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PHOTOCATALYTIC BLEACHING OF PHENOLPHTHALEIN USING ZnO SEMICONDUCTING POWDER

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ABSTRACT

The photocatalytic bleaching of phenolphthalein was monitored spectrophotometrically in the presence of zinc oxide powder. The effects of variation of different parameters like concentration of phenolphthalein, light intensity, pH, amount and particle size of semiconductor on the rate of photocatalytic bleaching was observed. A tentative mechanism for the photocatalytic bleaching of phenolphthalein was proposed.

Key words : Photocatalytic, ZnO, Semiconducting, Phenolphthalein

INTRODUCTION

Photoinduced electron transfer reactions have attracted the attention of photochemists all over the globe because these reactions are capable of converting toxic compounds into nontoxic or less toxic materials. A large amount of chemicals are produced in different industries, some of which are toxic to human life also. These pollutants are sometimes released into the environment either accidentally and and/or in the form of industrial effluents. Dyeing, printing and textile industries throw a lot of chemicals in the water resources around, thus causing water pollution. The coloured and polluted water can neither be used for irrigation purposes nor for any domestic use. A number of attempts have been made to remove these dyes from polluted water. These are adsorption by charcoal, thermal dehydration, chemical transformation, etc. but photocatalytic reactions seem to be promising for this purpose.

Photochemical decolouration of azo dyes was studied by Bugaeva et al.[1] whereas Hatsui and Takeshita et al.[2] reported methylene blue sensitized photoreaction of quadricyclane. Kamat et al.[3] investigated photochemistry of squarine dyes whereas Isak and Eyring[4] observed chemistry and photophysics of cresyl violet in various solvents and micelles. Paul et al.[5] reported photobleaching of oligoanthrylenes in the film state while Chen and Chou[6] observed photocatalytic bleaching of methyl orange. Sharma et al.[7,8] observed photocatalytic degradation of xylidine ponceau and orange–G, whereas Artemer et al.[9] carried out photocatalytic decomposition of methylene blue in ozonized aqueous TiO_2 and Nb_2O_5 suspensions. Fang et al.[10] observed sensitized photocatalytic oxidation of some dyes. Laxmi et al.[11] reported titanium dioxide mediated photocatalytic degradation of methylene blue whereas Moger and

Paroczay[12] investigated in detail some environmental effects in the cationic dye sensitized photochemical transformation of β–naphthol.

Zang and Shen[13] observed photocatalytic reduction of methyl yellow on CdS nanoparticles mediated in reverse micelles. Recently, Rappon and Syritski[14] studied kinetics of photobleaching of aberchrome 540 in various solvents. Rao et al.[15] carried out photobleaching of crystal violet.

A great deal of literature survey reveals that no work was reported on photocatalytic bleaching of phenolphthalein, over zinc oxide, although it is extensively used as indicator, because of its sensitivity towards the action of alkali solution. It is the most important member of phenolphthalein group. It is used in the determination of the hydrogen ion concentration of solutions.

EXPERIMENTAL

Phenolphthalein (E. Merck) and zinc oxide (sd fine) were used in present investigations. Stock solution of phenolphthalein (1.0×10^{-4}M) was prepared in double distilled water. The photocatalytic bleaching of phenolphthalein was observed by taking dye solution. 0.30 g of zinc oxide was added to it. Irradiation was carried out keeping the whole assembly exposed to a tungsten lamp (light intensity = 60.0 mW cm^{-2}). Sunlight was used for higher intensity of light. The intensity of light at various distances from the lamp was measured with the help of a solarimeter (SuryaMapi Model CEL 201). A water filter was used to cut out thermal radiations. The pH of the solution was measured by the digital pH meter (Systronics Model 335). The desired pH of the solution was adjusted by the addition of previously standardized sulfuric acid and sodium hydroxide solution. The necessary condition for the correct measurement of the optical density is that the solution must be free from semiconductor particles and other impurities, for that centrifuge (REMI–1258) and Whatmann filter paper were used, but both were not found suitable. Thus G–3 sintered glass crucible was used for filtration to obtain the desired accuracy in measurement of absorbance (Optical Density) of the dye solutions.

