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SYNTHESIS, CHARACTERIZATION AND PHOTOCATALYTIC APPLICATION OF BOVINE SERUM ALBUMIN CAPPED CADMIUM SULPHIDE NANOPARTILCES

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Cadmium sulphide nanoparticles (NPs) have been synthesized in aqueous phase at temperature range 70^0C using Bovine Serium Albumin (BSA) as the capping agent. Cadmium sulphide nanocrystals are synthesized by dissolving 0.1 M $CdSO_4$, 0.1 M Na_2S and BSA as stabilizing agent. Cadmium sulphide nanoparticles have been characterized with the help of X-ray diffraction (XRD), Transmission electron microscopy (TEM), Thermal analysis (TGA/DTA) and UV-Visible spectroscopy. The average particle size were found to be in the range of 3.1 – 3.8 nm from the peak broadening of X-ray diffraction. The CdS Nanoparticles have been effectively used for the removal of methylene blue from water samples in presence of visible sunlight and sodium lamp source.

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1. Introduction

Nano sized particles have attracted great deal of attraction in the recent years due to their unique optical, electrical, chemical properties. 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 nanocrystals, CdS is one of the most important II-VI group elements possessing size tunable optical transitions. Cadmium sulphide is a solid hexagonal or cubic crystal. CdS is an important n – type semiconductor with a direct band gap of 2.42 eV at 300K. Much effort has been given to the synthesis and to study the optical property of CdS related nano particles and quantum dots because they have wide applications for laser light emitting diodes, solar cells and some optoelectronic devices based on nonlinear properties [1-5]. The optoelectronic applications including solar cells, photodiodes, light emitting diodes, nonlinear optics, photoelectrochemical cells and heterogeneous photo catalysis [6-8]. The photoconductive and electroluminiscent properties of cadmium sulphide have been applied in manufacturing a variety of consumer goods. Several methods have been reported different shape controlled morphologies of CdS nanoparticles [9-12].

The appropriate use of nanoparticles for biological labeling requires the coating with biological receptor. The biomolecules have strong affinity for the nanocrystal structures. Therefore, this application of nanoparticles is achieved if the synthesis is carried out in presence of appropriate biomolecules. With surfactant assisted synthesis, the surfactants are the best suitable for the charge and steric stabilization to attain colloidal stability. When instead of surfactant, amphiphilic biomolecules are used for the synthesis of bioconjugate nanoparticles the same stability can be achieved [13].

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Bovine serum albumen (BSA) a low molecular weight, water soluble and active carrier protein as a capping agent to synthesize BSA-CdS biocounjugate nanoparticles have been taken in the present study. BSA is an important blood protein with molecular weight of 66500 Da, is composed of 580 amino acid residue [14]. It is versatile carrier protein with wide hydrophobic, hydrophilic, anionic and cationic properties. The synthesis of various metal and semiconductor nanoparticles has been reported using BSA as capping agent [15-17]. BSA is weakly reducing and can act as shape directing agent to promote anisotropic growth [16]. Numbers of studied have reported the heat induced denaturation of BSA [18]. It remains stable up to 60^0C, above this temperature the unfolding progresses and β–aggregation begins. The main advantage of this method is that the nanoparticles obtained at the end of the reaction can directly be used for specific bioactive functionalities.

In last decade photocatalytic degradation using semiconductors have been shown to be effective for destruction of pollutants. Several semiconductors such as ZnO, ZnS, TiO_2, Fe_2O_3 have been used for heterogeneous photocatalytic destruction of organic pollutants in waste water [19-22]. Dyes are the impotant class of organic water pollutants and therefore, many studies have been conducted on the photodegradation [23]. Methylene blue is one of the stable dyes extensibly used in textile industry, and is resistant to biodegradation.

Thus in the present work BSA is used as capping agent for the synthesis of CdS nanoparticles at 70^0C temperature. We have also explored the phocatalytic properties of synthesized BSA capped CdS nanoparticles for the degradation of methylene blue in presence of sunlight and light source.

