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SYNTHESIS AND CHARACTERIZATION OF La_2CoO_4 AND ITS USE AS A PHOTOCATALYST

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ABSTRACT

La_2CoO_4 is synthesized by a fast and simple microwave method using lanthanum nitrate and cobalt nitrate as starting reagents. La_2CoO_4 is synthesized using microwave heating for 6 mins. without calcination step. The synthesized product is characterized by X-Ray powder diffraction (XRD). The photocatalytic behaviour of La_2CoO_4 was studied spectrophotometrically through bleaching of azure-B and yellowish orange dyes. The effect of variation of different parameters i.e. pH, amount of La_2CoO_4, concentration of dye and light intensity was studied on the rate of photocatalytic degradation. A tentative mechanism for photocatalytic degradation of dyes has been proposed.

Key words: Photocatalyst, La_2CoO_4, Photocatalytic degradation, Yellowish orange, Azure-B.

INTRODUCTION

Dyes are quite useful to humanity but these are toxic and carcinogenic in nature too. Attempts are being made to degrade these dyes by using different photocatalysts. Generally, binary chalcogenides (oxides and sulphides) are being used as photocatalysts[1-3]. The use of ternary oxides like $SrTiO_3$ is limited as its λ_{max} falls in the near UV or at the border of visible region. Therefore, extensive research has been carried out using 3d transition metal ions for the preparation of ternary oxides. By changing the size of semi conducting particles, it is possible to enhance the redox potential of valence band holes and conduction band electrons[4] and hence, the photocatalytic activity[5-7]. Microwave assisted synthesis of different nanoparticles and their photocatalytic activity have been reported i.e. $MnFe_2O_4$[8], CuO[9], Bi_2WO_6[10], Bi_2O_3[11], Co_3O_4[11] and TiO_2[12] etc.

In the present work, lanthanum cobalt oxide (La_2CoO_4) was synthesized, characterized and used as a photocatalyst for degradation of azure-B and yellowish orange

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dyes. A comparison between the rates of photocatalytic degradation of two dyes has been made.

EXPERIMENTAL

Synthesis of photocatalyst

0.2 M aqueous solution (100 mL) of Co $(NO_3)_2.6H_2O$ was added to 0.2 M aqueous solution (100 mL) of La $(NO_3)_3.6H_2O$. Aqueous NH_4OH solution was added rapidly to the mixed nitrate solutions at room temperature maintaining pH. The solution is continuously stirred for 10 hrs. at room temperature so that hydroxides may be completely precipitated.

Microwave treatment

The filtered precipitate was kept for drying in oven at 60°C for 24 hrs. Dried precipitate was grounded with the help of mortar and pestle. The grounded material was irradiated with microwave radiations for 6 min. The synthesized ternary oxide was then washed with dil. acetic acid to separate unreacted La_2O_3 and CoO.

Materials and method

Yellowish orange and azure-B were used as dyes while La_2CoO_4 (synthesized) was used as a photocatalyst in the present investigation. 1.0×10^{-3} M solution of both dyes was prepared in doubly distilled water. This solution was used as a stock solution. The irradiation was carried out keeping the whole assembly under a 200 W tungsten lamp (Philips). The intensity of light was measured at various distances by Solarimeter (CEL model SM 201). The pH of the solution was measured by a digital pH meter (Systronics 335). The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solutions. The optical density was measured by a U.V. spectrophotometer (Systronics Model 106) following the necessary condition that the solutions are free from semiconductor particles and impurities. The photocatalytic bleaching of dyes was observed by taking dye solution of 3.33×10^{-5} M and 0.3 g La_2CoO_4 for azure-B and 1.66×10^{-5} M and 0.2 g La_2CoO_4 for yellowish orange.

