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Synthesis, Characterization and Photocatalytic capability of CdO Nanoparticle for methyl red

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Abstract:
Nano-sized cadmium oxide was synthesized by a simple hydrothermal method using $CdCl_2.H_2O$ as a metal precursor in the presence of polyethylene glycol and urea. The spectral study of the synthesized nanoparticle was characterized by using UV-Visible Spectroscopy and FT-IR.In addition, we evaluated adsorption of organic dye i.e. methyl red from water using the prepared CdO nanoparticle. UV-visible absorption spectroscopy was used to recordthe adsorption behavior. The result showsthat the degradation percentage was decreases with increase in concentration of the total organic carbon pollutant.
Keywords : CdO nanoparticles, hydrothermal method. Methyl red.

I. Introduction:

In the past few years, much attention has been focused on the research field of nano-crystalline oxide materials both because of their fundamental importance and the wide range of potential technological applications [1–6]. CdO is a degenerate, n-type semiconductor used in optoelectronic applications such as photovoltaic cells [7], solar cells [8], phototransistors [9], IR reflectors [10], transparent electrodes [11], gas sensors [2, 12, and 13] and a variety of other materials. These applications are based on its specific optical and electrical properties [14]. Ethylene glycol in aqueous solution are highly mobile molecules with a large exclusion volume, mostly free of charges, which can avoid the strong interaction between the constituents [15]. There are some reports on the synthesis of CdO nanoparticles for nanowires and nanofilms by chemical co-precipitation or sonochemical methods [2, 16–18], but to the best of our knowledge, there are no reports in the literature dealing with the use of ethylene glycol for the synthesis of CdO. In this work, we report a new and simple method for the synthesis of nano-sized cadmium oxide by autoclave method. The best use of this method is that it requires very less time for synthesis, easy to operate and gives high yield.

The photocatalytic activity of this synthesized dye was studied by using methyl red dye as an organic pollutant. Organic dyes are one of the major groups of pollutants in wastewaters released from textile and other industrial processes. Among various Physical and biological techniques for the treatment of pollutants, precipitation, adsorption, air stripping, flocculation, reverse osmosis, and ultra-filtration can be used for color removal from textile effluents [19]. One of the main environmental applications of nanotechnology is in the water sector. Heterogeneous photocatalysis, one of the advanced oxidation processes (AOPs), is a cost-effective treatment method for the removal of toxic pollutants from industrial waste water sowing to its ability to convert these into safer end products such as CO_2, H_2O, and mineral acids [20-21]. Semiconductor nanoparticles, as heterogeneous photocatalysts, have attracted much interest due to their size tunable physical and chemical properties.

In this context CdO has been synthesized by autoclave combustion method and the kinetics of photocatalytic degradation of methyl red dye using as synthesized CdO nanoparticles as photocatalyst have been reported. Also, effects of CdO photocatalyst of same concentration to different concentration on the degradation of methyl red (MR) have been reported.

II. EXPERIMENTS:

(A) Preparation of ZnO Nanoparticle:

30ml of ethylene glycol used as a stabilizer and 50ml of 1M cadmium choride was stirred for 30 minutes. To that solution 1M of urea was added. The solution turns milky white in colour after addition of urea. The solution was then kept in autoclave so as to reach the reaction temperature time. After autoclaving the system, the white ppt. of the CdO formed. The synthesized ppt. was then washed with distilled water 3 times and alcohol. The ppt. was then dried in oven at 150°C for 5 hours. This synthesized ppt. were then used for characterization and also for the degradation of organic pollutant.

(B) Photocatalytic activity test:

The photocatalytic activity of CdO nanoparticle can be studied using Methyl red $[(CH_3)_2N.C_6H_4.N.N.C_6H_4CHO]$, a widely used dye. The CdO nps synthesized were mixed in methyl red solutions and were examined by using a UV-Visible Spectrophotometer at an wavelength of 650nm (Max. absorbance at 650nm in visible region).The concentration of methyl orange prepared to be 5 ppm, 10 ppm, 15 ppm and 20 ppm.

