Scientific Reviews
&
Chemical Communications

Sci. Revs. Chem. Commun.: 5(1), 2015, 43-50
ISSN 2277-2669

PHOTOCATALYTIC DEGRADATION OF ERYTHROSINE USING NANOPARTICLES OF N, S-CODOPED TITANIUM DIOXIDE

AJAY SINGH SISODIYA*, PARAS TAK, RAKSHIT AMETA and K. L. AMETA[a]

Department of Chemistry, PAHER University, UDAIPUR – 313003 (Raj.) INDIA
[a]Department of Chemistry, Mody University of Science and Technology, LAKSHMANGARH – 332311 (Raj.) INDIA

(*Received : 16.02.2015; Accepted : 24.02.2015*)

ABSTRACT

The nanophotocatalytic process using semiconducting oxides with a nanostrucrure is one of the technologies used for the destructive oxidation of organic compound such as dyes. In this paper, photocatalytic degradation of erythrosine using N, S-codoped TiO_2 as semiconductor prepared by sol-gel method is reported. The rate of photocatalytic degradation of dye was monitored spectrophotometrically. The effect of variation of different parameters like pH, concentration of erythrosine, amount of photocatalyst, dopant percentage and light intensity on the rate of photocatalytic degradation of dye was also observed. A tentative mechanism for photocatalytic degradation of the dye has also been proposed.

Key words: Photocatalytic degradation, Erythrosine, N, S-codoped titanium dioxide.

INTRODUCTION

The uncontrolled release of colored waste water contaminated with dyes from textile paper, rubber and plastic industries have led to serious environmental. Over the past few years, the degradation of organic pollutants in wastewater has been a serious concern throughout the world. Several methods, such as Fenton technology[1], catalytic wet oxidation[2], hydrogen peroxide[3] and photocatalysis[4] have been developed. Recently, the heterogeneous photocatalytic process has been a rapidly growing research area for the purification and complete mineralization of organic pollutants in industrial waste water and air.[5] The unique properties of titanium dioxide (TiO_2) such as high photocatalytic activity, high chemical stability and low toxicity have made it a suitable photocatalyst in recent decades.[6] However, it is unavoidable to face two issues to make it the favorite catalyst for this process. One of which is to improve the low photo-quantum efficiency of TiO_2 that arises from the fast recombination of photo-generated electrons and holes. The other, is to extend its photocatalytic activity into the visible light region in order to use solar energy as the light source.[7] In recent years some of the studies reported the possibility of producing these characteristics by chemical additives such as noble metals and ion doping. To reach these ends the use of noble metals such as gold[8], silver[9], transition metals such as Fe[10], Cr[11], Cu[12], Mn[13], Zn[14], V[15], W[16], non-metals such as nitrogen[17], carbon[18] has been reported. In the present work, N, S-doped titania has been prepared and used for degradation of erythrosine and also its activity has also been compared with pure titania.

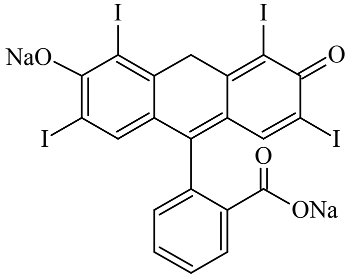
---

*Author for correspondence; E-mail: ajaymsc1@gmail.com

EXPERIMENTAL

Materials and methods

The dye erythrosine (ES) was obtained from sd-fine chem and was used as such without purification (λ_{max} = 530 nm). The dye solutions were prepared using doubly distilled water as and when required. A 200 W tungsten lamp (Phillips) was used for irradiating the solution in the visible range. UV-Visible spectrophotometer (Systronics Model 106) was used for measuring optical density at different time intervals. The pH of the solution was adjusted with previously standardized H_2SO_4 and NaOH solutions. Other chemicals materials such as $Ti(OiPr)_4$ and thiourea were purchased from Spectrochem and Himedia, respectively.