2. Experimental

Synthesis of cadmium sulphide nanoparticles

Cadmium sulfide nanoparticles were prepared in aqueous phase at temperature range of 70^0C by using BSA as the capping agent. In a typical procedure, 10 ml of aqueous BSA (15×10^{-4} g ml^{-1}) was taken in a round bottom glass flask. To this solution 0.1 M $CdSO_4$ (50 ml), 0.1 M CH_3 COOH (5 ml) was added with constant stirring. This mixture was stirred at room temperature for 15 minutes. Then 0.1 M Na_2S solution by added drop wise with continuous stirring to the above mixture. The resulting solution was kept on magnetic stirrer for three hours at 70^0C. After three hours orange coloured solution was obtained. This solution was centrifuged at rate of 10000 RPM for 15 minutes on cooling. The precipitates obtained were washed several times using methanol and distilled water to remove the impurities. Finally the wet precipitates were dried in hot air oven at 50^0C for 24 hours.

Characterization

The phase composition of the nanoparticles were determined by using X- ray diffractometer (Panalytical S X. Pert Pro) using CuKα radiation. The morphology was taken with a transmission electron microscope (Hitachi TEM System).Thermal analyses were determined with Mettler Toledo (DSC-851E). FTIR analysis was done using Infrared spectrophotometer (Perkin Elmer Spectrum 400). The concentrations of dye were determined using UV-Visible spectrophotometer (Systronics 117).

Photocatalytic activity

The photocalatytic activities of the CdS nanoparticles were carried out in a glass reactor of 100 ml capacity for degrading Methylene blue (MB) in water solution. A certain initial concentration of MB dye and the 0.5 gram of photocatalyst were taken in a reactor. This solution was stirred for half an hour in a dark. The resulted concentration was taken as initial concentration of MB. After exposure to the visible sunlight and sodium lamp source the dye concentrations were determined at different time for kinetic analysis. The light from the visible and sodium lamp

source were passed to the samples mixture through the glass filter. During the degradation study the samples were collected at regular interval, centrifuged to remove the catalyst portion prior to analysis. The supernatant solution was analyzed for dye concentrations by UV-visible spectrophotometer at wavelength of 653 nm.

Gel electrophoresis

The polarity of the BSA capped nanoparticles was determined by gel electrophoresis using tris-HCl buffer as a gel running medium with pH 7. For this purpose, 1% aqueous agarose solution was first brought to the boil in a microwave and then ethidium bromide dye was added in the boiled solution. This solution was left in the gel plate to harden. Wells were made in the gel plate with the help of comb. Then, 20 microlitre of colloidal CdS aqueous suspension made in acetic acid was loaded in the gel wells using methylene blue as staining agent. The direct voltage of 90 V was applied for 30 mints to determine the movement of nanoparticles.

3. Results and discussion

Fig. 1 shows the X- ray diffraction pattern of the CdS nanoparticles. The results obtained are very well matched with standard published data (JCPDS 10-454). The nanoparticles synthesized have good crystallinity and they are in the cubic form (zincblende phase) as all the peaks are prominent. The XRD patterns exhibits prominent broad peaks at 2θ values of 24.94, 47.85 and 51.92. These results are in agreement with 111, 220 and 311 planes. The intensity of the (111) is much higher than that of (220). Average particle size was found from XRD measurement value of FWHM using Debye- Sherrer formula [24]. The Peak broading in the XRD pattern indicates that small nanocrystals are present in the sample.

Scherrer equation (D) = $K\lambda/(\beta\cos\theta)$

Where K is constant (0.9), λ is the wavelength (λ= 1.5418 A^0), β is the full width at the half maximum of the line and θ is the diffraction angle. The average particle size of CdS nanoparticles were found in the range of 3.1 to 3.8 nm according to Debye- Scherrer formula.

