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Research Article

PHOTOCATALYTIC DEGRADATION ANALYSIS OF METHYLENE BLUE BY ALUMINIUM DOPED CADMIUM OXIDE NANOPARTICLES

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ABSTRACT

Environmental pollution from human activities is a major challenge of civilization today. This study aimed to use Al doped CdO nanoaprticles for the purification of polluted water from dye. Al doped CdO nanoparticles have been synthesized using a simple chemical method and characterized by SEM and Raman spectra. The degradation efficiency of Al/CdO nanoparticles was studied against methylene blue by using a UV-vis spectrophotometer. The results demonstrated that the photocatalyst was efficient at 200 mg/L, the maximum amount of degradation (90.2 %) has been observed for MB after 2 hrs. The photocatalytic performance of the Al/CdO nanoparticles was stable after the nanoparticles were reused five times. The photocatalytic ability of the Al-dopedCdO NPs allowed the development of a low cost, high efficiency, and environmentally friendly material for water treatment applications using sunlight.

Keywords: Al, CdO, Methylene blue, Nano particles, Photocatalyst.

1. INTRODUCTION

Discharging toxic contaminants from industries such as textiles, food, paper, cosmetics etc. into the environment requires refining and therefore various techniques such as coagulation, flocculation, membrane filtration, photocatalytic degradation etc. have been used to eliminate coloured contaminants. Discharged waste water from textile industry is contaminated mainly with dyes that consume oxygen and thus affect the aquatic life [1]. Methylene blue (MB) is one such cationic dye, extensively used for dying cloth would cause severe carcinogenic and mutagenic effects to human beings and wildlife. Therefore, the removal of MB is essentially a challenging task to protect the environment. One of the most effective and applicable methods for the elimination of environmental pollutants is the photocatalytic degradation process in which nanoparticles have been used in view of solar energy utilization that results two different electron transfer quenching pathways, *i.e.* reductive or oxidative quenching [2]. Thanks to the growth of nanoscience and nanotechnology for providing ample techniques for the production of nanoparticles. Scientists have investigated many semiconductors that consume visible light to degrade a large number of recalcitrant materials in aqueous system and as a matter of fact nano-sized metal oxide semiconductor materials gained a wide-reaching recognition as the preferable compounds for purification of water [3]. Different type of metal oxide semiconductors such as, ZnO [4], SnO_2 [5], TiO_2 [6], few metal particles Ag [7], Au [8], Pd [9], Pt [10] and few doped metal oxides [11] have been used widely to degrade organic pollutants. Studies have been already initiated to degrade methylene blue using palladium and golden drimer [12], La doped ZnO nanoflowers [13], ZnO/Ag/CdO nanocomposite [14] and polyaniline/CdO nanocomposite [15]. However, in best of our knowledge, the synthesis of Al doped CdO nanoparticles and its particle size related photocatalytic in photo degradation of methylene blue has not been reported yet. Hence the present study was meant to study the photocatalytic degradation of methylene blue using the Al doped cadmium oxide photocatalyst synthesized by the chemical co-precipitation method.

2. MATERIAL AND METHODS

2.1. Material

All the Chemicals $(CH_3COO)_2Cd{\cdot}2H_2O$, $Al_2SO_4.5H_2O$, Methylene blue and solvents were purchased from Merck and were used without further purification.

2.2. Synthesis of Al doped CdO nanoparticles

Cadmium acetate dihydrate [$(CH_3COO)_2Cd{\cdot}2H_2O$] was used as the metal salt precursor. In order to hydrolyze the metal salt precursors, ammonium hydroxide [NH_4OH] was added drop-wise to cadmium acetate. Possible reaction may be,

$$(CH_3COO)_2Cd{\cdot}2H_2O + 2NH_4OH \rightarrow Cd(OH)_2 + 2H_2O + 2CH_3COONH_4$$