Structure of erythrosine

Preparation of pure TiO_2

A mixture of 10 mL of $Ti(OiPr)_4$, 50 mL of isopropyl alcohol and 100 mL of double distilled water was vigorous stirred and the solution was stand overnight at room temperature. Then the solution was dried in oven at 80ºC for 2 hrs, and calcined at 400ºC for 3 hrs in air. Pure TiO_2 was obtained in the form of white powder.

Preparation of N, S-codoped TiO_2

A mixture of 10 mL of $Ti(OiPr)_4$, 50 mL of isopropyl alcohol and 0.5, 1, 1.5, 2.0 and 2.5 g of thiourea in 100 mL of doubly distilled water was taken in five different beakers. The solution was vigorously stirred and was stand overnight at room temperature. Then each solution was dried in oven at 80ºC for 2 hrs and calcined at 400ºC for 3 hours to get N, S- codoped TiO_2. The pale yellow N, S codoped titania powder was thus prepared with different amount of dopant source i.e. 0.5, 1.0, 1.5, 2.0 and 2.5%, respectively.

RESULTS AND DISCUSSION

A stock solution of erythrosine (1.0×10^{-3} M) was prepared in doubly distilled water. This stock solution was further diluted as and when required. The absorbance of dye solutions was determined with the help of UV-visible spectrophotometer (Systronics model 106) at λ_{max} = 530 nm. The dye solution of 1.40×10^{-5} M concentration was prepared in doubly distilled water and 0.14 g of N, S-doped TiO_2 was added to it. The pH of reaction mixture was kept 6.5 and this solution was exposed to a 200 W tungsten lamp. A decrease in absorbance of erythrosine dye solution was observed with increasing time of exposure.

The absorbance of erythrosine solution decreases with an increase in the time of irradiation indicating that the dye is degraded on irradiation. The plot of 1 + log O.D. against time was linear, following pseudo-first order kinetics. The rate constant was measured with the expression; $k = 2.303 \times \text{slope}$.

The typical run for the photocatalytic degradation of erythrosine in presence of pure TiO_2 and N, S-doped TiO_2 has been presented in Table 1 and graphically represented in Fig. 1.

Table 1: A typical run

pH = 6.5 [Erythrosine] = 1.40×10^{-5} M

N, S–codoped TiO_2 = 0.14 g (1.0%) Light Intensity = 50.0 $mWcm^{-2}$

Time (min)	**Pure TiO_2**		**N, S-doped TiO_2**	
	Optical density (O. D.)	**1 + log O. D.**	**Optical density (O. D.)**	**1 + log O. D.**
0	0.947	0.9763	0.947	0.9763
20	0.934	0.9703	0.901	0.9547
40	0.907	0.9576	0.857	0.9329
60	0.880	0.9444	0.803	0.9047
80	0.850	0.9294	0.752	0.8762
100	0.823	0.9153	0.708	0.8500
120	0.795	0.9003	0.669	0.8254
140	0.771	0.8870	0.631	0.8000
160	0.750	0.8750	0.596	0.7752
180	0.728	0.8621	0.560	0.7481
200	0.708	0.8500	0.525	0.7201
220	0.684	0.8350	0.496	0.6954
240	0.669	0.8254	0.468	0.6702
260	0.646	0.8102	0.442	0.6454
280	0.629	0.7986	0.415	0.6180
300	0.610	0.7853	0.391	0.5921

Rate constant for N, S-doped TiO_2; k = 4.91×10^{-5} sec^{-1}

Rate constant for pure TiO_2; k = 2.44×10^{-5} sec^{-1}

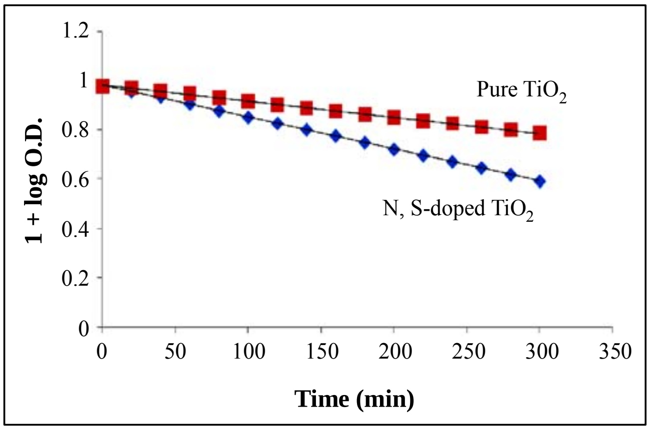


Fig. 1: A typical run

Different rate affecting parameters influence the photocatalytic degradation of the dye and therefore, these were varied to find out the optimum conditions for the degradation of the dye.

