COMPARISON OF PHOTO CATALYTIC DEGRADATION OF METHYLENE BLUE USING NANO-SIZED CDO AND PBO CATALYSTS

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Abstract:

The PbO and CdO nanoparticles were synthesized and characterized by X-ray diffraction (XRD), Scanning Electron microscopy (SEM),FT-IR and UV-Vis spectroscopy. The photocatalytic properties of PbO and CdO nanoparticles were investigated for the degradation of methylene blue (MB) dye under UV light irradiation. The activity for the degradation of methylene blue using PbO and CdO was found to be 76% and 46% respectively after 120 minutes. The overall kinetics of photodegradation of methylene blue dye using PbO and CdO photocatalysts was found to be of first order.

Keywords: *Sol-gel and precipitation techniques, PbO and CdO nanoparticles, Photocatalysts, Methylene blue (MB).*

1. INTRODUCTION

The textile industries use large amounts of dyes in aqueous solutions and the effluents are released to water bodies. This becomes the main cause of water pollution [1-3]. Methylene blue (MB) is one of the cationic dyes used for dyeing and cloth completion processes. From the previous researches it was known that the organic dye pollutants can be removed from waste water by photodegradation using nanoparticles. The use of zinc oxide and titanium oxide nanoparticles have attracted researchers in the photocatalytic degradation due to their stability and

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reactivity. The photocatalytic activity of bare and modified zinc oxide [4-5] and titanium oxide [6] on the degradation of methyl orange have been explored. Evaluation of activity of cadmium oxide in the photodegradation of C.I Reactive yellow-84 [7] and methylene blue [8] under visible light irradiation have been investigated. Photocatalytic activities of two kinds of lead magnesium niobate for decomposition of organic compounds have been compared [9]. The absorption of PbO and CdO nano particles fall on UV region and the wide band gap of PbO and CdO limit its applications to photochemical process under UV light irradiation. The aim of the present study is to compare the photocatalytic activity of bare lead oxide and cadmium oxide nano particles under UV irradiation for the degradation of methylene blue.

2. EXPERIMENTAL SECTION

2.1. Materials

All chemicals were obtained from Merck & Co. and used without purification. Tetraethyl Ortho Silicate (TEOS), Ethanol, Hydrochloric acid, Lead acetate, Sodium borohydride($NaBH_4$), methanol, Sodium Hydroxide, Cadmium Chloride, Ethylene glycol. Acetone(CH_3COCH_3). The solvents ethanol and methanol were used after purification by the standard method described in the literature [10,11].

2.2. Synthesis of Lead oxide nanoparticles by Sol-gel method

A fresh solution (A) was made by taking Lead acetate(0.1 M), 50 ml of ethanol and 5 ml of distilled water and the prepared solution, placed in ice bath, was stirred by a magnetic stirrer for one hour. Solution B was made by taking 0.05M TEOS, Ethanol, and few drops of HCl was stirred for 1 hour in ice bath. The solution A and B were mixed and stirred for 20minutes. The transparent part of the solution was transferred to the Petri dish and kept for few days for gelation. After the complete "Gel" formation, the sample was crashed to powder and a solution was prepared dispersing the sample into distilled water. The solution was placed in the ice bath and stirred for 20 minutes. To this solution saturated solution of $NaBH_4$ in distilled water was added and a black precipitate was obtained. The mixture was stirred for 10 minutes and then the products

were collected by centrifugation. The resultant precipitate was dried to get PbO nano composite.

2.3. Synthesis of Cadmium oxide nanoparticles by precipitation method

0.1 M of NaOH (100 mL) solution was continuously stirred and 5 mL of ethylene glycol in methanol was added to NaOH solution. The resulting solution was stirred for one hour and 0.1 M of $CdCl_2$ (100 mL) solution was added. After three hours of constant stirring a milky white solution was obtained. Size selective precipitation was carried out using acetone as a non-solvent. The precipitate was washed in methanol and methanol was allowed to evaporate at room temperature to obtain cadmium hydroxide nanoparticles in white powder form. Cadmium hydroxide nanoparticles were then placed in the furnace and heated to 250°C for five hours. After five hours cadmium oxide powder was obtained in brown colour.

