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SYNTHESIS AND CHARACTERIZATION OF $CeCrO_3$ AND ITS USE AS A PHOTOCATALYST IN PHOTOCATALYTIC DEGRADATION OF DYES

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ABSTRACT

The photocatalytic degradation of alizarin red and gentian violet on $CeCrO_3$ powder has been observed spectrophotometrically. The effects of variation of different parameters like pH, concentration, amount of semiconductor and light intensity on the rate of degradation has been observed. A tentative mechanism for the photocatalytic bleaching of alizarin red and gentian violet has been proposed.

Key words: $CeCrO_3$, Gentian violet, Alizarin red, Photocatalyst.

INTRODUCTION

The world is facing an ever increasing pace of water pollution. Various pollutants like acids, alkalies, detergents, soaps, phenols, cyanides, pesticides, insecticides, fungicides, etc. are released for different chemical industries and pollute our water resources. Pollution is also caused by industrial wastes of leather tanneries, paper, breweries, sugar, slaughter houses, textile, dyeing, printing, steel mills, distilleries and pharmaceutical units. Such contaminated water containing obnoxious toxic substances damage the biological activity and kills useful organisms; thus, posing a serious threat to human life and aquatic biota. One of the oldest and largest industry in our country; the textile industry is in no way different than other chemical industries, which cause water pollution. Dyes present in effluents from the textile industries are difficult to remove by conventional methods as each method has its own limitation. Photocatalytic treatment has been proved to be most effective and economical method for the removal of contaminants found in the textile effluents.

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Photochemistry has played a significant role in many reactions of biological, synthetic and industrial importance in which energy received from Sun can be better utilized for converting the pollutants into less toxic materials.

Alton and Ferry[1] used $SiW_{12}O_4$ as a photocatalyst for the photocatalytic degradation of acid orange-7. Preparation, characterization and photocatalytic activity of boron and cerium-codoped TiO_2 was studied by Wel et al.[2] Kako et al.[3] have suggested some preventive methods against catalytic poisoning of TiO_2 photocatalyst by H_2S. Photocatalytic degradation of methylene blue on Bi_2MNbO_7 (M= Al, Fe, ln,Sm). Sol-gel catalysts have been studied by Lorenal et al.[4] while Chittora et al.[5] studied the photoreduction of CO_2 in presence of some photocatalysts like ZnO, Fe_2O_3, etc. Jose et al.[6] synthesized lanthanum chromium oxide catalyst using co-precipitation method and specific heating cycles and it was characterized by using X-ray diffraction patterns. They also studied the photocatalytic bleaching of azure-B using lanthanum chromium oxide while the photocatalytic behaviour of a new composite ternary system: $WO_3/SiC\text{-}TiO_2$ and effect of coupling of semiconductors and oxides in photocatalytic oxidation of methylethylketone in gas phase was investigated by Kellar and Garin[7].

Photocatalytic degradation of nitrobenzene with combustion synthesized nano - TiO_2 was investigated by Priya and Madras[8]. Kale et al.[9] synthesized a novel photocatalyst, $ZnBiVO_4$ for the photodecomposition of H_2S. Kim et al.[10] used ZnO coated TiO_2 nanoparticles for the flexible dye-sensitized solar cells. Use of semiconducting iron (III) oxide in photocatalytic degradation of methylene blue has been reported by Ameta et al.[11] Photoreduction of CO_2 and water into formaldehyde and methanol on aqueous suspension of $SrTiO_3$ and TiO_2 was investigated by Blajeni et al.[12] Photodegradation of dye pollutants on one dimensional TiO_2 nanoparticles under UV and visible irradiation was investigated by Chen et al.[13]. Adalgisa et al.[14] studied electrochemically assisted photocatalytic degration of reactive dyes while Wang et al.[15] studied photocatalytic degradation and kinetics of orange-G using sized Sn (IV) - TiO_2 as a photocatalyst.

