



Degradation of some dyes using nanosized CeCuO₃ photocatalyst: synthesis and characterization

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Abstract

CeCuO₃ nanoparticles with diameter 4.36 nm was synthesized by a fast and simple microwave method using ceric sulphate tetra hydrate and copper sulphate pentahydrate as starting reagents. CeCuO₃ was synthesized under microwave heating for 6 min without calcining steps. The synthesized products were characterized by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM) and the photocatalytic behaviour of nanosized CeCuO₃ was also studied spectrophotometrically through decolorization of yellowish orange and fast green dyes, a prompt water pollutant from textile industries. The effect of variation of different parameters i.e. pH, amount of CeCuO₃, concentration of dye and light intensity was observed on the rate of photocatalytic bleaching. A Tentative mechanism for the photocatalytic bleaching of dyes has been proposed.

Keywords: Photocatalyst; CeCuO₃; Fast green; Yellowish orange; Dye; Bleaching.

1. Introduction

Dyes are quite useful humanity but are toxic and carcinogenic in nature also. An attempt is made to degrade these dyes by using photocatalysts. Semiconductor photocatalysis has been predicted as a promising technology for solving the problem of environmental pollution. Generally, binary chalcogenides (i.e. oxides and sulphides) are being used as photocatalysts [1-3]. The use of ternary oxides like SrTiO₃ 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 3-d transition metal ions for the preparation of ternary oxides. By changing size of semiconducting particles, it is possible to enhance the redox potential of valence band holes and conduction band electrons [4] and hence, photocatalytic activity [5-7].

Nanocrystalline anatase and rutile TiO₂ has been synthesized by controlled hydrolysis of titanium tetraisopropoxide and used for the degradation of acetophenone, nitrobenzene, methylene blue and malachite green by Tayade et al. [8]. Microwave assisted synthesis of different nanoparticles and their photocatalytic activity have been reported by various researchers i.e. MnFe₂O₄ [9], CuO [10], Bi₂WO₆ [11], Bi₂O₃ [12], Co₃O₄ [12] and TiO₂ [13] etc.

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Semiconducting photocatalysis has been used by Hachem et al. [14] for the degradation of orange-11, orange-G, congo red, indigo carmine, crystal violet, malachite green, remazol blue and methyl yellow. In the present work, nanosized cerium copper oxide was synthesized, characterized and used as photocatalyst for the degradation of fast green and yellowish orange dyes. A comparison between the rates of photocatalysis of two dyes was also established.

2. Experimental

2.1. Synthesis of Precursor

0.1 mol L⁻¹ aqueous solution of copper sulphate pentahydrate was mixed with the 0.1 mol L⁻¹ aqueous solution of ceric sulphate tetrahydrate followed by the quick feeding of aqueous sodium hydroxide (6 mol L⁻¹) with pH maintaining at 10. It is established that dictating the size of the nanoparticle [15] and the morphology and particle size [16] is controlled by the molar ratio of starting materials and the type of anion respectively. The precipitation of respective hydroxides at different pH (9, 9.5, 10 and 10.5) was performed and it was concluded that the pH 10 is most suitable for the precipitation of hydroxides of ternary oxide. The solution is continuously stirred for 10 hrs. at room temperature so that hydroxides might completely precipitate.

2.2. Microwave Treatment

The filtered precipitate was kept in an oven at 60 °C for 24 hours for drying the precipitate. Dried precipitate was grounded in acetone with a pestle and mortar. Grounded material was irradiated with microwave radiations for 6 min. Then the synthesized nanosized bimetal oxide was washed with dil. acetic acid to separate CeO₂ and CuO side products.

