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PHOTOCATALYTIC ACTIVITY OF CdS-ZnO COMPOSITE

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ABSTRACT

A composite of CdS and ZnO was prepared by simple solid state mechanochemical method and it was used for photocatalytic degradation of azure A. The photocatalytic efficiency of CdS-ZnO composite was compared with pure CdS and ZnO. The effect of various parameters such as pH, concentration of dye, amount of semiconductor and light intensity was observed. The optimum conditions obtained for this degradation were: Azure A = 3.00×10^{-5} M, pH = 8.5, amount of composite = 0.10 g and light intensity = 50.0 mWcm^{-2}. It was found that coupled chalcogenide CdS-ZnO shows better photocatalytic activity as compared with pure CdS and ZnO for the degradation of azure A in the presence of visible light.

Keywords: ZnO, CdS, Composite, Photocatalytic activity, Azure A.

INTRODUCTION

Water pollution is increasing day by day due to rapid industrialization, transportation, construction, etc. This is further supported by domestic discharge and some other anthropological activities. The release of organic pollutants, such as dyes, drugs, aromatic compounds, polymers, insecticides, pesticides, etc., in the water resources are posing a great nuisance to the surroundings due to their carcinogenic, mutagenic and toxic effects. Particularly, the discharge of synthetic dyes and pigments by many industries is prime source of water pollution, which disturbed the ecosystem and created eutrophication and perturbation to marine life[1]. Many traditional technologies have been used to treat waste water. Photocatalysis (Advanced Oxidation Process) is considered a promising technology for waste water treatment[2].

Photocatalysis is a term, which is a combination of two terms, photo (means light) and catalysis (means a process of enhancing rate of a chemical reaction)[3]. This process involves a semiconductor, which absorbs light radiations and acts as a catalyst. Normally, all

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photocatalysts are semiconductors but a particular semiconductor may or may not be a photocatalyst. It has been reported that these photocatalysts can completely mineralize almost all toxic organic pollutants like pesticides, dyes, drugs, aromatic compounds, halo-organics, surfactants, etc.[4,5]

Metal oxide photocatlysts have been widely studied for photocatalytic environmental remediation especially waste water treatment[6]. Zinc oxide (ZnO), a direct wide bandgap (3.2 eV) semiconductor, is deemed to be one of the most important semiconductor photocatalysts because of its high photosensitivity and stability[7-11]. CdS is a well known photocatalyst that has been used as a visible-light photocatalyst. CdS has a narrow direct band gap (2.4 eV), so it is also used as a photosensitizer of various wide band gap semiconductor photoanodes in photoelectrochemical cell[12-14]. Nanostructured CdS microspheres have been prepared by hydrothermal synthesis and these were used in complete degradation of methylene blue, phenol red and methyl red in presence of UV and blue LED radiation by Repo et al.[15]

It was demonstrated that the nano-heterostructures of different semiconductors can improve the photocatalytic efficiency by mutual transfer of photogenerated charge carriers[16-19]. Integration of two or more desirable semiconductors based on the electron transfer process, where photogenerated electrons can flow from one semiconductor with a higher conduction band minimum (CBM) to the other with a lower CBM is of great importance in better treatment of organic pollutants[20-22]. Compared to single phase photocatalysts, the heterostructures possess significant advantages of promoting the separation of electron–hole pairs and keeping reduction and oxidation reactions at two different reaction sites. Many successful examples have been developed in recent years, such as as ZnO/CdS[23], SnO_2/ZnO[24], ZnS/ZnO[25], etc.

Nayak et al.[26] synthesized the nanorods of CdS-ZnO composite by chemical method and investigated their structure, optical and electrical properties by suitable techniques. The catalytic activity of CdS-ZnO and the photodegradation of 3,4-dihydroxybenzoic acid has been investigated under visible irradiation from a halogen lamp. Liu et al.[27] prepared ZnO/CdS composite by combining a solvothermal route with a homogeneous precipitation process. They were able to degrade some organic dyes, such as methyl orange, rhodamine B, safranine T and methylene blue. Li et al.[28] successfully deposited ZnO nanorods on transparent conductive oxide (TCO) glass by electrochemical deposition. CdS nanoparticles were coated outside as-prepared ZnO nanorods by chemical bath deposition forming ZnO/CdS nanoarrays. The ZnO/CdS nanoarrays showed promising photocatalytic activity with respect to the degradation of eriochrome black T.

