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ORIGINAL ARTICLE

Photocatalytic degradation of 2, 4, 6-Trichlorophenol with CdS nanoparticles synthesized by a microwave-assisted sol-gel method

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Abstract

This paper reports the synthesis and characterization of CdS nanoparticles for investigation of photocatalytic degradation of 2, 4, 6-Trichlorophenol CdS nanoparticles were synthesized by microwave-assisted sol-gel method. Nano particles was characterized by various techniques such as X-ray diffraction, filed emission scanning electron microscopy, energy dispersive spectroscopy, fourier transform infrared spectroscopy and UV-visible spectroscopy. The average crystallite size was found to be 46 nm. The influences of catalyst amount, contaminant concentration and pH of the reaction solution were evaluated and optimized. After photocatalytic degradation, the remained of 2, 4, 6-Trichlorophenol was measured by UV-vis spectrophotometer. In the optimum condition, the highest degradation was obtained 90% after 3hours UV-C light irridiation.

Keywords: *Degradation; Microwave-assisted; Photocatalyst; UV-C light; 2, 4, 6-Trichlorophenol.*

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INTRODUCTION

Chlorophenols are important chemicals for various types of industries such as pesticides, antiseptics and wood preservers, as a consequence, the presence of these chemicals in environment is very common [1-5]. Their high toxicity makes them a group of dangerous chemicals even at low concentrations [1, 6-8]. 2, 4, 6-Trichlorophenol (2, 4, 6-TCP) is a frequently used chlorophenols [1, 3] that due to its high toxicity even in trace level, is of a vital significance to remove from industrial effluents before being discharge into environment. Many techniques have been used to remove this contaminant such as adsorption technology, reductive treatment with zero-valet iron, electrochemical and catalytic wet oxidation, radiation-induced degradation, and Fenton technology [1, 6, 7].

Over the last few years, the application of photocatalysts for the removal of toxic materials attracted numerous attention [9-13]. A high number of organic compounds were degraded from both aquatic and atmospheric environments with photocatalytic methods. This method is anticipated to be suitable for the removal of this 2, 4, 6-TCP from water due to its simplicity, non-toxicity and cost-effective operation [4, 10]. Photocatalysis is a process based on electron–hole pairs generation produced in a semiconductor material by the absorption of photons of relevant light with energy more than or equal to its band gap, causing valence band electrons to be excited into the conduction band giving electron-hole pairs which in turn create free radicals to redox the compounds that are absorbed on the surface of photocatalyst. These free radicals, especially hydroxyl radical ($^{\cdot}OH$), are powerful oxidizers that can decompose pollutants [2, 8, 10, 11, 13-16].

CdS is a well-known semiconductor with a band gap of 2.42 eV. It is one of the most promising photocatalysts due to its amazing properties such as narrow band gap, fine optical transmittance, and appropriate band potentials under different thermodynamic conditions for photocatalytic

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redox reactions [9, 13, 14, 17]. CdS has been used successfully to degrade large number of pollutants including 2, 4, 6-TCP [18,19].

Different methods have been used to synthesize CdS such as sol-gel, chemical bath deposition, mechanical alloying process, pyrolysis of single source precursor, arrested precipitation, co-precipitation, microwave assisted, solvothermal, and hydrothermal [9, 13, 14, 20-23]. Among these methods, microwave irradiation is considered a good candidate for synthesis of nanocrystals for its advantageous proprieties such as short reaction time, narrow particle size distribution, small particle size, and high purity [24, 25].

In this present study, we prepared CdS nanoparticles a by microwave-assisted sol-gel method. The synthesized CdS nanoparticles were characterized by different techniques. The photocatalytic ability of CdS nanoparticles was investigated by the degradation of 2,4,6-trichlorophenol. Furthermore, the influences of important parameters like pH of solution, catalyst mass and substrate concentration were studied and optimized.