The following fundamental reaction has been observed for the preparation of CdS nanoparticles

$$CdSO_4 + Na_2S \rightarrow CdS + Na_2SO_4$$

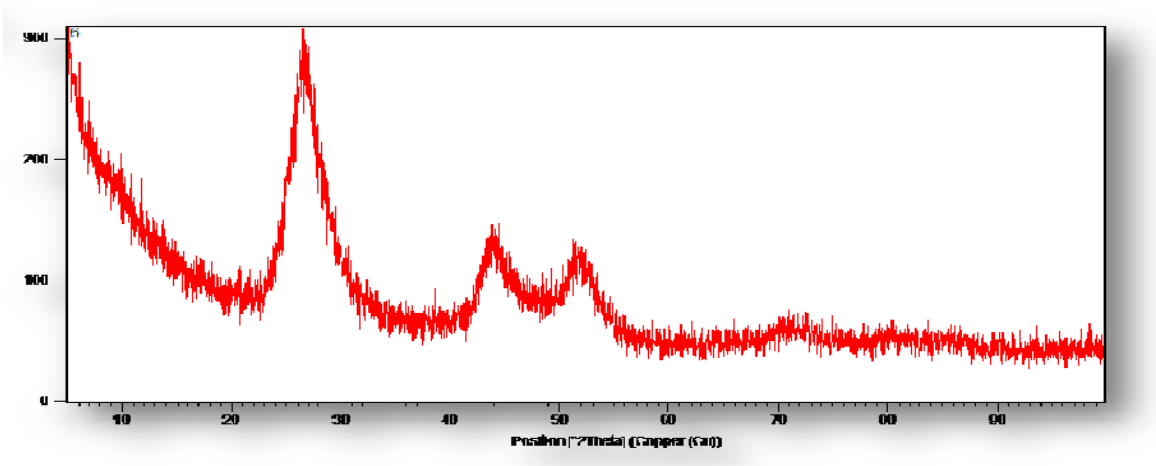

Fig. 1 XRD pattern of CdS nanoparticles

BSA capped CdS nanoparticles morphology are observed using TEM at different magnifications as shown in Fig. 2 (a-d). It is revealed from the TEM study that the BSA capped

BSA capped CdS nanoparticles morphology are observed using TEM at different magnifications as shown in Fig. 2 (a-d). It is revealed from the TEM study that the BSA capped CdS nanoparticles show the spherical morphology and their average sizes are less than 4 nm which is consistent with XRD results. Further, TEM study shows the smooth morphologies apparently because of predominant growth of CdS nanoparticles capped with BSA.

Fig. 3 shows the results of thermogravimetric analyses (TGA) of CdS nanoparticles. The TGA analyses shows a weight loss of 16.583 % sharply in the range of 800 – 845^0 C. TGA analyses indicate that BSA capped CdS nanoparticles are stable upto 800^0 C.

