



Photo degradation of synthetic dyes using cadmium sulfide nanoparticles synthesized in the presence of different capping agents

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ARTICLE INFO

Article history:

Received 24 November 2010
Received in revised form 30 November 2011
Accepted 30 November 2011
Available online 8 December 2011

Keywords:

Capping agents
Photo-catalyst
CdS nanoparticles
Synthetic dyes' photo-degradation
Water color removal

ABSTRACT

Photo-degradation of synthetic dyes by cadmium sulfide nano-particles synthesized by micro-emulsion/arrested precipitation routes using thioglycolic acid; potassium pyrosulfate and disodium salt of ethylene diamine tetra acetic acid (EDTA) as capping agents have been investigated. Synthesized nanoparticles have been characterized by X-ray diffraction, thermo-gravimetric analysis, high-resolution transmission electron microscopy, BET surface area analysis and UV–Vis spectro-photometry. The synthesized cadmium sulfide nano particles are observed to be a mixture of cubic and hexagonal phases and have crystallite size and surface area of 3.7, 6.8 and 13.9 nm and 32.11, 29.54 and 8.63 m²/g for thioglycolic acid, potassium pyrosulfate and EDTA capping agents, respectively. As expected, the photo-catalytic efficiency of nano-particles for degradation of dyes is observed to increase with increase in surface area (decrease in particulate size).

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1. Introduction

Cadmium sulfide nano particles have been extensively studied due to their unique photocatalytic, phosphorescence, photoluminescence and tunable emission properties [1–12]. The decrease in particles size in nano meter scale of CdS causes an increase in its band gap leading to an enhancement of the redox potential [13] and thus making it useful for applications in water decomposition [14,15], color removal [13,16,17], etc. In addition to mechanical milling [18], solvo/hydro thermal synthesis [19–21], micro-emulsion [22–27], sono-chemical [28,29] and capped precipitation from aqueous solutions [30–34] have been reported in literature. A number of capping agents such as thioglycerol [1], dodecanethiol [23], *n*-trioctyl phosphine oxide [30], starch [31], bio-molecules [32,33], polyvinyl pyrrolidone [34], thiophenol [35], HMP [36], flufenamic acid [37] and glucose [38] have been used. Generally emulsion methods are observed to give nano powders of smaller size as compared to capped precipitation. In the present work, reverse emulsion and chemical precipitation methods, in the presence of capping agents have been used to synthesize CdS nano powders. The powders have been characterized for their phase analysis, particle size, photoluminescence and band gap properties. The synthesized CdS nano powders have been used for photocatalytic degradation of synthetic dyes – methylene blue and crystal violet which are toxic but

are still used in textile industry and create difficulty for their effluent discharge. The results of these studies are presented in this paper.

2. Experimental details

2.1. Chemicals

Cadmium nitrate (RANKEM) LR and cadmium acetate (CDH) AR grade sodium sulfide (RANKEM) LR and potassium pyrosulphate (MERCK) LR, thioglycolic acid (MERCK) LR, disodium salt of ethylene diamine tetra acetic acid (CDH) AR, diethyl ether (MERCK) GR, sodium dodecyl sulfosuccinate (Loba chemie) LR were used as received. Aqueous solutions were made using double distilled water.

2.2. Methods

2.2.1. Synthesis of CdS nano powders by arrested precipitation method

To an aqueous solution of 10 g capping agent (potassium pyrosulfate or disodium salt of ethylene diamine tetra acetic acid (EDTA), 10 ml of 0.25 M cadmium acetate solution was added drop wise and then heated to boiling. After cooling 10 ml 0.25 M sodium sulfide solution was added drop wise under vigorous stirring to obtain yellow colored fine precipitate. The precipitate was filtered using Whatman filter paper (No. 42), washed thoroughly with water and then dried in an air oven at 80 °C.