Ivetic et al.[29] prepared ternary and coupled binary zinc oxide/tin oxide nanocrystalline powders by simple solid-state mechanochemical method. The degradation of alprazolam, a short acting anxiolytic of the benzodiazepine class of psychoactive drugs by ternary (Zn_2SnO_4 and $ZnSnO_3$) and coupled binary (ZnO/SnO_2) oxides under UV irradiation were observed and compared with pure ZnO and SnO_2.

In the present work, composite of cadmium sulphide with zinc oxide was prepared by simple solid state mechanochemical method and it was used for photocatalytic degradation of azure A.

EXPERIMENTAL

Preparation of composite

A composite of CdS and ZnO was prepared by simple solid state mechanochemical method. Composite (CdS – ZnO) was prepared by mixing the same amount of CdS and ZnO (in ratio 1:1) and then ground with pestle and mortar. It was then used for photocatalytic degradation of azure A.

Characterization of composite

X-rays diffraction pattern of the pure CdS-ZnS composite samples is shown in Fig. 1. Average particle size of the crystalline composite powder was calculated by Debye-Scherrer's equation and it was found to be 35.18 nm.

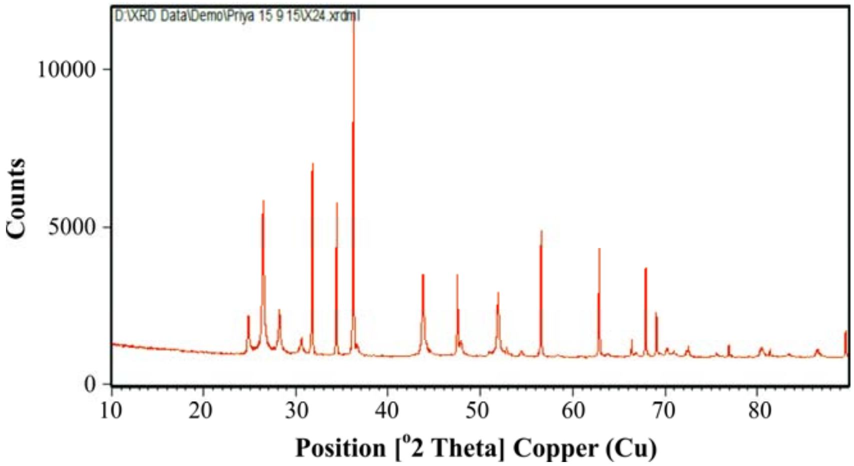

Fig. 1: X-ray diffraction spectrum of composite

The surface morphology and elemental composition were observed out by scanning electron microscope well equipped with an energy dispersive X-ray spectrophotometer. The SEM image of CdS-ZnO composite is shown in Fig. 2. It shows that particles have rough surface with irregular size.

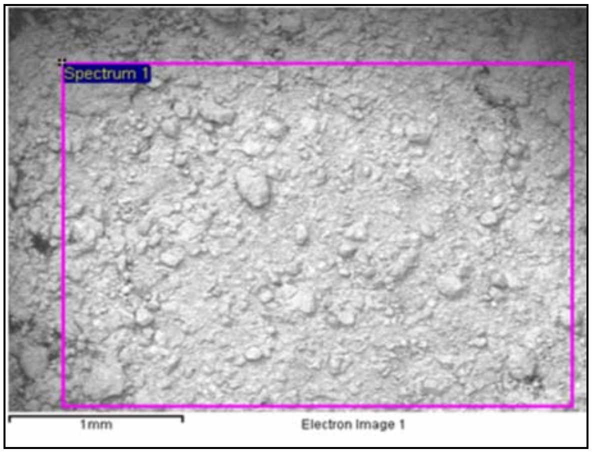

Fig. 2: SEM of composite

EDX analysis was performed to analyze the elemental constituent of mixed CdS-ZnO, which reveals that all the four elements are present in composie i.e. Cd, S, Zn, and O.

