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Photo catalytic degradation of Alizarin red S using ZnS and cadmium doped ZnS nanoparticles under unfiltered sunlight

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ABSTRACT

Zinc sulphide (ZnS) and cadmium doped ZnS (Cd-ZnS) nanoparticles were prepared by co-precipitation method and characterized by UV–Visible spectroscopy, X-ray diffraction (XRD) studies, Transmission electron microscopy (TEM) and Scanning electron microscopy (SEM). The optical band gaps of the synthesized materials were calculated from UV–Visible absorption spectra using Tauc plots. The band gap of ZnS was decreased from 3.4 eV to 2.44 eV due to substitution of Cd^{2+} ions in ZnS lattice at 0.5 M cadmium content. This variation in the optical bandgap effectively monitored degradation of the dye. Photo catalytic degradation of Alizarin red S (ARS) by the nanoparticles showed that the cadmium doped ZnS acted as a potential photo catalyst under unfiltered natural sunlight of irradiation 300 W/m^2. The ARS dye was degraded about 50% and 96.7% in the presence of ZnS and Cd-ZnS (Cd 0.5 M) nanoparticles respectively in 120 min. Furthermore the effect of various parameters, i.e., photocatalyst concentration, dye concentration, and pH of the solution on the percentage of degradation was also studied. Degradation followed first order kinetics.

1. Introduction

Dyes constitute a major class of organic compounds, which find numerous applications in our daily life such as in leather, paper, plastics, cosmetics, clothing, drugs, electronics, and printing. Modern textile industries consume about 80% of the synthetic dyes. Synthetic material dyes and other industrial dyestuffs are the major groups of water pollutants in the world [1]. Approximately 1–15% of the synthetic textile dyes used in manufacturing process, are lost in wastewater streams and finally settled into water bodies [2,3].

Industrial wastes contain different chemicals particularly synthetic dyes which are oncogenic in nature [4]. Dyeing also produces effluents that contain 10–15% of the dye [5]. So, the critical issue is to reduce the toxicity levels to permissible limits before releasing the dye to aquatic bodies. Various treatment methods like aerobic, and anaerobic biological treatments, flocculation, neutralization of acidic and alkaline effluents, advanced oxidation processes [6] like ultraviolet (UV) photolysis, UV/H_2O_2 process, UV/O_3 process, UV/Fenton process, and photo catalytic processes have gained significance due to their effective decontamination efficiencies. The textile industry produces large quantity of highly colored effluents which decrease light penetration and prevent photosynthesis [7]. Alizarin red-S dye is one of them which produces 'red and' purple colored solution depending on the pH of water.

Photocatalytic degradation by semiconductors is a new, effective and rapid technique for removal of pollutant from water. Nanophotocatalyst are non-toxic, non-corrosive, inexpensive and chemically and thermally stable [8,9].

Semiconducting nanoparticles engaged in photo conversion systems present a temperately wide energy gap between the conduction band (CB) and the valence band (VB). This separation is known as the band-gap energy (Egap). The absorption of energy by a semiconductor results in electron transfer from the valence band to the conduction band and leave vacancies in the valence band termed as holes. The photo generated electron-hole pair encourages the reduction and oxidation of species adsorbed at the surface of the semiconducting nanoparticles and encourages oxidative degradation of species in solution through radical reactions [10,11].

Various binary, ternary and modified semiconductors have been successfully used for removal of a number of organic pollutants. ZnS nanoparticles could be used as good photo catalysts due to rapid generation of the electron-hole pairs by photo-excitation and highly negative reduction potentials of the excited electrons; as conduction band position of ZnS in aqueous solution is higher than that of other semiconductors such as TiO_2 and ZnO [12]. Sharma et al. [13] examined photo degradation of Bromophenol blue,

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crystal violet and reactive red dyes using ZnS nanoparticles after 3.0 h of irradiation. Zinc sulphide semiconductor as a photo catalyst was used [14] for the removal of rose bengal dye. Warrier et al. [15] have reported that CdS and CdSe nanoparticles could act as very efficient and highly chemo selective photo catalysts for the reduction of aromatic azides to aromatic amines. Cerium iron oxide synthesized by Ameta et al. [16] by using co-precipitation method and specific heating cycles was utilized for the photo catalytic degradation of Alizarin red dye.

Decolorization of textile industry waste water by photo catalytic degradation process was reported by Hachem et al. [17] whereas semiconductor mediated photo catalyzed degradation of an anthraquinonoid dye Remazol Brilliant Blue was reported by Saquib et al. [18].

CdS nanoparticles were used by Zang et al. [19] for photo catalytic reduction of Methyl Yellow in reverse micelles. Takizawa studied N-dealkylation on Rhodamine B and Crystal Violet on CdS semiconductor as photo catalyst [20]. Nasr et al. [21] reported photo catalytic reduction of azo dyes like Naphthol Blue Black and Disperse Blue 79 while photo catalytic degradation of textile azo dye Acid Orange 7 was studied by Vinodgopal et al. [22]. Sesha et al. [23] made CdS/TiO_2 nano composite materials for photo catalysis in visible light. Recently Cu-doped ZnS has been used as a photocatalyst for the degradation of methylene blue [24] and the doped ZnS was found more effective in photo degradation than undoped ZnS.

