JIRCMS Vol.: 06 II Issue 01 II Pages 01-04 II Mar 2022

Photocatalytic Bleaching of Rose Bengal in Presence of Zinc Oxide As Photocatalyst

Seema Gulati, Sudha Sukhwal Shringi
Department of Chemistry, R. R. College, Alwar
seema.gulati1209@gmail.com, sudhashringi@gmail.com

Abstract: The photocatalytic bleaching of Rose Bengal in presence of zinc oxide has been carried out. The photocatalytic bleaching of Rose Bengal was observed spectrophotometrically. The effects of various parameters such as pH, dye concentration, amount of semiconductor and light intensity on the rate of photocatalytic bleaching was observed. A tentative mechanism has been proposed.

Keywords: Rose Bengal, zinc oxide, semiconductor, photocatalytic bleaching etc.

INTRODUCTION

Environmental photochemistry using semiconductor nanoclusters is a part of a general group of chemical remediation methods known as advanced oxidation process (OAP). These methods are based on distinguishing feature – the generation and use of hydroxyl radicals as the primary oxidant for the degradation of organic pollutants. AOPs such as UV-peroxide, ozonation, and photo-Fenton process have already been proved useful to carry out the oxidation of organic compounds. Three other AOPs, viz; semiconductor based photocatalysis, sonolysis and gamma radiolysis have also emerged as viable processes in recent years. In present work we are using semiconductor-based photocatalysis process for bleaching of dye in presence of zinc oxide. Rose Bengal is used as a dye in colouring edible products and cosmetics; therefore, it is important to remove this dye from the water resources.

S. Benjamin et al[1] have used natural pigments zinc oxide to enhance photocatalytic activity of zinc oxide. B Pare et al[2] have studied photocatalytic degradation of Lissamine Fast yellow dye in ZnO suspension. Al-Gheethi et al[3] worked on sustainable approaches for removing Rhodamine B dye using agricultural waste adsorbents. H. S. Rai et al[4] have carried work on removal of dye from the effluent of textile and dye-stuff manufacturing industry. M Antoniadou et al[5] have studied photocatalytic degradation of Pharmaceuticals and organic contaminants of emerging concern using nanotubular structures. R. Asahi et al[6] have used nitrogen doped Titanium oxide as photocatalysis in the presence of visible light. While, Y Gong et al[7] have used CdTe/ TiO_2 hetero structure Photocatalytic degradation of antibiotic waste water. S.K. Khore et al[8] have developed green sol-gel route for selective growth of 1D rutile N-TiO_2: A highly active photocatalyst for H_2 generation and environmental remediation under natural sunlight.

MATERIALS AND METHODS

Rose Bengal (H.M.), Zinc oxide (C.D.H.) were used in present investigation. 0.1050 gms of Rose Bengal was dissolved in 100 ml of distilled water so that the concentration of dye solution was $10X10^{-3}$ M. It was used as a stock solution. This solution was further diluted. The optical density of this dye solution was determined with the help of a spectrophotometer (λ_{max} = 545 nm). Then it was divided into four parts-

(I) The first beaker containing only dye solution was kept in dark.

(ii) The second beaker containing only dye solution was kept in sunlight.

(iii) 0.10g of semiconductor zinc oxide was added to the third beaker containing dye solution and was kept in dark.

(iv) 0.10g of semiconductor zinc oxide was added to the fourth beaker containing dye solution and it was exposed to sunlight.

These beakers were kept for 4 hours and then the optical density of solution in each beaker was measured with the help of a spectrophotometer. It was observed that the solutions of first three beakers had the same optical density while the solution of fourth beaker had a decrease in its initial value of optical density. The above experiment confirms that the reaction between Rose Bengal and semiconductor powder is neither thermal nor photochemical but it is a photo catalytic reaction. It was observed that the optical density of Rose Bengal solution in presence of semiconductor was much low as compared to sample without semiconductor at the same time intervals. It means that the rate of this photocatalytic degradation is favorably affected by a semiconductor in the case of Rose Bengal. The plot of log O.D. v/s time was linear and hence, this reaction follows pseudo-first order kinetics. The rate constants of this reaction was determined by the expression - (1)

$$k=2.303\times slope$$

RESULTS AND DISCUSSION

The photocatalytic beaching of Rose Bengal was observed at λ_{max} = 545 nm the result for typical run is given in Table 1 and graphically represented in figure 1

TABLE -1 A TYPICAL RUN

[Rose Bengal] = 1.0×10^{-5} M — pH=5.5

Light Intensity = 40.0 mW cm^{-2} — Zinc Oxide = 0.20 g

TIME (min)	Optical Density (O.D)	1+log O.D.
0.0	0.905	0.956
30.0	0.784	0.894
60.0	0.638	0.804
90.0	0.581	0.764
120.0	0.502	0.700
150.0	0.425	0.628
180.0	0.377	0.576
210.0	0.325	0.512

k=8.19×10^{-5}(sec^{-1})

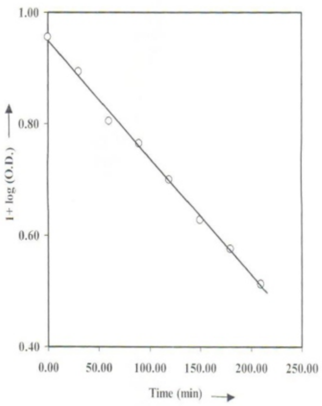

Fig 1. A Typical Run

EFFECT OF pH

The pH of the solution is likely to affect the bleaching of the dye. The effect of pH on the rate of bleaching of dye solution was investigated in the pH range (5.0 - 8.0) The results are reported in Table 2 and graphically presented in Figure 2.

