

## Synthesis and Characterization of CeFeO<sub>3</sub> Photocatalyst Used in Photocatalytic Bleaching of Gentian Violet

J. Ameta<sup>a</sup>, A. Kumar<sup>a</sup>, R. Ameta<sup>b,\*</sup>, V.K. Sharma<sup>a</sup> and S.C. Ameta<sup>a</sup>

<sup>a</sup>Photochemistry and Solar Energy Laboratory, Department of Chemistry, University College of Science, M.L. Sukhadia University, Udaipur, India

<sup>b</sup>Meera Girls Govt. College, Udaipur-313001 (Raj.), India

(Received 15 February 2008, Accepted 29 May 2008)

Ternary oxides have been used as effective photocatalyst for carrying out number of chemical reactions. Method of preparation has major effect on the performance of these mixed oxide catalysts. In the present work, cerium iron oxide catalyst was synthesized using co-precipitation method and specific heating cycle. Synthesized catalyst was characterized using X-ray diffraction patterns. Photocatalytic degradation on gentian violet dye was observed using this catalyst and progress of the reaction was monitored spectrophotometrically. The effect of variation of different parameters like concentration of gentian violet, pH, amount of semiconductor and light intensity was also studied. A tentative mechanism for the photocatalytic bleaching of gentian violet has been proposed.

**Keywords:** Photocatalysts, CeFeO<sub>3</sub>, Photocatalytic bleaching, Gentian violet

### INTRODUCTION

There are many methods for eliminating water pollutants like thermal dehydration, adsorption by charcoal *etc.* One of the most economical and ecofriendly methods is, however, the use of photocatalytic reactions. Following is a literature survey on the use of photocatalytic reactions in elimination of water pollutants.

Alton and Ferry used SiW<sub>12</sub>O<sub>4</sub> as photocatalyst for the photocatalytic degradation of acid orange 7 [1]. Photoreduction of CO<sub>2</sub> and water into formaldehyde and methanol on aqueous suspension of SrTiO<sub>3</sub> and TiO<sub>2</sub> was investigated by Blajeni *et al.* [2]. Domen *et al.* studied photocatalytic decomposing of water vapors over NiO-SrTiO<sub>3</sub> catalyst [3]. Photocatalytic degradation of nitrobenzene with

combustion synthesized nano TiO<sub>2</sub> was investigated by Priya and Madras [4]. Photodegradation of dye pollutants on one dimensional TiO<sub>2</sub> nanoparticles under UV and visible irradiation was investigated by Chen *et al.* [5]. Wang *et al.* studied photocatalytic degradation and kinetics of orange-G using nano sized Sn(IV) TiO<sub>2</sub> as a photocatalyst [6].

Kako *et al.* have suggested some preventive method against catalytic poisoning of TiO<sub>2</sub> photocatalyst by H<sub>2</sub>S [7]. Chittora *et al.* studied the photoreduction of CO<sub>2</sub> in presence of some photocatalyst like ZnO.Fe<sub>2</sub>O<sub>3</sub> *etc.* [8]. Pt/CdS colloidal particles were used for photocatalytic hydrogen production from H<sub>2</sub>S solution by Muradav *et al.* [9]. Swarnkar *et al.* observed the photocatalytic bleaching of gentian violet at CdS semiconductor surface [10]. Mansoori *et al.* used zinc oxide and lead oxide (PbO) as photocatalysts for the photocatalytic bleaching of rhodamine-B and rhodamine-6G [11,12].

\*Corresponding author. E-mail: ameta\_ra@yahoo.com

Photocatalytic degradation of azo dye acid readily in water using ZnO as photocatalytic has been investigated by Daheshvar *et al.* [13]. The photocatalytic bleaching of basic blue-24 in the presence of ZnO has been reported by Ameta *et al.* [14]. Kim *et al.* used ZnO coated TiO<sub>2</sub> nanoparticles for the flexible dye-sensitized solar cells [15]. Use of semiconducting iron(II) oxide in photocatalytic bleaching of some dyes (malachite green, crystal violet and methylene blue) has been reported by Ameta *et al.* [16]. Photocatalytic degradation of brilliant red dye and textile waste water has been suggested by Martins *et al.* [17]. The synthesis, characterization and photocatalytic activity of lanthanum cerium oxide (LaCeO<sub>3</sub>) catalyst was reported by Jose *et al.* [18].