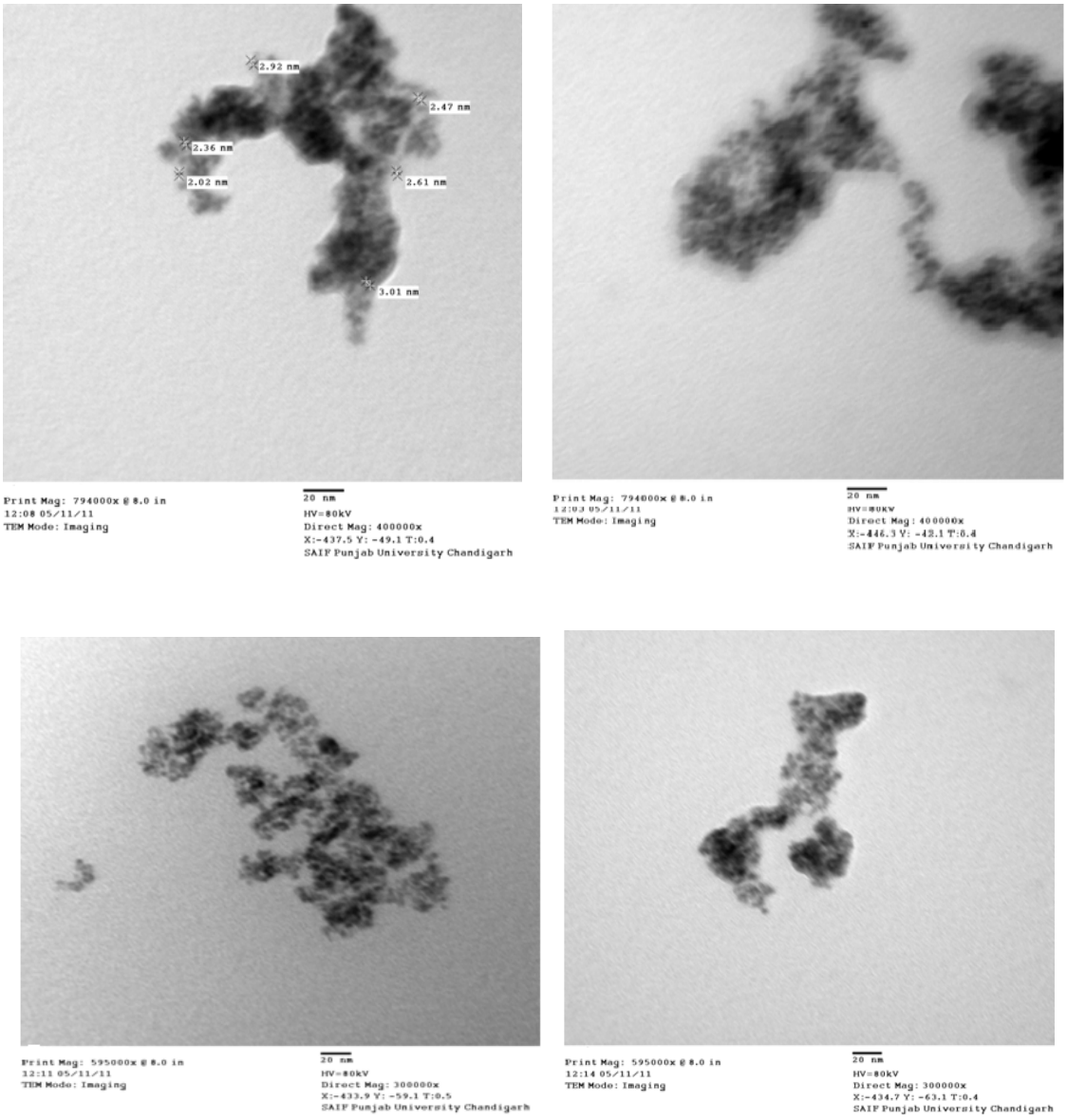

Fig. 2 (a-d) Transmission electron microscopy images of BSA capped CdS nanoparticles at different magnifications

