

## Effects of Operational Parameters on Degradation of Methyl Orange Dye over Nanosized CdS Photo-catalyst under UV Radiation

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### Abstract

*Nano-size CdS has been prepared by aqueous chemical method using glycine as a capping and stabilizing agent. X-ray diffraction (XRD) analysis of as-synthesized material revealed hexagonal wurtzite structure of CdS with average crystallite size 48.1 nm. The observed FTIR spectra support the template role of glycine in controlling the size of CdS nanoparticles. Photo-catalytic efficiency of CdS nanoparticles was investigated under UV irradiation following degradation of methyl orange (MO), as a probe. Effect of some operational parameters such as photo-catalyst load, pH of solution and substrate (MO) initial concentration on the photo-catalytic degradation of the dye have been investigated. Using methyl orange initial concentration 300 mg/L, optimum photo-catalyst load 120 mg /L and pH 4.0, as high as 92 % degradation of methyl orange could be achieved under UV radiation. The photo-catalytic method developed here can be used for large scale treatment of water bodies contaminated with methyl orange dye.*

**Keywords:** Nanoparticles; photo-catalytic; degradation; UV irradiation; FTIR

### 1. Introduction

The untreated effluents from paper and textile industries are contaminated with organic pollutants such as dyes and phenolic compounds. These chemicals being toxic and non-degradable, adversely affect the eco-system and are a health hazard for humans as well as animals. The usual methods, such as precipitation, absorption, flocculation and ultrafiltration, adopted for the removal of these chemicals from the polluted water are ineffective, costlier and generate enormous solid waste requiring secondary treatment [1]. Photo-catalytic degradation process, over nanosize semiconductor photocatalysts, has emerged as an efficient and cost-effective alternative for the removal of organic pollutants from contaminated water [2]. This process involves the formation of electron-hole pairs at the surface of semiconductor particles exposed to photons of

suitable radiation. The electron-hole pairs thus generated may either recombine or may interact with oxygen and water molecules at the semiconductor surface, generating highly reactive hydroxyl ( $\bullet\text{OH}$ ) free radicals responsible for the subsequent mineralizing of organic pollutants into harmless compounds, such as  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ . However, the re-combination of photo-generated electron-hole pairs can retard the solar energy conversion [3,4] and photo-catalytic efficiencies of semiconductors. In order to enhance these efficiencies, photo-excited electron-hole separation in semiconductor photo-catalysts, is necessary. To achieve this, researchers have adopted different strategies such as: photo-catalyst surface modification [5-11], use of dopants [12-17], compositing two or more photo-catalysts [18-21] and Use of Sensitizers [22-25]. Besides these, photo-catalytic efficiency may also be improved by

decreasing the photo-catalyst size down to the nanoscale [26].

In the recent years, nano-size particles, due to their unique optical, electrical and chemical properties, have attracted attention of several workers. Unlike the bulk materials, the emission wavelength of the nanoparticle (quantum dots) depends on their crystal dimension. Therefore, many researchers have focused on the production of nanomaterials that have controllable size. Among the semiconductor photocatalysts, CdS with band gap of 2.42 eV at 300 K, has wide applications for laser light emitting diodes, solar cells and some optoelectronic devices based on nonlinear properties [27]. Semiconductor CdS nanoparticles have been widely studied and synthesized because of their unique properties and photocatalyst application. The properties of CdS nanoparticles are mainly driven by two factors- (a) their high surface to volume ratio and (b) drastic change in the electronic structure of the material due to quantum mechanical effects with decreasing particles size.

Though various modification techniques have appeared in the literature to improve the photocatalytic efficiency of CdS yet to the best of our

knowledge, no work has been reported on the effect of operational parameters on photo-catalytic degradation of methyl orange (MO) over CdS nanoparticles under UV radiation. Methyl orange is an azo dye used in textile and dyestuff industries. Methyl orange has a deep orange color and its presence in effluents possess an environmental threat. In the present study, CdS nanoparticles have been prepared using aqueous chemical method and characterized by XRD, FTIR and spectroscopic techniques. The as-synthesized nanomaterial was used as a photo-catalyst for the degradation of methyl orange dye in aqueous solution under UV radiation. In order to achieve maximum degradation of the dye the operational parameters were also optimized.

