RJC
http://www.rasayanjournal.com

RASĀYAN *J. Chem.*
Vol.2, No.2 (2009), 516-520
ISSN: 0974-1496
CODEN: RJCABP

PHOTODEGRADATION OF ROSE BENGAL USING MnO_2 (MANGANESE DIOXIDE)

Naveen Mittal[*], Arti Shah[1], Pinki B. Punjabi[2] and V.K. Sharma[2*]
[1] Department of Chemistry, Govt. J.D.B. Girls College, Kota-324001, India.
[2] Department of Chemistry, College of Science, Sukhadia University, Udaipur-313002, I*ndia.*
*E-mail: anaveen275@gmail.com

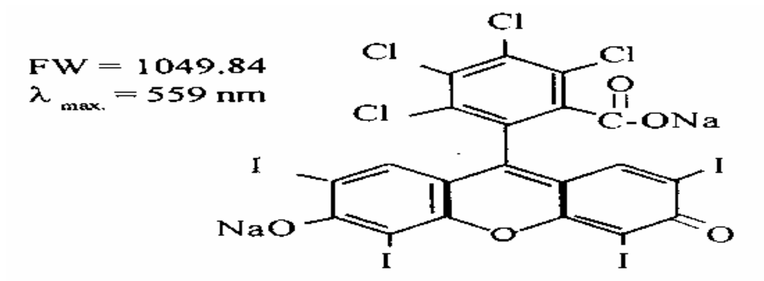
ABSTRACT
Photocatalytic reaction of Rose Bengal (RB) on Manganese dioxide powder has been carried out in presence of light. The photocatalytic bleaching of the dye was observed spectrophotometrically. The effects of variation of different parameters, like concentration of RB, pH, amount of semiconductor and intensity of light on the rate of photocatalytic bleaching was observed. The rate constants (k) for this reaction were determined using the ching was observed. The rate constants (k) for this reaction were determined using the expression, k = 2.303 x slope. A tentative mechanism for the photocatalytic bleaching of Rose Bengal has been proposed.
Keywords: Photocatalytic bleaching, Rose Bengal dye, Semiconductor, Manganese dioxide.

INTRODUCTION

The removal of the non biodegradable organic chemical is a crucial ecological problem. Dyes are an important class of synthetic organic compounds which are commonly used in textile industries and therefore are common industrial pollutants. Due to the stability of modern dyes, conventional biological treatment methods for industrial waste water are ineffective. Heterogeneous photocatalysis by semiconductor particles is a promising technology for the reduction of global environmental pollution. The solar photochemical Detoxification and Disinfection for water with TiO_2 has been studied by Cooper et-al[1-2] Oxidation process with Tio2 semi conductor has been shown by Malato et-al [3-6], and some other by an effective regard. The photocatalytic degradiation of methyl orange by TiO_2 in aqueous phase is studied by .M. N. Rashed and A.A.El-Amin[7] Lanthanum Chromium Oxide were also used as photocatalyst for the photodegradation of Azure-B dye by Ameta et-al [8]. Many other attempts has been done to study the photocatalytic activity of different semi conductors such as SnO_2, ZrO, CdO, ZnO[9-11]. Punjabi et-al [12] studied the photoreduction of Congored by ascorbic acid and EDTA as reductants and cadmium sulphide as a photocatalyst. The Fluoroscein dye Rose Bengal is extensively used in dyeing and printing industries, also used as insecticide has not received the attention of researchers. This was the motivation for the present work.The present work deals with photocatalytic degradation of aqueous solution containing Rose Bengal Dye using MnO_2.

EXPERIMENTAL

Rose Bengal (HM) and manganese dioxide (Merck) were used. The solution of RB was prepared in double distilled water. The photocatalytic bleaching of RB was studied in the presence of semiconducting mangznese dioxide. A 1.0 x 10^{-4} M RB solution in double distilled water was used as a stock solution. The dye solution (3.0 x 10^{-5} M) in presence of manganese dioxide semiconductor (0.50 g) was irradiated with magnetic stirring under light (intensity 60.0 mW cm^{-2}) using a 200 W tungsten lamp (Bajaj). Sunlight was used for higher intensities of light. The intensity of light was measured by Suryamapi (CEL-SM 201). A water filter was used to cut off thermal radiations. The pH was measured by a pH meter(MAC 552 Modal). The desired pH of the solution was adjusted by the addition of previously standardised sulfuric acid and sodium hydroxide solutions. A U.V. spectrophotometer (Systronics Model 106) was used for measuring optical density at different time intervals, whereas $\lambda_{max.}$ for the dye was determined with the help of an U.V. spectrophotometer (Systronics Model 106).