2.4. Instrumentation

The UV –Vis spectrum of the nanoparticles and the dye were recorded in acetone solvent by Shimadzu 1800 UV Double beam spectrophotometer. The infrared spectra was recorded in KBr disc on a SHIMADZU double beam infrared spectrophotometer and measuring the relative intensity of transmitted light energy versus wave number in the region of 4000 - 400 cm^{-1}. The XRD spectrum was recorded by X-Ray diffractometer with Cu kα radiation at 25°C. The SEM image was recorded by JEOL Model 6390 computer-controlled microscope. The photocatalytic activity studies of the synthesized catalysts on the photodegradation of methylene blue was done using photo reactor HIPR- compact-P-8/125/250/400/

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3. RESULTS AND DISCUSSION

3.1 Characterization of nano particles by UV-Visible Spectrum

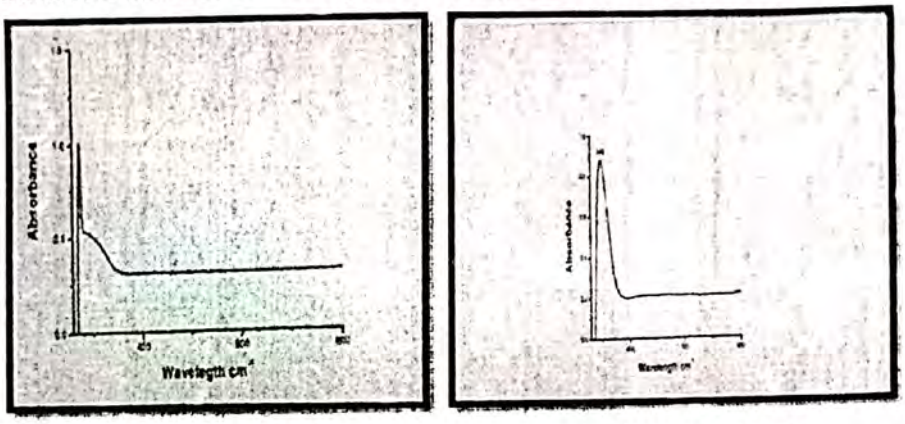

Figure 1: UV-Visible spectrum for a) PbO b)CdO

From UV-Vis spectra the λ_{max} for PbO and CdO was observed at 337 nm and 349 nm respectively. This indicates the absorption shift towards the shorter wavelength, because of the particle size reduction. From these data it is evident that resultant nanoparticles were embedded in silica matrix and exhibited the significant blue shift. This is an indication of strong quantum confinement. From UV spectra band gap for PbO and CdO were calculated and fond to be 4.5 eV and 3.85 eV respectively. The optical band gap was slightly enhanced compared to the bulk samples. The data was shown in Table 1. The UV Visible spectrum of the dye methylene blue exhibited peaks at 292 nm and 630 nm. The FT-IR spectra of the synthesized PbO and CdO exhibited intensive band at 674 cm^{-1} and 1034 cm^{-1} respectively which matches with the previous report [12]. XRD data was used to determine the average particle size using the Debye - Scherrer's equation. The XRD pattern of CdO is given in Figure 2. The observed "2θ" values (2θ = 34.2479 for PbO and 29.6249 for CdO) are in good agreement with standard "2θ" values. This confirms that powder prepared was PbO and CdO nano structure. The particle size of the PbO and CdO nanoparticles were found to be 3.96 nm and 4.08 nm respectively. The morphologies of the synthesized nano particles were

characterized by SEM. The SEM images are shown in Figure 3 illustrates the particle size of the PbO and CdO particles to be in the nano meter range.

Table 1. UV absorption data and particle size for the nanoparticles

Nano particles	Band gap of bulk (eV)	Band gap of nanoparticle (eV)	Particle size (nm)	Absorption peak λ_{max} (nm)
PbO	2.7	3.82	3.96	337
CdO	2.3	3.4	4.08	349