The progress of the photocatalytic reaction was observed by taking optical density at regular time intervals using spectrophotometer (JASCO 7800).

The photocatalytic bleaching of phenolphthalein was monitored at λ_{max} = 522 nm. The results of a typical run are given in Table 1 and presented graphically in Figure 1.

Table 1. A Typical Run

[Phenolphthalein] = 4.00×10^{-5}M
Zinc oxide = 0.30 g

Light Intensity = 60.0 $mWcm^{-2}$
pH = 11.0
Temperature = 308 K

Time (min.)	Optical Density (O.D.)	1 + log O.D.
0.0	0.739	0.8686
30.0	0.708	0.8500
60.0	0.669	0.8254
90.0	0.635	0.8027
120.0	0.604	0.7810
150.0	0.575	0.7596
180.0	0.543	0.7347
210.0	1.518	0.7143
240.0	1.494	0.6946
270.0	1.469	0.6711

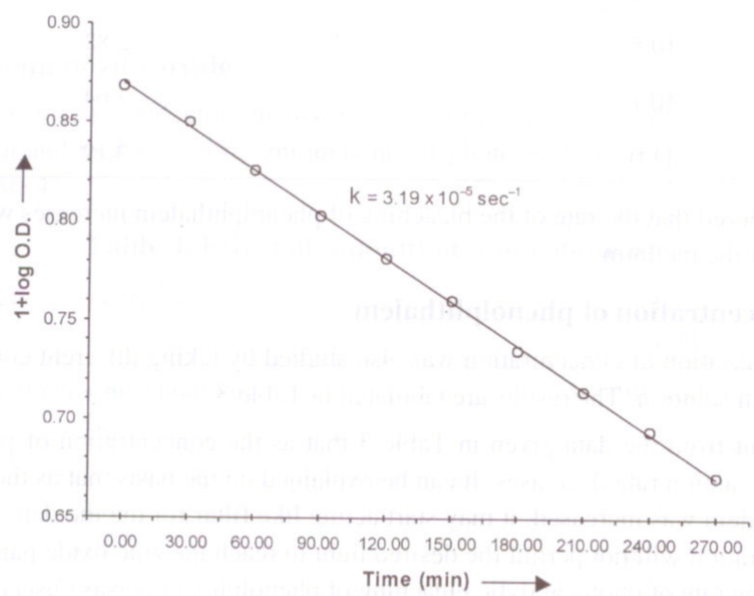

Fig. 1. A TYPICAL RUN

It was observed that optical density of phenolphthalein solution decreases with an increase in the time of irradiation, thus indicating that phenolphthalein is consumed on irradiation.

RESULTS AND DISCCUSION

Effect of pH

The effect of pH on the rate of bleaching of phenolphthalein was investigated in the pH range (pH = 9.5 to 11.5). The semiconductor zinc oxide dissolves in presence of highly acidic media and, therefore, photocatalytic bleaching could not be investigated in lower pH range. The rate constants for this reaction were determined using the expression $k = 2.303 \times$ slope.

Table 2. Effect of pH

[Phenolphthalein] = 4.00×10^{-5}M
Zinc oxide = 0.30 g

Light Intensity = 60.0 $mWcm^{-2}$
Temperature = 308 K

pH	$k \times 10^5$ (sec^{-1})
9.5	1.18
9.8	1.74
10.0	2.10
10.2	2.46
10.5	2.82
10.7	3.04
11.0	3.19

It was observed that the rate of the bleaching of phenolphthalein increases with increase in the pH value of the medium.

Effect of concentration of phenolphthalein

Effect of variation of concentration was also studied by taking different concentrations of phenolphthalein solution. The results are tabulated in Table 3.

