Synthesis and Characterization of CdO Nanomaterial and their Photocatalytic Activity

A.K.Barve[1], S.M.Gadegone[1], M.R. Lanjewar[2]and R.B.Lanjewar[3*].

[1.] Kamla Nehru Mahavidyalaya, Sakkardara, Nagpur 440009.

[2.] Department of Chemistry, R.T.M Nagpur University, Nagpur 440012.

[3.]Dharampeth M.P. Deo Memorial Science College, Nagpur 440033.

E-mail: rb_lanjewar@rediffmail.com

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 synthesized nanoparticles were characterized by X-Ray diffraction (XRD), transmission electron microscopy (TEM), UV-visible spectroscopy and FT-IR.Also adsorption of methyl red dye was carried out using CdO nanoparticles. The XRD analysis of the nanoparticle showed the crystalline phase with particle size 65nm. UV-Visible spectra and FTIR shows the formation of CdO bond. The TEM studies show the formation of spherical ring structure of the CdO nanomaterial.The photocatalytic activities of CdO nanoparticles were evaluated by measuring the degradation of Methyl red (MR) in water under the UV region. The degradation percentage were found to decrease with increase in concentration of the organic pollutant.

Keywords: *Hydrothermal method, Nanomaterial, Degradation*

*****

1. 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[12-13] 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[16-18]. Liu et al. synthesized CdO nanoneedles by chemical vapour deposition[17]. Zou et al. have prepared CdO nanoparticles by the micro-emulsion method employing AOT reverse micelles[18].Theadvantage of hydrothermal method is that it requires very less time for synthesis, easy to operate and gives high yield.

The photocatalytic activity of CdO nanomaterial was studied using methyl red dye as an organic pollutant. Organic dyes are the main 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 removal of contamination 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 showing 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 paper CdO has been synthesized by hydrothermal method. The nanoparticle has been characterized by TEM, XRD, UV-Visible spectroscopy and FTIR. The photocatalytic activity was also studied for the degradation of organic dye.

2. EXPERIMENTS

2.1 Materials:

The chemicals used (Cadmium chloride, Ethylene glycol and urea) in the preparation were of analytical reagent grade purchased from S-D fine lab. The dye Methyl red was of AR grade from Merck.

2.2 Preparation of CdO Nanoparticle:

30 ml of ethylene glycol used as a stabilizer and 50ml of 1M cadmium chloride was stirred for 30 minutes. To this solution 1M of urea was added. The solution turns milky white after addition of urea. The reaction mixture was kept for 1 hrs. in autoclave. After autoclaving the system, the white precipitate of the CdO formed. The synthesized compound so obtained was then washed with distilled water three times andthen finally with alcohol. The precipitate was then dried in oven at 150^oC for 5 hours. This product were

then used for characterization and also for the degradation of organic pollutant.

2.3 Photocatalytic activity test:

The photocatalytic activity of CdO nanoparticle was studied using Methyl red[$(CH_3)_2N.C_6H_4.N.N.C_6H_4CHO$], a widely used dye. The CdO nanoparticle in a fixed proportion (1g/l) were mixed in methyl red solutions and absorbance were recorded 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 as 5, 10, 15, 20 ppm were prepared and to each solution fixed amount of CdO nanoparticle was added. The concentration of the oxide added to be 1g/lit. The λmax for the dye solution was determined and to that wavelength absorbance was noted for the degradation of the dye. The absorbance was recorded 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:

$$Degradation\ (\%) = \frac{A_o - A_t}{Ao}\ X\ 100 \quad ..(1)$$

whereA_0represents 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.

3. Physiochemical techniques

3.1 Infrared Spectrum:

The infrared spectrum of the solid Cadmium oxide nanoparticle was recorded by Shimazdu FT-IR Spectrometer. The nanoparticle was mixed with KBr powder and spectra was measured.

3.2 TEM:

The particle size of the synthesised nanoparticles was determined by high resolution transmission electron microscopy (HRTEM) operating on TEM, EDAX Boronusing an accelerating voltage of 200 kV.