EXPERIMENTAL

Materials

Cadmium nitrate tetrahydrate ($Cd(NO_3)_2.4H_2O$), thioacetamide (C_2H_5NS), ammonia solution (25%) and hydrochloric acid (37%) were purchased from Merck Co in analytical gradeand used as received without further purification. Distilled water was used in all experiments to prepare solutions.

Synthesis of nano CdS

For the preparation of CdS nanoparticles, Cadmium nitrate tetrahydrate (1 mol) and thioacetamide (3 mol) were dissolved in 30 mL distilled water with vigorous stirring. A sufficient amount of ammonia solution (25%) was added to the solution in order to adjust pH. Subsequently, the solution was heated at 70 ^{0}C until the gel appeared. The gel was then transferred into a microwave oven (LG, MC-2002-JR) and operated at 1680 W power for 8 minute to yield an orange powder. Finally, the powder was calcined at 400^{0}C for 2 hours.

Instruments

The X-ray diffraction (XRD) pattern of the synthesized CdS nanoparticles was recorded on a Panalytical diffractometer with Cu Kα radiation (λ= 1.54060 $^\circ$A) as an X ray source, operated at 40 kV$^\circ$. Fourier transform infrared Spectrum (FTIR) of CdS nanoparticles was recorded on (Thermo Nicolet) in the range of 4000-400 cm^{-1} using KBr pellets. The UV-vis absorption spectrum of CdS nanoparticles was recorded with UV-vis spectrophotometer (Varian, Cary Conc100). The surface morphology of CdS nanoparticles was obtained by field emission scanning electron microscope (FESEM) (Zeiss, Sigma, Germany) at various magnifications. FESEM was equipped with the detector of EDS in order detect the elemental composition of the CdS powder.

Photocatalytic activity

Photocatalytic activity of the synthesized CdS nanoparticles was investigated by degradation of 2, 4, 6-TCP under UV-C (High pressure Hg lamp 30 W, Osram, Germany). A series of 2, 4, 6-TCP solutions of initial concentration (20-200 $mg.L^{-1}$) were prepared for the photocatalytic reactions. Additionally, CdS nanoparticles with different loads (0.02-0.08 g) were tested. Prior to the irradiation, contaminant solution was stirred for 1h in the dark to ensure adsorption-desorption equilibrium between CdS and 2, 4, 6-TCP. Then, the solution was exposed to UV-C light with constant stirring at room temperature for 3h. At particular time intervals, 5 mL of the solution was collected and centrifuged to obtain a clear solution. Afterwards, the remind 2, 4, 6-TCP was monitored by recording the absorbance from 200 to 600 nm using UV-vis spectrophotometer. The degradation efficiency was calculated by the following formula:

$$\text{Degradation} = \frac{C_0 - C}{C_0} \times 100 = \frac{A_0 - A}{A_0} \times 100 \quad (1)$$

Where A_0, A, and C_0, C are the absorbance and concentration of 2, 4, 6-TCP when the reaction time is 0 and t, respectively.

RESULT AND DISCUSSION

Characterization

XRD: The XRD pattern for CdS nanoparticles is shown in the Fig.1. The pattern consists of eight peaks within the region between 2θ, 20°-80°. The determined characteristics 2θ values correspond to mixed phases of CdS according to standard card No. 00-006-0314. The average crystallite size of CdS was calculated by Scherrer's equation

$$d = 0.9\lambda/\beta \cos\theta \quad (2)$$

Where d means the average crystallite size, λ is wavelength, β is full width at half maximum [FWHM] that can be measured from the XRD

peaks and θ is scattering angle [8, 9, 16, 26, 27]. The average crystallite size was around 46 nm.

FESEM: The field emission scanning electron microscopy (FESEM) image is shown in Fig. 2. a. The surface morphology of the CdS is confirmed to be nanoparticles. EDS was recorded in the binding energy between 0 and 15 keV, and is shown in Fig. 2.b. The peaks of the spectrum show the presence of Cd and S at 3.13 and 2.30 keV, respectively, which confirms the formation of CdS. The atomic quantity of cadmium and sulphur were found to be 78.8 and 21.2%, respectively. No other elements peak was seen in EDS spectrum, which indicates the high purity of the synthesized CdS nanoparticles.