ROSE BENGAL

RESULTS AND DISCUSSION

The photocatalytic bleaching of RB was observed at λ_{max} 559 nm. The results for a typical run are given in Table 1. It was observed that the absorbance of solution decreases with increasing time intervals which indicates that the dye is photocatalytically degraded on irradiation (Control experiments were also performed which indicated that the dye degrades only in the presence of semiconductor and light) . A plot of 2+log O.D. with time was linear and follows pseudo first order kinetics. The rate constant was determined using following expression **K=2.303 x Slope**.

Table-1: Typical Run

[RB] = 3.0 x 10^{-5} M,		pH = 8.0,
Light intensity = 60.0 mW cm^{-2}		Temp. = 308 K
Manganese dioxide = 0.40 g		
Time (min)	*Optical density*	*2+log O.D.*
0.0	0.627	1.798
15.0	0.445	1.652
30.0	0.306	1.486
45.0	0.213	1.330
60.0	0.147	1.159
75.0	0.102	1.019
90.0	0.070	0.865
105.0	0.049	0.680
120.0	0.034	0.541
135.0	0.024	0.389
150.0	0.017	0.236
165.0	0.012	0.074
170.0	0.010	0.000

The optical density of RB solution was found to decrease with the increase in the time of irradiation, thus indicating that RB was consumed on irradiation.

Effect of pH Variation

The effect of pH change on the rate of photocatalytic bleaching of RB was investigated in the pH range 6.0-10.0. The dye solution was bleached and semiconductor Manganese dioxide dissolved in highly acidic media and, therefore, photocatalytic bleaching could not be investigated in lower pH range. The rate constants (k) for this reaction were determined using the expression, k = 2.303 x slope. The results are reported in Table 2.

The rate of the bleaching of RB was found to increase with increase in the pH value of the medium. In alkaline medium, there is a greater probability for the formation of hydroxyl radicals ($OH^{\cdot}$), which can act as an oxidant. Thus the rate of photocatalytic bleaching of the dye increases. But after a certain value of pH (8.0) a further increase in the pH of medium decreases the rate of photocatalytic degradation. It may due to the fact that the dye does not remain in its cationic form due to greater concentration of OH^- and as such the reaction rate decreases.

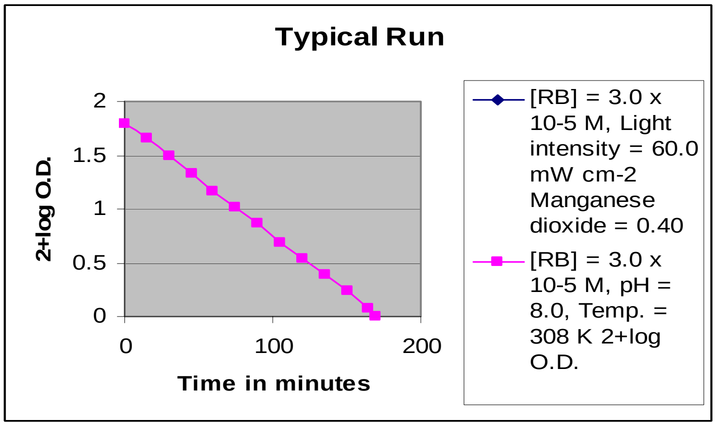


Table-2: Effect of Variation of pH

[RB] = 3.0 x 10^{-5} M	Manganese dioxide = 0.50 g
Light intensity = 60.0 mW cm^{-2}	Temp. = 308 K
pH	*10^{-4} x k (s^{-1})*
6.0	2.122
6.5	2.462
7.0	3.091
7.5	3.544
8.0	3.983
8.5	3.422
9.0	2.971
9.5	2.521
10.0	2.220

Effect of RB Concentration

Effect of variation of dye concentration was also studied and the results are tabulated in Table-3.

Table-3: Effect of Rose Bengal concentration

pH = 8.0	Manganese dioxide = 0.50 g
Light intensity = 60.0 mW cm^{-2}	Temp. = 308 K
[RB] x 10^{-5}M	*10^{-4} x k (s^{-1})*
2.00	2.441
2.25	2.721
2.50	3.026
2.75	3.442
3.00	3.983
3.25	3.672
3.50	3.346
3.75	3.098
4.00	2.872

It is evident from the data that with the increasing [RB], reaction rate increase due to the increase in number of molecules participating in the reaction but after the optimum value of concentration $3.0x10^{-5}$ the rate of reaction decreases. It can be explained on the basis that as the concentration of dye was increased, it may start acting like a filter for the incident light and dose not allow light to reach the semiconductor surface.

Effect of manganese dioxide

The results of effect of amount of semiconductor zinc oxide powder on the rate of bleaching are reported in Table 4.