Effect of CeO_2 and La_2O_3 on the activity of $CeO_2\text{-}La_2O_3/Al_2O_3$ supported Pd catalysts for steam reforming of CH_4 was investigated by Cassinelli et al.[16]. Jung et al.[17] studied the local structure and photocatalytic activity of $B_2O_3\text{-}TiO_2$ ternary mixed oxide prepared by sol-gel method. Enhancement of activity and self-reactivation of NSR-catalysts by temporary formation of $BaPtO_3$-perovskite was reported by Casapu et al.[18]. In present investigation, the semiconducting properties of synthesized $CeCrO_3$ photocatalyst are utilized for photocatalytic bleaching of alizarin red and gentian violet.

EXPERIMENTAL

Synthesis of ternary oxide by coprecipitation method

$CeCrO_3$ was prepared by coprecipitation of metal nitrates. The 0.2 M aqueous solution of chromium nitrate was added to the 0.2M aqueous solution of $(NH_4)_2$ Ce (NO_3) to make the volume upto 100.0 mL. Now, aqueous ammonium hydroxide solution was added rapidly to the aqueous mixed nitrate solution and the pH of the solution was maintained at 8.5 at room temperature.

Heat treatment

The precipitate along with the supernatant solution was kept in an oven at 110°C for 15-16 hours for drying the precipitate. Subsequently, stepwise calcinations were performed by heating. The precipitate was dried 0.5 h at 150°C, 2 h at 400°C, 3 h at 500°C and 24 h at 600°C. The dried precipitate was heated in the muffle furnace. The calcinations at 600°C was completed in four days with 6 h heating everyday. After the heating, the material was furnace-cooled everyday and was grounded in acetone with a pestle and mortar. The grounded material was further heated on the next day at the terminal temperatures. The calcinations temperature and heating treatment schedules are reported in Table 1.

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	1.0
6.	350	1.0
7.	400	2.0
8.	450	2.0
9.	500	3.0
10.	550	3.0
11.	600	24.0

XRD study

The prepared ternary oxide was characterized by X-ray diffraction method. Fig. 1 presents the X-ray diffraction patterns of $CeCrO_3$. Table 2 shows the characteristic peaks of $2\theta = 22^{o}.84$ to $86^{o}.61$, which correspond well with $CeCrO_3$ stoichiometry X-ray patterns.

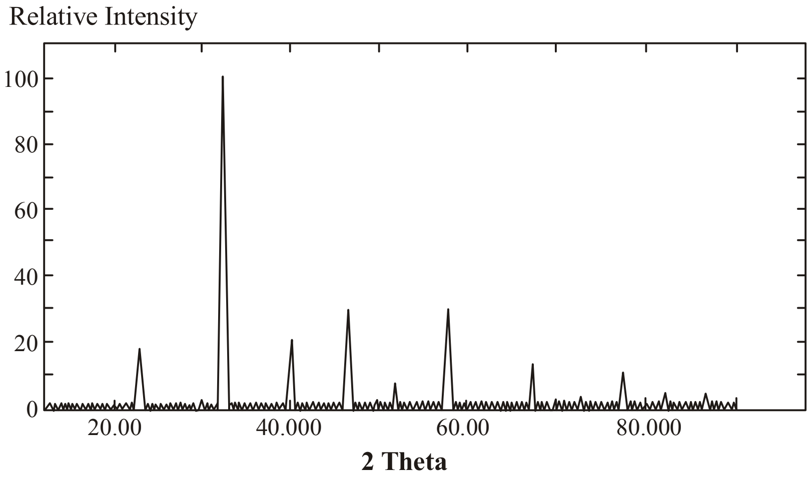

Fig. 1: XRD of $CeCrO_3$

Table 2: XRD data of $CeCrO_3$

No.	2theta (2θ)	d-value	Intensity	hkl
1.	22.841	3.890	18	100
2.	32.523	2.751	100	110
3.	40.115	2.246	20	111
4.	46.629	1.945	29	200
5.	51.370	1.683	7	210
6.	58.027	1.588	29	211
7.	68.119	1.375	13	220
8.	72.886	1.297	3	221
9.	76.590	1.195	4	310
10.	82.100	1.173	4	311
11.	86.615	1.123	4	222

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, these are matched with the 2θ values obtained from the sample.

The occurrence of prominent peaks (which are numbered from 1 to 11 in Table 2). indicated that there is a maximum possibility of phase $CeCrO_3$ stoichiometry in the sample prepared.