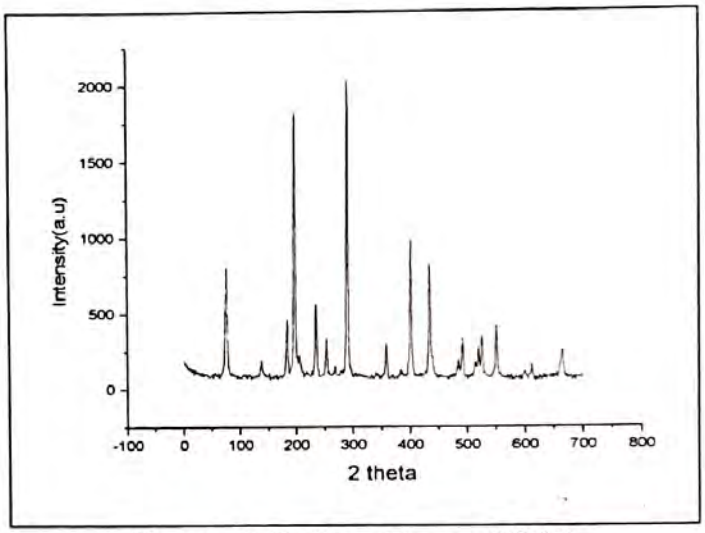

Figure 2: XRD pattern of CdO

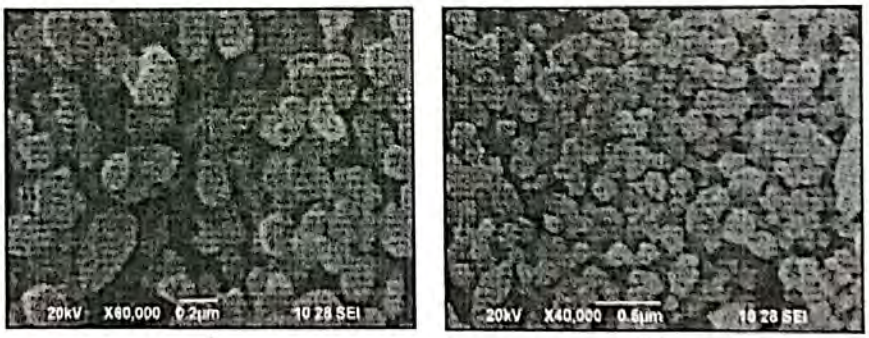

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Figure 3: SEM Images a)PbO b)CdO nanoparticles

3.2. Photocatalytic studies

In order to study the photodegradation of methylene blue dye, the absorbance of the dye at 630 nm was measured by Shimadzu 1800 UV Double beam spectrophotometer. The initial concentration of the dye solution was taken as 0.027 M and the weight of the nanoparticle taken was 100 mg. The mixture was taken in the photocatalytic vessel and was exposed to UV light with stirring in the photo reactor. The reaction was carried out at room temperature and at pH 7. The extent of degradation of the dye in solution was studied at definite intervals of time (30 minutes) by measuring the absorbance of the dye. The intensity of the absorption peak λ_{max} = 630 nm diminished gradually with increase of irradiation time and it is almost disappeared at 60 min for PbO. The UV-Vis spectra showing the decrease in intensity is depicted in Figure 4a and 4b. The photodegradation curves of MB in the presence of the prepared catalysts are shown in Figure 5. Photodegradation experiments were also conducted in the absence of catalyst to study the effect of photolysis and it is observed that the degradation of MB is negligible (12%) without any photocatalyst.

For PbO nanoparticle the dye was bleached after 60 minutes and for CdO the time taken was more than 120 minutes. The photodegradation efficiency of MB was calculated applying the following equation:

% photodegradation efficiency = $100(C_o - C) / C_o$

Where C_o =Initial concentration of dye C =Final concentration of dye.

The efficiency for PbO was found to be 76 % and that of CdO was 46 %.

