Lanthanum Chromium Oxide Catalyst: Synthesis, Characterization and Photocatalytic Activity Shown in Azure-B

Justin Jose, Jyoti Ameta, P.B. Punjabi, V.K.Sharma and Suresh C.Ameta
Photochemistry and Solar Energy Laboratory, Department of Chemistry,
M. L. Sukhadia University, Udaipur –313002, Rajasthan, India.
e-mail: pb_punjabi@yahoo.com

Abstract: The photo-catalytic activity of number of semiconducting materials has been established and photo catalysis has been predicted as a promising technology for waste water treatment. Ternary oxides have been used as effective photocatalysts for carrying out number of chemical reactions. In the present work, lanthanum chromium oxide catalyst has been synthesized using co-precipitation method and specific heating cycles. Synthesized catalyst was characterized using x-ray diffraction patterns. Photocatalytic bleaching of azure-B dye was observed by spectrophotometric method using above catalyst and progress of the reaction was monitored spectrophotometrically. The effect of variation of different parameters like concentration of azure-B, pH, amount of semiconductor and light intensity was observed on the rate of photocatalytic bleaching. A tentative mechanism for the photocatalytic bleaching of azure-B has been proposed.

1. Introduction:

Photocatalysis has become an emerging technology for the treatment of waste water all over the world. It is being used for solving the problem of environmental pollution and even has remedial effect from harmful bacteria as reported by Toshiyuki *et al*. [1]. The field of photocatalysis has been extensively reviewed by Stein Bach [2], Gratzel [3] and Pelizzetti and Serpone [4]. Photocatalytic decomposition of water vapors over NiO-SrTiO$_3$ catalyst has been studied by Domen *et al*. [5]. Tang *et al*. [6] investigated the photocatalytic decomposition of the organic contaminants by Bi$_2$WO$_6$ under visible light irradiation. Generally, binary chalcogenides(specially oxides and sulphides) are being used as photocatalysts. Luo *et al*. [7] studied the structure and redox properties of

CexPr1-xO$_2$ delta mixed oxides and their catalytic activities for CO, CH$_3$OH and CH$_4$ combustion. The search for new photocatalysts has led to the study of ternary oxides. The use of ternary oxides like SrTiO$_3$ is limited as its λ_{max} falls in the near U.V. or at the border of visible region. Chaudhary *et al*. [8] performed carbon free dry reforming of methane to syngas over NdCoO$_3$ perovskite type mixed metal oxide catalyst. Therefore, extensive research has been carried out using 3d-transition metal ions for the preparation of ternary oxides including perovskites.

The way in which these ternary oxides are prepared is most important. Method of preparation, calcination temperature and heating schedule has major effect on the photocatalytic activity of the mixed oxides. Tascon *et al*. [9] prepared, characterized and tried

to find out the catalytic properties of LaMeO$_3$ oxides (here Me denotes 3d-metals).The ternary oxides of Lanthanum were prepared by co-precipitation of its hydroxide along with hydroxides of 3d series. The precipitation of hydroxides was preferred over other precipitations like oxalates, carbonates and citrates due to reasons cited by Keshavaraja and Ramaswamay [10] followed by calcinations at higher temperatures. Novio *et al*. [11] observed partial or complete heterogeneous photocatalytic oxidation of neat toluene and 4-picoline in liquid organic oxygenated dispersions containing pure and iron doped titania photocatalysts. These synthesized ternary oxides have been used in the photobleaching of dyes. Fuerte *et al.* [12] observed effect of doping level in the photocatalytic degradation of toluene using nanosized Ti-W mixed oxides in the sunlight.