$$Cd(OH)_2 \rightarrow CdO + H_2O$$

Al doped CdO nanoparticles have been synthesized using a simple chemical solution method. The stock solutions of starting materials 50 mM $(CH_3COO)_2Cd{\cdot}2H_2O$, 0.003 M $Al_2SO_4.5H_2O$ and 100 mM NH_4OH were prepared using deionised water as solvent for each sample. The solution of NH_4OH was dropped into the solution of $(CH_3COO)_2$ $Cd{\cdot}2H_2O$ under continuous magnetic stirring till the formation of white precipitates of $Cd(OH)_2$. The precipitates were filtered off and washed with distilled water. The precipitates of $Cd(OH)_2$ were first dried in air at room temperature and then calcined at 250°C for 24 hours to attain fine crystalline CdO nanoparticles. For the preparation of Aldoped CdO, 0.003M $Al_2SO_4.5H_2O$ was added to 5g of calcined CdO nanoparticles. The sample was agitated and heated at 110°C for 30 minutes. The powder was cooled to room temperature, calcined at 300°C for 2 hours and then grounded. Total preparation time of solid product was 25 hrs. The product obtained was labelled as Al-doped cadmium oxide (Al-CdO).

2.3. Scanning Electron Microscope

The synthesized products were characterized using a VEGA3 TESCAN (Czech Republic) scanning electron microscope (SEM).

2.4. Raman Spectroscopy

Make: HORIBA, Model: LabRAM HR Evolution Laser (in Wave length): 514nm, 785nm, From UV to near IR, Automated laser switching Detectors: CCD, InGaAs

2.5. Photocatalytic Degradation Experiment

The photocatalytic activity of the prepared Al-CdO photocatalyst was evaluated for simultaneous degradation of MB dye. Batch tests were performed as per the following procedure: 0.2 g Al-CdO nanoparticles photocatalyst was added in 100 ml solution prepared by mixing MB (10-50mg/l) in a beaker and the mixture was stirred in dark for 40 min to allow the physical adsorption of dye molecules on catalyst particles reaching the equilibrium. The photodegradation experiments were carried out under natural sunlight. Reaction samples were collected at regular intervals and immediately centrifuged to remove suspended particles before recoding absorbance. The concentration of MB was determined by measuring the absorption intensity at their maximum absorbance wavelengths of 661 nm and 540 nm respectively, by using a UV-vis spectrophotometer (Sl-210 Double Beam UV Visible Spectrophotometer (Elico)) with a 1cm path length spectrometric quartz cell, and then calculated from calibration curve. The percentage of dye degradation was calculated from the following equation:

$$\%\ \text{dye degradation} = (A_0\text{-}A_t/A_0)\text{X } 100$$

Where A_0 is absorbance of dye at initial stage, A_t is absorbance of dye at time "t".

2.6. Effect of Al/CdO load on the degradation of MB

The effect of amount of photocatalyst on the rate of photocatalytic degradation of MB was observed by taking different amounts of Al-CdO (100 to 300 mg/L) keeping other factors constant.

2.7. Effect of initial concentration of MB

The effects of MB concentration on the rate of their photocatalytic degradation were observed at different concentrations (10 mg/l to 50 mg/l) of MB.

2.8. Effect of pH of the solution

The effect of pH on the rate of photocatalytic degradation of MB was investigated in the pH range of 2 to 10. The pH was maintained each time by using 1 M HCl or 1 M NaOH and measured using a pH meter.

2.9. Recycling/reuse of the Al-CdOphotocatalyst

The recycling and reuse of the photocatalyst for the degradation of MB was also tested. For each experiment, the 200 mg/L of Al-CdO photocatalyst was added into the MB solution with an initial concentration of 10 mg/L MO; pH was maintained at 6. The degradation efficiency was calculated after contact time of 120 min. The experiment was carried out five times with the same, reused Al-CdO photocatalyst.

3. RESULTS AND DISCUSSION

3.1. Characterization of Al-CdO nanoparticles

Raman spectroscopy is the study of the interaction between light and matter in which the light that is inelastically scattered: a process called the Raman effect. In a Raman spectroscopy experiment, photons of a single wavelength (in the visible range this would be light of a single colour) are focused onto a sample. Most commonly a laser is used as it is a powerful monochromatic source. The photons interact with the molecules and are either reflected, absorbed, transmitted or scattered. With Raman spectroscopy, we study the scattered photons.