3.3 XRD:

The obtained nanoparticles were examined by a Brucker D8 advance X-ray Diffractometer with Cu K radiation (λ = 1.54 Å) to check the phase system and purity of the sample.

3.4 UV-Visible Spectrophotometer:

For absorbance spectra and study of photocatalytic activity, Shimazdu 1800 double-beam UV–visible spectrophotometer was used.

4. Result and discussion

a) XRD pattern for CdO nanoparticle:

Fig.1 shows the XRD patterns of the synthesized CdO nanoparticle using Cu Kα radiation (λ = 0.1546 nm). All the diffraction peaks can be well indexed to the cubiccrystalline phase of the CdO nanomaterial, with lattice constants of a=4.689Å. The results indicate that the samples consist of pure phase and are crystalline in nature.The XRD peaks of CdOat 2θ =17.33°,23.53°, 29.48°, 30.32°, 38.74°, 49.79 ° and 53.13°can be respectively indexed to the (200), (220), (331), (222), (331), (440) and (531) plane of crystalline phase(JCPDS 011049).The grain crystalline size of CdO can be calculated using Scherrar's formula:

$$D = \frac{0.94\ \lambda}{\beta\ Cos\ \theta} \quad ..... (2)$$

Where 'λ' is the wavelength of X-rays (1.5406 for Cu kλ), θ is the Bragg's angle, β is the full width at half maximum.

The grain size calculated using the relative intensity peak (222) for CdO nanoparticles was found to be 65 nm.

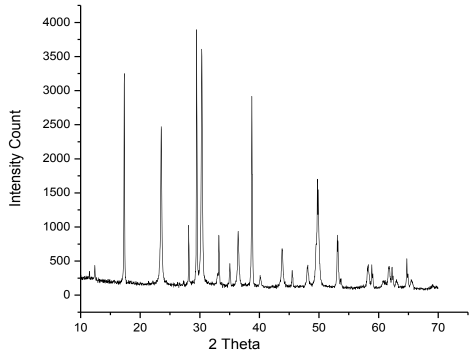

Fig. 1 XRD pattern for CdO nanoparticle

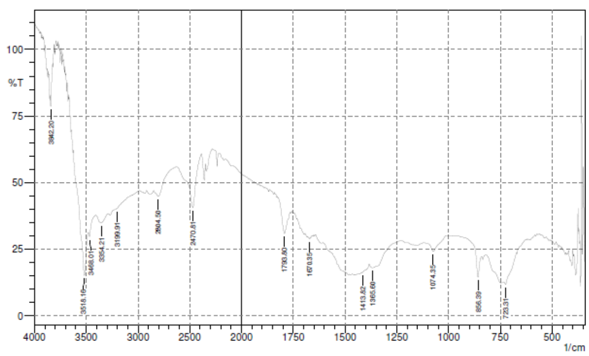

Fig. 2 FTIR spectra for CdO nps

b) FTIR Spectra:

Fig. 2 shows the IR spectra for the sample product CdO nanoparticle. IR spectra shows four characteristic absorption peaks at 3518, 3468, 3354, and 3199 cm^{-1} whichare attributed to the N-Hantisymmetrical and symmetrical stretching vibrations, respectively, and also can be assigned to -OH stretching vibration of water absorbed from the surrounding. The overlapping of –OH bands of H_2O molecule to the vibration bands of NH_2 molecule can results in the broadening of the bands.The other peak at 1793-1365 cm^{-1} corresponds to the C=O and O-C-O stretching vibrations of the carbonyl group. However, the FTIR peaks at 856 and 723 cm^{-1} confirms the formation of CdO bond in the product.

c) UV-Visible Spectroscopy:

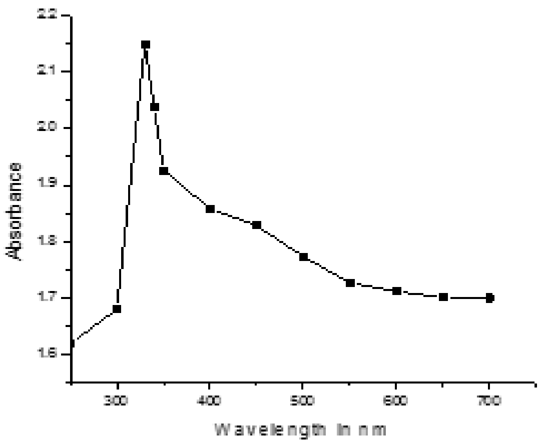

Fig. 3 UV-Visible absorbance spectra of CdO nanoparticle in water

UV– visible absorption of synthesized Cadmium oxide solution illustrates a wide absorption peak centered at 330 nm with a long tail.The band gap of semiconductor materialsincreases with the decrease in particles size, which leads to the shift of the absorption edge toward high energy; this is the so-called quantum size effectThe 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 peak observed at 390 nmcorresponds to the band-edge emission of the CdO nanocrystals[23].The maximum absorption of the nanoparticles shows at 330nm and band gap energy was calculated to be 3.75eV. The optical band gap, Eg, of thesamples are determined from the absorbance spectra, from the given equation:

$$E = \frac{hC}{\lambda} \qquad \ldots\ldots (3)$$

$E = 1240/\lambda$

Where λ is the maximum wavelength and E is the band gap energy.

d) TransmissionElectron Microscopy:

Fig4. Shows the TEM images of the as-synthesized CdO nanoparticle. The particle shows spherical nature and particle size found to be 60-70 nm which are in agreement with the calculation of Scherrer's equation. The fig also shows the selected area electron diffraction (SAED) patterns indicating sharp rings which confirms the crystalline nature of the CdO nanomaterial. It is evidentfrom these images that CdO nanomaterial has spherical and rod shaped nanostructures. Sphericalparticles have size distributions lie in therange of 50-60 nm. Sphericalparticles are assembled in the linear manner andmake rod shaped nanostructure of 500 nm in length.

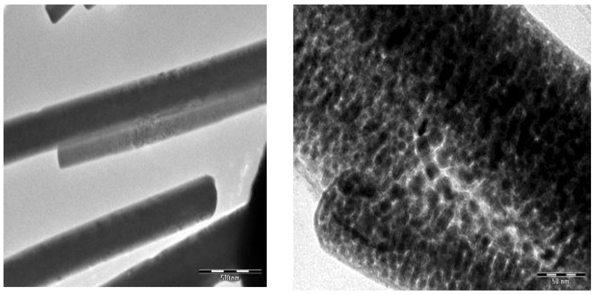

Fig. 4: (a) and (b) TEM micrograph of CdO nanoparticle

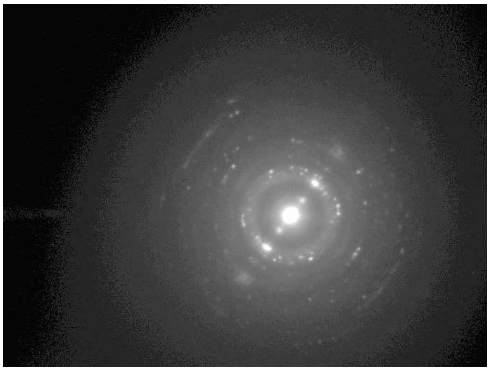

Fig. 4c. SAED pattern of CdO nanoparticle

e) Photocatalytic test:

To evaluate the potential application in water treatment of cadmium oxide nanoparticles, the photocatalysis capacities for the organic pollutant were investigated. Methyl red was chosen as the model organic pollutant. According to the principles of CdO photocatalysts [24], the energy gap are generated on the surface of Cadmium oxide when are irradiated in photon light which can 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 adsorbed species [25].

The degradation of methyl red was recorded as a function of time in the presence of UV-Visible light. 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.