2.2.2. Micro-emulsion method

To a 100 ml solution of 0.5 M sodium dodecyl sulfosuccinate (AOT) in diethyl ether, 20 ml of 0.4 M cadmium nitrate aqueous

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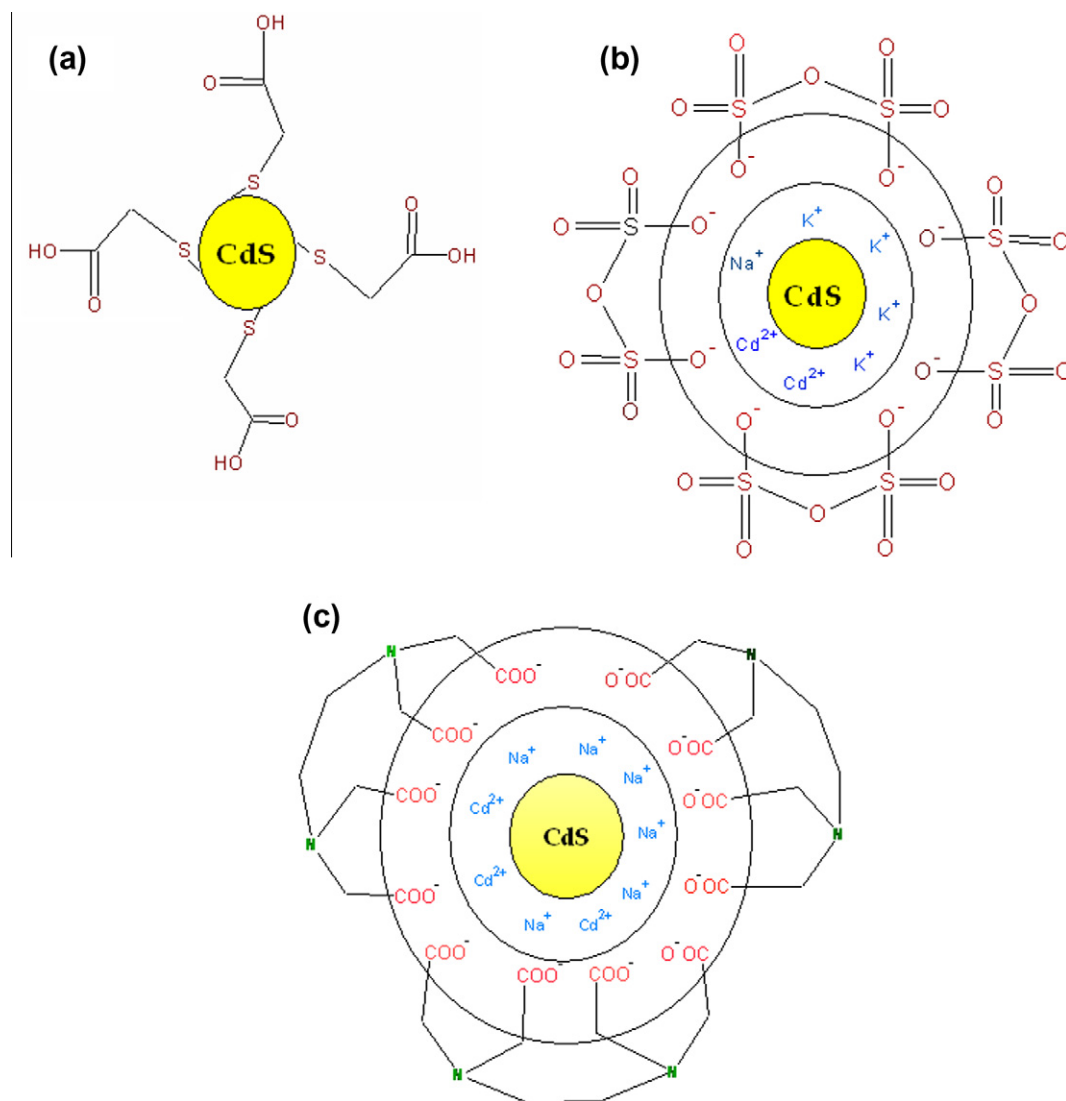


Fig. 1. Mechanism for CdS nanoparticles using different capping agents (a) CdS-T, (b) CdS-K and (c) CdS-E.

solution was added drop wise under continuous stirring using a magnetic stirrer and Teflon sleeved magnetic bit to form a micro emulsion. After drop wise addition of 1 ml thioglycolic acid to the emulsion, 20 ml of 0.4 M aqueous sodium sulfide solution was added slowly under continuous stirring to obtain very fine precipitate, which was filtered, washed thoroughly with ethanol and then dried in an air oven at 80 °C.