2.3. Materials and Methods

Yellowish orange (CDH) dye, fast green (CDH) dye and CeCuO₃ (synthesized) as a photocatalyst were used in the present investigation. 1.0 × 10⁻³ mol L⁻¹ solution of both dyes were prepared in doubly distilled water and stored as a stock solution in dark. The photocatalytic degradation of dyes was observed by taking dye solution of 1.33 × 10⁻⁵ mol L⁻¹ and 0.02 g CeCuO₃ for fast green and 1.50 × 10⁻⁵ mol L⁻¹ and 0.06 g CeCuO₃ for yellowish orange. Irradiation was carried out keeping whole assembly exposed to a 200 W tungsten lamp (Philips, light intensity = 70.0 mWcm⁻²). 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.) was measured spectrophotometrically (Systronics Model 106) following the necessary conditions that the solutions are free from semiconductor particles and impurity. The progress of the photocatalytic reaction was observed by taking optical density at room temperature with regular time intervals.

2.4. Photocatalytic activity of CeCuO₃

A cutoff water filter was placed outside the beaker (Pyrex) to completely remove any thermal radiation just to ensure illumination by visible light. A 50 mL beaker was filled with 30 mL of dye solution containing photocatalyst. The mixture was sampled to assay at given time intervals by recording variation of the absorbance at 620 and 480 nm for fast green and yellowish orange, respectively. The change in the maximum absorption versus irradiation time was obtained. The typical run has been presented in Table 1. It was observed that the O.D. of dye solutions decreases in presence of the semiconductor and light. The plot of log O.D. 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 $k = 2.303 \times \text{slope}$. The rate constant for these reactions at the optimum conditions were determined as $k = 3.71 \times 10^{-4}$ and $9.75 \times 10^{-5} \text{ s}^{-1}$ for fast green and yellowish orange, respectively.

Table 1

A typical run.

Yellowish orange [Yellowish orange] = $1.50 \times 10^{-5} \text{ mol L}^{-1}$ [CeCuO ₃] = 0.06 g pH = 8.0 Light intensity = 70.0 mW cm^{-2}			Fast green [Fast green] = $1.33 \times 10^{-4} \text{ mol L}^{-1}$ [CeCuO ₃] = 0.02 g pH = 8.0 Light intensity = 70.0 mW cm^{-2}		
Time (min.)	Absorbance	1 + log (Absorbance)	Time (min.)	Absorbance	1 + log (Absorbance)
0	0.212	0.3268	0	0.739	1.8686
15	0.192	0.2842	10	0.587	1.7688
30	0.177	0.2483	20	0.456	1.6589
45	0.162	0.2091	30	0.367	1.5653
60	0.149	0.1743	40	0.295	1.4683
75	0.135	0.1313	50	0.231	1.3638
90	0.125	0.0964	60	0.187	1.2733
105	0.116	0.0625	70	0.151	1.1789
120	0.106	0.0241	80	0.121	1.0836
$k = 9.75 \times 10^{-5} \text{ s}^{-1}$			$k = 3.71 \times 10^{-4} \text{ s}^{-1}$		

3. Results and discussion

3.1. Characterization

The prepared nanosized CeCuO₃ was characterized by X-ray diffraction method and scanning electron microscopy. Fig. 1 presents the X-ray diffraction patterns of CeCuO₃. The graph has been plotted between intensity (cycles per second) and 2θ values (in degree), for general consideration 2θ value ranges from 20° - 80° .

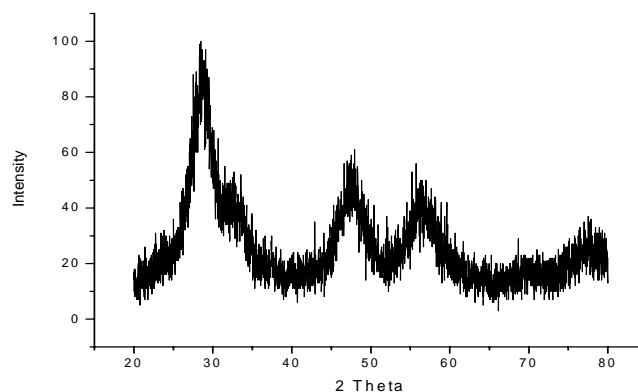
**Fig. 1.** X-ray diffraction of CeCuO₃.

