Int. J. Chem. Sci.: 14(3), 2016, 1768-1776
ISSN 0972-768X
www.sadgurupublications.com

PHOTOCATALYTIC DEGRADATION OF ERYTHROSINE BY USING MANGANESE DOPED TiO_2 SUPPORTED ON ZEOLITE

RINKU BAIRAGI and RAKSHIT AMETA*

Department of Chemistry, PAHER University, UDAIPUR – 313003 (Raj.) INDIA

ABSTRACT

In present work, manganese doped TiO_2 supported on zeolite has been used as a photocatalyst for the degradation of erythrosine dye. It was prepared by sol gel method. Rate of photocatalytic degradation of erythrosine was measured spectrophotometerically. Effect of various rate affecting parameters has been studied to obtain the optimum conditions for degradation of dye. It has been observed that rate of photocatalytic degradation of erythrosine was higher in case of Mn doped TiO_2 as compared to pure TiO_2.

Key words: Photocatalytic degradation, Erythrosine, Mn doped TiO_2, Zeolite.

INTRODUCTION

Today, the world is facing many environment problems; out of which, water pollution is a major one. Dyes are toxic and sometimes even carcinogenic in nature and cause water pollution. Although dyes are harmful, in spite of that we cannot avoid its use. Dyes can be removed from industrial effluents by different methods like adsorption[1], air stripping[2], biological methods[3], etc., but these do not provide complete solution to the problem. Photocatalysis is an important part of Advanced Oxidation Processes (AOPs) is a modern technique, which is eco-friendly and a green chemical method. In this technique, a semiconductor is used as a photocatalyst in presence of light.

TiO_2 is the most commonly used photocatalyst, because it is non-toxic, chemically stable, low cost and very efficient[4-6]. TiO_2 has been used for degradation of many dyes like rose Bengal[7], crystal violet[8], ect. TiO_2 has a band gap of about 3.2 eV and it exists in three crystal line forms; antase, rutile and brookite. Anatase form is mostly used under UV light. It has two problems - (i) It floats in solution and forms suspension; hence, creats problem in

*Author for correspondence; E-mail: rakshit_ameta@yahoo.in

measuring absorbance during monitoring and (ii) It is white colour in nature and does not utilize major incident light in visible region. Researchers have doped TiO_2 with different metals and non-metals such as nitrogen[9], nitrogen-sulphur[10], silver[11], iron[12], lanthanum[13], zinc[14], chromium[15], copper[16], carbon[17], vanadium[18] and tungsten[19], etc. so as to decrease its band gap and as a consequence, titania may utilize visible light too. In the present investigation, an effort has been made to solve these problems of titania by doping it with manganese and supported on zeolite. Further, it has been successfully used for degradation of erythrosine.

EXPERIMENTAL

Materials and method

Erythrosine, also known as Red No. 3, is an organoiodine compound, specifically a derivative of fluorone. It is cherry-pink synthetic dye and primarily used for food coloring. It is the disodium salt of 2,4,5,7-tetraiodofluorescein. Its maximum absorbance is at 530 nm in an aqueous solution. Its chemical structure is shown in Fig. 1.

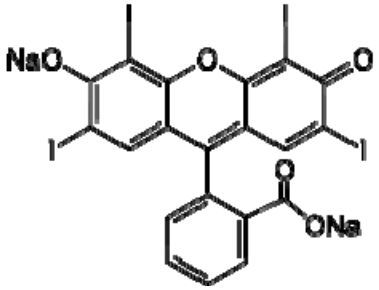

Fig. 1: Chemical structure of erythrosine

The solution of the dye was prepared in doubly distilled water. A 200 W tungusten lamp was used for irradiation in the visible range. UV-visible spectrophotometer (Systronic 106) was used for measuring absorbance of the dye at regular time intervals. The pH of the dye solution was adjusted with previously standardized H_2SO_4 and NaOH solutions and monitored by pH meter (Systronic 335). Erythrosine and $MnSO_4$ (Himedia) and titanium tetraisopropoxide (spectrochem) were purchased and used as received.

Preparation of Mn doped TiO_2/zeolite

Sol-gel method was used for the preparation of Mn doped titania. Ethanol and nitric oxide were mixed first and then titanium tetraisopropoxide solution was added dropwise. In this solution, manganese sulphate was added as a dopant. The sol was stirred for 10-12 hours

at 4°C. After stirring, this solution was kept in ice bath for three days. Then solution was evaporated at 35°C and as a result a gel was formed. Gel was dried in an oven for 5-6 hours and calcined at 450°C for 20-30 min. It was mixed with zeolite slurry in 1:2 ratio and thus, Mn doped TiO_2/zeolite was prepared.

