



## “Synthesis, characterization and photocatalytic activity of nanocrystalline cadmium carbonate.”

### KEYWORDS

Nanocrystalline CdCO<sub>3</sub>, photodegradation, acid violet dye

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**ABSTRACT** In the present study, nanocrystalline CdCO<sub>3</sub> have been synthesized via simple hydrothermal method by using Cd(NO<sub>3</sub>)<sub>2</sub>, triton and dodecylbenzyl sulphonic acid as reagents. The product was characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDAX), Fourier transform infrared spectroscopy (FT-IR) and Brunauer Elmer Teller (BET) Surface area. The obtained product was further used for photocatalytic degradation of acid-violet dye from its aqueous medium.

### 1. Introduction

Nowadays, Due to the wide range of technological applications of nanostructured CdCO<sub>3</sub> there has been great research interest in the synthesis of CdCO<sub>3</sub>. Cadmium carbonate is an important catalyst in many organic and polymerization processes. It has been used as one of the starting components in the production of photoconductive materials [1]. Their study can be useful in applications such as insulators, composite electrodes, sensors among other devices [2], and stable capsules [3]. Capsules templated on these cores have a higher surface to volume ratio that is valuable for applications related to drug delivery, functional properties of the shells and absorption of proteins and other biologically relevant molecules. CdCO<sub>3</sub> was introduced to give better access to steroidal aryl glucuronides, ortho esters and -anomers whose reactivity is insufficient with other catalysis [4]. The CdCO<sub>3</sub>-In<sub>2</sub>O<sub>3</sub> composite is used as sensors [5]. CdCO<sub>3</sub> is used in industries as one of the main components for the production of high quality inorganic pigments. CdCO<sub>3</sub> finds its main applications in the production of Ni-Cd batteries and for indirect determination of cyanide in a single line FI system. CdCO<sub>3</sub> reagent used is cheap, safe, stable and readily available in every lab [6]. Reaction of the fungus with Cd ion results in Cadmium Carbonate. The reaction leads to detoxification of aqueous solution, potential for bioremediation of heavy metals [7]. CdCO<sub>3</sub>/CdS or CdCO<sub>3</sub>/CdS/CdO photoconductor is produced which works in copying machines without memory problems [8]. CdCO<sub>3</sub> is an important additive in plastics, stabilizers and catalysts. It is also an attractive intermediate for synthesizing terylene [9]. Polyelectrolyte multilayer capsules templated on CdCO<sub>3</sub> cores were found to be less permeable than MF derived capsules [10].

Nanostructured cadmium carbonate has been previously reported in several morphologies including particles [11], wires [12], belts [13,14] and some complex nanostructures [15]. Recently, quasi monocrystals of cadmium carbonate polygonal Cadmium carbonates nanoparticles in crystalline or amorphous state have been used for many applications including diagnostic imaging [16], drug delivery [17], biological separation [18], solar energy transformation, magnetic storage media, electronics industry [19], and catalysts [20]. Especially, amorphous Cadmium carbonates nanoparticles with large surface area may be a good candidate for gas sorption, sensors, and electrode materials [21]. Their disturbed surface structure with a large number of unsaturated bonds endows them with a high catalytic activity and superparamagnetic behavior of nanoparticles in colloidal solutions led to their use as magnetic fluids. Moreover, amorphous nanopowder was found to be a suitable precursor for solid-state systems [22]. Many articles have reported on the preparation of cadmium carbonates and their characteristics.

There have been a number of research on the manufacture of the crystalline cadmium carbonates nanoparticles such as chemical [23,24], physical [25] methods. Whereas, there are limited researches on producing amorphous cadmium carbonate nanoparticles because it requires a high cooling rate to prepare amorphous cadmium carbonates.

Photocatalysis is a promising method among advanced oxidation process, which can be used for degradation of various organic pollutants in water and in waste water [26-29]. In photocatalysis systems a combination of semiconductors (such as PbO, MgO, ZnO, CdS etc.) and UV or visible lights can be used. It is well known that a variety of organic molecules e.g. pesticides, dyes, phenol, halogenated aliphatics and other waste products in water can be effectively decomposed using this technology.

In this study, we have examined the photocatalytic degradation of acid violet dye using nanocrystalline CdCO<sub>3</sub> photocatalyst. Textile industry waste waters are well known to have a wide variation in their composition and treatment with such a pollutant has not been easy. The main contaminant in textile waste water is the color that comes from the dyeing and finishing processes. We have considered that CdCO<sub>3</sub> concentrations can degrade the dye present in aqueous medium.