TABLE 2

EFFECT OF pH

Rose Bengal = 1.0×10^{-5}M — Zinc oxide = 0.20 g

Light Intensity = 40.0 mW cm^{-2}

pH	K x 10^5 (sec^{-1})
5.0	7.31
5.5	8.19
6.0	6.24
6.5	4.90
7.0	4.54
7.5	3.03
8.0	2.47

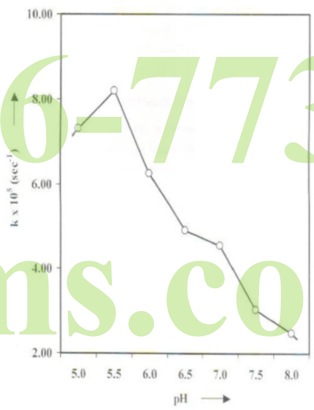

Fig. 2 Effect of pH

It was observed that with increase in the pH of medium, the rate of photocatalytic bleaching of Rose Bengal increases up to 5.5 and a further increase in pH value will decrease the rate of photocatalytic bleaching. This may be explained on the basis that at lower pH values (< 5.5), the dye remains in its protonated form and this will facilitate the approach of dye molecules towards the surface of the semiconductor which is electron rich due to presence of an electrons in its conduction band and, therefore, the rate of photocatalytic bleaching will increase. But after a certain value of pH i.e. 5.5, a further decrease in pH will make semiconductor surface positively charged due to the adsorption of H^+ ions on its surface. In this situation, the approach of protonated dye molecules towards the semiconductor surface will face an electrostatic repulsion and, therefore, the rate of photocatalytic bleaching will again decrease.

EFFECT OF ROSE BENGAL CONCENTRATION

Effect of variation of dye concentration was also studied by taking different concentrations of Rose Bengal. The results are tabulated in Table 3 and graphically represented in Figure 3.

TABLE-3
EFFECT OF ROSE BENGAL CONCENTRATION

pH = 5.5

Light Intensity = 40.0 mW cm^{-2} — Zinc oxide = 0.20 g

[Rose Bengal] x 10^5M	K x 10^5 (sec^{-1})
0.50	5.95
0.75	6.78
1.00	8.19
1.25	5.39
1.50	3.82
1.75	3.08

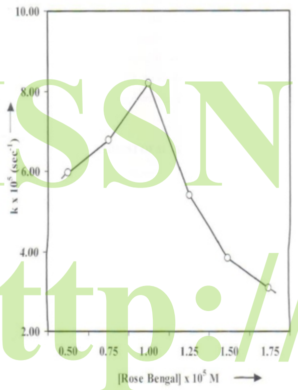

Fig. 3 Effect of Rose Bengal Concentration

It has been observed that the rate of photocatalytic bleaching increases with an increase in the concentration of the dye. It may be due to the fact that as the concentration of Rose Bengal was increased, more dye molecules were 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 an increase in the concentration of the dye further. 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; thus, decreasing the rate of photocatalytic bleaching of Rose Bengal.

EFFECT OF AMOUNT OF SEMICONDUCTOR

The amount of semiconductor is also likely to affect the process of dye bleaching. Different amounts of photocatalysts were used and the results are reported in Table 4 and graphically represented in Figure 4.

T-4:EFFECT OF AMOUNT OF SEMICONDUCTOR

[Rose Bengal] = 1.0×10^{-5}M pH=9.5

Light Intensity = 40.0 mW cm^{-2}

Amount of Semiconductor (g)	$K \times 10^5$ (sec^{-1})
0.04	5.62
0.08	6.15
0.12	6.81
0.16	7.48
0.20	8.19
0.24	8.20
0.28	8.18

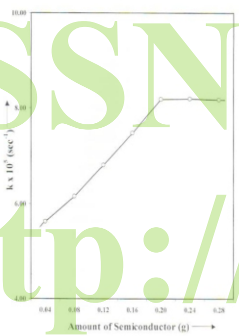

Fig.4 Effect of Amount of Semiconductor

It has been observed that the rate of photobleaching of Rose Bengal increases with an increase in the amount of semiconductor but ultimately it becomes almost constant after a certain amount. This may be due 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 or no effect on the rate of photocatalytic bleaching of Rose Bengal. 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 confirmed on the basis of geometry of the reaction vessel. This was observed by taking reaction vessels of different dimensions. The point of saturation was shifted to 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

To observe the effect of intensity of light on the photocatalytic bleaching of Rose Bengal, light sources of different wattage were used or the distance between the light source and the exposed surface area was varied. The intensity of light at each distance was measured by suryamapi (CEL Model SM 201). The results obtained are reported in Table 5 and graphically represented in Figure 5.