Fig. 2 represents the scanning electron microscopy (SEM) of CeCuO₃ nanoclusters. It shows size of nanocluster 2 μm at 7500x magnification. It was performed on JEOLJSM 5600 operated at 0.5 to 30 KV, whose resolution power is up to 3.5 nm. The number-weighted average particle size was found to be comparable with the volume-weighted mean size obtained from the broadening of the X-ray diffraction lines (Scherer Formula).

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where D is crystallite size and its calculated value is 4.36×10^{-9} m; K is a constant depending upon crystal structure; λ is the wavelength used in XRD (5.4×10^{-10} m); β is full width of half maxima (FWHM) and θ is Bragg's angle.

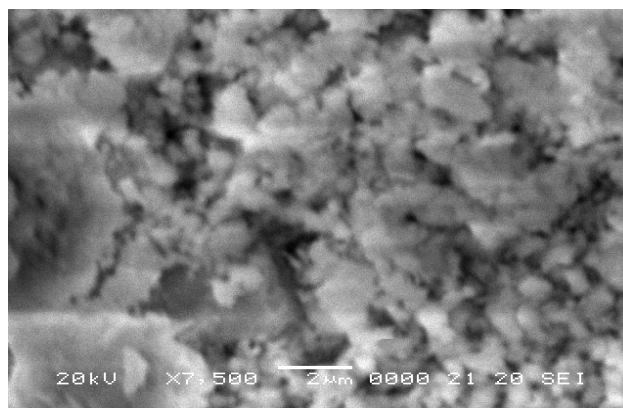


Fig. 2. Scanning electron Microscopy of CeCuO₃.

3.2. Effect of pH

The effect of pH on photocatalytic degradation was also investigated. The results are reported in Table 2.

Table 2
Effect of pH.

Yellowish orange [Yellowish orange] = 1.50×10^{-5} mol L ⁻¹ [CeCuO ₃] = 0.06 g Light intensity = 70.0 mW cm ⁻²		Fast green [Fast green] = 1.33×10^{-4} mol L ⁻¹ [CeCuO ₃] = 0.02 g Light intensity = 70.0 mW cm ⁻²
pH	k × 10⁵ s⁻¹	k × 10⁴ s⁻¹
4.5	-	0.83
5.0	-	1.06
5.5	4.25	1.16
6.0	4.59	1.20
6.5	4.85	1.70
7.0	4.90	2.04
7.5	5.74	2.42
8.0	9.75	3.71
8.5	6.64	2.70
9.0	6.54	-

It is evident from the data that the rate of bleaching of both dyes increases with increasing pH of mixture up to 8.0 and above this value of pH, there is a decrease in the rate of photocatalytic bleaching of dye. It may be explained on the basis that at higher pH the surface of the semiconductor becomes negatively charged and the dye remains in its neutral form; however, the dye is electron rich due to presence of lone pairs on two nitrogen atoms. Therefore, these electron rich molecules of dye will face a force of repulsion from negatively charged surface of the semiconductor; thus, resulting into a decrease in the rate of reaction.

3.3. Effect of concentration of dyes

The concentration of dye was varied from 0.33×10^{-5} to 1.50×10^{-5} M and 0.06×10^{-5} to 1.83×10^{-5} mol L⁻¹ for fast green and yellowish orange, respectively. The results are reported in Table 3. It has been observed that the rate of photocatalytic bleaching increases with increase in the concentration of the dye up to 1.33×10^{-5} and 1.50×10^{-5} mol L⁻¹ for fast green and yellowish orange, respectively. It may be due to the fact that as the concentration of the dye was increased, more dye molecules were available for excitation and consecutive degradation 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 starts acting as a filter for the incident light and it does not permit the desired light intensity to reach the semiconductor surface in a limited time domain; thus, decreasing the rate of photocatalytic bleaching of dyes.

Table 3

Effect of concentration of dyes.