In present investigation, the semiconducting properties of a synthesized CeFeO<sub>3</sub> photocatalysts are utilized for photocatalytic bleaching of gentian violet. Like other inorganic semiconductor photocatalysts, CeFeO<sub>3</sub> also acts as an inorganic semiconductor. It absorbs photons to create electron-hole pair, which can subsequently participate in the redox reaction.

## EXPERIMENTAL PROCEDURE

### Materials and Methods

Gentian violet (CDH) as a modal dye and CeFeO<sub>3</sub> as a photocatalyst were used in this investigation. A stock solution of gentian violet ( $1.0 \times 10^{-3}$  M) was prepared in doubly distilled water. The photocatalytic degradation of gentian violet was started by adding 0.10 g of CeFeO<sub>3</sub> to the dye solution. Irradiation was carried out keeping whole assembly exposed to a 200 W tungsten lamp (Philips, light intensity = 60.0 m W cm<sup>-2</sup>). This intensity of light at various distances from the lamp was measured with the help of solarimeter (SM CEL 201). The pH of the solution was measured by a digital pH meter (Systronics modal 335). The desired pH of the solution was adjusted by the addition of previously standardized sulfuric acid and sodium hydroxide solutions. The necessary condition for the correct measurement of optical density (O.D.) is that the solution must be free from semiconductor particles and impurity. The progress of photocatalytic reaction was followed by taking optical density at regular time intervals using an UV-Vis spectrophotometer (Systronics Modal 106).

### Synthesis and Heat Treatment of Photocatalyst

CeFeO<sub>3</sub> was prepared by co-precipitation of metal nitrates upon addition of ammonium hydroxide. The methodology was as follows: 25 ml of 0.2 M aqueous solution of ferric nitrate was added to 25 ml of 0.2 M aqueous solution of (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> to make the volume up to 100 ml. Then enough concentrated aqueous ammonium hydroxide was added rapidly to the mixture to adjust the pH of solution at 8.5.

The resulting precipitate along with the supernatant solution was kept in an oven at 110 °C for 15-16 h for drying of precipitate. Subsequently, stepwise calcinations were performed in a muffle furnace by heating the dried precipitate from 150 to 600 °C according to the heating schedule given in Table 1. The calcination at 600 °C was completed in four days 6 h heating everyday. After each heating, the material was furnace-cooled and ground in acetone with a pastel and mortar. The ground material was further heated in the next day and the procedure was repeated.

**Table 1.** Calcinations Temperature and Heating Schedule

S. No.	Temperature	Duration (h)
1	150	½ h
2	200	½ h
3	225	½ h
4	250	½ h
5	300	1 h
6	350	1 h
7	400	2 h
8	450	2 h
9	500	3 h
10	550	3 h
11	600	24 h