The photocatalytic performance of the as-prepared photocatalyst was studied by measuring degradation rate of erythrosine dye. A standardized solution of 1.0×10^{-3} M of erythrosine was prepared in doubly distilled water. This stock solution was further diluted as and when required. pH of the solution was measured by pH meter. The reaction mixture was exposed to 200 W tungsten lamp. The intensity of light was varied by changing the distance between the light source and reaction mixture. Absorbance of dye solution was measured at 530 nm wavelength for regular time intervals.

Effect of various rate affecting parameters like pH, concentration of erythrosine dye, amount of Mn doped TiO_2/zeolite and light intensity was observed. Absorbance of solution was found to decrease with time of irradiation, which indicated that molecules of erythrosine dye was degraded. A plot between time and 1 + log A was found linear, which shows that this reaction followed pseudo-first order kinetics. The rate constant was calculated using this equation; $k = 2.303 \times$ slope.

RESULTS AND DISCUSSION

In a typical run, rates were determined at optimum conditions in presence of pure TiO_2 and Mn doped TiO_2. The higher rate constants were obtained for Mn doped TiO_2 as compared to pure TiO_2.

Table 1: Typical run

pH = 6.5, [Erythrosine] = 9.00×10^{-6} M, Mn doped TiO_2/zeolite = 0.1 g,
Light intensity = 50.0 $mWcm^{-2}$

Time	Mn doped TiO_2		Pure TiO_2	
	Absorbance (A)	**1 + log A**	**Absorbance (A)**	**1 + log A**
0	0.569	0.7551	0.635	0.8028
15	0.483	0.6839	0.610	0.7853
30	0.480	0.6812	0.586	0.7679

Cont…

Time	Mn doped TiO_2		Pure TiO_2	
	Absorbance (A)	**1 + log A**	**Absorbance (A)**	**1 + log A**
45	0.422	0.6253	0.560	0.7482
60	0.413	0.6160	0.551	0.7412
80	0.380	0.5798	0.541	0.7332
100	0.333	0.5224	0.532	0.7259
120	0.287	0.4579	0.527	0.7218
			Rate constant of pure TiO_2; $k = 4.19 \times 10^{-5}$ sec^{-1}	
			Rate constant of Mn doped TiO_2; $k = 1.15 \times 10^{-4}$ sec^{-1}	

Effect of pH

The effect of pH of photocatalytic degradation of erythrosine was studied by changing the pH of the dye solution from 5.0 to 10.0. The results are reported in Table 2.

Table 2: Effect of pH

[Erythrosine] = 9.00×10^{-6} M, Mn doped TiO_2/zeolite = 0.1 g,
Light intensity = 50.0 $mWcm^{-2}$

pH	Rate constant (k) × 10^4 (sec^{-1})
5.0	0.60
5.5	0.67
6.0	0.83
6.5	**1.15**
7.0	0.63
7.5	0.53
8.0	0.51
8.5	0.42
9.0	0.39
9.5	0.36
10.0	0.31

When the pH of the dye solution was increased from 5.0 to 6.5, an increase in the rate of photocatalytic degradation of erythrosine was observed. It may be due to generation of oxygen anion radicals, $O_2^{-\bullet}$, which were produced from the reaction between dissolved O_2 and electron of the semiconductor. This is less stable in acidic medium and will form $HO_2^{\bullet}$ radical, which acts as an oxidizing agent. A decrease in the rate of photocatalytic degradation of the dye was observed above pH 6.5. It may be due to the fact that after this pH, erythrosine was present in its anionic form, which will experience a force of repulsion with negatively charged surface of the semiconductor due to adsorption of more ^{-}OH ions on the surface of the semiconductor.

Effect of erythrosine concentration

The concentration of erythrosine dye was varied from 5.00×10^{-6} M to 1.20×10^{-5} M to know its effect on photocatalytic degradation rate. The observations are given in Table 3.

Table 3: Effect of erythrosine concentration

pH = 6.5, Mn doped TiO_2/zeolite = 0.1 g, Light intensity = 50.0 $mWcm^{-2}$

[Erythrosine] × 10^5 M	**Rate constant (k) × 10^4 (sec^{-1})**
0.50	0.83
0.60	0.87
0.70	0.93
0.80	1.11
0.90	**1.15**
1.00	0.63
1.10	0.59
1.20	0.59

This observations shows that as the concentration of erythrosine dye was increased from 5.00×10^{-6} M to 9.00×10^{-6} M, degradation rate was also increased. It may be due to the reason that on increasing the dye concentration, more dye molecules were available for excitation and energy transfer so that reaction rate was enhanced. After 9.00×10^{-6} M concentration of the dye, the degradation rate of the dye was decreased because beyond this stage, dye acts as an internal filter for incident light and it will not permit desired light intensity to approach the semiconductor surface.