FTIR: Fig. 3 shows FTIR spectrum of CdS nanoparticles. Sharp peaks at 584 cm^{-1} and 678 cm^{-1} are attributed to the Cd-S stretching mode of vibrations; that confirmed the formation of CdS. The band at 1053 cm^{-1} is due to the C-O bending mode that may be ascribed to intermediates resulted from remained thioacetamide in the reaction medium. Similarly, the bands at 1444 cm^{-1} and 2171 cm^{-1} may belong to C-N and C=S bending mode from remained thioacetamide, respectively [9, 15, 26, 28].

Photocatalysis evolution of CdS

Effect of pH: pH is one of the most important parameters which effects on photocatalytic removal rate of organic contaminants. Experiments were conducted between pH 2-11. Fig. 4 shows the effect of pH during 2, 4, 6-TCP photocatalytic degradation. The pKa of 2, 4, 6-TCP is 6.23. Thus, in acidic conditions, 2, 4, 6-TCP appears in molecular shape (Eq.3).

$$PhOH(Cl)_3 \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} {}^-O\ Ph(Cl)_3. \quad (3)$$

Therefore, low degradation is obtained in acidic medium [4]. In neutral and mild acidic medium, CdS surface is cationic. As a consequence, highest degradation reached at pH 6, which is near to pKa of 2, 4, 6-TCP [5]. A decrease in 2, 4, 6-TCP degradation rate was observed as pH is increased. This observation may be attributed to the repulsion of 2,4,6-trichlorophenoxide by CdS which has its surface covered with the excess hydroxide ions in base medium.

Effect of catalyst amount: The effect of catalyst dosage on photodegradation of 2, 4, 6-TCP was studied by varying CdS amount from 0.02 to 0.08 g in 65 $mg.L^{-1}$ 2, 4, 6-TCP solution. As shown in Fig. 5, the degradation increased as CdS amount is increased up to 0.06 g owing to the presence of more catalyst sites for pollutant degradation. Above 0.06 g of CdS amount, decreasing in degradation was obtained which could be accredited to light scattering by excess CdS and lower light penetration. Thus, 0.04 g CdS was chosen to be optimum catalyst mass for 2, 4, 6-TCP degradation in this study [4, 8, 9, 29].