## RESULTS AND DISCUSSION

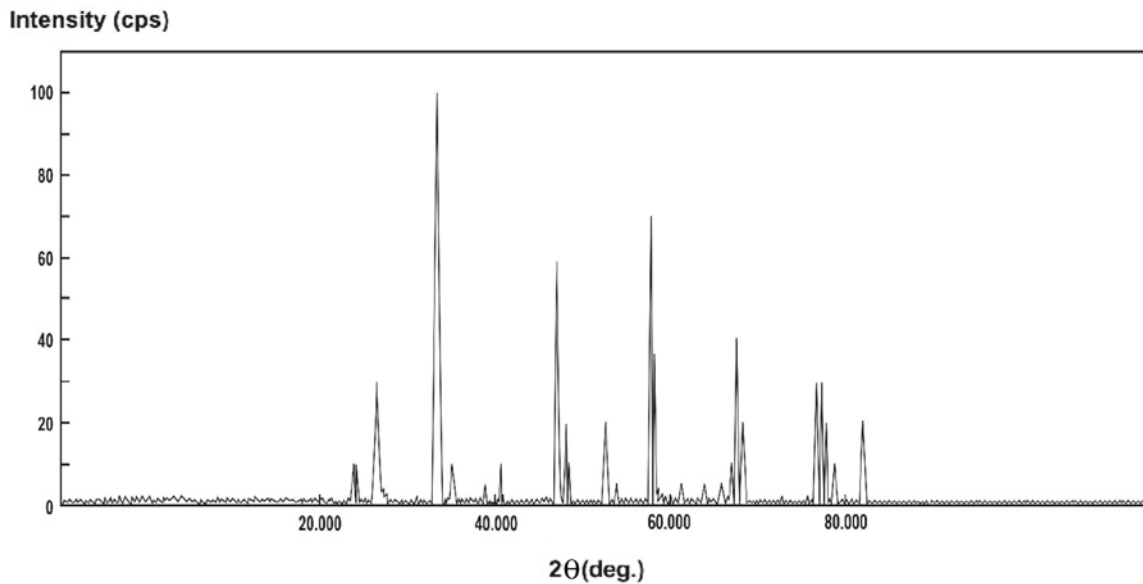
The prepared ternary oxide was characterized by X-ray diffraction method and the results are shown in Fig. 1 and the corresponding characteristic XRD data are summarized in

## Synthesis and Characterization of CeFeO<sub>3</sub> Photocatalyst

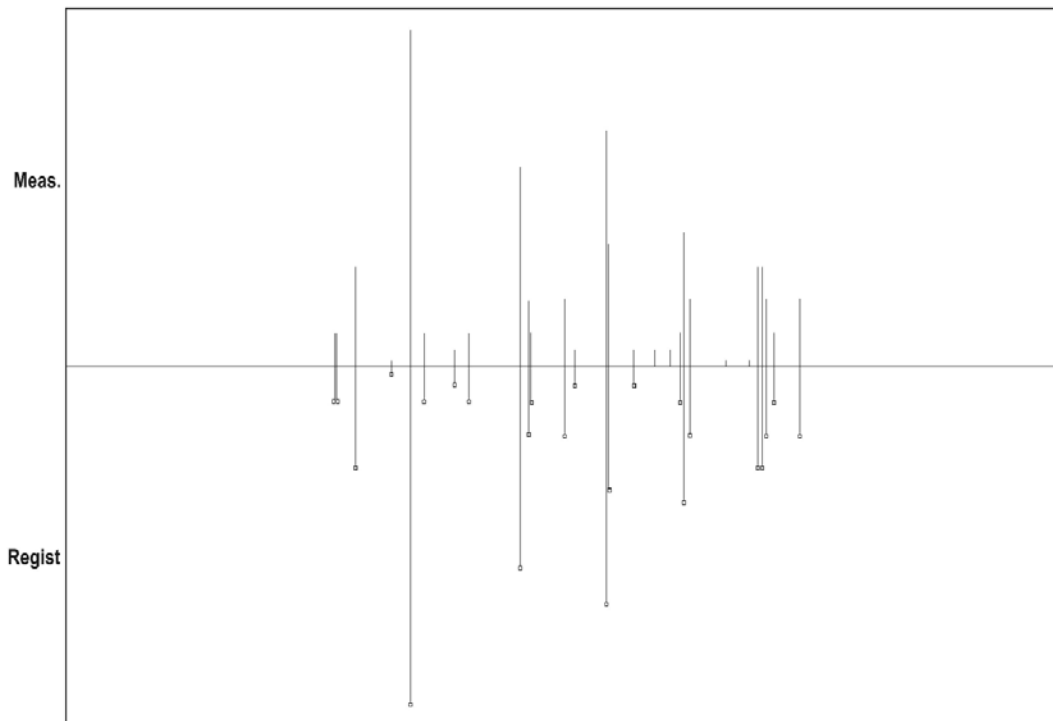
Table 2. The stoichiometry of the ternary oxide sample has been established with the help of published diffraction data file-JCPDS (Joint Committee on Power Diffraction

Standards).

Matching of mirror imaged XRD with XRD of CeFeO<sub>3</sub> from JCPDF file is shown in Fig. 2.