Effect of amount of Mn doped TiO_2/zeolite

Effect of amount of modified semiconductor on photocatalytic degradation of erythrosine was observed by taking different amounts of the semiconductor. The observed data are reported in Table 4.

Table 4: Effect of amount of Mn doped TiO_2/zeolite

pH = 6.5, [Erythrosine] = 9.00×10^{-6} M, Light intensity = 50.0 $mWcm^{-2}$

Mn doped TiO_2/zeolite (g)	Rate constant (k) × 10^4 (sec^{-1})
0.02	0.85
0.04	0.97
0.06	0.98
0.08	1.12
0.10	**1.15**
0.12	0.93
0.14	0.91
0.16	0.87

It was observed that as the amount of Mn doped TiO_2/zeolite was increased from 0.02 to 0.10 g, degradation rate of the dye was also increased. After attaining the optimum rate at 0.10 g, when the amount of the modified semiconductor was further increased, the rate become almost constant. It may be explained on the basis that as the amount of Mn doped TiO_2/zeolite increases, exposed surface area of semiconductor was increased. But after its limiting value (0.10 g), only thickness of the semiconductor layer was increased and not its exposed surface area.

Effect of light intensity

The light intensity also affect the degradation rate of the dye and therefore, its effect on photocatalytic degradation of erythrosine was studied by varying light intensity. The results are given in Table 5.

These data revealed that an increase in light intensity increases the number of photons striking per unit area of semiconductor surface per unit time and as a result, rate was increased. But after 50.0 $mWcm^{-2}$, there was a slight decrease in degradation rate, which may be due to some side reactions or thermal effects.

Table 5: Effect of light intensity

pH = 6.5, [Erythrosine] = 9.00×10^{-6} M, Mn doped TiO_2/Zeolite = 0.10 g

Light intensity ($mWcm^{-2}$)	Rate constant (k) $\times 10^4$ (sec^{-1})
20.0	0.50
30.0	0.67
40.0	0.97
50.0	**1.15**
60.0	1.03

Mechanism

Erythrosine (E) absorbs light of suitable frequency and its molecules are excited from ground state to first excited singlet state. Then the dye molecules are converted to triplet state via intersystem crossing system (ISC). The Mn doped TiO_2 semiconductor also absorbs light and as a result an electron-hole pair is generated, where electron jumps from valence band to conduction band leaving behind a hole in valence band. This electron will be abstracted by oxygen molecule (dissolved oxygen) generating superoxide anion radical ($O_2^{-\bullet}$). It will further react with H^+ to form $HO_2^{\bullet}$, which will oxidize the dye molecule to its leuco form. Ultimately, dye molecules are degraded to harmless products.