Literature study revealed that both wide and low band-gap semiconducting nanoparticles can cause the photo-catalytic degradation of various dyes absorbing in the ultraviolet and visible region. The wide and low band gap semiconductors can be combined to extend their light capturing potential and regulate their band gap for monitoring photocatalytic degradation effectively. This report is an endeavor to achieve the above target by decreasing band gap of zinc sulphide nanoparticles by cadmium substitution in ZnS lattice and study its potential for the photocatalytic degradation of Alizarin red dye. To the best of our knowledge this is the first time that such an appreciable decrease in bandgap and increase in the photocatalytic degradation potential of ZnS has been recorded using direct and unfiltered sunlight instead of simulated light.

Mechanism of photo catalysis: When a photo catalyst is exposed to light, electrons on the surface of catalyst are excited from valance band into conduction band. This leaves positive holes in the valance band which reacts with water and produce radicals that can degrade dye [11]

The mechanism of the photo catalytic degradation is as under.

$$\text{Catalyst} + h\upsilon \rightarrow e^-_{cb} + h^+_{vb}$$

$$H_2O + h^+_{vb} \rightarrow OH^{\cdot} + H^+$$

$$O_2 + e^-_{cb} \rightarrow O^{-2}$$

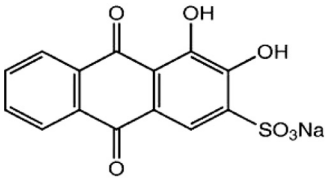
$$O^{-2} + H^+ \rightarrow HO_2^{\cdot}$$

$$2HO^{\cdot}_2 \rightarrow H_2O_2 + O_2$$

$$H_2O_2 \rightarrow 2\ OH^-$$

$$OH^- + \text{Dye} \rightarrow CO_2 + H_2O$$

To explore possible photocatalytic application of ZnS and Cd-ZnS nanoparticles, the catalytic degradation of ARS is carried out in the presence of sunlight, as it is a water-soluble dye and is used extensively as a coloring agent for fibers, leather, etc. [25–27]. The chemical structure of ARS is shown in Scheme 1.



Scheme 1. The chemical structure of Alizarin Red S.

2. Experimental

2.1. Synthesis of ZnS nanoparticles

Wet chemical method was adopted for the synthesis of ZnS nanoparticles [28]. The synthesis was carried out in a mixture of analytical grade (Sigma Aldrich) ethanol and distilled water both taken in equal proportions. Zinc acetate (Zn (CH3COO) $_2$•2H2O) and sodium sulfide nanohydrate (Na_2S•9H2O) were used as starting materials. 0.5 M of zinc acetate was dissolved in 50 ml of distilled water. In the next step 0.5 M solution of Na_2S•$9H_2O$ was added dropwise to the solution of zinc acetate while stirring the mixture continuously at 60 °C until a homogenous solution was obtained. The solution was cooled to room temperature. After 50 min, a white precipitate of ZnS was obtained. The precipitate was carefully settled down and washed thrice with a mixture of ethanol and distilled water. It was dried in oven at 120 °C for 2 h.

2.2. Synthesis of $Zn_{1-x}Cd_xS$ nanoparticles

In a typical experiment, the synthesis of $Zn_{1-x}Cd_xS$ nanoparticles was carried out in two steps. In the first step, 1 M solution of Zn (CH_3COO) $_2$•$2H_2O$ and 0.5 M solution of cadmium acetate were dissolved in 20 ml of distilled water separately. These solutions were mixed and the resulting mixture was stirred for 30 min. In second step, 1 M solution of sodium sulfide in the same solvent was slowly added to above mixed solution drop wise. The mixture was stirred vigorously for 1 h at 60 °C. The precipitate was separated by centrifugation at 6000 rpm for 10 min and washed thrice with distilled water and freshly distilled ethanol. Therafter the doped ZnS nanoparticles were dried in oven at 120 °C for 2 h.

2.3. Degradation of Alizarin red S (ARS)

Alizarin Red S (ARS), a water-soluble dye was tested for its degradation by ZnS and cadmium doped ZnS semiconducting nanoparticles. The degradation of ARS was carried out in the presence of unfiltered sunlight. A 30 mg sample of nanoparticles was dispersed in a 30 ml of distilled water under ultrasound irradiation. Then the solution was mixed with 30 ml of 5×10^{-5} M ARS solution. The solution was stirred in dark at room temperature for 1 h to make the absorption/desorption between ARS and catalysts to reach the equilibrium state. Then, the solution was stirred by the magnetic stirrer in the presence of sunlight.2 ml of the of the reaction mixture was periodically withdrawn after every 30 min to check the progress of photocatalytic degradation of ARS dye by recording UV–Visible absorption spectra. The decrease of intensity of absorbance of dye after irradiation at definite time intervals gave the efficiency of photocatalytic degradation of nanoparticles. This efficiency was calculated as:

$$\%D = 100 \times [(\text{Ao-At})/\text{Ao}]$$

Where Ao and At are the values of initial absorbance and absorbance at time t respectively. 't' is the irradiation time of sample.