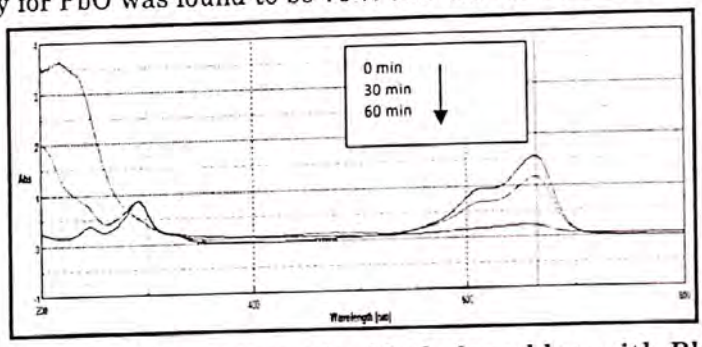


Figure 4a: UV spectrum for Methylene blue with PbO

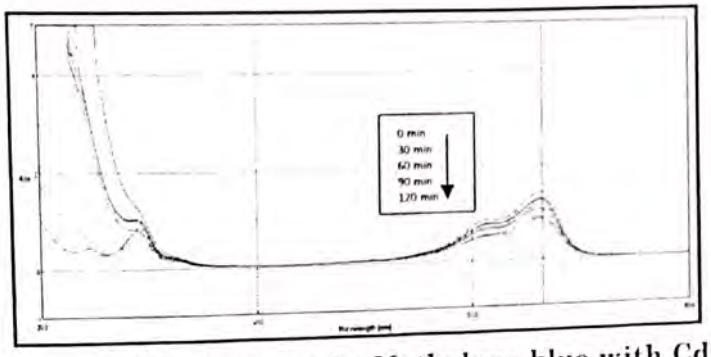


Figure 4b: UV spectrum for Methylene blue with CdO

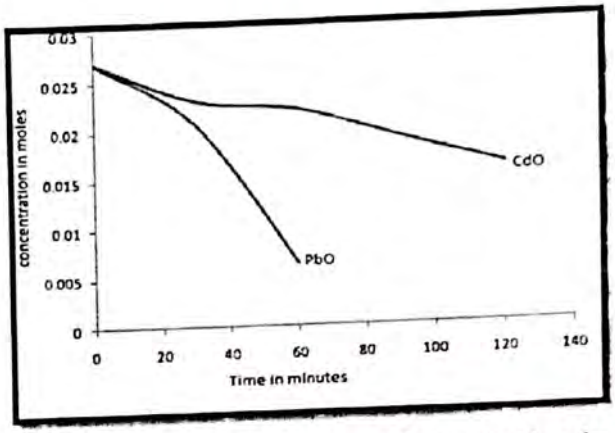


Figure 5: Photodegradation of methylene blue solution by nano particles

3.3. Kinetics of photodegradation

The kinetics for the photo degradation of methylene blue using synthesized catalyzed was also investigated and results are shown in Figure 6. The photo degradation of methylene blue can be described by pseudo-first order equation [13] and it can be expressed as follows:

$$\ln (C_0/C) = kt \text{ and } \quad k = 1/t \times \ln (C_0/C)$$

Where C_0 is the concentration of methylene blue at irradiation time t = 0, C is the concentration of methylene blue at irradiation time of 't' and k is the rate constant. The plot of ln (C_0/C) versus time (t) represents a linear relationship. The Kinetic Plot of ln (C_0/C) versus irradiation time for the photo degradation of Methylene blue by PbO and CdO nanoparticle is given below

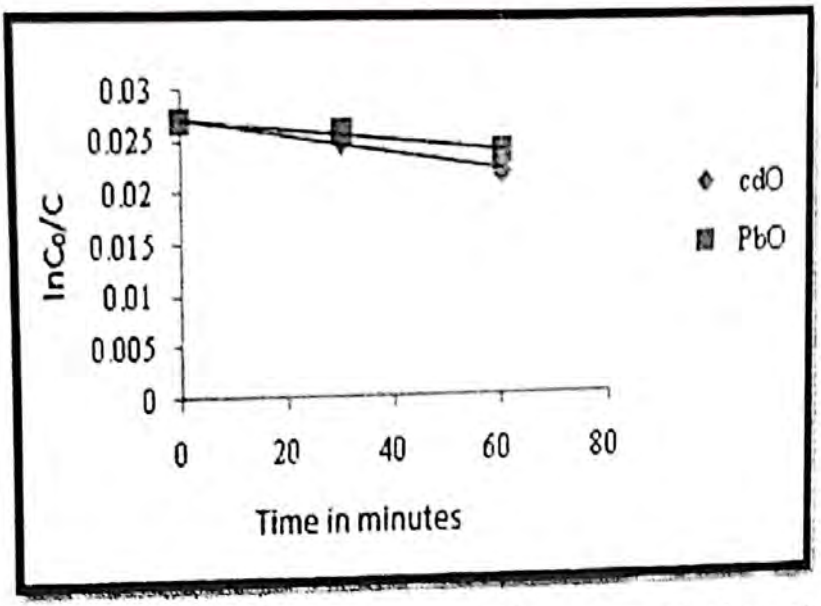


Figure 6: Kinetic Plot of ln (C_0/C) vs irradiation time

3.4 Effect of pH of dye solution on photo degradation

The effect of pH in the range of pH 4.0 – 10.0 on the photo-catalytic degradation rate of methylene blue was studied. The initial concentration of the dye solution was taken as 0.027 M and the weight of the nanoparticle taken was 100 mg. The initial pH of the dye solution was varied (4 to 10) by adding the required volume of 1N solution of HCl and NaOH. Then pH was measured by using digital pen pH meter. The removal of methylene blue with both lead oxide nano particles and cadmium oxide nanoparticles was high when the pH was 7. Above the pH value 7 the photodegradation decreases. It is known that the surface properties are responsible for photocatalytic process [14]. The nano-sized particles are negatively charged when the pH is above 7. The surface charge on semiconductor induces the reaction when it is positive. This surface charge depends upon the pH of the solution, being positive in acidic media and negative in alkaline media. After a particular pH the net charge on the surface of the particles becomes zero and is called zero discharge (PZC). Therefore the optimum pH for this study can be fixed as 7. The variation can be graphically represented as in Figure 7.