2.3. Characterization of CdS synthesized by precipitation and micro-emulsion methods

Identification of the phases present in the synthesized CdS nanoparticles was carried out using X-ray diffraction spectrometer (Bruker – Model D-8) using Cu K α radiation ($\lambda = 1.54$ nm), operated at 40 kV and 40 mA at a scan rate of 1° 2 θ /s in the range 2 θ = 10–70° and comparing the inter planar distances and intensity values with those of the corresponding standard peaks using JCPDS files. The TGA measurements were performed on a Mettler Toledo TGA/DSC-1 STAR^E SYSTEM instrument at a heating rate of 5 °C/min. For studying particle morphology high-resolution transmission electron microscope (HRTEM) (JOEL 3010), operated at 100 kV, was used. For morphology studies, the synthesized samples were sonicated in acetone for 15 min followed by ambient drying and mounted on carbon coated copper grids. The Brunauer–Emmett–

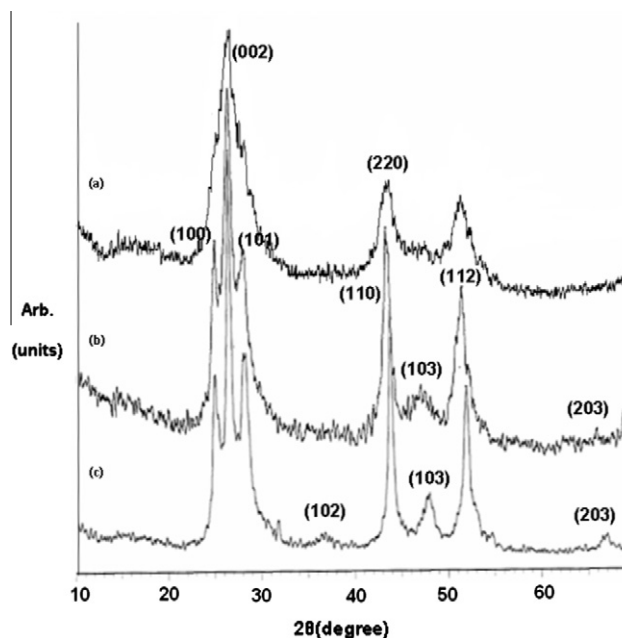


Fig. 2. XRD pattern of CdS nanoparticles (a) CdS-T, (b) CdS-K and (c) CdS-E.