Experimental procedure of photocatalytic bleaching of dye (alizarin red and gentian violet)

Alizarin red, gentian violet and $CeCrO_3$ were used in the present investigation. The stock solutions of dyes were prepared in doubly distilled water. The photocatalytic degradation of dyes was observed by taking dye solution and adding different amounts of $CeCrO_3$ to it. Irradiation was carried out keeping whole assembly exposed to a 200 W tungsten lamp (Philips). The intensity of light was measured with the help of solarimeter (SM CEL 201). The pH of the solution was measured by the digital pH meter (Systronics Model 335). The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solutions. The optical density (O.D) of the dye solution was measured spectrophotometrically (Systronics Model 106). The necessary condition is that the solution must be free from semiconductor particles and impurity. The progress of the photocatalytic reaction was observed by taking optical density of the dye solution at regular time intervals.

RESULTS AND DISCUSSION

The photocatalytic degradation of gentian violet and alizarin red was observed at λ_{max} = 580 nm and λ_{max} = 555 nm, respectively. The typical run has been presented in Table 3 and graphically presented in Fig. 2. Its was observed that the optical density (O.D) of dye solution decreases in presence of the semiconductor and light. The plot of log OD v/s time was linear and hence, this reaction follows pseudo- first order kinetics. The rate constant for this reaction was determined using the expression.

$$K = 2.303 \text{ x slope} \qquad \ldots(1)$$

Effect of pH

The effect of pH on photocatalytic degradation was also investigated. The results are reported in Table 3.

Table 3: Effect of variation of different parameters

Rate constant x 10^4 (s^{-1})			Rate constant x 10^4 (s^{-1})			Rate constant x 10^4 (s^{-1})			Rate constant x 10^4 (s^{-1})		
pH	**AR**	**GV**	**[Dye] x 10^5 M**	**AR**	**GV**	**Amount of $CeCrO_3$ (g)**	**AR**	**GV**	**Light intensity (mWcm^{-2})**	**AR**	**GV**
4.0	0.61	-	0.6	-	0.81	0.02	1.13	-	10	0.90	-
4.5	0.82	-	0.8	-	0.93	0.03	-	-	20	1.14	0.76
5.0	0.95	-	1.0	0.70	1.10	0.04	1.19	-	30	1.40	0.98
5.5	1.22	-	1.1	0.85	-	0.05	-	0.78	40	1.60	1.03
6.0	1.53	0.93	1.2	1.12	1.56	0.06	1.24	-	50	1.70	1.21
6.5	1.70	1.16	1.3	1.62	-	0.07	-	1.09	60	2.06	1.33
7.0	1.58	1.39	1.4	1.70	1.38	0.08	1.48	-	70	2.30	1.39
7.5	1.30	1.43	1.5	1.49	-	0.09	-	1.12	80	2.51	1.48
8.0	1.10	1.56	1.6	1.45	1.02	0.10	1.70	-	90	-	1.56
8.5	-	1.32	1.6	1.45	1.02	0.11	-	1.56	-	-	-
9.0	-	1.14	1.8	-	0.78	0.12	1.73	-	-	-	-
-	-	-	-	-	-	0.13	-	1.54	-	-	-
-	-	-	-	-	-	0.14	1.76	-	-	-	-
-	-	-	-	-	-	0.15	-	1.56	-	-	-
-	-	-	-	-	-	0.16	1.72	-	-	-	-
-	-	-	-	-	-	0.17	-	1.53	-	-	-