From the Raman pattern in Fig.1 and Fig.2 , the comparison of Raman data for pure CdO and Al doped CdO nanoparticles with similar morphology at the nano/mesoscale allows to investigate the relation between Raman features (peak or band positions, width, relative intensity) and material properties such as local structural order, stoichiometry and doping. Moreover Raman measurements with four different excitation lines (559, 774, 1088 and 3127 cm^{-1}) point out a strong correlation between vibrational and electronic properties. This observation confirms the relevance of a multi-wavelength Raman investigation to obtain a complete structural characterization of advanced doped oxide materials.

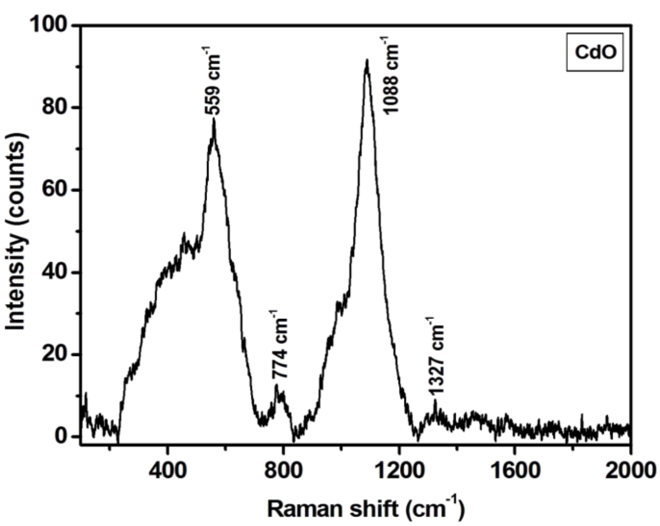

Fig. 1: Raman Spectrum of undopedCdO

3.2. Characterization by Scanning Electrom Microscope

The microstructure and morphology of nanoparticles were analyzed using SEM. Fig.3 and Fig.4 shows the micrographs of the samples of Al/CdO nanoparticles. The Al/CdO nanoparticles are heterogeneous in nature.From the Fig.3, it is seen that the particles have irregular shape about 1 μm diameter. But the second image, the particles shapes are like rectangle.