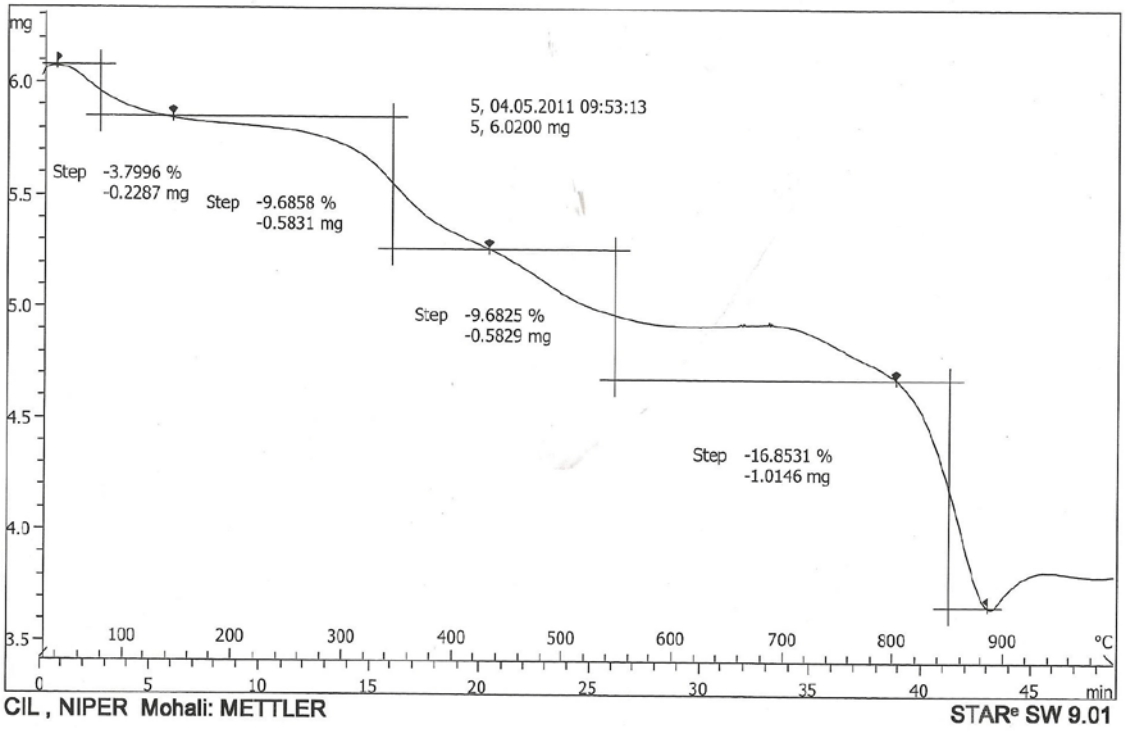

Fig. 3 TGA curve for the CdS nanoparticles obtained.

FTIR measurements (Fig. 4) have been made in the wave number range 400 cm^{-1} to 4000 cm^{-1}. From the Figure it is revealed that the strong absorption bands at 616.47 cm^{-1} and 756.72 cm^{-1} correspond to Cd-S stretching [25]. The IR peaks at 3411.58, 3041.37, 1654.00, and 1530.66 cm^{-1} are assigned to the stretching vibration of –OH, amide A (mainly –NH stretching vibration), amide (mainly C=O stretching vibrations), and amide (the coupling of bending vibrate of N–H and stretching vibrate of C–N) bands, respectively [26]. These results clearly reveal that the nanoparticles are coated with BSA.

Preliminary studies on the photocatalytic properties of the CdS nanoparticles powders were made on methylene blue dye degradation under visible sunlight and sodium lamp radiation. The synthesized CdS nanoparticles was dispersed in aqueous solution of methylene blue dye and was irradiated with visible sunlight and sodium lamp in a reactor while the suspension was kept under stirring. The degradation of the dye was monitored at different time intervals using UV–Visible spectrophotometer.

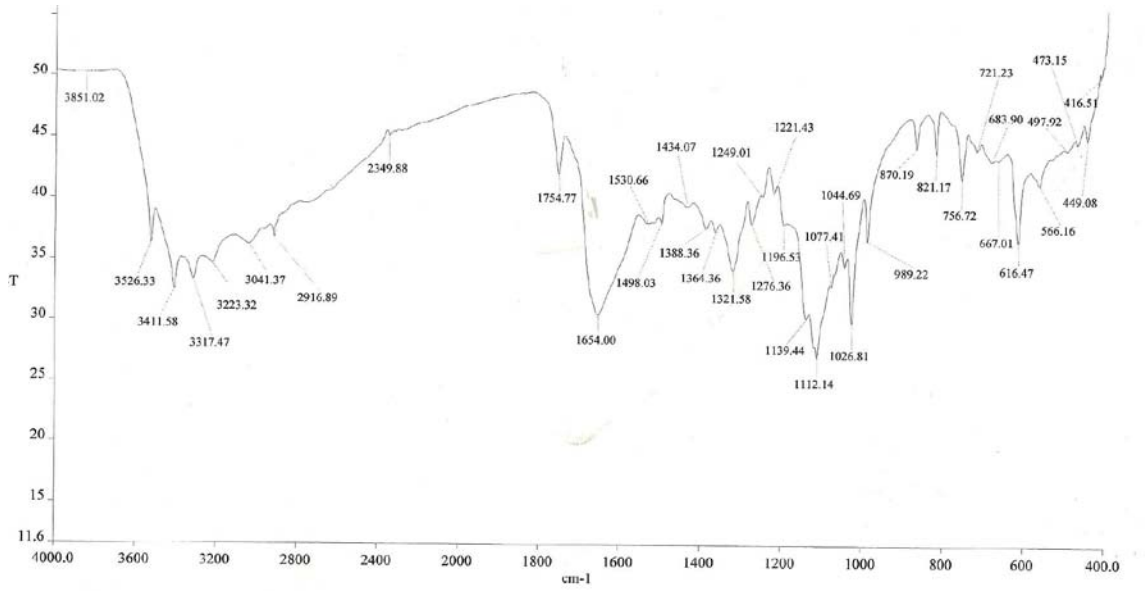

Fig. 4 FTIR spectra of CdS nanoparticles.