It is evident from the data given in Table 3 that as the concentration of phenolphthalein increases, the reaction rate decreases. It can be explained on the basis that as the concentration of phenolphthalein was increased, it may start acting like filter for the incident light, where its larger concentration will not permit the desired light to reach the zinc oxide particles and thus, a decrease in the rate of photocatalytic bleaching of phenolphthalein was observed.

Table 3. Effect of phenolphthalein concentration

Light Intensity = 60.0 mWcm^{-2} pH = 11.0
Zinc oxide = 0.30 g Temperature = 308 K

[Phenolphthalein] × 10^5M	k × 10^5 (sec^{-1})
1.00	2.04
1.50	2.42
2.00	2.73
2.50	2.85
3.00	3.02
3.50	3.10
4.00	3.19
4.50	3.12
5.00	3.04
5.50	2.81
6.00	2.69
6.50	2.32

Effect of amount of zinc oxide

The amount of semiconductor zinc oxide powder may also affect the rate of bleaching of phenolphthalein and therefore, different amounts of photocatalyst were used. The results are reported in Table 4.

Table 4. Effect of amount of semiconductor

[Phenolphthalein] = 4.00 × 10^{-5} M Light Intensity = 60.0 mWcm^{-2}
pH = 11.0 Temperature = 308 K

Amount of semiconductor (g)	k × 10^5 (sec^{-1})
0.05	2.04
0.10	2.32
0.15	2.87
0.20	3.02
0.30	3.19
0.35	3.19
0.40	3.18

As evident from the data shown in Table 4, the value of k increases with increase in the amount of zinc oxide but the time taken for bleaching of phenolphthalein solution decreases with the increase in the amount of semiconductor zinc oxide. This increase in the rate of bleaching may be attributed to increase in the exposed surface area of the semiconductor. But after a certain limit (0.30 g), if the amount of zinc oxide is increased further, 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 no additional or negligible effect on the rate of photocatalytic bleaching of phenolphthalein. As any increase in the amount of semiconductor after this saturation point will only increase the thickness of the layer at the bottom of the vessel, once the complete bottom of the reaction vessel is covered by the photocatalyst.

It may be also explained on the basis of the geometry of the reaction vessel. 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 vessels of larger capacities were used. A reverse trend was observed, when vessels of smaller capacities were used.

Effect of light intensity

The effect of intensity of light on the photocatalytic bleaching of phenolphthalein was also observed. The results obtained are reported in Table 5.

Table 5. Effect of light intensity

[Phenolphthalein] = 4.00×10^{-5}M Zinc oxide = 0.30 g
pH = 11.0 Temperature = 308 K

Light Intensity ($mWcm^{-2}$)	$k \times 10^5$ (sec^{-1})
20.4	1.24
30.0	1.76
40.4	2.24
50.2	2.87
60.0	3.19
70.4	3.70
81.6	4.10

The results given above indicates that bleaching action is accelerated as the intensity of light was increased. A further increase in the intensity of light will also increase the temperature of the dye solution, thus thermal reactions may occur in the place of photocatalytic reaction and, therefore, higher intensities were avoided.

Effects of particle size

The effect of particle size on the rate of bleaching of phenolphthalein was also investigated by taking zinc oxide particles of different sizes. The results are summarized in Table 6.

Table 6. Effect of particle size

[Phenolphthalein] = 4.00×10^{-5} M | Zinc oxide = 0.30 g

pH = 11.0 | Light Intensity = 60.0 $mWcm^{-2}$

Particle size (μm)	$k \times 10^5$ (sec^{-1})
0.80	3.19
1.60	2.83
2.40	2.46
3.20	2.14
4.00	1.70

It is clear from the data given in Table 6 that as the particle size of the semiconductor was 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 into a decrease in the rate of bleaching of phenolphthalein.

Mechanism

On the basis of the observed data, the following tentative mechanism may be proposed for photocatalytic bleaching of phenolphthalein.

The semiconductor (SC) will be excited on exposure to give SC^*. The excited state will provide on electron (e^-) in conduction band and a hole in the valence band. The electron in the conduction band may be utilized for reducing the phenolphthalein to its leuco form.

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

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

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

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