Photocatalytic activity of La_2CoO_4

A cut off filter was placed outside the beaker to remove any thermal radiations just to ensure illumination by visible light only. A 50 mL beaker was filled with 30 mL dye solution containing photocatalyst. The O.D. was recorded at 630 nm and 480 nm for azure-B and yellowish orange, respectively. The change in O.D. versus irradiation time was observed. The typical run has been presented in Fig. 1 and Fig. 2 for azure-B and yellowish orange respectively. It was observed that the O. D. of dye solutions decreases in presence of semiconductor and light. A plot of 1 + log O.D. versus time was linear and hence, this reaction follows pseudo-first order kinetics. The rate constant for this reaction was determined using the expression k = 2.303 x slope. The rate constants for these reactions at optimum conditions were determined as k = 2.09 x 10^{-4} s^{-1} and 3.74 x 10^{-4} s^{-1} for azure-B and yellowish orange, respectively.

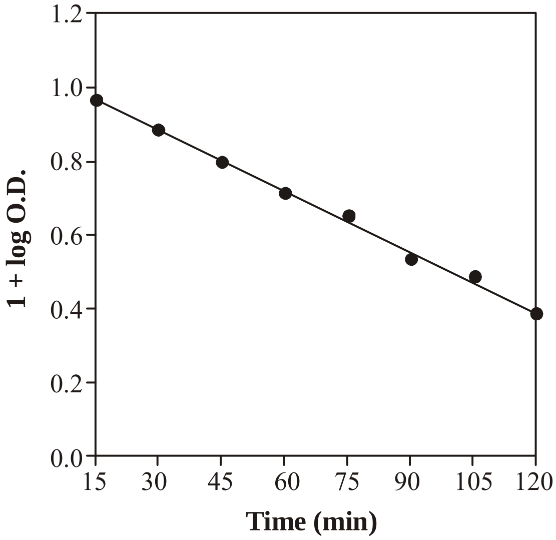

Fig.1: A typical run

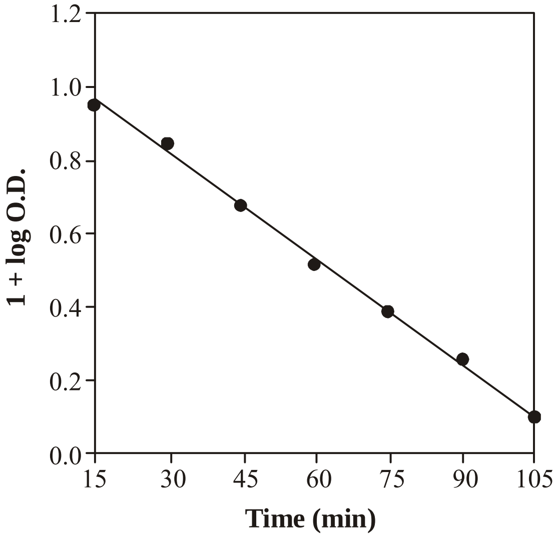

Fig. 2 A typical run

RESULTS AND DISCUSSION

Characterization of La_2CoO_4

The prepared La_2CoO_4 was characterized by X-ray diffraction method. The X-ray diffraction pattern of La_2CoO_4 has been shown in Fig. 3. The graph has been plotted between intensity and 2θ values in degrees (2θ value ranges from 20°-80°).