Figs. 5 - 7 and Tables 1 - 2 shows the absorbance characteristics of methylene blue at different time intervals in visible sunlight and sodium lamp irradiations. It has been observed that from the figures that there is considerable degradation of the dye after exposure to about 3 hours. It was observed that concentration of methylene blue is reduced to about 25% of its initial value after exposure to UV radiation for about 3 hours. The photocatalytic activity of CdS nanoparticles for degradation of the methylene blue dye is more in presence of visible sunlight than sodium lamp irradiations.

It is concluded from the absorbance of dye before and after radiation at regular intervals that with increase in reaction time the photocatalytic activity of CdS nanoparticles increases. The CdS nanoparticles are able to decompose methylene blue dye upto 70% and 65% in two hours in the presence of visible sunlight and sodium lamp respectively. Thus BSA capped CdS nanoparticles can effectively be used as photocatalysts in the treatment of wastewater effluents and degradation of absorbed dyes.

Table 1. Absorbance of MB by CdS nanoparticles in different time at wavelength 653 nm in sodium lamp

Sr. No.	Degradation time	Absorbance	A/A_0
1.	1 hr	1.938	0.713
2.	2 hr	1.180	0.434
3.	3 hr	0.995	0.366
4.	4 hr	0.782	0.288
5.	5 hr	0.640	0.235
6.	6 hr	0.519	0.191
7.	7 hr	0.435	0.160

Methylene blue Absorbance (A_0) is 2.715

Table 2. Absorbance of MB by CdS nanoparticles in different time at wavelength 653 nm in visible sunlight

Sr. No.	Degradation time	Absorbance	A/A_0
1.	1 hr	1.657	0.611
2.	2 hr	0.980	0.361
3.	3 hr	0.756	0.278
4.	4 hr	0.680	0.250
5.	5 hr	0.598	0.220
6.	6 hr	0.472	0.174
7.	7 hr	0.395	0.145

Methylene blue Absorbance (A_0) is 2.710

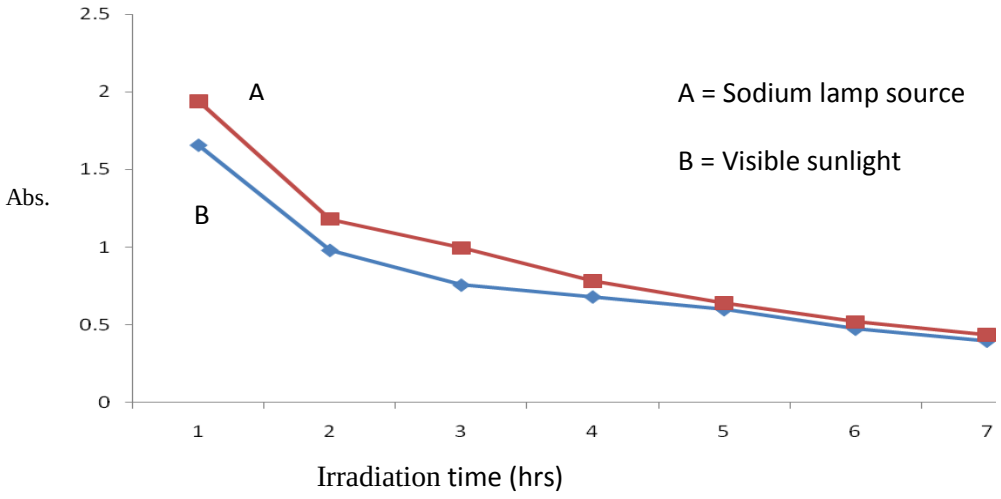

Fig. 5 Degradation of methylene blue with photocatalyst under visible sunlight and sodium lamp radiations