Effect of pH

The pH of the solution is likely to affect the degradation rate of erythrosine. The effect of pH on the rate of degradation of the dye was investigated in the pH range 5.0 – 9.5 and the results are reported in Table 2.

Table 2: Effect of pH

[Erythrosine] = 1.40×10^{-5} M N, S-codoped TiO_2 = 0.14 g

Light Intensity = 50.0 $mWcm^{-2}$ % of dopant = 1.0

pH	$k \times 10^5$ (sec^{-1})
5.0	4.36
5.5	4.59
6.0	4.73
6.5	**4.91**
7.0	4.77
7.5	4.52
8.0	4.32
8.5	4.13
9.0	3.87
9.5	3.71

It has been observed that the rate of photocatalytic degradation of erythrosine was increased with increase in pH upto 6.5. A further increase in pH above 6.5 results in a decrease in the rate of reaction. An increase in the rate of photocatalytic degradation of erythrosine with increase in pH may be due to generation of oxygen anion radical, $O_2^{-\bullet}$ which are produced from the reaction between O_2 and electron of the semiconductor. This is less stable in acidic medium and will form $HO_2^{\bullet}$ radical, which act as oxidizing agent. Above pH 6.5, a decrease in the rate of photocatalytic degradation of the dye may be due to the fact that erythrosine is 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 photocatalyst.

Effect of dye concentration

The effect of dye concentration was also observed by taking different concentrations of the erythrosine. The results are tabulated in Table 3.

It is evident from the data that the rate of photocatalytic degradation of dye increases with an increase in concentration of the dye. It may be explained on the basis that as the concentration of the dye was increased, more dye molecules were available for excitation and consecutive energy transfer and hence, an increase in the rate of photocatalytic degradation of the dye was observed. The rate of photocatalytic degradation was found to decrease with an increase in the concentration of dye above 1.40×10^{-5} M. It may be due to the fact that the dye itself may start acting as an internal filter for the incident light and it will not permit the desired light intensity to reach the semiconductor particles and as a result, the degradation rate decreases.

Table 3: Effect of dye concentration

pH = 6.5 N, S-codoped TiO_2 = 0.14 g

Light Intensity = 50.0 $mWcm^{-2}$ % of dopant = 1.0

[Erythrosine] × 10^5 M	k × 10^5 (sec^{-1})
1.00	4.15
1.10	4.45
1.20	4.63
1.30	4.69
1.40	**4.91**
1.50	4.76
1.60	4.51
1.70	4.24
1.80	4.03
1.90	3.90
2.00	3.78

Effect of amount of semiconductor

The effect of amount of N, S-codoped TiO_2 was observed by taking different amount of semiconductor. The results are reported in Table 4.

Table 4: Effect of amount of semiconductor

pH = 6.5 [Erythrosine] = 1.40 × 10^{-5} M

Light intensity = 50.0 $mWcm^{-2}$ % of dopant = 1.0

Amount of N,S doped semiconductor (g)	k × 10^5 (sec^{-1})
0.02	3.47
0.04	3.75
0.06	3.98
0.08	4.14
0.10	4.38
0.12	4.57
0.14	**4.91**
0.16	4.85
0.18	4.87

It was observed that the rate of reaction was increased with increase in the amount of semiconductor N, S-codoped TiO_2. The rate of degradation was optimum at 0.14 g of the photocatalyst. Beyond 0.14 g, the rates of reaction become virtually constant. This may be due to fact that as the amount of semiconductor was increased, the exposed surface area of the semiconductor also increases. However, after this limiting value (0.14 g), an increase in the amount of semiconductor only increases the thickness of the semiconductor layer and not the exposed surface area. This was also confirmed by using reaction vessels of different dimensions. It was observed that the point of saturation is shifted to a higher value for vessels of larger capacities while it is shifted to lower value for vessels of smaller capacities.