On the contrary, bleached dye solution is non toxic and harmless. Secondly, dye containing coloured water is of almost no use, but if this coloured solution is bleached to colourless, then it may be used for washing, cooling, irrigation and cleaning purpose. Therefore, photocatalytic bleaching will provide low cost method to solve this problem. From the literature survey, it is evident that lot of attention has been given on the photocatalytic activity shown by binary chalcogenides compounds. Devi and Krishnaiah *et al*. [13] reported that heat treated TiO$_2$ acts as photocatalysts in the photocatalytic degradation of p-amino azobenzene and p-hydroxy azobenzene. Likewise, Calvert *et al*. [14] used ZnO as a photocatalyst for photochemical synthesis of H$_2$O$_2$. Domenech and Munoz [15] studied the photocatalytic reduction of Cr(VI) over

CdS. Looking to the importance of photocatalysts for pollution control there is a need to synthesize some newer photocatalysts. In the present work, lanthanum chromium oxide was synthesized, characterized and used as a photocatalyst for the degradation of azure-B which is extensively used in printing and dyeing industries.

2. Experimental procedure:

2.1. Synthesis of ternary oxide by co precipitation method:

Lanthanum chromium oxide was prepared by co-precipitation of hydroxide from a mixture of aqueous solution of chromium nitrate and lanthanum nitrate by the addition of ammonium hydroxide solution. The procedure is as follows: La(NO$_3$)$_3$.6H$_2$O was dissolved separately in distilled water (50.0 mL. each) and both solutions were mixed and made up to 100 mL solution (0.4 M La, 0.4 M Cr). Aqueous ammonium hydroxide solution was added rapidly to the mixed nitrate solutions at room temperature, a dark green coloured precipitate was formed. The pH of the solution was maintained at 7.5 which insured co-precipitation of La and Cr ions as hydroxides.

2.2. Heat treatment:

The precipitate along with the supernatant solution was kept in an oven at 110° C for 15-16 hours for drying. The dried precipitate was subjected to stepwise calcinations by heating from 150°C to terminal temperature 725°C. For the heat treatment, the dried precipitate was heated in the muffle furnace with increase in the temperature at a rate of 10° C per minute from one temperature to the subsequent higher temperature. After heating at 600°C for 12 hours, the material was furnace cooled and

grounded in acetone in a gap of 6 hours, using a pastel and mortar. Later on the ground material was further heated at 650°C for 12 hours. Here it is also grounded in acetone, in a gap of 6 hours. Now the material is finally heated at 725°C for 5 hours. In this way we see that the calcined material at 600°c and 650°C is ground in between two times. The calcination at 725°C was completed without in between grinding of the material.

Table.1
CALCINATION TEMPERATURE AND HEATING SCHEDULE

S. No.	Temperature °C	Duration (Hrs)
1.	150	0.5
2.	200	0.5
3.	225	0.5
4.	250	0.5
5.	300	1
6.	350	1
7.	400	2
8.	450	2
9.	500	3
10.	550	3
11.	600	12
12.	650	12
13.	725	5

2.3. XRD characterization:

The prepared ternary oxide was characterized by X-ray diffraction method. Figure-1 present the x-ray diffraction patterns of $LaCrO_4$ synthesized from the co-precipitation of $La(NO_3)_3.6H_2O$ and $Cr(NO_3)_3.9H_2O$ in hydroxide form and calcined at 600°C, 650°C and 725°C for different periods. In the first illustration of figure-1 First illustration of figure-1 show the characteristic peaks of 2θ = 25.5°, 27.2°, 29.2°, 30.5°, 36.3°, 41.1°, 49.7°, 50.0°, 53.8°, 54.0°, 57.3°, 58.1°, 74.8° and 79.9° which accurately corresponds with $LaCrO_4$ stoichiometry X-ray patterns. Above mentioned intensity peaks indicate values of 2θ where Bragg's law $n\lambda=2dsin\theta$ is fulfilled. The stoichiometry of the ternary oxide sample has been established with the help of published diffraction data file - JCPDS (Joint Committee on Powder Diffraction Standards). Since values are known from JCPDS files, the 2θ setting of each peak which corresponds to certain wavelength was determined and matched with the 2θ values obtained from the sample.