AR = Alizarin red; GV = Gentian violet

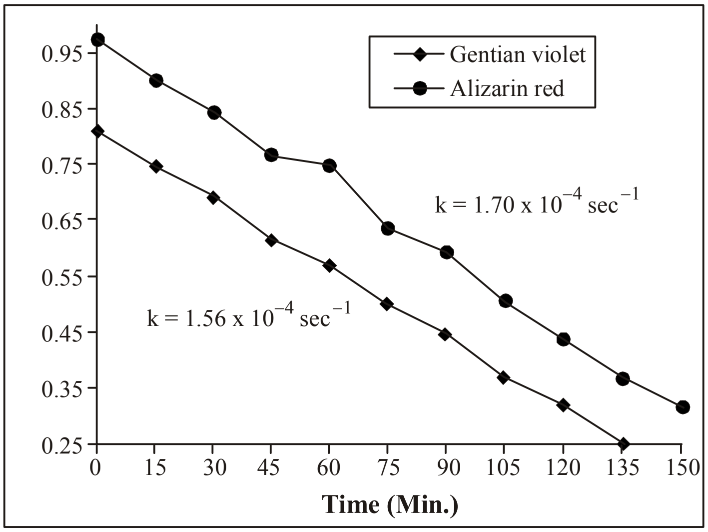

Fig. 2: A typical run

It is evident from the data that the rate of photocatalytic bleaching of dyes increases with increase in pH. The increase in the rate of photocatalytic bleaching may be due to availability of the dye in its anionic form, which is attracted towards positively charged surface of the semiconductor.

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 but is electron rich due to presence of lone pair on two nitrogen atoms. Therefore, these molecules will face a force of repulsion form negatively charged surface of the semiconductor, thus, resulting into a decrease in the rate of reaction.

Effect of dye concentration

Effect of variation of dye concentration was studied by taking different concentrations of dye. The results are reported in Table 3.

It has been observed that the rate of photocatalytic bleaching increases with an increase in the concentration of the dye. It may be due to the fact that as the concentration of the 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 further increase in the concentration of dye. The may be attributed to the fact 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; thus, decreasing the rate of photocatalytic bleaching of dye.

Effect of amount of semiconductor

The effect of amount semiconductor is also likely to affect the process of dye bleaching and therefore, different amounts of semiconductor were used. The results are reported in Table 3.

It has been observed that as the amount of semiconductor was increased, the rate of photodegradation of dye increases but ultimately, the rate becomes constant after a certain limit. If the amount of $CeCrO_3$ was further increased, then 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 semiconductor has negligible or no effect on the rate of photocatalytic bleaching of dye, 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 it is covered by a photocatalyst. Vessels of different dimensions were used to confirmed this fact.

Effect of light intensity

To investigate the effect of light intensity on the photocatalytic bleaching of dye, the distance between the light source and the exposed surface area was varied. The results are reported in Table 3.

The data indicate that 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. An almost linear behaviour between light intensity and rate of reaction was observed.

Mechanism

On the basis of experimental observations, a tentative mechanism for photocatalytic degradation of dye may be proposed as –

$$^{1}\mathrm{Dye}_{o} \xrightarrow{h\nu} {}^{1}\mathrm{Dye}_{1} \qquad \ldots(2)$$

$$^{1}\mathrm{Dye} \xrightarrow[\mathrm{ISC}]{h\nu} {}^{3}\mathrm{Dye}_{1} \qquad \ldots(3)$$

$$^{3}\mathrm{Dye}_{1} + \mathrm{CeCrO_3} \longrightarrow \mathrm{Dye}^{\cdot+} + [\mathrm{CeCrO_3}]^{-} \qquad \ldots(4)$$

$$[CeCrO_3]^- + O_2 \longrightarrow O_2^{-\bullet} \quad \ldots(5)$$

$$^3Dye +\cdot\ OH^- \longrightarrow Dye + {}^\bullet OH \quad \ldots(6)$$

$$^3Dye + {}^\bullet OH \longrightarrow \text{Colourless products} \quad \ldots(7)$$

Dye absorbs radiations of suitable wavelength and it goes to its first excited state. It then undergoes intersystem crossing (ISC) to give the triplet state of the dye. This triplet state may donate an electron to the semiconductor and the dye becomes positively charged. The dissolved oxygen of the solution may pull an electron form the conduction band of semiconductor; thus, regenerating the semiconductor and forming superoxide anion radical. The positively charged molecule of dye will immediately react with hydroxyl ion to form $^\bullet$OH radical. These $^\bullet$OH radicals act as an active oxidizing species to oxidize dye molecules to final products of degradation, which was confirmed by carrying out the reaction in presence of $^\bullet$OH radical scavenger, where the reaction rate was drastically retarded.

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