Yellowish orange [CeCuO ₃] = 0.06 g pH = 8.0 Light intensity = 70.0 mW cm ⁻²		Fast green [CeCuO ₃] = 0.02 g pH = 8.0 Light intensity = 70.0 mW cm ⁻²	
[Yellowish orange] × 10 ⁵ mol L ⁻¹	k × 10 ⁵ s ⁻¹	[Fast green] × 10 ⁵ mol L ⁻¹	k × 10 ⁴ s ⁻¹
0.66	2.31	0.33	2.13
0.83	3.28	0.50	2.36
1.00	3.72	0.66	2.41
1.16	4.23	0.83	2.60
1.33	5.64	1.00	2.97
1.50	9.75	1.16	3.33
1.66	8.72	1.33	3.71
1.83	5.54	1.50	2.97

3.4. 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 are reported in Table 4. 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 (0.02 and 0.06 g for fast green and yellowish orange, respectively) of semiconductor. This may be due the fact that after a certain limit, if the amount of CeCuO₃ was further increased; there is no increase in the exposed surface area of the photocatalyst. It may be considered like a saturation point, after this saturation point, with any increase in amount of semiconductor, the thickness of the layer only increases, as the bottom of the reaction vessel is

covered by the photocatalyst. This was also confirmed by taking reaction vessels of different dimensions.

Table 4

Effect of amount of semiconductor

Yellowish orange [Yellowish orange] = 1.50×10^{-5} mol L ⁻¹ pH = 8.0 Light intensity = 70.0 mW cm ⁻²		Fast green [Fast Green] = 1.33×10^{-4} mol L ⁻¹ pH = 8.0 Light intensity = 70.0 mW cm ⁻²	
CeCuO₃ (g)	k × 10⁵ s⁻¹	CeCuO₃ (g)	k × 10⁴ s⁻¹
0.02	3.35	0.008	2.79
0.03	5.01	0.009	3.04
0.04	5.94	0.01	3.30
0.05	6.96	0.02	3.71
0.06	9.75	0.03	3.45
0.07	8.88	0.04	3.42
0.08	8.14	0.05	3.57
0.09	8.17	0.06	3.33
-	-	0.07	3.39
-	-	0.08	3.35

3.5. 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 5. The data indicate that 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 time per unit area of the semiconductor powder. An almost linear behavior between light intensity and the rate of reaction has been observed. However, higher intensities were avoided due to thermal effects.

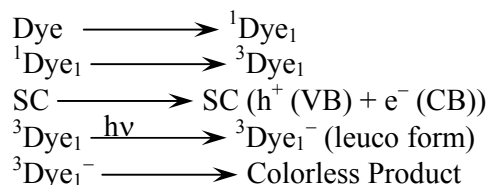
Table 5

Effect of light intensity.

Yellowish orange [Yellowish orange] = 1.50×10^{-5} mol L ⁻¹ [CeCuO ₃] = 0.06 g pH = 8.0		Fast green [Fast green] = 1.33×10^{-4} mol L ⁻¹ [CeCuO ₃] = 0.02 g pH = 8.0	
Light intensity (mW cm⁻²)	k × 10⁵ s⁻¹	k × 10⁴ s⁻¹	
10.0	5.44	2.73	
20.0	6.85	2.94	
30.0	7.55	3.01	
40.0	7.62	3.10	
50.0	8.30	3.21	
60.0	8.94	3.21	
70.0	9.75	3.71	

3.6. Mechanism

On the basis of experimental observations, a tentative mechanism for photocatalytic degradation of yellowish orange may be proposed as:



In the reaction, dye molecules absorb radiations of suitable wavelength and give rise to excited singlet state. Then it undergoes intersystem crossing (ISC) to give the excited triplet state of the dye. Semiconductor also utilizes the radiant energy to excite its electron from valence band to the 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 products. This was also confirmed that $\bullet\text{OH}$ radicals do not act as oxidizing species as the reaction rate remains almost unaffected in the presence of hydroxyl radical scavenger, 2-propanol.

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