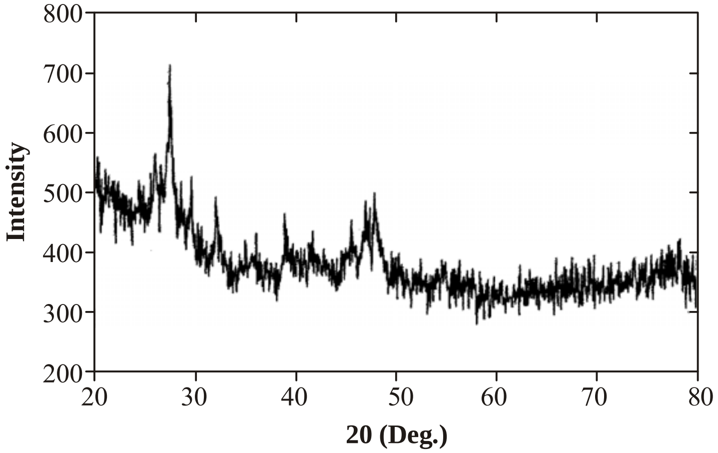

Fig. 3: X-Ray diffraction pattern of La_2CoO_4

Table 1: A typical run

[Azure-B] = 3.33 x 10^{-5}M Light intensity = 70.0 mW/cm^2 La_2CoO_4 = 0.3 g ; pH = 8.0			[Yellowish orange] = 1.66 x 10^{-5}M Light intensity = 70.0 mW/cm^2 La_2CoO_4 = 0.2g ; pH = 6.5		
Time (min.)	**O.D**	**1+ log O.D**	**Time (min.)**	**O.D**	**1+ log O.D**
15	0.915	0.961	15	0.901	0.954
30	0.768	0.885	30	0.690	0.838
45	0.628	0.797	45	0.475	0.676
60	0.514	0.711	60	0.330	0.518
75	0.442	0.645	75	0.245	0.389
90	0.346	0.539	90	0.179	0.252
105	0.299	0.476	105	0.126	0.100
120	0.243	0.385	120	-	-
k = 2.09 x 10^{-4} (s^{-1})			k = 3.74 x 10^{-4} (s^{-1})		

Effect of pH

The effect of pH on the rate of photocatalytic degradation of both dyes were investigated in the range of 6.0- 8.5. The results are reported in Table 2.

Table 2: Effect of pH

[Azure-B] = 3.33×10^{-5}M Light intensity = 70.0 mW/cm^2 La_2CoO_4 = 0.3g		[Yellowish orange] = 1.66×10^{-5}M Light intensity = 70.0 mW/cm^2 La_2CoO_4 = 0.2 g	
pH	**k x 10^4 (s^{-1})**	**pH**	**k x 10^4 (s^{-1})**
6.0	1.74	6.0	3.17
6.5	1.82	6.5	3.74
7.0	1.86	7.0	2.92
7.5	1.90	7.5	2.81
8.0	2.09	8.0	2.61
8.5	1.64	8.5	1.87

It is evident from the data that the rate of degradation of azure-B increases with increase in pH upto 8.0 and above this value of pH, there is a decrease in the rate of photocatalytic degradation of dye. It may be explained on the basis that at higher values of pH, the dye does not remain in its cationic form due to greater concentration of OH^- ions and as such, the force of attraction between dye molecules and negatively charged semiconductor surface decreases. Therefore, the approach of dye molecules towards photocatalyst becomes slow. As a result, the rate of reaction decreases.

In case of yellowish orange, the rate of degradation of increases with increase in pH upto 6.5 and above this value of pH, there is a decrease in the rate of photocatalytic degradation of dye. It may be explained on the basis that at higher values of pH, the surface of photocatalyst become negatively charged due to greater concentration of OH ions and the dyes in its anionic form will face a force of repulsion and as such rate of reaction decreases.

Effect of amount of semiconductor

The amount of semiconductor also affects the rate of degradation of dye. The effect of variation of amount of semiconductor was studied by taking different amounts of La_2CoO_4 (0.15 g - 0.4 g). The results are reported in Table 3.

Table 3: Effect of amount of semiconductor

[Azure-B] = 3.33 x 10^{-5}M Light intensity = 70.0 mW/cm^2 pH = 8.0		[Yellowish orange] = 1.66 x 10^{-5}M Light intensity = 70.0 mW/cm^2 pH = 6.5	
La_2CoO_4 (g)	**k x 10^4 (s^{-1})**	**La_2CoO_4 (g)**	**k x 10^4 (s^{-1})**
0.15	1.26	0.15	3.21
0.20	1.72	0.20	3.74
0.25	1.91	0.25	3.40
0.3	2.09	0.3	3.37
0.35	1.59	0.35	3.31
0.40	1.20	0.40	3.15

It has been observed that as the amount of semiconductor was increased, the rate of photodegradation of dyes also increased but ultimately, the rate becomes constant after a certain amount (0.3 g and 0.2 g for azure-B and yellowish orange, respectively). It may be explained on the basis that as the amount of La_2CoO_4 was further increased, there is no increase in the exposed surface of the photocatalyst. It may be considered like a saturation point. After this saturation point, increase in amount of photocatalyst increases the thickness of layer only, as the bottom of the reaction vessel was already covered by photocatalyst.