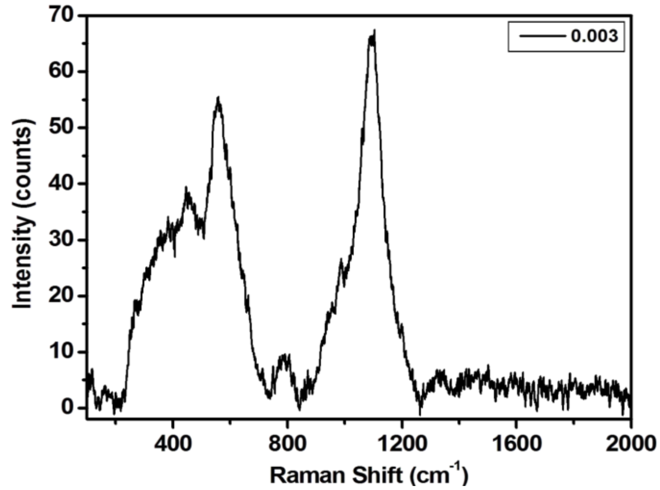

Fig. 2: Raman spectrum of Al doped CdO

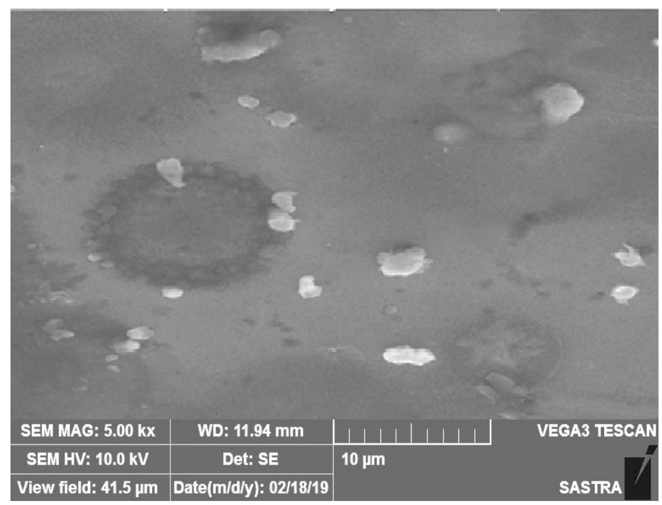

Fig. 3 shows scanning electron micrographs (SEM) of the undopedCdO NPs

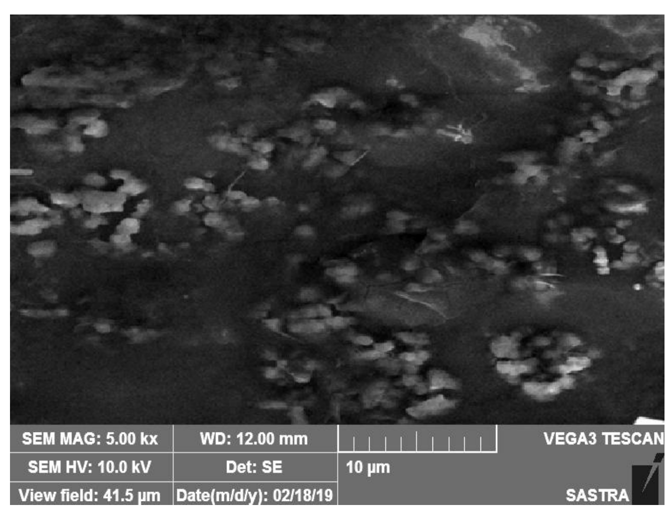

Fig. 4 shows scanning electron micrographs (SEM) of Al–doped CdO NPs

3.3. Effect of Al/CdO load on the degradation of MO

It is necessary to find out the optimum loading of photocatalyst for efficient removal of dye [16]. Hence, a series of experiments were carried out to find the optimum amount of the photocatalyst Al/CdO by varying its amount from 100-300 mg/L. The percent degradation of dye versus time of degradation by varying the photocatalyst weight is recorded is given in Fig.5. To achieve highest photocatalytic reaction rate, the optimum amount of the photocatalyst was found to be 200mg/L. The observed dependence of reaction rate on the amount of photocatalyst can be explained in terms of the availability of active sites at the adsorbent surface and the level of light penetration in the reaction medium [17]. Upon increasing the amount of photocatalyst up to 200mg/L percent degradation increases due to the increase in the adsorbent total surface area and thus, the number of active sites, available for the photocatalytic reaction. However, excess photocatalyst, abovethis optimal load, would induce more aggregation (particle–particle interactions) of photocatalyst making a significant fraction of the catalyst inaccessible either to the adsorbing dye or to the radiation [18]. The degradation efficiency decreases after achieving an optimum value of photo-catalyst load. Therefore, 200mg/L of the photocatalyst was selected as the optimal amount of photocatalyst for the subsequent experiments (Fig.5).

3.4. Effect of initial concentration of MB

The % degradation of MB dye solution with the concentration of 200 mg/L for the Al/CdO nano-particles under sunlight shown in Fig. 6. The result shows that 90.2% degradation have been observed for MB at 2 h using initial concentration of MB 20 mg/l.

3.5. Effect of pH

The effect of pH on MB dye removal efficiency by Al/CdO nanoparticles was determined at pH 2, 4, 6, 8 and 10. For each experiment, 200 mg/L of Al/CdO nanoparticles was added into the MB solution with an initial concentration of 20 mg/L MB. The degradation efficiency was calculated after contact time of 120 min. The results were presented in Fig.7, from the results, the optimum pH for removal efficiency of Al/CdO was observed as 6.

Fig.8 shows the results obtained regarding the recycling and reuse of the photocatalyst for photocatalytic-degradation of MB solution**.** The experiment was carried out under the following conditions: for each experiment, the 200 mg/L of Al/CdO was added into the MB solution with an initial concentration of 20 mg/L MB. The degradation efficiency was calculated after contact time of 120 min. The results show that the photocatalytic activity remained nearly unchanged after five uses, which indicates that the photocatalyst is stable in the photocatalytic oxidation. This results also agreement with previous reports. Therefore, this photocatalyst can be separated and recycled while maintaining its stability, making it a promising material for environmental remediation. The total time spent on the entire work was 3 days.

