photodegradation of some textile dyes over zinc oxide. Zinc oxide in the slurry and thin film form was used for the photocatalytic degradation of acid green-16 (Sakthivel et al., 1999). Photocatalytic reduction of methyl yellow on CdS nanoparticals mediated in reverse micelles was observed by Zang and Shen (1996). Punjabi et al. (2005) studied the photoreduction of congo red by ascorbic acid and EDTA over cadmium sulphide as a photocatalyst. Nasr et al. (1997) reported photocatalytic reduction of azo dyes such as naphthol blue black and disperse blue – 79.

Mansilla and Viilasnov (1994) investigated the photodegradation of Kraft-black liquor using platinum-impregnated zinc oxide and reported complete discolouration after 60 min under UV irradiation. Photocatalytic degradation of crystal violet with semiconducting zinc oxide powder suspended in aqueous solution was observed by Rao et al. (1997) . Ameta et al. (1998) have used zinc oxide particles for photobleaching of basic blue – 24. From the literature survey it has been observed that no attention has been paid on the photocatalytic bleaching of rose bengal by ZnO photocatalyst coated with the extracts of natural pigments, although this dye is extensively used in textile industries.

Therefore, in the present investigation, ZnO coated with the extracts of natural pigments has been employed as a photocatalyst for photobleaching of rose bengal dye and the effect of various experimental parameters on the rate of the reaction to obtain optimum condition for the reaction has been studied.

2. 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 absorbance of the solution decreases with increasing time of exposure, indicating a decrease in the concentration of rose bengal dye. A plot of 1 + log [absorbance] versus time was linear and follows pseudo-first order kinetics (Figs. 1 and 2). The rate constant was measured with the expression:

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

The results are represented in Tables 1A and 1B.

O.D. refers to optical density.

2.1. 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 4.5–8.0 and 4.5–8.5 for chlorophyll and china rose-coated ZnO, respectively (Table 2).

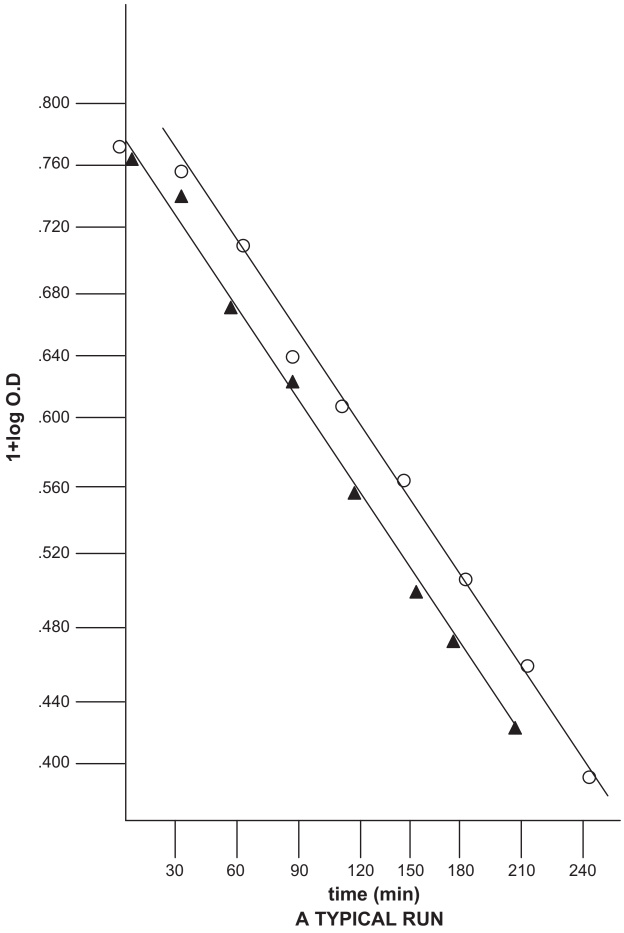

Figure 1 A typical run.

Photocatalytic degradation of rose bengal was maximum at pH 5.5 for both chlorophyll and china rose-coated ZnO. It was observed that the rate of photocatalytic bleaching of rose bengal increases with increase in pH up to 5.5 and on further increasing the pH beyond 5.5, the rate of reaction decreases.