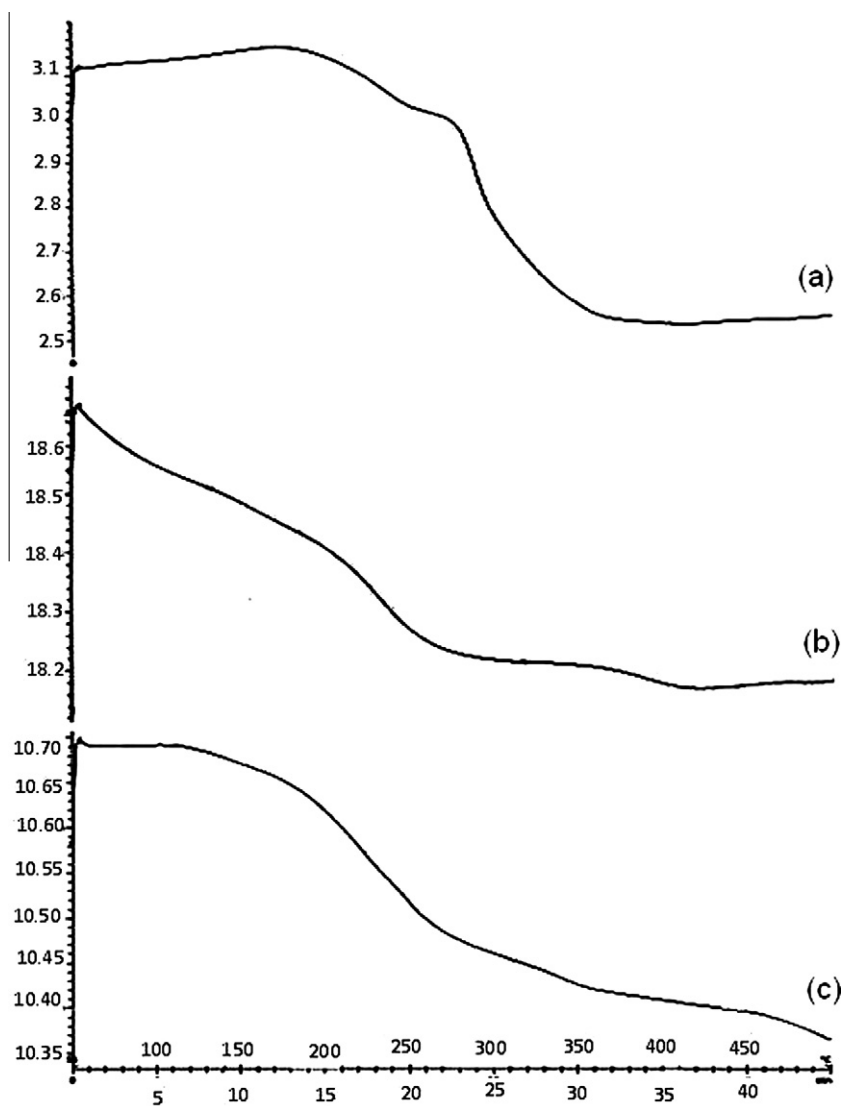


Fig. 3. TGA graph for CdS nanoparticles (a) CdS-T, (b) CdS-K and (c) CdS-E.

Teller surface area of the powders was analyzed by nitrogen adsorption in a Quantachrome – Autosorb – 01 apparatus. All the Samples were degassed at 100 °C prior to nitrogen adsorption measurements. The band gap of nano sized CdS samples and their photo-degradation efficiency for chosen dyes was estimated using UV–VIS Absorption Spectrometer (Varian Model: carry 100 conc).

2.4. Studies on photo catalytic dye-degradation

Photocatalytic activity of CdS nanopowders was studied by degradation of synthetic methylene blue and crystal violet dyes in aqueous solution. 0.1 g CdS nano particles were suspended in 200 ml solution of the dye in a reactor and exposed to light from top from a 160 W mercury vapor lamp for durations ranging between 5 and 105 min. The reactor was placed in a thermo stated bath to maintain its temperature at 30 °C. The contents in the reactor were continuously stirred using magnetic stirrer. The distance between light source and surface of the solutions was maintained at 15 cm to avoid excessive heating. From the absorbance data, with and without exposure to light, the photo catalytic degradation efficiency (C) of CdS nano powders was calculated using the formula:

$$C = (A_0 - A)/A_0 \times 100\% \quad (1)$$

'A₀' and 'A' are absorbance values of the dye before and after photo-irradiation.

3. Results and discussion

3.1. Mechanisms of CdS nanoparticles formation

3.1.1. Micro-emulsion method

The water-in-oil type of micro emulsion used in the present study comprises of dispersion of tiny aqueous droplets of Cd(NO₃)₂ in diethyl ether (oil) phase. These small nano size droplets act as nano reactors [23]. The small size of the droplets, coupled with low concentration restricts availability of material for growth of crystals and the presence of capping agents like thioglycolic acid prevents aggregation due to surface repulsion. Fig. 1a shows capping of CdS nanoparticles by thioglycolic acid.