The experiment was performed as follows:

Different concentration of dye solution were prepared and to each solution same concentration of oxide was mixed. The concentration of the dye solution was 1g/lit. The maximum absorbance of the methyl red solution was measured and then to that wavelength absorbance was noted for the degradation of the dye before the addition of Metal oxide and after addition of metal oxide. This absorbance is noted to be as A_o. And after UV irradiation, the absorbance was again measured at t intervals of time. The total irradiation time is 50 min. The extent of photocatalytic activity of CdO in Methyl red can be determined by measuring the absorbance of the solution. The degradation of methyl red can be evaluated by using the formula:

$$\textbf{Degradation (\%)} = \frac{A_o - A_t}{Ao} \, X\, 100$$

where A_0 represents the initial absorbance and A_t represents the absorbance after t min reaction of the methyl red at the characteristic absorption wavelength of 650 nm.

III. Result and discussion:

Fig1a. exhibits the absorbance spectra of the Methyl red degradation under the irradiation of UV light. According to the principles of CdO photocatalyst, the energy gap are generated on the surface of Cadmium oxide when are irradiated in photon light with either exceeding or equaling the band gap energy, an electron may be promoted from the valence band to the conduction band (e^-_{cb}) leaving behind an electronic vacancy or "hole" in the valence band (h^+_{vb}). If charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with the sorbed species.

Fig 1a-d. shows the UV-Visible absorption spectra of degradation of MR solution with different time. The experimental data was found to fit approximately a first order kinetics by the linear transform equation as:

$$\ln\frac{A_o}{A_t} = kt$$

where k is rate constant.

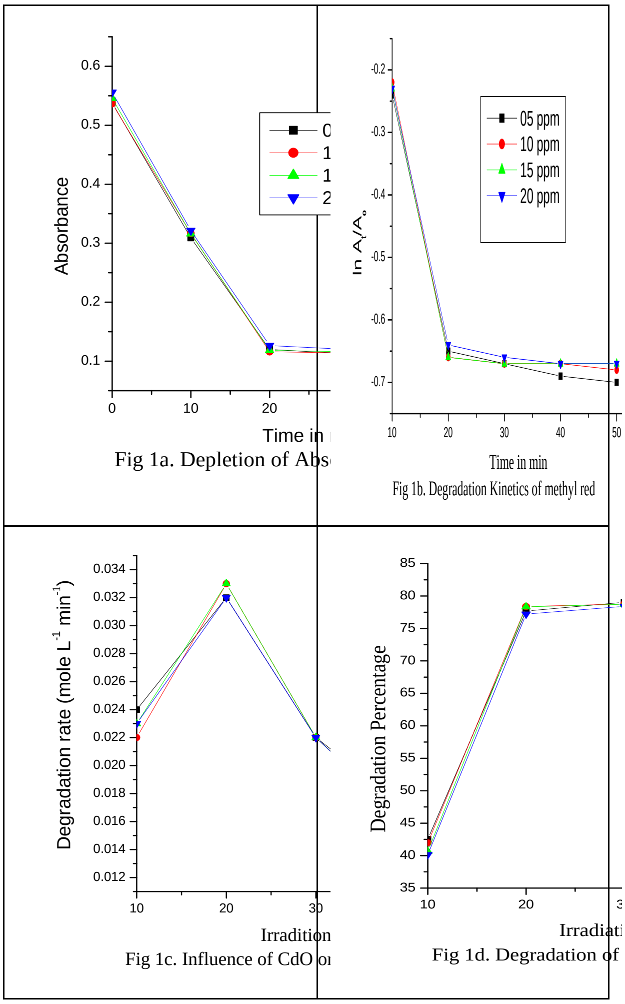

Fig 1a. Depletion of Abs
Fig 1b. Degradation Kinetics of methyl red
Fig 1c. Influence of CdO o
Fig 1d. Degradation of

The highest percent of MR photo degradation is observed for 5ppm solution while the lowest percent of MR photo degradation is observed for 20 ppm as shown in fig 4d. From fig 1b. Kinetics of reaction follows 1st order for the four different concentration of the pollutant. Comparison studies of the dye solution demonstrates the photocatalytic properties of the CdO material decreases due to higher surface areas. At lower concentration of the organic pollutant, loading much of light may be transmitted through the solution. However reaction rates is almost same for the different concentration of the dye but the degradation percentage of the pollutant decrease with the increase in pollutant concentration. The photocatalyst CdO was found to be efficient for the decomposition of the organic pollutant. The decrease in % degradation can be explained in terms of complete utilization of incident photons striking on the catalyst surface or may be possible explanation for this behavior is that as the concentration of the pollutant increases, more and more molecules of the compound get adsorbed on the surface of the catalyst therefore the requirement of the catalyst surface needed for the degradation also increases. Hence the generation of OH^- and O_2^- on the surface of catalyst does not increase; since the amount of catalyst is constant. Hence the degradation efficiency of the organic pollutant decreases with the increase in concentration.