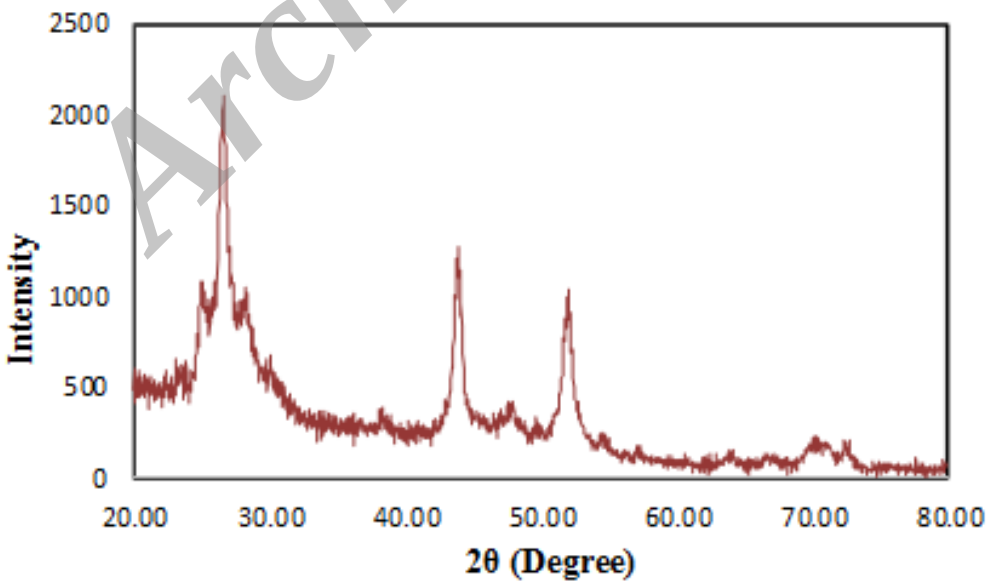

Fig.1: The XRD pattern of CdS nanoparticles

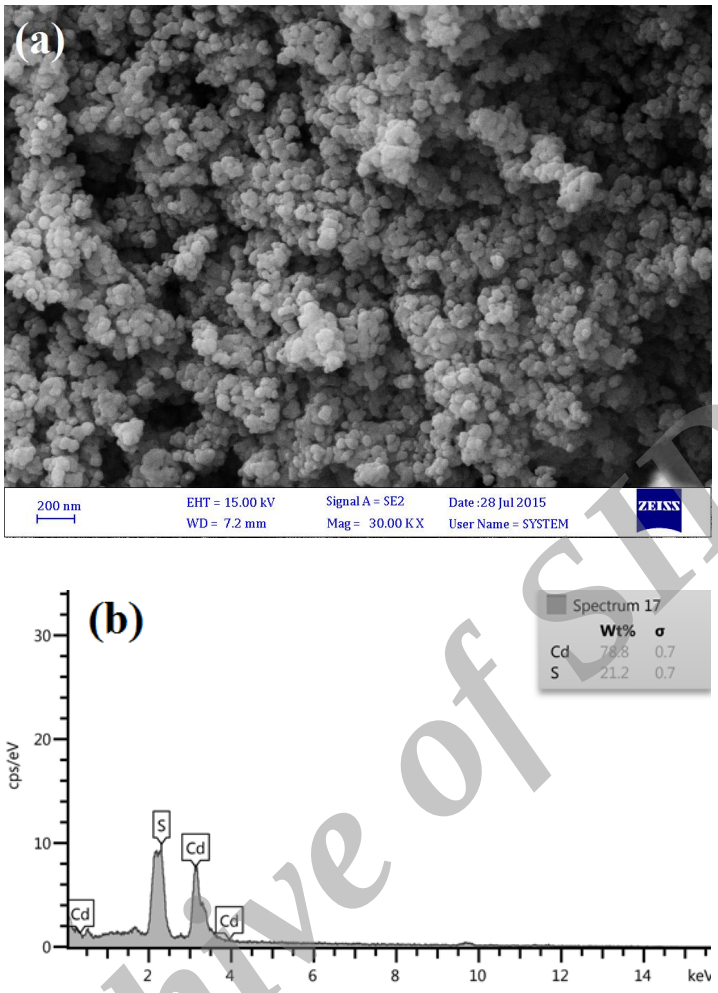

Fig. 2: (a) FESEM image of CdS nanoparticles at different magnifications and (b) EDS pattern of CdS nanoparticles