This behaviour may be explained on the basis that as pH is 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 from semiconductor. This will decrease the rate of reaction. On the other hand, the rate of photocatalytic bleaching of rose bengal also decreases with the increase in pH above 5.5. This may be due to the fact that at higher pH (alkaline), the $\bar{O}H$ ions are adsorbed on the surface of the semiconductor making it negatively charged and as a result, the anionic dye will experience repulsion from semiconductor, 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 (approx pH 5.5).

2.2. Effect of concentration of rose bengal

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

The rate of photocatalytic degradation was found to increase with the increasing concentration of rose bengal up

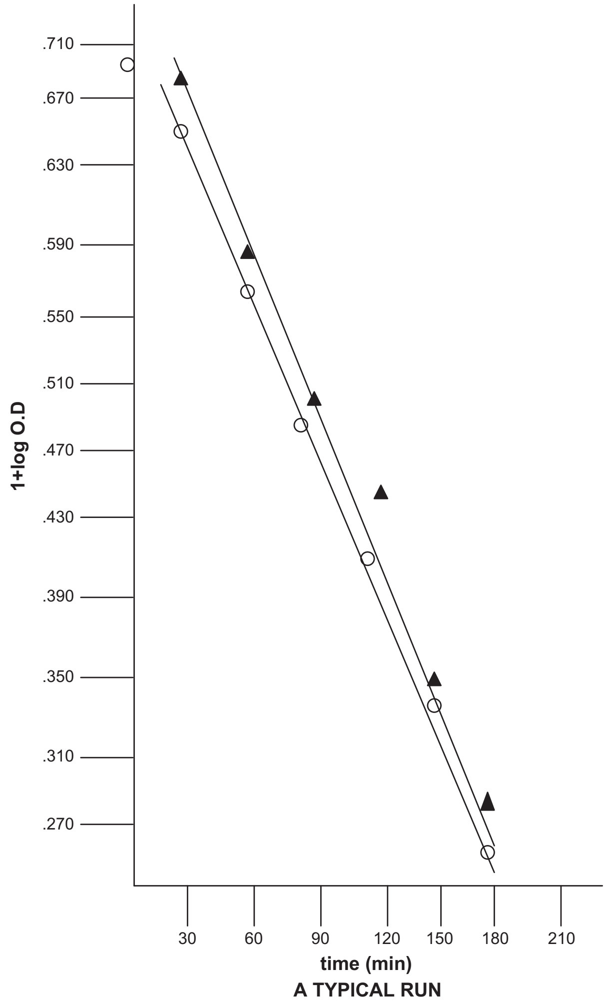

Figure 2 A typical run.

Table 1A A typical run. Chlorophyll-coated ZnO system.

Time (min)	1 + log O.D.	
	Treated	Untreated
0.0	0.769	0.761
30.0	0.755	0.742
60.0	0.708	0.673
90.0	0.635	0.611
120.0	0.604	0.555
150.0	0.563	0.502
180.0	0.498	0.468
210.0	0.460	0.404
240.0	0.394	0.296
	$k = 6.71 \times 10^{-5}\ \mathrm{s}^{-1}$	$k = 6.21 \times 10^{-5}\ \mathrm{s}^{-1}$

Rose bengal = 2.0×10^{-5} M, light intensity = 60.0 mW cm^{-2}, chlorophyll coated ZnO = 0.3 gm, pH 5.5, untreated ZnO = 0.3 gm, O.D. = optical density.

Table 1B A typical run. Anthocyanin (china rose)-coated ZnO.

Time (min)	1 + log O.D	
	Treated	Untreated
0.0	0.684	0.715
30.0	0.637	0.684
60.0	0.562	0.586
90.0	0.635	0.503
120.0	0.418	0.439
150.0	0.336	0.346
180.0	0.250	0.274
210.0	0.181	0.120
	$k = 10.96 \times 10^{-5}\ \mathrm{s}^{-1}$	$k = 9.30 \times 10^{-5}\ \mathrm{s}^{-1}$

Rose bengal = 2.0×10^{-5} M, light intensity = 50.0 mW cm^{-2}, china rose coated ZnO = 0.4 gm, pH 5.5, untreated ZnO = 0.4 gm, O.D. = optical density.