## 2. Material and methods

### 2.1. Material

Cadmium nitrate ( $\text{Cd}(\text{NO}_3)_2$ ), sodium sulfide ( $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ ), sodium hydroxide ( $\text{NaOH}$ ) and hydrochloric acid ( $\text{HCl}$ ), each from FLUKA (Switzerland) and glycine (BDH), were used as such. Methyl orange ( $\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$ ) dye was procured from BLULUX LABORATORIES (India). The molecular structure of methyl orange is shown in Figure 1.

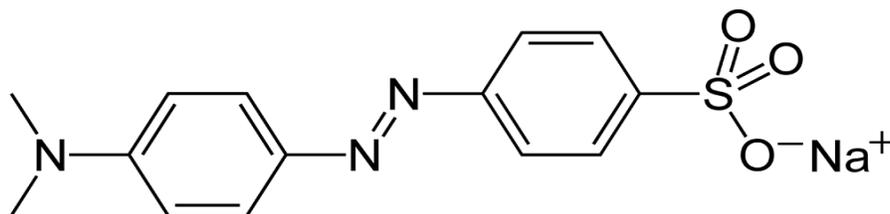


Figure 1. Molecular structure of methyl orange dye

## 2.2. Methods

### 2.2.1. Synthesis of CdS nanoparticles

Cadmium nitrate 100 mL aqueous solution (0.1M) was slowly mixed with an equal volume sodium sulfide aqueous solution (0.1 mL)- pre-mixed with 5 ml glycine and magnetically stirred for 15 h, at 80°C. The

yellow colored colloidal dispersion, thus obtained, was dried up by evaporating at room temperature and then calcined at 400 °C in a muffle furnace.



### 2.2.2. X-ray Diffraction (XRD) Study

The XRD pattern of as-synthesized CdS was recorded at an X-ray diffractometer (BRUKER D8 Advance XRD, AXS GMBH, Karlsruhe, West Germany) equipped with a Cu target generating a  $\text{CuK}\alpha$  radiation (wave length 1.5406 Å). The instrument was operated using accelerating voltage 40kV and applied current 30 mA under step scan with step time and degree ( $2\theta$ ) as 1s and 0.020°, respectively, over  $2\theta$  range: 4 to 64°

### 2.2.3. FTIR Spectroscopic Analysis

As-synthesized CdS powder (10 mg) was sandwiched between a pair of a KBr plates and the spectra over 400 to 4000 $\text{cm}^{-1}$  was recorded on a fourier transform infra-red (FTIR) spectrometer (Shimidazu).

### 2.2.4. UV/Vis Diffuse Absorption Study

For determining diffuse absorption edge and band gap energy of synthesized CdS nanoparticles, absorption spectra of its 0.1% aqueous suspension was recorded on a UV-visible spectrophotometer (SANYO, SP65, GALANAKAMP, made in U.K), over the wave length range: 200-800nm.

### 2.2.5. Photo-catalytic Degradation Study

Photo-catalytic degradation of methyl orange (MO) dye in aqueous solution was carried out under an ultraviolet radiation source having radiation intensity 2.3905  $\text{mW}/\text{cm}^2$  following batch operation method. A known amount of as-synthesized CdS powder was dispersed in 100mL methyl orange aqueous solution of specified initial concentration, taken in reactor tube made of quartz. Initial pH of the reaction mixture was adjusted by adding appropriate amount of 1M HCl or 1M NaOH solutions. The reaction mixture was continuously purged with air at 100 mL / min. Five mL each of the reaction mixture was withdrawn at regular intervals up to three hours and centrifuged at 4000rpm for 10minutes on a centrifuge ( $K_2$  series, Centerion Scientific ltd, U.K). The absorbance of clear

supernatant liquid was recorded at 462nm using a UV-visible spectrophotometer (Sanyo, SP65, Galanakamp, U.K). The degradation of dye was calculated using the following equation [28]:

$$\% \text{ Degradation} = [(A_0 - A_t) / A_0] \times 100 \quad (1)$$

where  $A_0$  and  $A_t$  are the absorbance values at the initial stage and at reaction time 't', respectively.