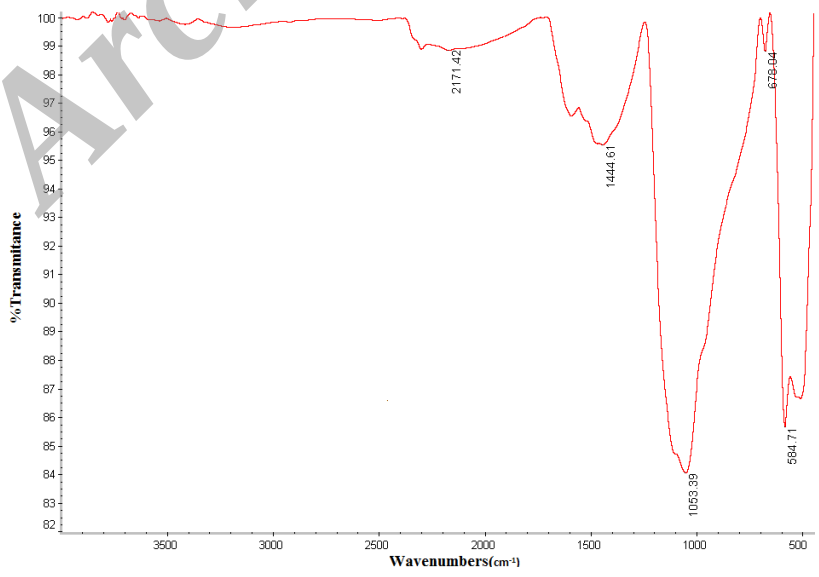

Fig. 3: FT- IR spectrum of CdS nanoparticles

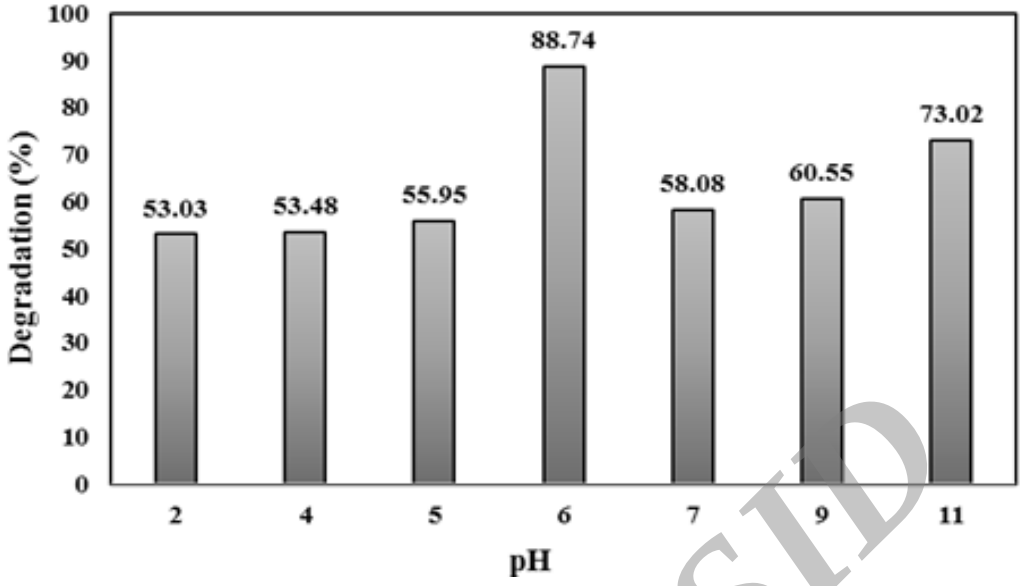

Fig. 4: The effect of initial pH of sample on the photo degradation of 2, 4, 6-TCP catalyzed by CdS nanoparticles (0.04 g)