Table 2 Effect of pH.

pH	Chlorophyll coated ZnO system $k \times 10^5\ \mathrm{s}^{-1}$	Anthocyanin (china rose) coated ZnO system $k \times 10^5\ \mathrm{s}^{-1}$
4.5	3.98	3.62
5.0	4.83	4.13
5.5	**5.11**	**6.23**
6.0	3.83	5.11
6.5	3.51	4.75
7.0	3.40	4.35
7.5	3.28	4.03
8.0	3.19	3.83

Table 3 Effect of dye concentration.

$[\mathrm{RB}] \times 10^{-5}$ M	Chlorophyll coated ZnO system $k \times 10^5\ \mathrm{s}^{-1}$	Anthocyanin (china rose) coated ZnO system $k \times 10^5\ \mathrm{s}^{-1}$
1.5	3.62	4.05
2.0	**3.65**	**4.22**
2.5	3.07	2.74
3.0	2.46	2.67
3.5	2.13	2.45
4.0	2.30	2.38

Sensitized (ZnO) = 0.1 gm, light intensity = 30 mW cm^{-2}, pH 5.5.
Sensitized (ZnO) = 0.1 gm, light intensity = 40 mW cm^{-2}, pH 5.5.

to 2.0×10^{-5} M, for both chlorophyll and china rose-coated ZnO. Further increase in concentration beyond this limit results in 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 are available for excitation and energy transfer and hence, an increase in the rate was observed. The rate of photocatalytic bleaching was found to decrease with a further increase in the concentration beyond 2.0×10^{-5} 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 bleaching of rose bengal.

2.3. Effect of amount of semiconductor

The amount of semiconductor is also likely to affect the rate of dye bleaching and hence photocatalytic bleaching was

Table 4 Effect of amount of semiconductor.

Semiconductor (gm)	Chlorophyll coated ZnO system $k \times 10^5\ s^{-1}$	Anthocyanin (china rose) coated ZnO system $k \times 10^5\ s^{-1}$
0.1	2.92	5.95
0.2	3.95	6.35
0.3	**5.11**	**6.90**
0.4	4.02	7.67
0.5	3.98	6.50
0.6	3.32	5.96

Rose bengal = 2.0×10^{-5} M, light intensity = 30 mW cm^{-2}, pH 5.5.
Rose bengal = 2.0×10^{-5} M, light intensity = 40 mW cm^{-2}, pH 5.5.

observed using different amounts of photocatalyst. The results are reported in Table 4.

It has been observed that the rate of photocatalytic bleaching of rose bengal increases with an increase in the amount of semiconductor and then ultimately it becomes almost constant after a certain amount of semiconductor. The rate is maximum at 0.3 and 0.4 gm for chlorophyll and china rose-coated ZnO, respectively. This may be attributed to 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 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 which any increase in the amount of semiconductor has negligible effect on the rate of photocatalytic bleaching of rose bengal, because any increase in the amount of semiconductor after saturation point will only increase the thickness of the layer at the bottom of the reaction vessel.

2.4. Effect light intensity

The effect of light intensity on the photocatalytic degradation of rose bengal was also investigated. The results are reported in Table 5.

The results indicate that as the light intensity was increased, the rate of reaction also increased and maximum rate of reaction has been found to be at 50 mW cm^{-2} for both the systems. With the increasing light intensity the number of photons striking per unit area of semiconductor powder is increased thereby increasing the rate of photocatalytic bleaching.

With further increase in the intensity, there is a decrease in the rate of reaction, which may be due to the thermal side reactions.

Table 5 Effect of light intensity.

Intensity (mW cm^{-2})	Chlorophyll coated ZnO system ($k \times 10^5\ s^{-1}$)	Anthocyanin (china rose) coated ZnO system ($k \times 10^5\ s^{-1}$)
30	3.65	4.36
40	3.69	4.75
50	**3.83**	**5.45**
60	3.69	4.75
70	2.74	4.75
80	3.95	4.60

Rose bengal = 2.0×10^{-5} M, sensitized (ZnO) = 0.3 gm, pH 5.5.
Rose bengal = 2.0×10^{-5} M, sensitized (ZnO) = 0.4 gm, pH 5.5.