3.1.2. Controlled precipitation method

The proposed mechanism of CdS nanoparticles formation is similar to that suggested by Warad et al. for ZnS nano-particles [39]. The growth process initially involves formation of primary nuclei or seeds of CdS which have very high surface energy. These seeds grow by reactive precipitation of anions and cations at-

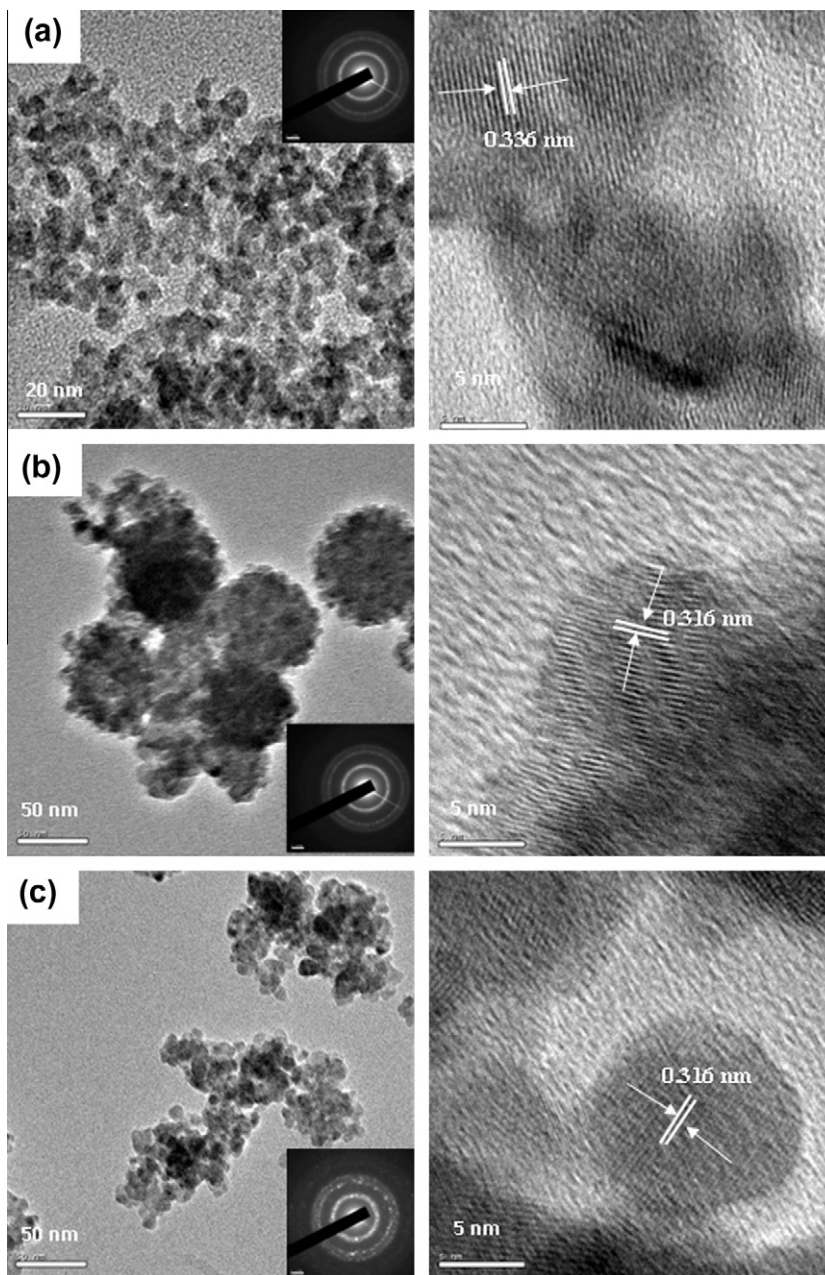


Fig. 4. HRTEM of CdS nanoparticles (a) CdS-T, (b) CdS-K and (c) CdS-E.

tracted towards the surface of the nuclei (seeds). The diffuse layer in the case of potassium pyrosulfate capped CdS nanoparticles is formed by pyrosulfate molecules (Fig. 1b). These bulky molecules create steric hindrance which impedes aggregation. Fig. 1c shows CdS nanoparticles capped by EDTA.