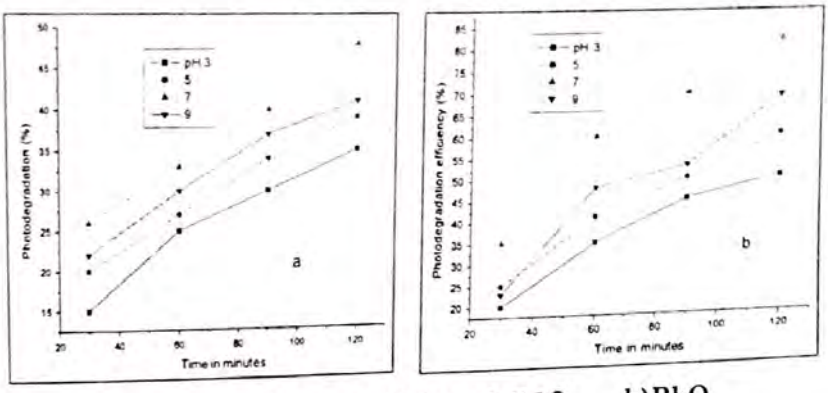
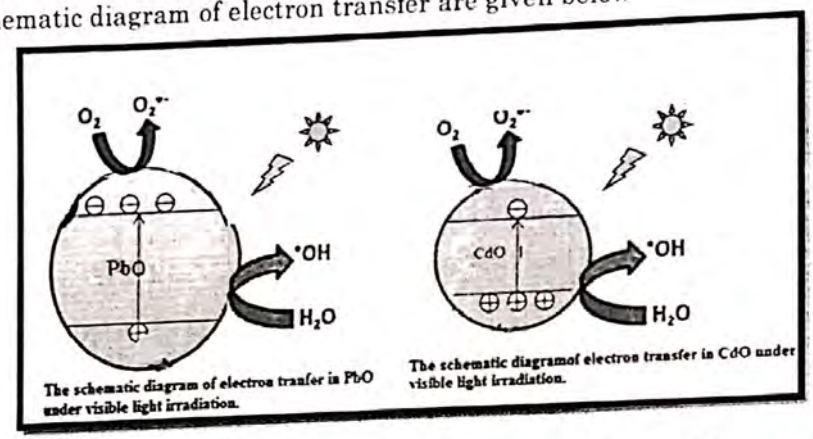


Figure 7: Effect of pH for a) CdO b)PbO

Proposed mechanism for the photocatalytic activity of PbO and CdO and the schematic diagram of electron transfer are given below



When PbO and CdO irradiated with light, PbO and CdO are excited by photons led to the formation of electrons and holes in the conduction and valance band of CdO. The electrons react with surface adsorbed O_2 to produced $O_2^{\cdot-}$ and holes react with H_2O to create $^{\cdot}OH$. The reactive species $O_2^{\cdot-}$ and $OH^{\cdot}$ are responsible for degradation of dye molecules.

4. Conclusion

The precipitation and sol-gel techniques have been used for the synthesis of PbO and CdO nanoparticles respectively. The two samples obtained by the precipitation and sol-gel techniques were characterized by XRD, FT-IR, UV and

SEM instrumental methods. The IR analysis of the spectra shows broad band between 601 – 648 cm^{-1} with shoulder shape, characteristic of PbO and CdO band. The images obtained by SEM of samples PbO and CdO shows sphere and pseudo-spherical like nanoparticles. From the XRD results the size of PbO and CdO nanoparticles were calculated to be 3.96 nm, 4.08 nm respectively. The PbO and CdO nanoparticles have been distributed well within the range of ≈100 nm which is the favourable property to exhibit better photo catalytic activity. The photo catalytic degradation of the dyes was carried out using UV radiation. The degradation efficiency was more for lead oxide than cadmium oxide at the pH of 7. So we can conclude that PdO and CdO nano particles can be used for photo catalytic degradation of methylene blue.

5. Acknowledgements

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