2.5. Mechanism

On the basis of the experimental observations and corroborating the existing literature, a tentative mechanism has been proposed for the photocatalytic degradation of rose bengal by the ZnO coated with extracts of chlorophyll and china rose.

$$^1\text{sens}_0 \xrightarrow{h\nu} {}^1\text{sens}_1$$

$$^1\text{sens}_0 \xrightarrow{\text{ISC}} {}^3\text{sens}_1$$

$$^3\text{sens}_1 + \text{ZnO} \rightarrow {}^1\text{sens}_0 + [\text{ZnO}]^*$$

$$[\text{ZnO}]^* \rightarrow \text{ZnO}(h^+) + \text{ZnO}(\text{e}^-)$$

$$\text{ZnO}(\text{e}^-) + \text{O}_2(\text{dissolved}) \rightarrow \text{ZnO} + \text{O}_2^{-\cdot}$$

$$\text{H}^+ + \text{O}_2^{-\cdot} \rightarrow \text{HO}_2^{\cdot}$$

$$4\text{HO}_2^{\cdot} \rightarrow 2\text{H}_2\text{O} + \text{O}_2$$

$$\text{OH}^- + \text{ZnO}(h^+) \rightarrow \text{ZnO} + \text{OH}^{\cdot}$$

$$\text{RB} + \text{OH}^{\cdot} \rightarrow \text{leuco[RB]}$$

$$\text{Leuco[RB]} \rightarrow \text{products}$$

where sensitizer = chlorophyll and china rose. RB = rose bengal.

The sensitizer (sens) absorbs radiations of suitable wavelength and gives rise to its excited singlet state, which then undergoes intersystem crossing (ISC) to its triplet state. This triplet state ($^3\text{sens}_1$) transfers its energy to the semiconductor ZnO which is in its ground state. Now this ZnO uses its energy to excite its electron from valence band to the conduction band, thus, leaving behind a hole (h^+). Dissolved oxygen reacts with the electron located in conduction band forming oxygen radical anion.

This reacts with proton, forming hydrogen peroxide radical, which ultimately decomposes to oxygen and water.

The hole abstracts an electron from –OH$^-$ ion to generate OH radical ($\hat{\text{O}}$H) which will oxidize the dye to its leuco form. The leuco dye ultimately degrades to the products.

3. Conclusion

The rate of photocatalytic degradation of rose bengal is enhanced by coating the semiconductor with natural pigments such as chlorophyll and anthocyanin from china rose. The increasing order of the rate of degradation of rose bengal with different sensitizers is as follows:

$$\text{China rose coated ZnO} > \text{Chlorophyll coated ZnO} > \text{pure ZnO}$$

4. Experimental

All solutions were prepared in doubly distilled water. Irradiation has been carried out with a 200 W tungsten lamp. The light intensity was measured with the help of a solarimeter (CEL, Model SM 201). A water filter has been used to cut off thermal radiations. A digital pH meter (Systronics, Model

335) is used to adjust the pH of the solutions by the addition of previously standardized 0.1 N sulfuric acid and 1 N sodium hydroxide solutions. The progress of the photocatalytic reactions was observed by measuring the absorbance at regular time intervals using UV–vis spectrophotometer (Systronics Model 106). Zinc Oxide (B.D.H.) and rose bengal (Himedia) have been used as received.

The effect of coating of ZnO by extracts of flowers on the band gap of ZnO was ascertained by their diffused reflectance spectra. It is known that pure ZnO absorbs radiations at the border of UV–vis region i.e. 388 nm. Coating of ZnO by these natural pigments has shifted the wavelength of absorption from UV–vis region to the IR region (for chlorophyll coated ZnO and for china rose-coated ZnO).

It reflects that the band gap of ZnO has been reduced considerably by coating of ZnO with these natural pigments. As a consequence, coated ZnO will utilise visible and infrared radiations more as evident from the increase in rate of photocatalytic degradation of rose bengal from that of pure ZnO to $k = 6.71 \times 10^{-5}\ \mathrm{s}^{-1}$ (for chlorophyll-coated ZnO) and $k = 10.96 \times 10^{-5}\ \mathrm{s}^{-1}$ (for china rose-coated ZnO).

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