3.2. X-ray diffraction

The X-ray diffractograms of the three nano sized CdS powders are given in Fig. 2. The CdS sample made by reverse emulsion method in the presence of thioglycolic acid capping agent (CdS-T) shows the presence of broad peaks with 'd' values 3.53, 3.34, 3.20, 2.06 and 1.76 nm, indicating the presence of a mixture of cubic and hexagonal phases of CdS (cf. Fig. 2a). It is notable that the intensity of 3.34 peak (common for cubic and hexagonal phases) is higher than the 100% peak ('d' value 3.20) for hexagonal phase alone. The crystallite size, calculated from the peak broadening

using Scherer's equation is observed to be 3.7 nm. The X-ray diffractograms of the CdS samples prepared by controlled precipitation method using $K_2S_2O_7$ and EDTA as capping agents (cf. Fig. 2a and c) show the presence of additional peak with 'd' value 1.89 nm, which also corresponds to hexagonal/cubic phases of CdS. The crystallite size, calculated from the broadening of the major peak using Scherer's equation for the CdS-T, CdS-K and CdS-E samples is observed to be 3.7, 6.8 and 13.9 nm, respectively. The increase in the crystallite size (CdS-T < CdS-K < CdS-E) is reflected in the well formed/sharpness of the peaks (cf. Fig. 2).

3.3. TGA analysis

The TGA plots of CdS samples prepared using different capping agents viz., thioglycolic acid, potassium pyrosulphate and EDTA are shown in Fig. 3a–c respectively. The weight loss in all the three cases is observed to be in two steps, the first up to a temperature

of approximately 250 °C may be attributed to removal of adsorbed moisture. The second step involves removal of adsorbed capping molecules from the surface of CdS nano particles. For CdS-T it takes place between 280 and 400 °C and is accompanied by 16.33% weight loss while for CdS-K and CdS-EDTA systems it occurs between 310 and 400 °C (accompanied by 0.2420% and 0.430% weight loss, respectively). The higher weight loss due to desorption of thioglycolic acid indicates more effective capping and in turn smaller size of the particles while lower weight loss by desorption of potassium pyrosulphate and EDTA indicates less effective capping leading to bigger particle size. This is confirmed by HRTEM particle size estimation of 5–10 nm, aggregates of 60–80 nm comprising of individual particles of 10–15 and 15–20 nm particles for CdS-T, CdS-K and CdS-EDTA systems, respectively.

3.4. HRTEM analysis

The HRTEM images of CdS-T, CdS-K and CdS-E samples are shown in Fig. 4. All the three samples appear to be agglomerated although the extent of agglomeration varies; cube shaped particles in CdS-T and CdS-E samples are less agglomerated (Fig. 4a and c, respectively) but in CdS-K sample (cf. Fig. 4b), comparatively more agglomerated ball like assemblies of ~70 nm dia are observed. The HRTEM image of a single particle of CdS-T exhibits a fringe spacing of 0.336 nm, which is in good agreement with the distance between (111) lattice planes of cubic CdS (JCPDS-10-454). For CdS-K and CdS-E the inter planar distance for an individual crystallite was estimated around 0.316 which corresponds to the (002) lattice plane of the hexagonal phase (JCPDS-16-0314).

3.5. BET surface area analysis

Fig. 5 shows nitrogen adsorption isotherms for the three CdS samples of present study. The surface area of CdS-T, CdS-K and CdS-E samples is observed to be 32.11, 29.54 and 8.63 m²/g, respectively. Higher the surface area, more are the number of active catalytic sites available for reaction. This is confirmed by the observations given later in this paper that photocatalytic activity is observed to follow the order thioglycolic acid > potassium pyrosulfate > EDTA capped samples for the photo degradation of crystal violet and methylene blue dyes.