In figure-1, the first graph has been plotted between intensity (cycles per second) and 2θ values in degrees. For general consideration we had taken the 2θ value ranging from 20.0° to 80.0°. here we see the occurrence of prominent peaks, which are numbered

1,2,3,4,5,6,9,10,11,13,16,17,21,23 and 24 respectively. In the second illustration of figure-1, a genuine comparison has been made between the X-ray diffraction data obtained for the ternary oxide sample and the original registered values of $LaCrO_4$ taken from JCPDS files. On comparing the X-ray patterns we came to a conclusion that there is a maximum possibility of phase having $LaCrO_4$ stoichiometry.
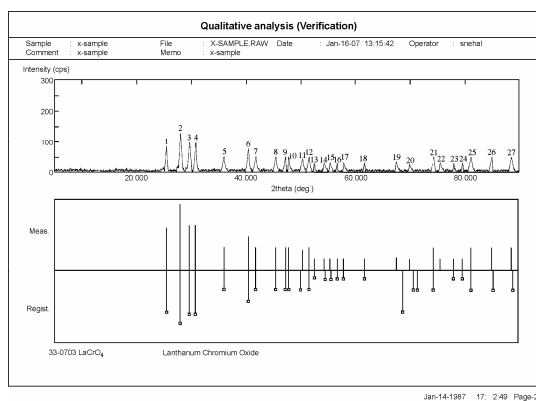

Fig.1

Table 2

Peak No.	2theta(2θ)	FWHM	d-value	Intensity	I/Io
1.	25.500	0.235	9.8173	84	63
2.	27.200	0.235	9.3017	132	100
3.	29.200	0.235	9.0176	99	74
4.	30.500	0.235	8.3128	99	74
5.	36.300	0.235	8.2176	50	41
6.	41.100	0.235	7.3298	76	70
7.	42.000	0.235	7.2150	50	41
8.	45.800	0.235	7.0157	51	42
9.	49.700	0.235	6.3921	51	42
10.	50.000	0.235	6.2168	50	41
11.	53.100	0.235	6.1094	48	39
12.	53.800	0.235	6.0236	50	41
13.	54.000	0.235	5.9124	37	25
14.	55.200	0.235	5.8793	36	24
15.	56.100	0.235	5.7872	36	24

16.	57.300	0.353	5.6389	36	24
17.	58.100	0.353	5.4321	37	25
18.	62.700	0.353	5.3976	37	25
19.	67.300	0.353	5.2174	37	25
20	69.800	0.353	5.1293	31	21
21.	74.800	0.353	5.0171	52	43
22.	75.400	0.353	4.8106	33	23
23.	78.900	0.235	4.7132	32	22
24.	79.900	0.235	4.6179	32	22
25.	81.800	0.235	4.6073	53	44
26	84.600	0.235	4.5901	53	44
27.	87.400	0.235	4.3270	53	44

2.4. Experimental procedure of photocatalytic bleaching of azure-B:

Azure-B and lanthanum chromium oxide were used in the present investigation. The solution of azure –B dye (AB) was prepared in doubly distilled water. The photocatalytic bleaching of azure-B was studied in the presence of semiconducting lanthanum chromium oxide catalyst and light. 0.0305 g of azure-B was dissolved in 100mL. of double distilled water so that the concentration of dye solution was 1.0×10^{-3} M. This solution was used as a stock solution. The photocatalytic bleaching of the dye was observed using different concentrations of the dye and semiconductor at different pH and light intensities. The irradiation was carried out keeping the whole assembly under light.
A 200 watt tungsten lamp (Philips) was used for irradiation purpose. The intensity of light at various distances was measured by Suryamapi (CEL model SM 201) . A water filter was used to cut off thermal radiations. The pH of the solution was measured by a digital pH meter (Systronics Model 324). The desired pH of the solution was adjusted by the addition of previously standardized 0.1N sulphuric acid (Rankem, 98%) and 0.1N sodium hydroxide (Rankem, 97%) solutions. The necessary condition for the correct measurement of optical density is that the solution must be free from semiconductor particles and other impurities. Therefore, a G-3 sintered glass crucible was used for filtration to obtain the desired accuracy in measurement of absorbance (optical density) of the dye solution. A U.V spectrophotometer (Systronics Model 108) was used for measuring absorbance at different time intervals.