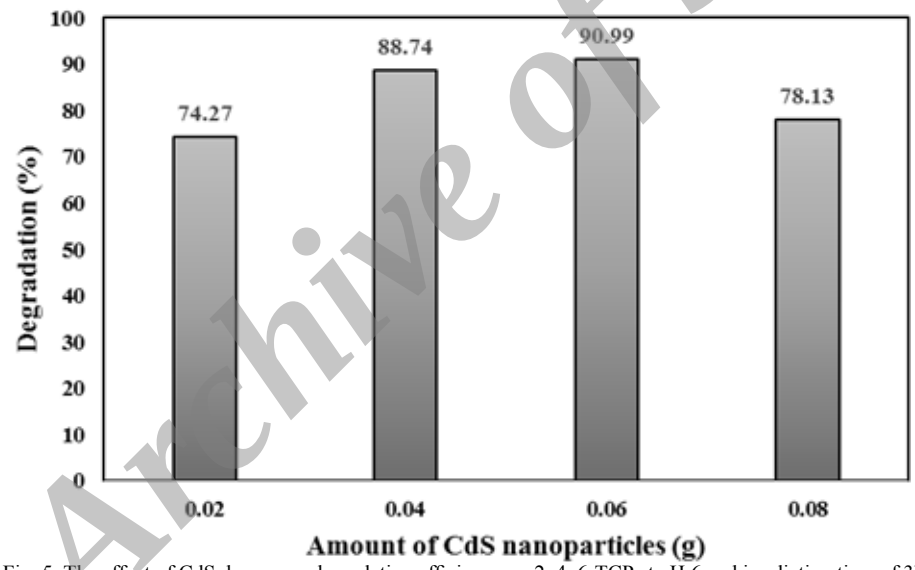

Fig. 5: The effect of CdS dosage on degradation efficiency on 2, 4, 6-TCP at pH 6 and irradiation time of 3h

Effect of contaminant concentration: The influence of contaminant concentration on its degradation was studied at different concentrations varying from 20-200 mg.L^{-1} in presence of 0.04 g CdS catalyst under UV-C light. As shown in Fig. 6, highest photodegradation is achieved at 65 mg.L^{-1} concentration as a result of abundant active sites to be occupied by the 2, 4, 6-TCP. A slight drop in degradation was acquired when concentration was less than 65 mg.L^{-1} , which may be attributed to insufficient substrate or coverage of active sites by solvent. A steady photodegradation was observed in range of 40-65 mg.L^{-1} that probably attributed to balance between the catalyst amount and the contaminant amount.

As the 2, 4, 6-TCP concentration exceeds 65 mg.L^{-1}, a decrease in the photocatalytic degradation was obtained which would be a result of excessive 2, 4, 6-TCP in solution and insufficient active sites on photocatalyst. Thus, 65 mgL^{-1} of 2, 4, 6-TCP was chosen as contaminant concentration for this study [8, 29].

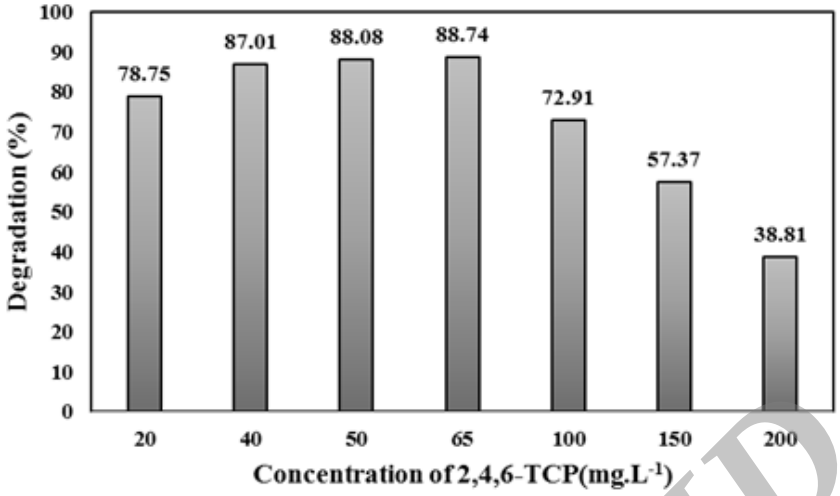

Fig. 6: The effect of 2, 4, 6-TCP concentration on its photo degradation catalyzed by CdS nanoparticles (0.04g) at pH 6 and irradiation time of 3h

CONCLUSION

In this present work, CdS nanoparticles were successfully synthesized by microwave-assisted sol-gel method. The average crystallite size of 46 nm was obtained for CdS nanoparticles. The EDS spectrum has shown high purity of synthesized CdS nanoparticles. The effect of important parameters such as pH, catalyst mass and contaminant concentration were investigated. The optimum condition for degradation of 2, 4, 6-TCP were catalyst mass and contaminant concentration 0.04 g and 65 $mg.L^{-1}$, respectively, at pH 6. Under ehich, 2, 4, 6-TCP was 88.74% degraded after 3h of UV-C light irradiation.

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