3.6. Estimation of band gap by UV–Visible absorption studies

The band gap of CdS-T, CdS-E and CdS-K samples was estimated using UV–Vis absorption spectra estimated using the formula: $E = hc/\lambda$, (where h = Plank constant, c = velocity of light and λ is the absorption edge obtained from absorption spectrum). The band gap for CdS-T, CdS-K and CdS-E samples is evaluated to be 2.96, 2.66 and 2.63 eV, respectively, (compared to ~2.4 eV for bulk CdS species), which follow the same order as their crystallite size.

3.7. Photo-catalysis studies

The plot of degradation efficiency vs. time is shown in Fig. 6. It is observed that the best photocatalytic decomposition of crystal violet occurs with CdS-T sample where ~81% degradation is over within 5 min and in 105 min ~96% degradation is completed. For CdS-K sample in 5 min, only ~42% degradation takes place but increases to ~78% in 30 min and then gradually increases to a value of ~95% in 105 min. For CdS-E, the degradation is observed to be lower than the other two samples and in 5 min 27% degradation occurs while in 105 min, it reaches a maximum value of ~76%. The plot of degradation efficiency vs. time is shown in Fig. 7. In this case also the best photocatalytic decomposition occurs with CdS-T sample where ~83% degradation is over within 5 min and in

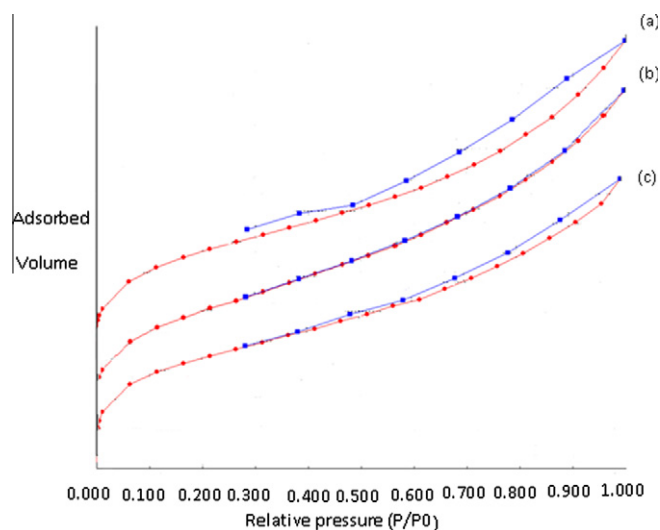


Fig. 5. Nitrogen adsorption and desorption isotherms of CdS nanoparticles (a) CdS-T (b) CdS-K and (c) CdS-E.

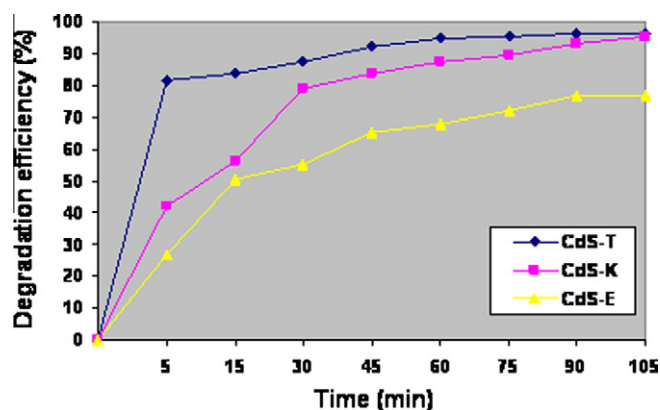


Fig. 6. Graph between degradation efficiency and time for crystal violet dye using CdS nanoparticles.