**Fig. 1.** X-ray diffraction pattern of CeFeO<sub>3</sub>.



**Fig. 2.** Matching of mirror imaged XRD with XRD of CeFeO<sub>3</sub> from JCPDF file.

**Table 2.** XRD data of CeFeO<sub>3</sub>

S. No.	2θ	D Value	Intensity	H k l
1	22.065	3.930	10	110
2	22.723	3.910	10	2
3	25.353	3.510	30	111
4	32.290	2.770	100	112
5	34.140	2.624	10	21
6	38.048	2.363	5	211
7	39.854	2.260	10	202
8	46.507	1.951	60	4
9	47.672	1.906	20	221
10	47.832	1.900	10	23
11	52.290	1.748	20	114
12	53.544	1.710	5	311
13	57.594	1.599	70	24
14	57.673	1.597	30	204
15	61.161	1.514	5	231
16	67.084	1.394	10	40
17	67.578	1.385	40	224
18	68.363	1.371	20	41
19	77.024	1.237	30	116
20	77.618	1.229	30	43
21	78.147	1.222	20	225
22	79.073	1.210	10	234
23	82.432	1.169	20	135

### Photocatalytic Degradation of GentianViolet

The photocatalytic degradation of gentian violet was followed at  $\lambda_{\max}$  of 580 nm. The optical density-time data for a typical run are given in Table 3 and graphically presented in Fig. 3. It was observed that the optical density of gentian violet solution decrease in presence of semiconductor and light. The plot of  $\log OD$  vs. time was leaner and hence, this reaction follows a pseudo first order kinetics. The rate constant for this reaction, as determined using the expression  $k = 2.303 \times \text{slope}$ , found to be  $k = 1.02 \pm 0.026 \times 10^{-4} \text{ s}^{-1}$ .

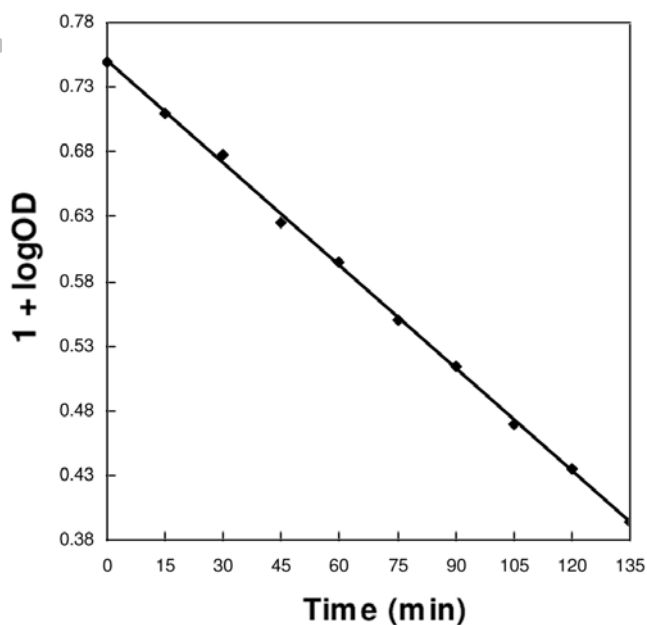
### Effect of pH

The effect of pH on photocatalytic degradation was also investigated and the results are reported in Table 4. As seen, the rate of reaction increased with increasing of pH of solution

**Table 3.** A Typical Run. [Gentian violet] =  $1.0 \times 10^{-5} \text{ M}$ ; pH = 6.0; Light intensity =  $60.0 \text{ mW cm}^{-2}$ ; CeFeO<sub>3</sub> = 0.10 g

Time (min)	Optical density (O.D.)	1 + logO.D.
0	0.562	0.7497
15	0.513	0.7101
30	0.476	0.6776
45	0.422	0.6253
60	0.393	0.5944
75	0.355	0.5502
90	0.327	0.5145
105	0.295	0.4698
120	0.272	0.4346
135	0.248	0.3945

$$k = 1.02 \pm 0.026 \times 10^{-4} \text{ s}^{-1}$$

**Fig. 3.** Plot of 1 + logOD vs. time for a typical run.

up to a pH of 6.0. However, a further increase in pH of solution resulted in decreased reaction rate. It may be explained on the basis that the surface of the semiconductor becomes negatively charged and the dye will remain in its neutral form, where it is electron rich due to the presence of