3. Results and discussion:

The photocatalytic bleaching of azure-B in presence of lanthanum chromium oxide semiconductor at different time intervals was observed at λ_{max} 650 nm.

For typical run setup the pH was taken 9.5, the concentration of azure-B was taken 5.0×10^{-5} M, the amount of semiconductor was taken 0.11 gm. and the intensity of light radiation was taken 80.0 mWcm^{-2}. The results for a typical run are graphically represented in the figure-2. It was observed that absorbance of azure-B solution decreases with the increase in the time of irradiation, thus indicating that azure-B is photocatalytically degraded (control experiments were also performed which indicated that dye degrades only in the presence of photocatalyst and light) on irradiation.
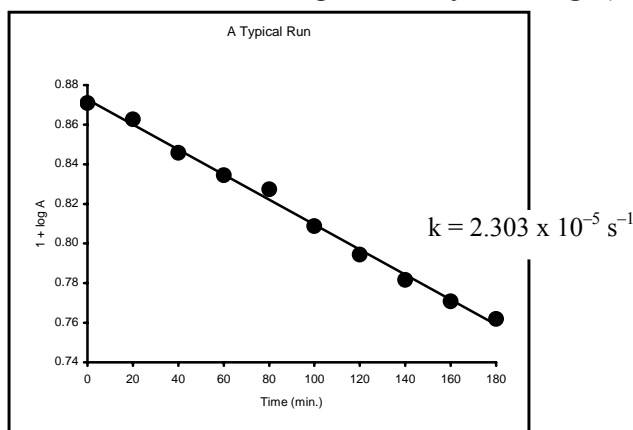
Fig.2

A plot of 1 + log A versus time was linear and follows pseudo first order kinetics. The rate constant was measured using following expression:

$$k = 2.303 \times \text{slope}$$

3.1 Effect of pH variation:

The effect of pH on the rate of photocatalytic bleaching of azure-B was investigated in the pH range (7.0-10.5). It is evident from the data given below that the rate of photocatalytic bleaching of azure-B increases with increase in pH. The increase in the rate of photocatalytic bleaching may be due to more availability of the OH ions at higher pH values. These OH ions will generate more OH radicals by combining with holes and these hydroxide radicals are considered responsible for this photocatalytic bleaching. But after a certain value of pH (pH=9.5), a further increase in the pH of the medium decreases the rate of photocatalytic bleaching. It may be due to the fact that the dye does not remain in its cationic form due to greater concentration of OH ions and as such, the reaction rate decreases. The results are reported in the Table-3 shown below.

3.2 Effect of variation of dye concentration:

Effect of variation of dye concentration was also studied by taking different concentrations of azure-B. It has been observed that the rate of photocatalytic bleaching increases with an increase in the concentration of dye. It may be due to the fact that as the concentration of dye 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 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 azure-B. The results are tabulated in Table-3 given below.
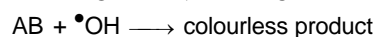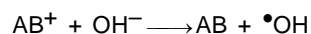
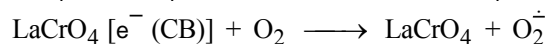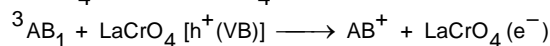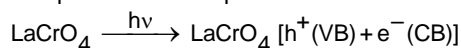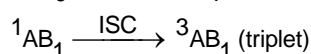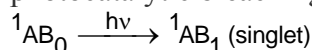### 3.3. Effect of amount of lanthanum chromium oxide:

The amount of photocatalyst is also likely to affect the rate of dye bleaching .Here different amounts of photocatalysts were used. It has been observed that initially the rate of bleaching of azure-B increases with an increase in the amount of semiconductor but ultimately it becomes almost constant after a certain amount of it. 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 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, any increase in the amount of it has negligible or no effect on the rate of photocatalytic bleaching of azure-B. As any increase in the amount of semiconductor after 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 photo catalyst. The results are reported in Table-3 given below.