TABLE 5

EFFECT OF LIGHT INTENSITY

[Rose Bengal] = 1.0×10^{-5}M Zinc oxide = 0.20 g

pH = 5.5

Intensity of light (mW cm^{-2})	$K \times 10^5$ (sec^{-1})
20.0	5.92
30.0	6.84
40.0	8.19
50.0	8.94
60.0	9.86
70.0	10.72

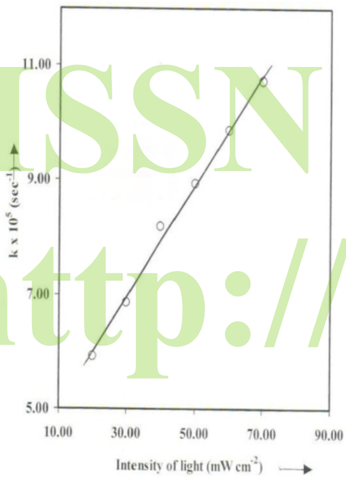

Fig. 5 Effect of Light Intensity

The result given in Table 5 indicates that bleaching action was accelerated as the intensity of light was increased, because any increase in the light intensity will increase the number of photons striking per unit area of semiconductor powder. A linear behavior between light intensity and rate of reaction was observed.

MECHANISM

On the basis of these observation, a tentative mechanism for photocatalytic bleaching of Rose Bengal may be proposed as

MECHANISM

On the basis of these observation, a tentative mechanism for photocatalytic bleaching of Rose Bengal may be proposed as

$$^1RB_o \xrightarrow{h\nu} {}^1RB_1 \quad \text{........(1.0)}$$

$$^1RB_1 \xrightarrow{ISC} {}^3RB_1 \quad \text{........(1.1)}$$

$$^3RB_1 + ZnO \longrightarrow RB^+ + ZnO\ (e^-) \quad \text{........(1.2)}$$

$$ZnO\ (e^-) + O_2 \longrightarrow ZnO + O_2^{\cdot -} \quad \text{........(1.3)}$$

$$H^+ + O_2^{\cdot -} \longrightarrow HO^{\cdot}_2 \quad \text{........(1.4)}$$

$$HO^{\cdot}_2 + RB^+ \longrightarrow RBH + O_2 \quad \text{........(1.5)}$$

When the solution of Rose Bengal (RB) was exposed to light, in presence of semiconductor; initially the dye molecules are excited to first excited singlet state. Then these excited singlet molecules are transferred to triplet state through inter system crossing (ISC). The triplet dye may donate its electron to the semiconductor and the Rose Bengal becomes positively charged. The dissolved oxygen of solution will pull an electron from conduction band of semiconductor; thus, regenerating semiconductor and $O^{\cdot}_2$ is formed. In acidic medium, oxygen ion radical reacts with proton to form HO_2 radical. This radical reduces the positively charged Rose Bengal (RB) molecules in leuco form (RBH) regenerating oxygen molecules.

The participation of HO_2 radical as an active species was confirmed by carrying out the reaction in presence of HO_2 ion scavenger e.g. 2-propanol, where the reaction rate was drastically retarded.

References

1. S. Benjamín, D. Vaya, P. B. Punjabi and S. C. Ameta, 2011, Arabian J. chem, 4, 205-209
2. B. Pare, P. Singh and S. B. Jannalyadda, 2009, Indian J. chem, 48A, 1364-1369
3. Al-Gheethi, A.A.; Azhar, Q.M.; Senthil Kumar, P.; Yusuf, A. A.; Al- Buriahi, A.K.; Radin Mohamed, R.M.S.; Al-Shaibani, M.M., 2022, Chemosphere, 287, 132080.
4. Rai, H.S.; Bhattacharyya, M.S.; Singh, J.; Bansal, T.K.; Vats, P.; Banerjee, U.C, 2005, Crit. Rev. Environ. Sci. Technol, 35,219-238
5. Antoniadou M.; Falara, P.P.; Likodimos, V., 2021, Curr. Opin. Green Sustain. Chem., 29, 100470
6. Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, 4, 2001,Science, 293, 269-271.
7. Gong, Y.; Wu, Y.; Xu, Y.; Li, L.; Li, C.; Liu, X.; Niu, L, 2018, Chem. Eng. J., 350, 257-267.
8. Khore, S.K.; Tellabati, N.V.; Apte, S.K.; Naik, S.D.; Ojha, P.; Kale, B.B.; Sonawane, R. S., 2017, RSC Adv., 7, 33029-33042