 ISSN: 2321-8169
2806 – 2810

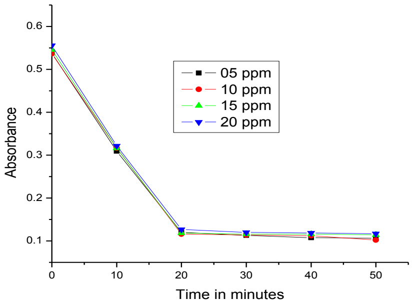

Fig 5a. Depletion of Absorbance with time

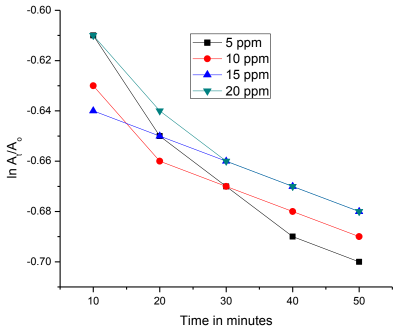

Fig. 5b Degradation of methyl red as a function of ln(At/Ao)versus time of exposure to UV light

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. Comparison studies of the dye solution demonstrates that the photocatalytic properties of the CdO material decreases with increase in higher concentration of pollutant.

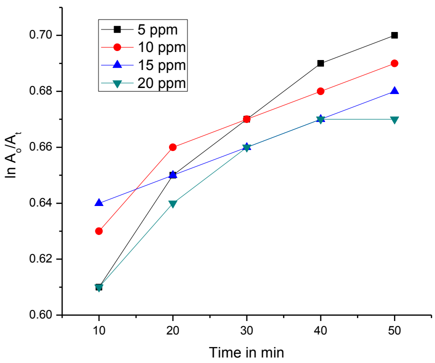

Fig. 5c Curve fit data for the first order degradation kinetics of methyl red

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 photocatalysts CdO was found to be efficient for the decomposition of the organic pollutant. The decrease in percentage 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 nanoparticle decreases with the increase in concentration of the pollutant.

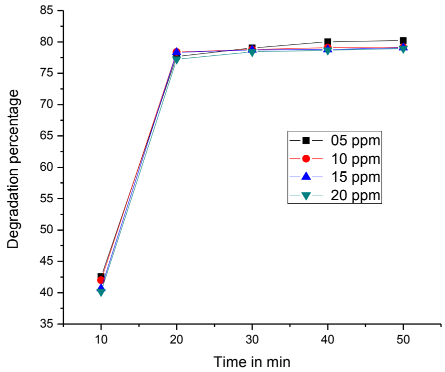

Fig. 5d Increase in degradation percentage as a function of time

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.From fig 1b. Kinetics of reaction follows 1^{st} order for the four different concentration of the pollutant and rate constant found to be 0.013 min^{-1}.

Table 1: Degradation percentage of Methyl red dye using as-synthesized nanoparticle

Concentration of Methyl red	Time in min	Degradation %	K (min/ l min)
5 ppm	50	80.21	0.013
10 ppm	50	79.14	0.013
15 ppm	50	79.08	0.013
20 ppm	50	78.95	0.013

5. Conclusion:

CdO nanoparticles has been synthesized by hydrothermal method using very easy, cheap and convenient process. XRD and TEM confirms the formation of spherical shape of nanocrystalline material. IR and UV-Vis spectral studies shows presence of CdO bonds. 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

ISSN: 2321-8169
2806 – 2810

indicates that it can be used as a photocatalysts for removal of organic contaminants present in water.

6. Acknowledgements:

This work was supported by author R.B.L and M.R.L are thankful to granting financial grant to our Minor Research Project File no. 47-2024/11 (WRO) sanctioned by UGC, New Delhi. The author is also thankful to Dr. M. Gupta and Dr. N. Lalla, UGC-DAE consortium Research Centre, Indore for the use of facilities for XRD and TEM.

References:

[1] B. L. Cushing, V. L. Kolesnichenko and C. J.ÓConnor*Chem. Rev*.vol. 104, 2004, pp. no. 3893.