## 3. Results and Discussion

### 3.1. XRD Analysis

XRD pattern of as-synthesized CdS photocatalyst is depicted in Figure 2. The observed diffraction peaks correspond to (002), (100), (101), (111) and (103) planes of hexagonal wurtzite structure of CdS nanocrystals. Average particle size of CdS was calculated using Debye Scherrer equation

$$D = K\lambda / (\beta \cos \theta) \quad (1)$$

where D is the average particle size in nm, K is the shape factor constant and is taken as 0.94,  $\beta$  is the full width at half maximum (FWHM) in radians,  $\lambda$  is wavelength (0.15406 nm) of the X-ray used and  $\theta$  is diffraction angle for (101) plane of wurtzite CdS. The average crystallite size of as-synthesized CdS photocatalyst powder was found to be 48.1nm.

### 3.2. FTIR Spectroscopy

The FTIR spectrum of as-synthesized CdS nanoparticles is shown in Figure 3. The absorption peak at 3420 $\text{cm}^{-1}$ , in the higher energy region, is assigned to O-H stretching of absorbed water on the surface of CdS nanoparticles and absorptions at 1625  $\text{cm}^{-1}$  and 1440 $\text{cm}^{-1}$  are due to carbonyl (CO) stretching and OH bending vibrations, respectively, within glycine's COOH group. Further, the observed two low intensity peaks near 3400 $\text{cm}^{-1}$  are assigned to  $\text{NH}_2$  group in glycine. These observations convincingly support template role of glycine in controlling the size of CdS particles.

Fikadu Tsehaye, Om Prakash Yadav and Lokesh Yadav

Effects of operational parameters on degradation of methyl orange dye over nanosized CdS photocatalyst ...