Effect of % variation of dopant

The effect of % variation of dopant was observed by taking different % of dopant i.e. thiourea. The results are reported in Table 5.

Table 5: Effect of % variation of dopant

pH = 6.5
N, S-codoped TiO_2 = 0.14 g
Light Intensity = 50.0 $mWcm^{-2}$
[Erythrosine] = 1.40×10^{-5} M

% of Dopant	$k \times 10^5$ (sec^{-1})
0.5	4.67
1.0	**4.91**
1.5	4.68
2.0	4.50
2.5	4.06

It was observed that as the % of dopant source was increased, the rate constant was also increased. At 1.0% of dopant, the rate of reaction was optimum and after that, rate of reaction was decreased. It may be due to the reason that freely active site decreases after this dopant concentration and therefore, the rate of reaction started decreasing.

Effect of light intensity

To investigate the effect of light intensity on the photocatalytic degradation of erythrosine, the distance between the light source and the exposed surface area was varied. The results are summarized in Table 6.

Table 6: Effect of light intensity

pH = 6.5
[Erythrosine] = 1.40×10^{-5} M
N, S-codoped TiO_2 = 0.14 g
% of dopant = 1.0

Intensity of light ($mWcm^{-2}$)	$k \times 10^5$ (sec^{-1})
20.0	4.24
30.0	4.50
40.0	4.67
50.0	**4.91**
60.0	4.79
70.0	4.60

The results indicate that photocatalytic degradation of a erythrosine was accelerated as the intensity of light was increased from 20.0 to 50.0 mWcm^{-2}, because an increase in the light intensity will increase the number of photons striking per unit area of semiconductor surface per unit time. On further increasing the intensity of light above 50.0 mWcm^{-2}, there was a decrease in the rate of reaction. This may be due to some side reactions or thermal effect.

Mechanism

On the basis of these observations, a tentative mechanism for photocatalytic degradation of erythrosine (ES) may be proposed as –

$$^{1}ES_0 \xrightarrow{h\nu} {}^{1}ES_1 \quad ....(1)$$

$$^{1}ES_1 \xrightarrow{ISC} {}^{3}ES_1 \quad ....(2)$$

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

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

$$\mathrm{H^+ + O_2^{-\bullet} \longrightarrow HO_2^{\bullet}} \quad ....(5)$$

$$HO_2^{\bullet} + {}^{3}ES_1 \longrightarrow Leuco\ \mathrm{ES} \quad ....(6)$$

$$Leuco\ \mathrm{ES} \longrightarrow \mathrm{Products} \quad ....(7)$$

Erythrosine (ES) absorbs radiations of suitable wavelength and gives rise to its excited singlet state. Then it undergoes intersystem crossing (ISC) to give the triplet state of the dye. On the other hand, the N, S-codoped TiO_2 (SC) also utilizes the radiant energy to excite its electron from valence band to the conduction band. This electron will be abstracted by oxygen molecule (dissolved oxygen) generating superoxide anion radical ($O_2^{-\bullet}$). It will further react with H^+ and will produce $HO_2^{\bullet}$, which will oxidize the dye molecules to its leuco form, which may ultimately degrade to products. It was also confirmed that this degradation proceeds through reduction and not oxidation. $^{\bullet}OH$ radical does not participate as an active oxidizing species as confirmed by using hydroxyl radical scavenger (2-propanol), where the rate of degradation was not affected appreciably.

CONCLUSION

Doping of titania with non-metal reduces its band gap and accordingly its activity is increased. In the present work, it was confirmed by using pure TiO_2 and N, S-TiO_2 semiconductor for photocatalytc degradation of erythrosine dye. The results showed higher rate constant for N, S-doped TiO_2 than pure TiO_2, which revealed that N, S-TiO_2 extended the absorption of TiO_2 into the visible light range.