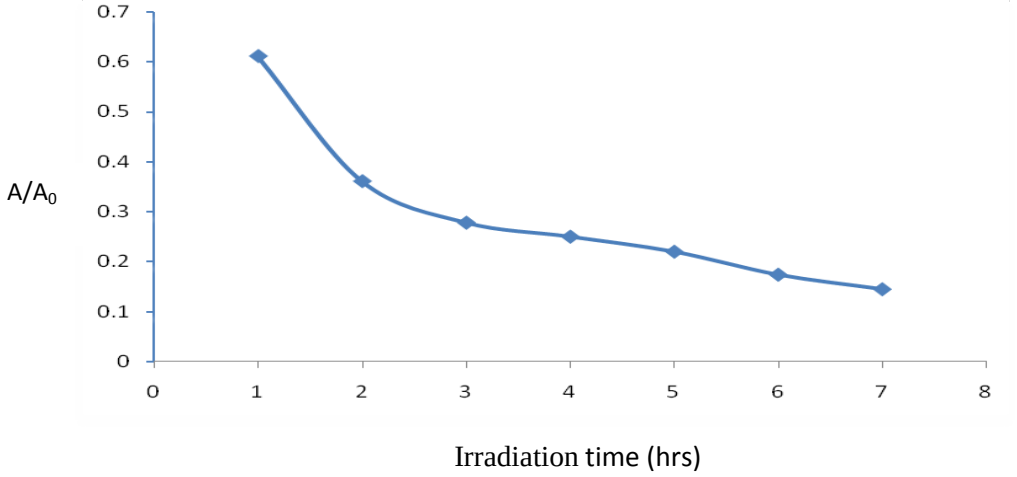

Fig. 6 Degradation of methylene blue with photocatalyst under visible sunlight radiations.

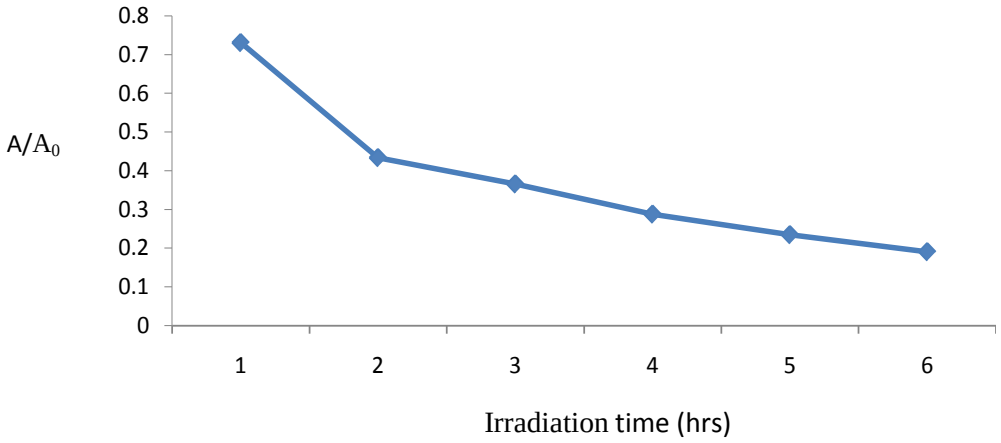

Fig. 7 Degradation of methylene blue with photocatalyst under sodium lamp radiations.

The scheme of CdS formation in the BSA solution is illustrated in Fig.8. Firstly, Cd^{2+} forms complex with BSA when $CdSO_4$ is added to BSA solution. Secondly, when Na_2S is added into the solution, the S^{2-} combines with Cd^{2+} cooperated by BSA to form CdS. Finally, some CdS absorb on or bond to BSA molecules and form large CdS capped BSA nanoparticles.

Fig. 7 Scheme of CdS nanoparticle formation

The Gel electrophoresis determines the polarity of BSA capped CdS nanoparticles. It was observed from the gel electrophoresis study that CdS nanoparticles show a displacement towards the positively charged electrode under the applied potential, suggesting that the surface of BSA capped nanoparticles is predominantly negatively charged.

4. Conclusion

The CdS nanoparticles were successfully synthesized by using BSA as the stabilizing reagent at 70^0 C. This method is fast, inexpensive, producing high yield and requires neither complex apparatus nor a long reaction time. The CdS obtained are approximately cubic, with a size distribution from 3.1 to 3.8 nm in diameter. Further the results from XRD and SEM also confirm the nanocrystal nature of synthesized CdS. The synthesized CdS nanoparticles have successfully used for degradation of methylene dye in presence of visible sunlight and sodium lamp radiations. These protein-assisted synthesized CdS nanomaterials have a great potential application in photocatalysis, biomedical engineering and microelectronics.

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