Effect of concentration of azure-B and yellowish orange

The concentration of dye was varied from 1.66 x 10^{-5} M - 10.0 x 10^{-5} M and 0.83 x 10^{-5} M - 5.0 x 10^{-5}M for azure-B and yellowish orange, respectively. The results are reported in Table 4.

It has been observed that the rate of photocatalytic degradation increases with increase in concentration of dye up to 3.33 x 10^{-5} M and 1.66 x 10^{-5} M for azure-B and yellowish orange, respectively. This can be explained on the basis that as the concentration of dye was increased, more dye molecules were available for excitation and consecutive degradation and hence, an increase in rate of reaction was observed. The rate of photocatalytic degradation was found to decrease with further increase in the concentration of dye. This may be due to the fact that the dye started acting as a filter for the incident light and it would not permit the desired light intensity to reach semiconductor surface; thus, decreasing the rate of degradation of dyes.

Table 4: Effect of concentration of dyes

La_2CoO_4 = 0.3 g Light intensity = 70.0 mW/cm^2 pH = 8.0		La_2CoO_4 = 0.2 g Light intensity = 70.0 mW/cm^2 pH = 6.5	
[Azure-B] x 10^5 M	**k x 10^4 (s^{-1})**	**[Yellowish orange] x 10^5 M**	**k x 10^4 (s^{-1})**
1.66	1.62	0.83	2.38
3.33	2.09	1.66	3.74
5.00	1.79	2.50	3.34
6.66	1.59	3.33	2.99
8.33	1.24	4.16	2.34
10.00	1.23	5.00	2.08

Effect of light intensity

The effect of light intensity was studied by changing the distance between light source and the exposed surface of area (30 mW/cm^2 - 70 mW/cm^2). The results are reported in Table 5.

Table 5: Effect of light intensity

[Azure-B] = 3.33 x 10^{-5}M pH = 8.0 La_2CoO_4 = 0.3 g		[Yellowish orange] = 1.66 x 10^{-5}M pH = 6.5 La_2CoO_4 = 0.2 g
Light intensity (mw/cm^2)	**k x 10^4 (s^{-1})**	**k x 10^4 (s^{-1})**
30.0	1.25	0.59
40.0	1.28	1.10
50.0	1.33	1.14
60.0	1.58	3.00
70.0	2.09	3.74

The degradation 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. However, higher intensities were avoided assuming that it may cause thermal effects.

Mechanism

On the basis of experimental observations, the following tentative mechanism may be proposed for the photocatalytic degradation of azure-B and yellowish orange (Dye).

$$^{1}\text{Dye}_0 \xrightarrow{h\nu} {}^{1}\text{Dye}_1 \quad \ldots(2)$$

$$^{1}\text{Dye}_1 \xrightarrow{I\text{SC}} {}^{3}\text{Dye}_1 \quad \ldots(3)$$

$$\text{SC} \xrightarrow{h\nu} \text{SC}^{*}\ [\text{h}^{+}\ (\text{VB}) + \text{e}^{-}\ (\text{CB})] \quad \ldots(4)$$

$$^{3}\text{Dye}_1 + \text{e}^{-} \longrightarrow {}^{3}\text{Dye}_1^{-}\ (\text{Leuco form}) \quad \ldots(5)$$

$$^{3}\text{Dye}_1^{-}\ (\text{Leuco form}) \longrightarrow \text{Colourless products} \quad \ldots(6)$$

When the solution of dye was exposed to light in presence of semiconductor; initially, the dye molecules were excited first to their excited singlet state. These excited singlet molecules were converted to the triplet state through inter system crossing (ISC). Semiconductor also utilizes radiant energy to excite its electron from valence band to conduction band; thus, leaving behind a hole. This electron present in conduction band may be utilized to reduce the dye in its leuco form, which ultimately degrades to colorless products.

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