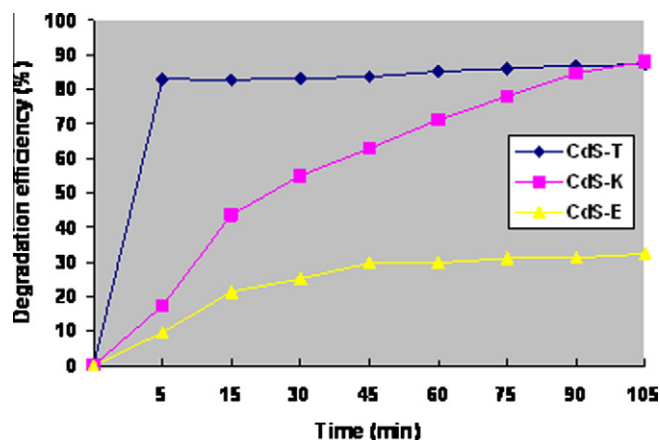


Fig. 7. Graph between degradation efficiency and time for methylene blue dye using CdS nanoparticles.

105 min ~87% degradation is completed. For CdS-K sample in 5 min only ~17% degradation takes place but increases continuously to reach a value of ~88% in 105 min while in the case of CdS-E, the degradation is observed to be poor and in 5 min only

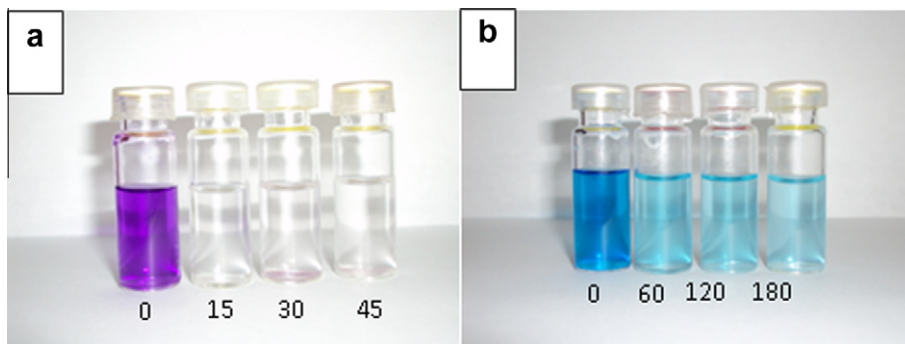


Fig. 8. Samples of (a) crystal violet and (b) methylene blue after photodegradation for different periods using CdS-T nanoparticles.

~9% degradation occurs while in 105 min, it reaches a maximum value of ~32%.

It is observed from above discussion that CdS-T sample shows best photo-catalytic efficiency for degradation of both, crystal violet and methylene blue dyes. The photographs of degraded crystal violet and methylene blue dye samples after exposure to different time intervals are shown in Fig. 8a and b, respectively, which further strengthen the discussions given above.

The observation of more efficient degradation of crystal violet as compared to the methylene blue molecules in aqueous solution by CdS nanoparticles prepared using different capping agents can be attributed to simple molecular structure of crystal violet as also suggested by Khataee and Kasiri [40] that dyes having anthraquinone ring are more difficult to degrade.

4. Conclusions

Based on the above studies, following conclusions can be drawn:

- CdS nanoparticles prepared by emulsion/arrested precipitation methods using thioglycolic acid, potassium pyrosulfate and EDTA as capping agents have been found to act as photo-catalysts for photo-degradation of crystal violet and methylene blue synthetic dyes.
- The nano particles prepared using thioglycolic acid, potassium pyrosulfate and EDTA as capping agents are observed to have crystallite size of 3.7, 6.8 and 13.9 nm, respectively.
- The photo-catalytic efficiency of nano-particles for degradation of crystal violet and methylene blue dyes is observed to decrease with increase in the particle size and thus follows the order thioglycolic acid > potassium pyrosulfate > EDTA capped samples.

Acknowledgments

The authors are thankful to Dr. S. Das, Scientist, AMPRI for carrying out X-ray diffraction studies, authors also thank Prof. T. Pradeep, IIT, Madras for HRTEM analysis, Dr. R.K. Shrivastava, R&D, HEG for BET surface area analysis and Dr. R.K. Pandey for many useful suggestions. MS and DKS are indebted to CSIR (India) and RKU to AMPRI, Bhopal for grant of fellowships and to Madhya Pradesh Council of Science and Technology (MPCST) for financial assistance.

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