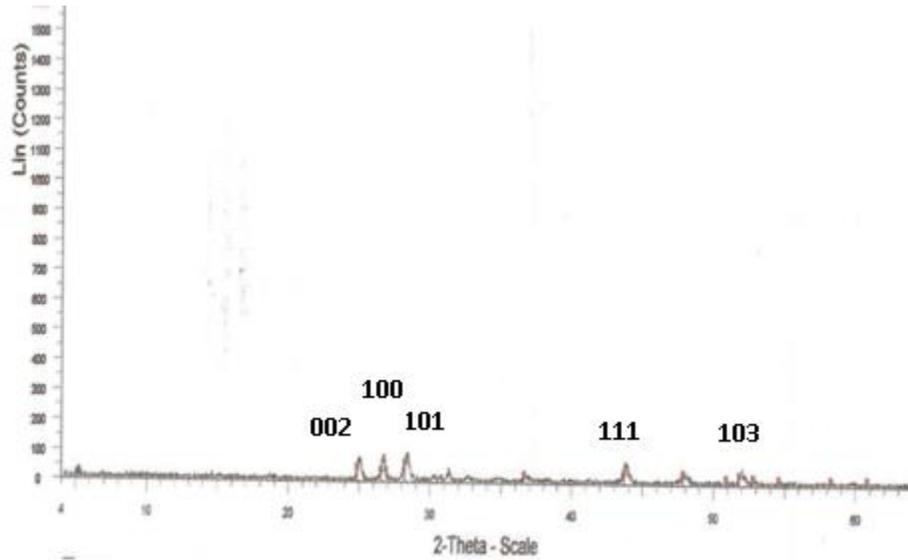


Figure 2. XRD pattern of as-synthesized CdS photo-catalyst

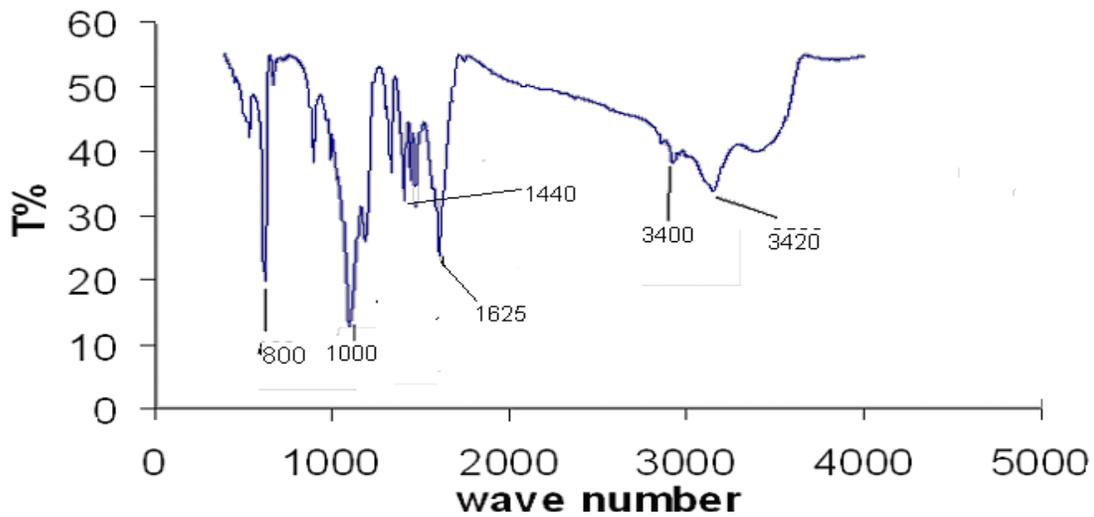


Figure 3. FTIR Spectrum of as synthesized CdS nanoparticles

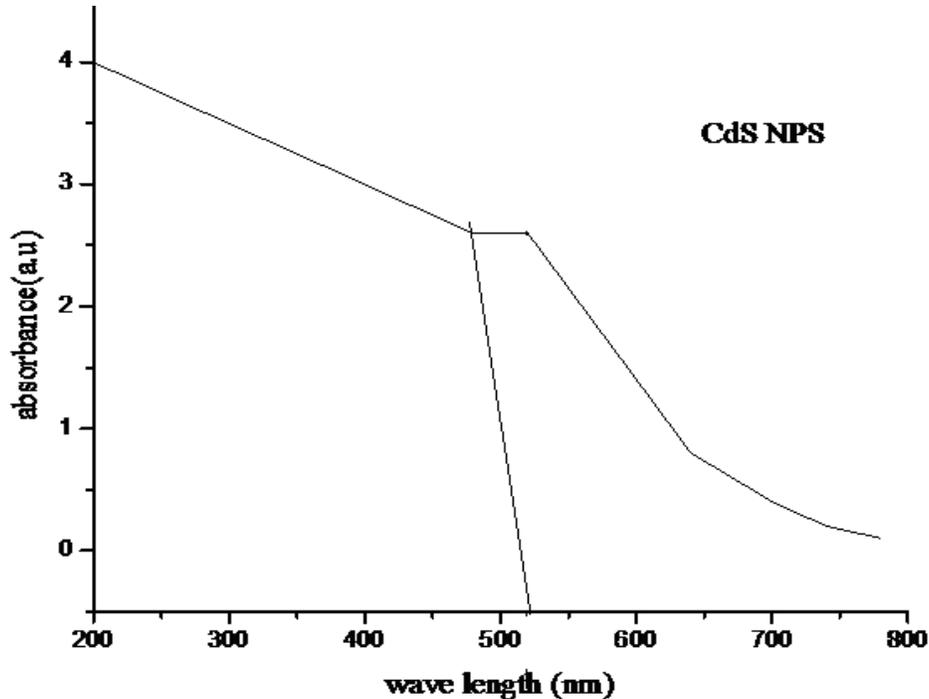


Figure 4. UV-visible absorption spectra of 0.1 % aqueous suspension of CdS nanoparticles (Absorption edge: 525 nm)

### 3.3. UV-Visible Absorption Study

The UV-Visible absorption spectra of as-synthesized 0.1 % aqueous suspension of CdS powder is shown in Figure 4 exhibiting the absorption edge at 525 nm. The broadening of the absorption spectrum could be due to the quantum confinement of the nanoparticles. Band gap energy ( $E_g$ ) of CdS nanoparticles was calculated using the relation:

$$E_g = 1240 / \lambda \quad (2)$$

where,  $E_g$  is band gap energy in electron volts (eV) and  $\lambda$  is wavelength (nm) at the absorption edge. The band gap energy of CdS photocatalysts thus obtained was 2.36 eV [29].