**Table 4.** Effect of pH. [Gentian Violet] =  $1.0 \times 10^{-5}$  M; Light Intensity =  $60.0 \text{ mW cm}^{-2}$ ; CeFeO<sub>3</sub> = 0.10 g

pH	$k \times 10^4 \text{ (s}^{-1}\text{)}$
4.0	0.57
4.5	0.60
5.0	0.69
5.5	0.73
6.0	1.02
6.5	0.90
7.0	0.83
7.5	0.73

**Table 5.** Effect of Concentration of Gentian Violet. pH = 6.0; Light Intensity =  $60.0 \text{ mW cm}^{-2}$ ; CeFeO<sub>3</sub> = 0.10 g

[Gentian violet] $\times 10^5 \text{ M}$	$k \times 10^4 \text{ (s}^{-1}\text{)}$
0.4	0.80
0.6	0.85
0.8	0.96
1.0	1.02
1.2	0.96
1.4	0.92
1.6	0.82

**Table 6.** Effect of Amount of Semiconductor. [Gentian Violet] =  $1.0 \times 10^{-5}$  M; pH = 6.0; Light Intensity =  $60.0 \text{ mW cm}^{-2}$

CeFeO <sub>3</sub> (g)	$k \times 10^4 \text{ (s}^{-1}\text{)}$
0.04	0.43
0.06	0.84
0.08	0.89
0.10	1.02
0.12	0.98
0.14	0.96
0.16	0.93

lone pairs on two nitrogen atoms. Therefore, these molecules will face a force of repulsion from negatively charged surface of the semiconductor; thus, resulting into a decrease in the rate of reaction.

### Effect of Concentration of Gentian Violet

Effect of variation of dye concentration was also studied by taking different concentrations of gentian violet. The results are reported in Table 5. It is seen that the rate of photocatalytic bleaching increases with an increase in the concentration of the dye up to  $1.0 \times 10^{-5}$  M. It may be due to the fact that as the concentration of the gentian violet 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 further increase in the concentration of dye. 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 surface. Also, some dye aggregates may also form to retard the reaction rate.

### Effect of Amount of Semiconductor

The effect of amount of semiconductor is also likely to affect the process of dye bleaching and therefore, different amounts of semiconductor were used. The results of this study are reported in Table 6.

It has been observed that, as the amount of semiconductor increases, the rate of photodegradation of gentian violet increases up to 0.10 g. A further increase in the amount of catalyst has no significant effect on the rate of reaction. This may be due to the fact that after a creation limit of 0.10 g, a further increase in CeFeO<sub>3</sub> will result in 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 gentian violet, 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 covered by a photocatalyst. This was also supported by taking vessels of different dimensions.

### Effect of Light Intensity

The effect of the variation of the light intensity on the rate was also investigated and the observations are reported in Table 7.

The data given in Table 7 indicate that the bleaching action is accelerated as the intensity of light was increased, because any increase in the light intensity will increase the number of

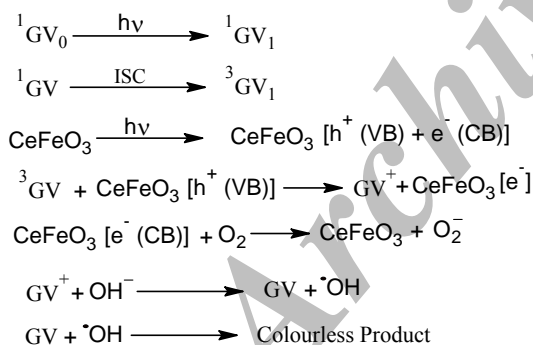
**Table 7.** Effect of Light Intensity. [Gentian Violet] =  $1.0 \times 10^{-5}$  M; pH = 6.0; Light Intensity = 60.0 mW  $\text{cm}^{-2}$ ;  $\text{CeFeO}_3 = 0.10$  g

Light intensity (mW $\text{cm}^{-2}$ )	$k \times 10^4$ ( $\text{s}^{-1}$ )
10	0.45
20	0.57
30	0.70
40	0.91
50	0.96
60	1.02

photons striking per unit area of the semiconductor powder. A linear behavior between light intensity and the rate of reaction was observed.