### 2. Experimental:

All chemicals used for synthesis of CdCO<sub>3</sub> were purchased from Aldrich Chemical and were used without further purification. CdCO<sub>3</sub> nanoparticles synthesized by hydrothermal method were characterized by Infrared spectroscopy (FT-IR) 2400s (Shimadzu). The structural properties of the synthesized materials were studied using X-ray diffractometer-DMAX-2500 (Rigaku) with CuK $\alpha$  radiation, having  $\lambda = 1.5406 \text{ \AA}$ . The surface morphology and chemical composition of synthesized catalyst were analyzed using a Scanning Electron Microscope-JSM-6300 (JEOL) coupled with an energy dispersive spectrophotometer-JEO-2300LA (JEOL). The surface area was recorded with the help of Quantochrome Autosorb Automated Gas sorption system.

#### Preparation of CdCO<sub>3</sub> nanoparticles

A mixture of Y<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub> (1.2 mol) and Triton and dodecyl benzylsulphonic acid (DBSA) (1.5 mol) in double distilled water (10 ml) was stirred for 3 hrs at room temperature. To basify the above solid solution mixture 2N sodium hydroxide (5 ml) was added. This reaction mixture was transferred into steel lined Teflon autoclave and kept in an oven at 120 °C. After the reaction time, the Teflon bottle was cooled naturally at room temperature. The solid product

obtained was filtered, washed with distilled water and dried in oven at 100 °C for 24 hrs. Further, the dried product was calcined at 570 °C for 4 hrs to remove organic matter.

### 3. Result and Discussion:

Figure 1 represents the UV-Visible diffused reflectance spectrum of the synthesized CdCO<sub>3</sub> photocatalyst. The diffused reflectance spectrum depict that absorption goes into UV-visible region. The DRS of the CdCO<sub>3</sub> has absorption edge cut-off at 365 nm with corresponding band in the visible region. The band gap energy ( $E_g = hc/\lambda$ ) for the compound was found to be 3.265 eV. The broad absorption edge shoulder reveals the formation of CdCO<sub>3</sub>. The presence of uneven shape and size of nanocrystals of CdCO<sub>3</sub> could be one of the reasons for the broad absorption peak. The result implies that the sample may possess excellent photocatalytic activity.

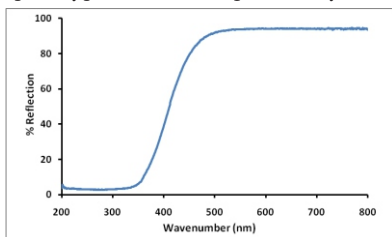


Fig. 1: UV-DRS spectra of CdCO<sub>3</sub> nanoparticles.

The FT-IR spectrum for the synthesized CdCO<sub>3</sub> powder in KBr matrix is depicted in Figure 2. The bands arising from the absorption of atmospheric CO<sub>2</sub> on the metallic cations at 1350 cm<sup>-1</sup> and bonding between Cd-C (639 cm<sup>-1</sup>) are clearly seen in spectra. There is a broad band with very low intensity at 3467 cm<sup>-1</sup> corresponding to the vibration mode of small amount of water adsorbed on the CdCO<sub>3</sub> nanocrystal surface. The band at 1628 cm<sup>-1</sup> is due to the OH bending vibration of water. A strong band at 500 cm<sup>-1</sup> is attributed to the Cd-C stretching band corresponding to the bulky particle was observed in the range from 400-500 cm<sup>-1</sup>.

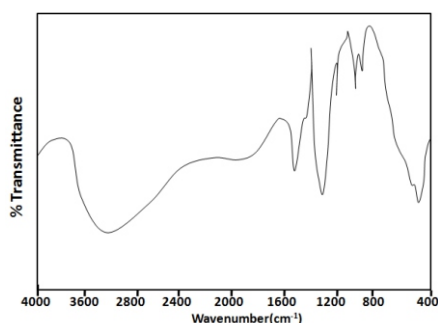


Fig. 2: FT-IR spectrum of CdCO<sub>3</sub> nanoparticles.

Figure 3 depicts XRD pattern of synthesized nanocrystalline CdCO<sub>3</sub> and have peaks due to crystal plane 110, 101, 200, 102, 201 for CdCO<sub>3</sub>. The obtained X-ray diffraction pattern (XRD) pattern is in good agreement with cubic structure of CdCO<sub>3</sub> nanoparticles. The particle size was calculated using Scherer's equation and is 87.50 nm.