3.4. Effect of light intensity:

To observe the effect of intensity of light on the photocatalytic bleaching of azure-B, 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 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. As we raised the intensity of light above 80.0 $mWcm^{-2}$, we found that the solution starts becoming turbid, so it was not possible to measure the absorbance of the solution. Hence we had measured the absorbance of the dye solution up to intensity 80 $mWcm^{-2}$. A linear behaviour between light intensity and rate of reaction was observed. The results obtained are reported in Table-3 given below.

4. Mechanism:

On the basis of the observed data, the following tentative mechanism may be proposed for the photocatalytic bleaching of azure-B.

$$^1AB_0 \xrightarrow{h\nu} {}^1AB_1 \text{ (singlet)}$$

$$^1AB_1 \xrightarrow{ISC} {}^3AB_1 \text{ (triplet)}$$

$$LaCrO_4 \xrightarrow{h\nu} LaCrO_4 \; [h^+(VB) + e^-(CB)]$$

$$^3AB_1 + LaCrO_4 \; [h^+(VB)] \longrightarrow AB^+ + LaCrO_4 \, (e^-)$$

$$LaCrO_4 \; [e^-(CB)] + O_2 \longrightarrow LaCrO_4 + O_2^{\dot-}$$

$$AB^+ + OH^- \longrightarrow AB + {}^\bullet OH$$

$$AB + {}^\bullet OH \longrightarrow \text{colourless product}$$

When the solution of the dye was exposed to light in the presence of a semiconductor, initially the azure-B molecules are excited first to their singlet state. These excited singlet molecules are converted to the triplet

state through inter system crossing (ISC).These triplet state may donate its electrons to the semiconductor and the azure-B 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 azure-B will immediately react with hydroxyl ions to form OH radicals and these OH radicals will oxidize the azure-B molecule into colorless products. The participation of OH radicals as an active oxidizing species

was confirmed by carrying out the reaction in the presence of hydroxyl radical scavenger e.g ; 2-propanol, where the reaction was drastically retarded.

Acknowledgments:

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Table 3: Effect of variation of different parameters

Effect of pH		Effect of azure-B concentration		Effect of amount of LaCrO$_4$		Effect of intensity of light	
[Azure-B] = 5.0 x 10^{-5} M LaCrO$_4$ = 0.11gm Light Intensity = 60.0 mWcm^{-2} Temperature = 308 K		pH = 9.5 LaCrO$_4$ = 0.11gm Light Intensity = 60.0 mWcm^{-2} Temperature = 308 K		pH = 9.5 [Azure-B] = 5.0 x 10^{-5} M Light Intensity = 60.0mWcm^{-2} Temperature = 308 K		pH = 9.5 [Azure-B] = 5.0 x 10^{-5} M LaCrO$_4$ = 0.11gm Temperature = 308 K	
pH	Rate Constant x 10^5 (s^{-1})	[Azure-B] x 10^5 M	Rate Constant x 10^5 (s^{-1})	Amount of LaCrO$_4$ (gm)	Rate constant x 10^5 (s^{-1})	Light intensity (mWcm^{-2})	Rate Constant x 10^5 (s^{-1})
7.0	1.79	3.0	1.94	0.05	2.03	20.0	1.78
7.5	1.91	3.5	2.07	0.07	2.10	30.0	1.85
8.0	2.17	4.0	2.12	0.09	2.17	40.0	2.00
8.5	2.21	4.5	2.21	0.11	2.30	50.0	2.08
9.0	2.26	5.0	2.30	0.13	2.23	60.0	2.15
9.5	2.30	5.5	2.03	0.15	2.17	70.0	2.22
10.0	2.26	6.0	1.94	0.17	2.10	80.0	2.30
10.5	2.08	-	-	-	-	-	-