Furthermore, the obtained values of the rate constant of the reaction up to 50min and the percent of degradation of MR solution on cadmium oxide nanoparticles are summarized in the table. The results revealed that photodegradation of MR dye solution obeyed the rules of pseudo first order kinetics reaction.

Concentration of Methyl red	Time in min	Degradation %	K (min/ l min)
5 ppm	50	80.21	$1.39 X 10^{-2}$
10 ppm	50	79.14	$1.34 X 10^{-2}$
15 ppm	50	79.08	$1.34 X 10^{-2}$
20 ppm	50	78.95	$1.34 X 10^{-2}$

FTIR Spectra:

Fig. 2 shows the FT-IR spectra of the obtained precursor of the oxide nanoparticles. The observed peaks are related to the organic groups of the precursor. The absorption bands at 3433 cm^{-1} are attributed to the N-H antisymmetrical and symmetrical stretching vibrations, respectively.

Probably, the overlapping O-H vibration bands of the H_2O molecules with the vibration bands of the functional groups of NH_2 can lead to broaden these bands. The appeared peaks at 1633 and 1346 cm^{-1} are assigned to C=O and C-O stretching vibrations of the carbonyl groups, respectively.

The observed peaks at 812, and 439 cm^{-1} can be attributed to the ν(CO) and ν(CO_2) . Likewise, the appeared peak at 694 and 682 cm^{-1}can be corresponded to the vibration band of formed Cd-O in the precursor.

UV-Visible Spectra:

The UV–visible absorption spectra of CdO nanoparticles are shown in Figure 3.The absorption band of the CdO nanoparticles have been shows a blue shift due to the quantum confinement of the exactions present in the sample compare with bulk CdO particles. This optical phenomenon indicates that these nanoparticles show the quantum size effect. The maximum absorption of the nanoparticles shows at 330nm and band gap energy was calculated to be 3.75eV.

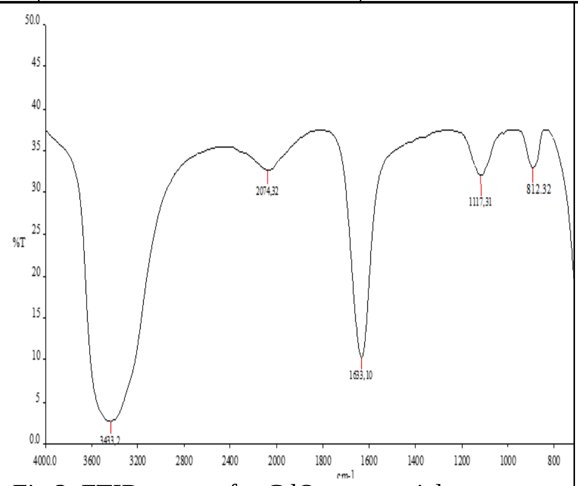

Fig 2. FTIR spectra for CdO nanoparticles

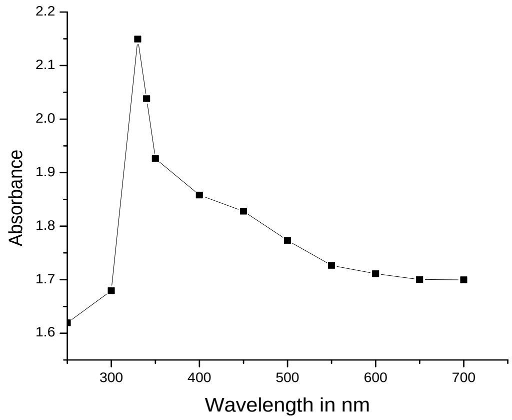

Fig 3. UV-Absorption spectra of CdO nanoparticles

IV. Conclusion:

CdO nanoparticles has been synthesized by autoclave combustion method using very easy, cheap and convenient process. IR and UV-Vis spectral studies The photocatalytic activity of the CdO nanoparticles studied with the help of spectrophotometer by using degradation of methyl red dye solution. Photocatalytic study revealed that CdO decomposes Methyl red. The performance of CdO nanoparticles indicates that it can be used as a photocatalyst for removal of organic contaminants present in water.

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