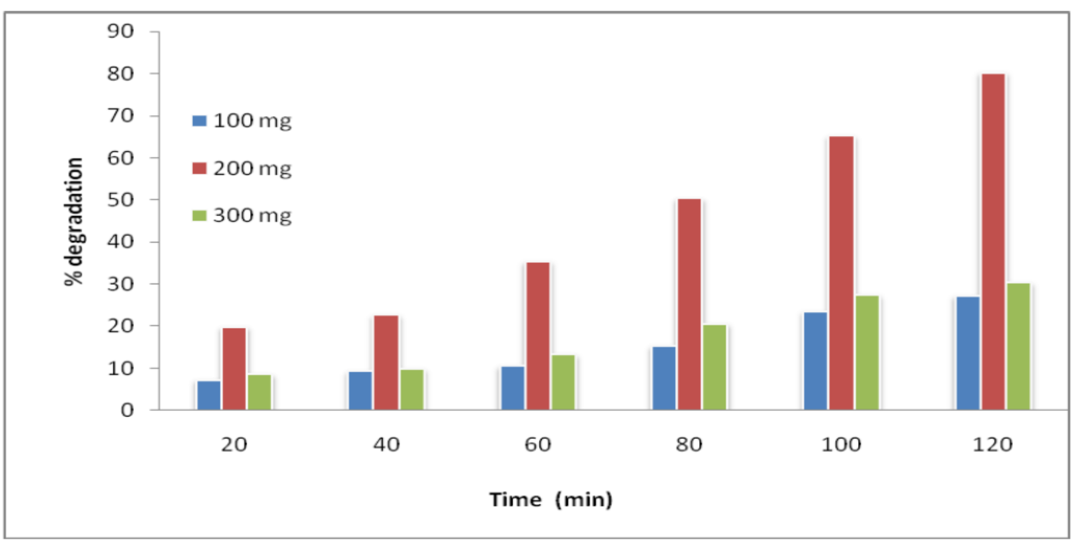

Fig. 5: % degradation of MB Vs. time by varying the amount of Al/CdO (100 mg to 300 mg)