Table -4: Effect of amount of manganese dioxide

pH = 8.0	[RB] = 3.0 x 10^{-5} M
Light intensity = 60.0 mW cm^{-2}	Temp. = 308 K
Amount of MnO_2 (g)	*10^{-4} x k (s^{-1})*
0.10	2.098
0.20	2.342
0.30	2.877
0.40	3.322
0.50	3.983
0.60	3.980
0.70	3.980
0.80	3.980
0.90	3.980

As evident from the above data, the value of k increases with the increase in the amount of manganese dioxide but the time taken for bleaching of RB solution decreases with the increase in the amount of semiconductor manganese dioxide. This increase in the rate of bleaching may be attributed to increase in the exposed surface area of the semiconductor. But after certain limit (0.60 g), if the amount of manganese dioxide 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 increase in the amount of semiconductor has no additional or negligible effect on the rate of photocatalytic bleaching of RB.

Effect of variation of light intensity

The effect of intensity of light on the photocatalytic bleaching of RB was observed and the results are reported in Table 5.

Table-5: Effect of Light Intensity

pH = 8.0	Manganese dioxide = 0.50 g
[RB] = 3.0 x 10^{-5} M	Temp. = 308 K
Intensity of light (mW cm^{-2})	*10^{-4} x k (s^{-1})*
10.0	1.432
20.0	1.744
30.0	2.122
40.0	2.682
50.0	3.210
60.0	3.983
70.0	3.712

The results indicate that bleaching action is increases with the increase in the intensity of light. Further increase in the intensity of light will increase the temperature of the dye solution, thus thermal reactions may occur in place of photocatalytic reactions.

MECHANISM

On the basis of the observed data, the following tentative mechanism has been proposed for photocatalytic bleaching of RB. 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 in the valence band. The hole in the valence band will generate hydroxyl radical ($OH^{.}$) from hydroxyl ions, which will oxidize the dye to its leuco form.

$$SC \rightarrow SC^* \quad (1)$$

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

$$h^+ + OH^- \rightarrow OH^{.} \quad (3)$$

$$RB + OH^{\cdot} \rightarrow \text{leuco RB} \rightarrow \text{Products.} \quad (4)$$

Dyes absorb light radiation of suitable wave length and goes to excited singlet state. It then undergoes inter system crossing (ISC) to give the triplet state of dyes. The semiconducting manganese dioxide also utilises the radiant energy to excite its electron from valence band to conduction band, thus leaving behind a hole.
The hole abstracts an electron from OH^- ion generating OH * radical. Now the excited dyes are oxidised by OH * free radicals to give the product. The participation of OH * radical was confirmed by use of scavenger iso-propanolol which stops the bleaching reaction almost completely.

CONCLUSION

Manganese dioxide is an effective semiconductor for photodegradation of Rose Bengal dye.

ACKNOWLEDGEMENT

We are thankful to Prof. Suresh C. Ameta for his critical and valuable suggestions from time to time.

REFERENCES

1. A.T. Cooper, D.Y. Goswami and S.S. Block, *J. Adv. Oxid. Technol.*, **3**, 151 (1998).
2. A.T. Cooper, 'Solar photochemical Technology for portable water treatment', University of Florida, Gainesville, Fl (1998).
3. I.A. Mlato, I.A. Balcioglu and O.W. Bahnemann, *Water Res.*, 36, 1143 (2002).
4. A. Marinas, G. Chantal, M.M. Jes, P.A. Amadeo, A. Ana and J. Marie, *Appl. Catal. B. Environ.*, **34**, 241 (2001).
5. V. Augugliaro, C. Baiocchi, A.B. Prevot, E. Garca-Lopez, V. Laddo, S. Malato, G. Marc, L. Palmisano, M. Pazzi and E. Parmauro, *Chemosphere*, **49**, 1223 (2002).
6. I. Konstantinou and T.A. Albanis, *Appl. Catal. B. Environ.*, **49**, 1 (2004).
7. M.N. Rashed and A.A. El-Amin, *Int. J. Phys. Sci.*, **2**, 73 (2002).
8. J. Jose et al., *Bulletin of the catalysis Society of India*, **6**, 110 (2007).
9. K. Vinod Gopal and P.V. Kamat, *Environ. Sci. Technol.*, **29**, 841 (1995).
10. C. Lizama, J. Freer, J. Baeza and H.D. Mansilla, *Catal. Today*, **76**, 235 (2002).
11. A. Akyel, H.C. Yatmaz and M. Bayramglu, *Appl. Catal. B: Environ.*, **54**, 19 (2001).
12. P.B. Punjabi, R. Ameta, R. Vyas and S. Kothari, *Ind. J. Chem.*, **44 A**, 2266 (2005).

(Received: 13 May 2009 Accepted: 25 May 2009 RJC-392)