### Mechanism

On the basis of experimental, a tentative mechanism for photocatalytic degradation of gentian violet may be proposed as:



Gentian violet (GV) absorbs radiations of suitable wavelength and goes to excited state. It then undergoes intersystem crossing (ISC) to the triplet state of the dye. This triplet state may donate its electrons to the semiconductor and the gentian violet becomes positively charged. The dissolved oxygen of the solution may pull an electron from the conduction band of semiconductor, thus regenerating the semiconductor and forming superoxide anion radical. The positively charged molecule of gentian violet will immediately react with hydroxyl ion to form  $\cdot\text{OH}$  radicals and these  $\cdot\text{OH}$

radicals will oxidize the gentian violet molecule into colorless product. The participation of  $\cdot\text{OH}$  radicals as an active oxidizing species was confirmed by carrying out the reaction in the presence of a  $\cdot\text{OH}$  radicals scavenger *e.g.*, 2-propanol, where the reaction rate was drastically retarded.

### ACKNOWLEDGEMENTS

Authors are thankful to the Head of the Chemistry Department, Sukhadia University, Udaipur for providing necessary facilities and to Dr. Pinki B. Punjabi, Mukesh Paliwal and Justin Jose for critical discussions.

### REFERENCES

- [1] A. Alton, J.L. Ferry, *J. Photochem. Photobiol.* 152A (2003) 175.
- [2] B.A. Blajeni, M. Halmann, J. Manassen, *Solar Energy* 25 (1980) 165.
- [3] K. Bomen, T. Anishi, S. Naifo, K. Tamuru, *Phys. Chem.* 86 (1982) 3657.
- [4] M.H. Priya, G. Madras, *J. Photochem. Photobiol.* (2006) 178.
- [5] J.Y. Li, W.H. Ma Chen, *J. Mol. Catal.* 2619 (2007) 131.
- [6] J.H. Sin, X.L. Wang, J.Y. Sun, *J. Mol. Catal.* 260 (2006) 235.
- [7] T. Kako, H. Irie, K. Hashimoto, *J. Photochem. Photobiol.* 171A (2005) 131.
- [8] A.K. Chittora, B. Sharma, M. Balo, S.C. Ameta, *Natt. Conv. Solar Energy Udaipur (India)* (1990) 169.
- [9] N.Z. Muradov, M.I. Rustamov, A.D. Guseinova, Y.V. Bazhutin, *Rect. Kinet. Catal. Lett.* 33 (1987) 279.
- [10] H. Swarnkar, D. Mogra, J. Vardia, S.C. Ameta, *Poll. Res.* 23 (2004) 233.
- [11] R.A. Mansoori, S. Kothari, R. Ameta, *J. Indian Chem. Soc.* 81 (2004) 335.
- [12] R.A. Mansoori, S. Kothari, R. Ameta, *Arabian J. Sci. Eng.* 11 (2004) 29.
- [13] N. Daheshvar, D. Salari, R. Khataee, *J. Chem. Soc. Farady. Trans.* 157A (2003) 111.
- [14] R. Ameta, C. Kumari, V. Bhat, S.C. Ameta, *Indust. Quim.* 33 (1998) 36.
- [15] S.S. Kim, J.H. Yun, Y.E. Sung, *J. Photochem.*

Synthesis and Characterization of CeFeO<sub>3</sub> Photocatalyst

- Photobiol. 171A (2005) 275.
- [16] R. Ameta, J. Vardia, P.B. Punjabi, S.C. Ameta, Indian J. Chem. Tech. 13 (2006) 114.
- [17] A.F. Martins, M.L. Wilde, C. Dasilveria, Indian. J. Chem. Tech. 13 (2006) 14.
- [18] J. Jose, J. Ameta, P.B. Punjabi, V.K. Sharma, S.C. Ameta, Bull. Catal. Soc. India 6 (2007) 110.

Archive of SID