### 3.4. Photocatalytic Degradation of Methyl Orange

#### 3.4.1 Effect of Catalyst Load

The optimization of the photo-catalyst load is important for achieving maximum substrate (dye) degradation as well as for the cost-effectiveness of the process. The percent photo-catalytic degradations of methyl orange (MO) dye over as-synthesized CdS nanoparticles as a function of reaction time under UV radiation at different loads of catalyst (300 mg/L to 1.80 g/L).using MO initial concentration 100 mg/L; pH = 6.8, are presented in Figura 5. It is observed that the percent photo-catalytic degradation of dye increases on raising the photo-catalyst load from 300 mg/L up to 1.20 g/L, however, upon further increasing the photo-catalyst load MO degradation falls. The observed increase in degradation of dye on raising the photo-catalyst load from 300 mg/L to 1.20 g/L, may be due to an enhanced availability of number of active sites per substrate (dye) molecule at the catalyst surface. However, the observed fall in dye degradation above

Fikadu Tsehaye, Om Prakash Yadav and Lokesh Yadav

Effects of operational parameters on degradation of methyl orange dye over nanosized CdS photocatalyst ...

the optimum photo-catalyst load (1.20 g/L) may be attributed to the diminished photons penetration into

the bulk reaction mixture due to the light scattering as well as the screening effects.

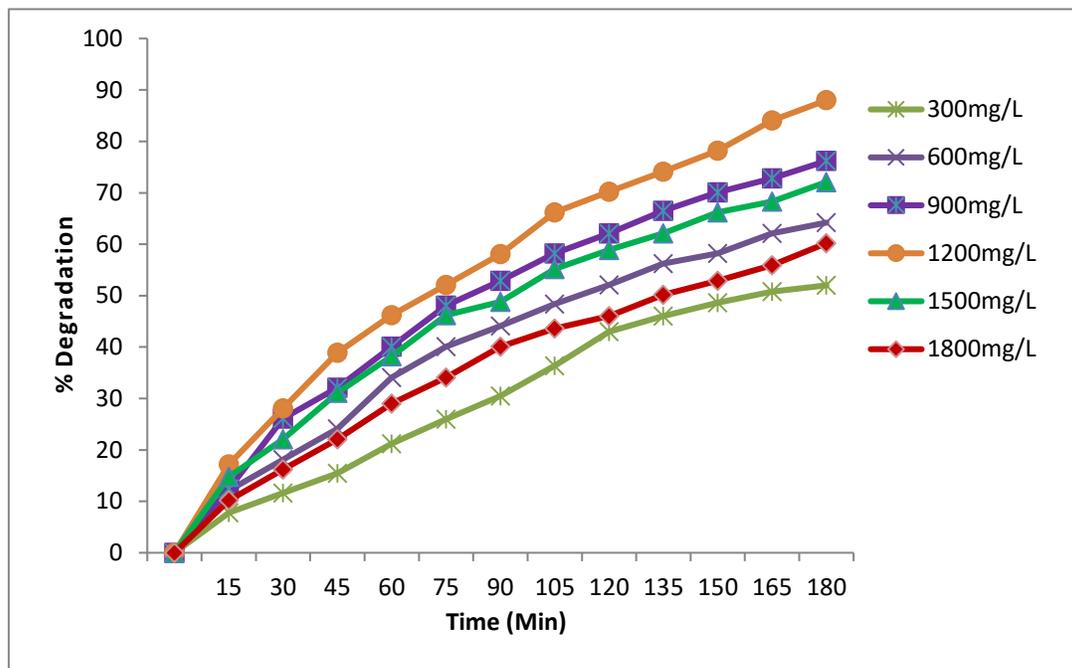


Figure 5. Percent photo-catalytic degradation of methyl orange as a function of reaction time under UV radiation using different loads of CdS photo-catalyst (MO initial concentration 100 mg/L; pH = 6.8)

### 3.4.2. Effect of pH on photocatalytic degradation

Electrostatic interactions of semiconductor surface with the solvent as well as substrate (dye) molecules and also with charged radicals formed during photo-catalytic oxidation, strongly depend on the pH of the reaction medium. In addition, protonation or deprotonation of the substrate (dye) can take place and hence affecting the photo-catalytic degradation of pollutants in water.