[2] R. B. Waghulade, P. P.Patil and R.Pasricha*Talanta*vol. 72, 2007,pp.no.594.

[3] G. N. Chaudhari, A. M. Bende,A. B.Bodade, S. S.Patil andV. S. Sapkal*Sens. Actuators B*vol. 115**,** 2006, pp. no. 297.

[4] A. Srivastava,K. Jain, A. K. Rashmi, S. T. Srivastava and Lakshmikumar,*Mater. Chem. Phys*. Vol. 97, 2006,pp.no. 85.

[5] G. N. Chaudhari, A. M. Bende, A. B. Bodade, S. S. Patil and S. V. Manorama*Talanta*vol. 69,2006, pp. no.187.

[6] C. Aifan, H. Xiaodong, T.Zhangfa, B. Shouli, L. Ruixianand L.Chiun*Sens. Actuators B*vol.115, 2006, pp. no.316.

[7] C. H. Champness andK. Ghoneim andJ. K. Chen *Can. J. Phys*. Vol.63, 1985,pp.no.767.

[8] L. M. Su, N. Grote andF. Schmitt,*Electron. Lett*.Vol. 20, 1985,pp. no.716.

[9] Su L M, Grote N and Schmitt F,*Electron Lett*.Vol20, 1984,pp. no.717.

[10] I. M. Ocampo, A. M. Ferandez andP. J. SabastianSemicond. *Sci. Technol*. Vol**8**, 1993,pp. no.750.

[11] F. A. BenkoandF. P. Koffyberg,*Solid State Commun*.Vol57, 1986,pp. no.901.

[12] K. Gurumugan, D. Mangalarag, A. Narayandass, K. Sekar, and C. P. GirijaVallabham*Semicond. Sci. Tech*. Vol9, 1994,pp. no.1827.

[13] C. Xiangfeng, L. Xingqin andM. Guangyao*Sens. Actuators B*Vol65, 1995,pp. no.64.

[14] R. S. Mane,H. M. Pathan, C. D. Lokhande and S. H. Han *Solar Energy*Vol80, 2006,pp. no.185.

[15] C. Qiu, X. Xiao andR. Liu *Ceramics International*Vol34, 2008,pp. no.1747.

[16] A. Askarinejad andA. Morsali*Mater. Lett*.Vol62, 2008,pp. no.478.

[17] Y. Liu, C. Yin, W. Wang, Y. Zhan, and G. WangJ. *Mater. Sci. Lett.*Vol21, 2001,pp. no.137.

[18] B. Zou, V. Volkov and Z. Wang Chem*. Mater*. Vol11, 1999,pp. no.3037.

[19] R. R. Salunkhe, V. R. Shinde andC. D. Lokhande*Sens. Actuators B*Vol133, 2008,pp. no.296.

[20] Y. W. Wang, C. H. Liang, G. Z. Wang, T. Gao, S. X. Wang, J. C. Fan and L. D. Zhang*J. Mater. Sci. Lett.*Vol20, 2001,pp. no.1687.

[21] T. Robinson,G. McMullan, R. Marchant andP. Nigam, *Bioresource Technology*.Vol77, 2001, pp. no.247-255.

[22] D. F. Ollis and C. Turch*Journal of Enviromental Programs.*Vol9, 1990,pp. no.229-234.

[23] S. Y. Kato, M. Hirano, T. Iwata, K. Sano, T. Takeuchiand S. Matsuzawz Journal *of Applied Catalysis of Enviornmental Biology*.Vol57, 2005,pp. no.109-115.

[24] R. F. Mulligan, A. A. IliadisandP. Kofinas*Journal of Applied Polymer Science*Vol1, 2003,pp. no.1058.

[25] A. S. Lang,R. S. Ningthoujam, S. J. Sharma and R. B. Pode*Indian J. Pure& Appl. Phys*. Vol.49, 2011,pp. no.234–238.