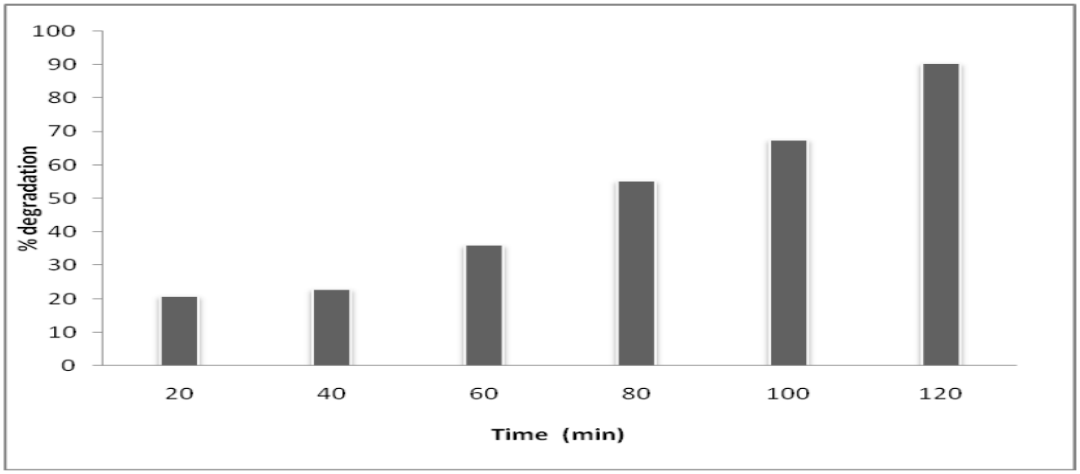

Fig. 6: % degradation of MB Vs. time

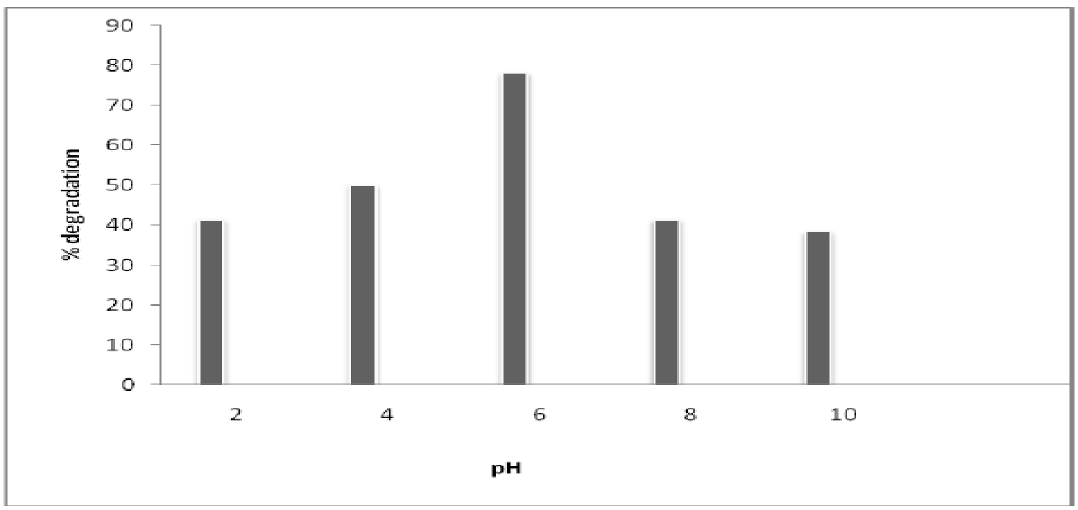

Fig. 7: % degradation of MB at 120 min by varying the pH of the solution keeping MB concentration and Al/CdO amount as constant

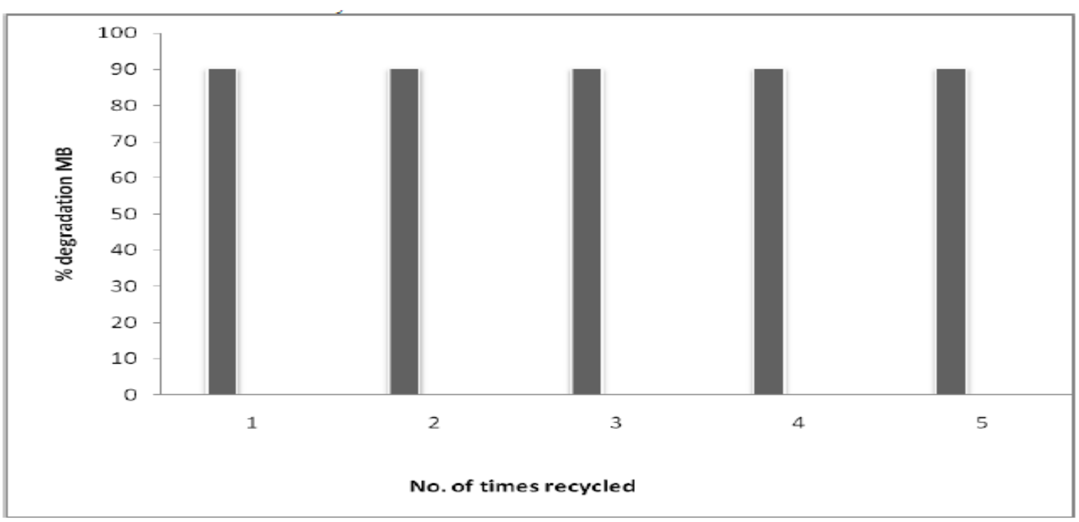

Fig.8: Recycling of the photocatalyst for degradation of MB

4. CONCLUSION

In this study, the Al doped CdO nanoparticles were successfully synthesized via chemical method and calcinedat 300ºC. Photocatalytic performances of Al/CdO nanoparticles were evaluated using MB solution as the indicator under the natural sunlight. The results demonstrated that the photocatalyst was very efficient, 90.2 % degradation have been observed for MB dye solution after 2 hrs. Our research provided asimple yet efficient way to synthesize Al/CdO based photocatalysts in large scale. Also, Al doped CdO nanoparticles suggests that the photocatalysts are recyclable. In order to provide more stable and better performance in degradation of recalcitrant organic pollutants in larger scale of application, future research should look into overcoming the weak points of CdO and the practical issues that still exist.

5. ACKNOWLEDGEMENT

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