Plots of percent degradation of methyl orange dye under UV irradiation as a function of time at varying pH (2 to 7) using dye initial concentration (300 mg/L) and optimum photo-catalyst load 1.20 g/L, are presented in Figure 6. Percent degradation of dye at 3 hrs as a function of pH are shown in Figure 8. It is observed that the degree of degradation of MO increases upon raising pH from 2 to 4 and then decreases until pH 7 is reached. Such a result can be

better understood taking into account that both the surface state of the photocatalyst and the ionization state of dye (MO) depending on pH of the solution. Since the pH at point of zero charge (PZC) for CdS is 3.7 [30], the CdS surface above pH 3.7, acquires negative charge and below this pH, it becomes positively charged. Methyl orange molecules have negative charges in a wide pH value range. Therefore, when the pH of MO solution is below the PZC, the MO anions should be readily adsorbed on the surfaces of nanosize CdS particles leading to higher photo-catalytic degradation. However, the lowering of dye degradation going down the optimum pH 4, may be due to diminishing over all negative charge on MO due to protonation of its amino group. At higher pH, above the optimum pH 4, the photo-catalyst surface as well as methyl orange molecules acquire negative charge causing diminishing of dye adsorption at the similarly charged photo-catalyst resulting in the decrease of

Fikadu Tsehaye, Om Prakash Yadav and Lokesh Yadav

Effects of operational parameters on degradation of methyl orange dye over nanosized CdS photocatalyst ...

dye degradation. Moreover, at higher pH, hydroxyl radicals ( $\bullet\text{OH}$ ) are rapidly scavenged missing opportunity to interact with the dye in the degradation process.

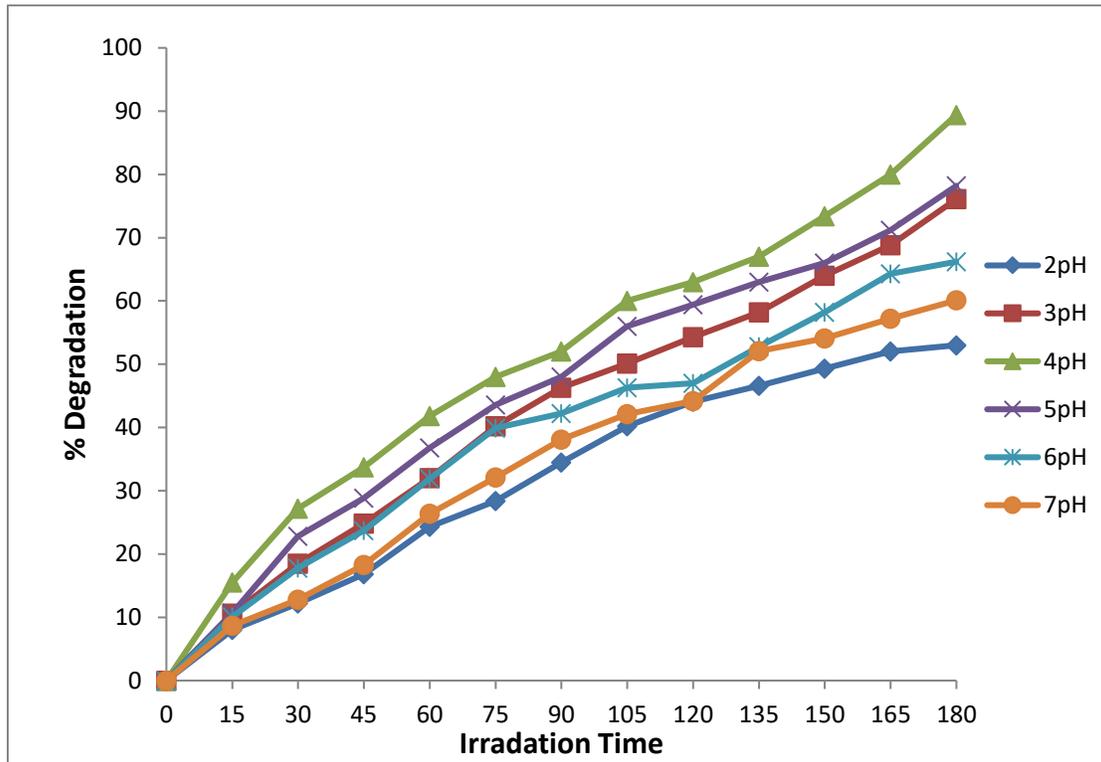


Figure 6. Percent photo-catalytic degradation of methyl orange (MO) as a function of time at different pH (MO initial concentration: 300 mg/L; photo-catalyst optimum load:1.20 g/L).