REFERENCES

1. J. H. Ma, W. J. Song, C. C. Chen, W. H. Ma, J. C. Zhao and Y. L. Tang, Fenton Degradation of Organic Compounds Promoted by Dyes under Visible Irradiation, J. Environ. Sci. Technol., **39**, 5810-5818 (2005).
2. D. B. Akolekar, S. K. Bhargava, I. Shirgoankar and J. Prasad, Catalytic Wet Oxidation: An Environmental Solution for Organic Pollutant Removal from Paper and Pulp Industrial Waste Liquor, J. Appl. Catal. A: general, **236**, 255-262 (2002).

3. Y. Z. Zhan, H. L. Li and Y. L. Chen, Copper Hydroxyphosphate as Catalyst for the Wet Hydrogen Peroxide Oxidation of Azo Dyes, J. Hazard. Mater., **180**, 481-485 (2010).

4. A. L. Linsebigler, G. Q. Lu and J. T. Yates, Photocatalysis on TiO_2 Surfaces: Principles, Mechanisms and Selected Results, J. Chem. Rev., **95**, 735-798 (1995).

5. B. Pal, M. Sharom and N. Nogami, Preparation and Characterization of TiO_2/Fe_2O_3 Biner Mixed Oxidses and its Photocatalytic Properties, J. Mater. Chem. Phys., **59**, 254-261 (1999).

6. S. Bilgi and C. Demir, Identification of Photooxidation Degradation Products of CI RO 16 Dye by Gas Chromatography- mass Spectrometry, Dye Pigments, **66**, 69-76 (2005).

7. T. Tong, J. Zhang, B. Tian, F. Chen and D. He, Preparation of Fe^{+3} Doped TiO_2 Catalysts by Controlled Hydrolysis of Titanium Alkoxide and Study on their Photocatalytic Activity for Methyl Orange Degradation, J. Hazard. Mater., **155**, 572-579 (2008).

8. V. Subramanian, E. Wolf and P. Kamat, Semiconductor Metal Composite Nanostructers, to What Extent Do Metal Nanoparticles Improve the Photocatalytic Activity of TiO_2 films ? J. Phys. Chem B, **105**, 11439-11446 (2001).

9. C. He, Y. Yu, X. Hu and A. Hu, Influence of Silver Doping on the Photocatalytic Activity of Titania Films Appl. Surf. Sci., **200**, 239-247 (2002).

10. P. Sathishkumar, S. Anandan and P. Maruthamuthu, Synthesis of Fe^{+3} Doped TiO_2 Photocatalysts for the Visible Assisted Degradation of an Azo Dye, Colloid Surface A: Physicochem Eng. Aspects, **375**, 231-236 (2011).

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

12. 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).

13. L. G. Devi, S. G. Kumar, B. N. Murthy and N. Kottam, Influence of Mn^{+2} and Mo^{+6} Dopants on the Phase Transformations of TiO_2 Lattice and its Photocatalytic Activity under Solar Illumination, Catal. Commun., **10**, 794-798 (2009).

14. L. G. Devi, B. N. Murthy and S. G. Kumar, Photocatalytic Activity of TiO_2 Doped with Zn^{+2} and V^{+5} Transition Metal Ions: Influence of Crystallite Size and Dopant Electronic Configuration on Photocatalytic Activity, Mater Sci. Eng. B, **166**, 1-6 (2010).

15. 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).

16. 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).

17. A. R. Gandhe and J. B. Fernandes, A Simple Method to Synthesize N-doped Rutile Titania with Enhanced Photocatalytic Activity in Sunlight, J. Solid State Chem., **178**, 2953-2957 (2005).

18. H. Li, D. Wang, H. Fan, P. Wang, T. Jiang and T. Xie, Synthesis of Highly Efficient C- Doped TiO**2** Photocatalyst and its Photogenerated Charge Transfer Properties, J. Colloid Interface Sci., **354**, 175-180, (2011).