$$^1E_0 \xrightarrow{h\nu} {}^1E_1 \quad \ldots(1)$$

$$^1E_1 \xrightarrow{ISC} {}^3E_1 \quad \ldots(2)$$

$$SC \xrightarrow{h\nu} e^- (CB) + h^+ (VB) \quad \ldots(3)$$

$$e^- + O_2 \longrightarrow O_2^{-\bullet} \quad \ldots(4)$$

$$h^+ + O_2^{-\bullet} \longrightarrow HO_2^{\bullet} \quad \ldots(5)$$

$$HO_2^{\bullet} + {}^3E_1 \longrightarrow \text{Leuco E} \quad \ldots(6)$$

$$\text{Leuco E} \longrightarrow \text{Products} \quad \ldots(7)$$

REFERENCES

1. M. F. R Pereira, S. F. Soares, J. J. M Orfao and J. L. Figueiredo, Adsorption of Dyes on Activated Carbons: Influence of Surface Chemical Groups, Carbon, **41**, 811-821 (2003).
2. X. Shibin, X. Shuichun and Z. Changqing, Removal of Organic Pollutants from 2, 2′, 5,5′-Tetrachlorobenzidine (TCB) Industrial Wastewater by Micro-Electrochemical Oxidation and Air-Stripping, J. Hazard. Mater., **144**, 159-163 (2007).
3. N. P. Tantak and S. Chaudhari, Degradation of Azo Dyes by Sequential Fenton's Oxidation and Aerobic Biological Treatment, J. Hazard. Mater., **136,** 698-705 (2006).
4. A. Ameta, I. Bhati, R. Ameta and S. C. Ameta, Photocatalytic Degradation of Methylene Blue by Nanosized Vanadium Doped TiO_2 Loaded on Zeolite, Int. J. Chem. Sci., **13**, 1485-1494 (2015).
5. S. Lakshmi, R. Renganathan and S. Fujita, Study on TiO_2-Mediated Photocatalytic Degradation of Methylene Blue, J. Photochem. Photobiol. A, **88**, 163-167 (1995).
6. R. Jain and S. Sikarwar, Semiconductor-Mediated Photocatalyzed Degradation of Erythrosine Dye from Wastewater using TiO_2 Catalyst, Environ. Technol., **31**, 1403-1410 (2010).
7. X. Z. Li, H. L. Liu, P. T. Yue and Y. P. Sun, Photoelectrocatalytic Oxidation of Rose Bengal in Aqueous Solution using a Ti/TiO_2 Mesh Electrode, Environ. Sci. Technol., **34**, 4401-4406 (2000)
8. S. Samira, A. Raja, P. Mohan and J. M. Modak, Photocatalytic Degradation of Crystal Violet (C.I. Basic Violet 3) on Nano TiO_2 Containing Anatase and Rutile Phases (3:1), J. Thermodynam. Cat., **3**, doi:10.4172/2157-7544.1000117 (2012).
9. T. Tachikawa, Y. Takai, S. Tojo, M. Fujitsuka, H. Irie, K. Hashimoto and T. Majima, Visible Light-Induced Degradation of Ethylene Glycol on Nitrogen-Doped TiO_2 Powders, J. Phys. Chem. B, **110**, 13158-13165 (2006).
10. A. S. Sisodiya, P. Tak, R. Ameta and K. L. Ameta, Photocatalytic Degradation of Erythrosine using Nanoparticles of N, S-Codoped Titanium Dioxide, Sci. Revs. Chem. Commun., **5**, 43-50 (2015).
11. C. Sahoo, A. K. Gupta and A. Pal, Photocatalytic Degradation of Methyl Red Dye in Aqueous Solutions under UV Irradiation using Ag^+ Doped TiO_2, Desalination, **18**, 91-100 (2005)

12. X. H. Wang, J. G. Li, H. Kamiyama, Y. Moriyoshi and T. Ishigaki, Wavelength-Sensitive Photocatalytic Degradation of Methyl Orange in Aqueous Suspension Over Iron(III)-Doped TiO_2 Nanopowders under UV and Visible Light Irradiation, J. Phys. Chem. B, **110**, 6804-6809 (2006).

13. K. Dai, T. Peng, H. Chen, J. Liu and L. Zan, Photocatalytic Degradation of Commercial Phoxim over La-Doped TiO_2 Nanoparticles in Aqueous Suspension, Environ. Sci. Technol. **43**, 1540-1545 (2009).

14. H. M. Zhao, Y. Chen, X. Quan and X. L. Ruan, Preparation of Zn-Doped TiO_2 Nanotubes Electrode and its Application in Pentachlorophenol Photoelectrocatalytic Degradation, Chin. Sci. Bull., **52**, 1456-1461 (2007).

15. K. Wilke and H. D. Breuer, The Influence of Transition Metal Doping on the Physical and Photocatalytic Properties of Titania, J. Photochem. Photobiol. A: Chem., **121**, 49-53 (1999).

16. R. S. Wong, J. Feng, X. Hu and P. L. Yue, Discoloration and Mineralization of Nonbiodegradable Azo Dye Orange Second by Copper-Doped TiO_2 Nanocatalysts, J. Environ. Sci. Health A, **39**, 2583-2595 (2004).

17. N. Kunwar, R. Ameta and S. Sharma, Preparation of C-TiO_2 Nanophotocatalyst for the Degradation of Livofloxacin from Waste Water, Sci. Revs. Chem. Commun., **4**, 124-129 (2014).

18. B. Tian, C. Li, F. Gu, H. Jiang, Y. Hu and J. Zhang, Flame Sprayed V-Doped TiO_2 Nanoparticles with Enhanced Photocatalytic Activity under Visible Light Irradiation, J. Chem. Eng., **151**, 220-227 (2009).

19. Saepurahman, M. A. Abdullah and F. K. Chong, Preparation and Characterization of Tungsten Loaded Titanium Dioxide Photocatalyst for Enhanced Dye Degradation, J. Hazard. Mater., **176**, 451-458 (2010).

Accepted : 10.06.2016