3.4.3. Effect of Dye Initial Concentration

Plots of percent photo-catalytic degradation of MO under UV radiation using varying dye initial concentrations (optimum photo-catalyst load 1.20 g/L and pH = 4) as a function of time are presented in Figure 7. It is observed that degradation of MO decreases with increasing dye initial concentration. It may be because on raising dye initial concentration (a) the number of available photo-catalyst active sites per substrate (dye) molecule decreases and (b) photons intensity reaching the photo-catalyst surface diminishes. Both these effects result in generation of fewer reactive  $\bullet\text{OH}$  radicals responsible for the lowering of dye degradation [31].

Conclusion

Cadmium Sulphide (CdS) nanoparticles with average crystallite size 48.1 nm and band gap energy 2.38 eV have been synthesized by a simple chemical route using glycine as a capping agent. FTIR spectra has supported the template role of glycine in controlling the size of CdS photo-catalyst nanoparticles. The effects of photo-catalyst load, pH and substrate concentration on the degradation of methyl orange have been studied. Using optimum photo-catalyst load, 120 mg /L and pH 4.0, as high as 92 % degradation of methyl orange could be achieved under UV radiation. The photo-catalytic method developed in the present study for efficient removal of methyl orange may be used for the treatment of dye

Fikadu Tsehaye, Om Prakash Yadav and Lokesh Yadav

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contaminated industrial effluent on a commercial scale.

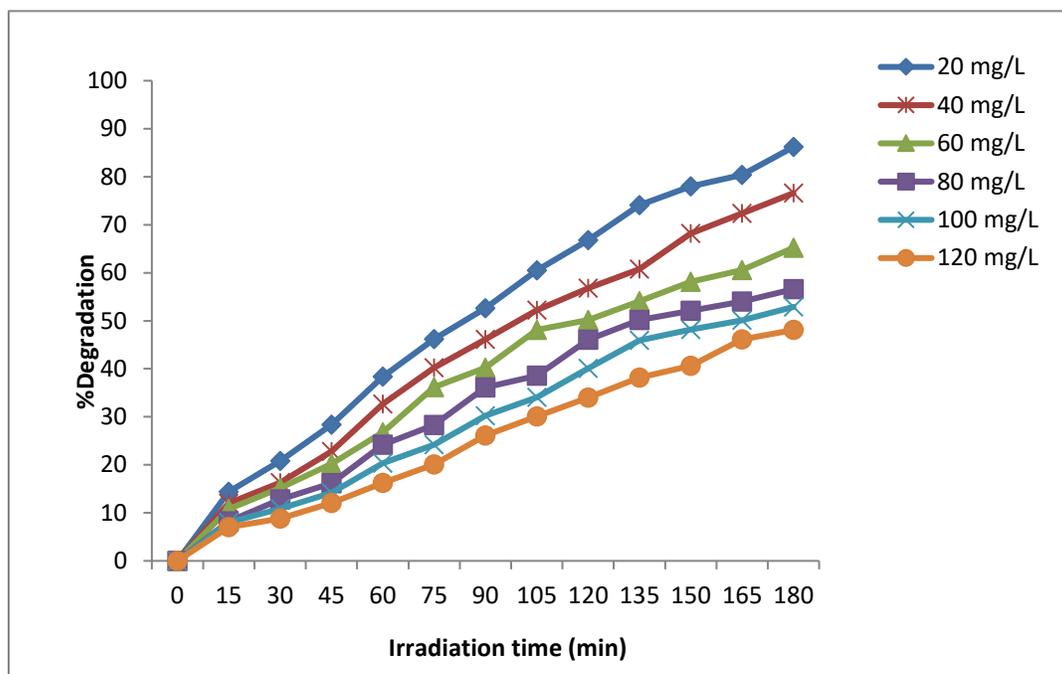


Figure 7. Plots of percent photo-catalytic degradation of MO under UV radiation using varying dye initial concentrations (optimum photo-catalyst load 1.20 g/L and pH = 4) as a function of time

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### Conflict of Interest:

There is no conflict of interest for publishing the paper.

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Fikadu Tsehaye, Om Prakash Yadav and Lokesh Yadav

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Fikadu Tsehaye, Om Prakash Yadav and Lokesh Yadav

Effects of operational parameters on degradation of methyl orange dye over nanosized CdS photocatalyst ...

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