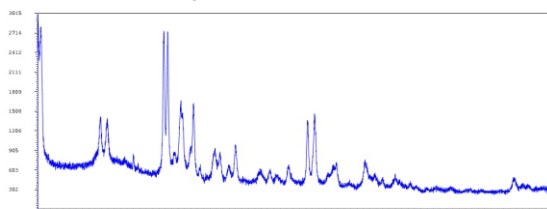


Fig. 3: XRD pattern of CdCO<sub>3</sub> nanoparticles.

In order to investigate surface morphology, the SEM image (Fig. 4) showed crystal morphology and size of the synthesized CdCO<sub>3</sub>

nanoparticles. It shows few crystals are big hexagonal, circular and some are spongy and discrete in appearance.

Figure 4b shows EDAX analysis of CdCO<sub>3</sub> nanoparticles which indicates that presence of carbonates with appropriate stoichiometric amount and confirmed the formation of CdCO<sub>3</sub> nanoparticles.

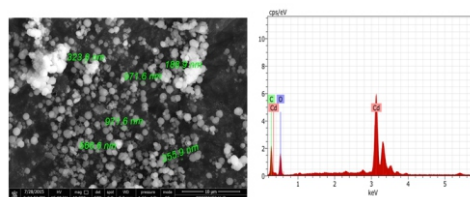


Fig. 4: SEM and EDAX analysis of CdCO<sub>3</sub> nanoparticles.

The BET surface area measurement curve for synthesized nanocrystalline catalyst CdCO<sub>3</sub> are presented in Fig. 5. The N<sub>2</sub> adsorption-desorption isotherm and BJH pore size distribution of both catalyst reveals that the samples have typical IV N<sub>2</sub> adsorption-desorption isotherm with <sup>1</sup>H hysteresis. Both samples show a narrow pore diameter range. Based on the N<sub>2</sub> adsorption-desorption isotherms the specific surface area ( $S_{BET}$ ) of CdCO<sub>3</sub> is 49.46 m<sup>2</sup>/g (Fig. 5a), the average pore volume ( $V_p$ ) and pore diameter ( $d_p$ ) were 0.268 cc/g and 15.67 Å respectively (Fig. 5b).

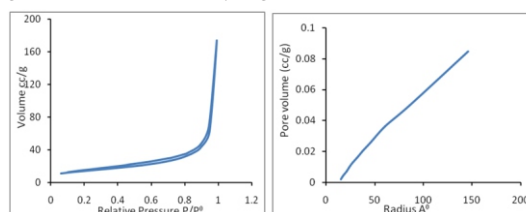
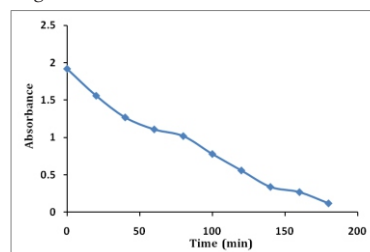


Fig. 5: BET Surface area analysis of CdCO<sub>3</sub> nanoparticles.

### Photodegradation of Dye:

Photodegradation of acid violet dye in aqueous media was investigated using the synthesized catalyst. Photocatalysis experiments were carried out with 1 % (w/w) catalyst sol in, dye concentration of 30 mg/l, 2 hr reaction time and at natural pH. The photodegradation experiments were carried out with UV-visible light. The reaction of the photocatalytic decolorization of acid violet dye was carried out in a 250 cm<sup>3</sup> glass beaker containing 100 cm<sup>3</sup> of a dye solution and 0.5 gm/lit photocatalyst under UV-visible light.

For the subsequent experiments, the dye solution was kept in the dark for 15 min before irradiating to make sure that adsorption was achieved. In the photolysis experiments no variation in acid violet dye concentration was observed. The mixture was then irradiated under UV light. The samples were collected at regular intervals of time (30 min) and concentration changes of dye solution were measured using a UV-Visible spectrometer at 543 nm ( $\lambda_{max}$ ) corresponding to the maximal absorption of the dye. Figure 6 illustrates the photocatalytic degradation of acid violet dye using cadmium carbonates over time by decreasing absorbance to almost zero within 180 min. Figure 6 also shows the decrease in absorbance at various time intervals of acid violet dye under irradiation of simulated UV light with different time interval.



**Fig. 6:** Degradation of Acid violet dye at various time intervals using CdCO<sub>3</sub> catalyst.

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