Table 1: Elemental composition

Elements	Weight (%)	Atomic (%)
Zn	46.69	29.54
Cd	25.98	9.54
O	19.78	51.15
S	7.54	9.72

The diffuse reflectance spectrum of the synthesized sample was scanned between 200-800 nm using UV Vis-3000+ spectrophotometer. The band gap of composite was calculated by following equation-

$$E_g = hc / \lambda = 1240 / \lambda \qquad \text{…(1)}$$

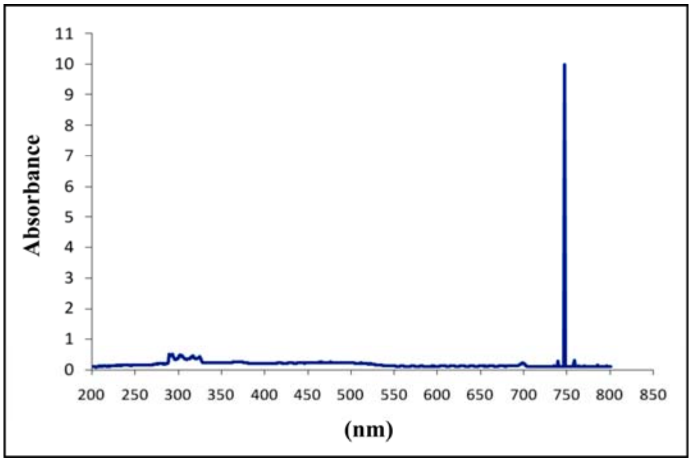

Fig. 3: DRS of composite

Band gap of composite was found to be 1.66 eV.

Photocatalytic degradation

0.0291 g of azure A was dissolved in 100.0 mL of doubly distilled water so that the concentration of dye solution was 1.0 x 10^{-3} M. It was used as a stock solution and further diluted to working solutions as and when required. The absorbance of azure A solution was observed with the help of spectrophotometer (Systronic model 106) at λ_{max} = 630 nm. It was irradiated with a 200 W tungsten lamp. Reaction solution was exposed to visible light.

A water filter was used between light source and solution to cut off thermal radiations.

The dye solution was placed in equal amounts in four beakers.

- The first beaker containing azure A solution was kept in dark.
- The second beaker containing azure A solution was exposed to light.
- The third beaker containing azure A solution and 0.10 g CdS-ZnS composite was kept in dark.
- The fourth beaker containing azure A solution and 0.10 g CdS-ZnS composite was exposed to light.

After exposing these beakers for 3 hours, absorbance of solution of each beaker was measured with the help of a spectrophotometer. The absorbances of the solution of first three beakers were found almost constant, but the solution of the fourth beaker absorbance had a decrease as compared to initial value of absorbance. It is clear from all these observations that the degradation required both; light and semiconductor composite.

A solution of 3.0×10^{-5} M azure A was prepared in doubly distilled water and 0.10 g of ZnO, CdS and CdS-ZnO composite were added to it in separate beakers. The pH of reaction mixture was adjusted to 8.5 and then this mixture was exposed to a 200 W tungsten lamp (50.0 mWcm^{-2}). The absorbance was measured with increasing time of exposure. Here, a linear plot between 1 + log A and time was found, which shows that azure A degradation followed pseudo-first order kinetics.

The rate constant was calculated with the help of given formula –

$$k = 2.303 \times \text{slope} \qquad \ldots(2)$$

RESULTS AND DISCUSSION

Table 2: A typical run

[Azure A] = 3.00×10^{-5} M pH = 8.5
Amount of composite = 0.10 g Light intensity = 50.0 mWcm^{-2}

Time (min.)	Absorbance (A)	1 + log A (ZnO-CdS)
0.0	0.538	0.7307
10.0	0.506	0.7041
20.0	0.471	0.6730
30.0	0.416	0.6191
40.0	0.379	0.5786
50.0	0.340	0.5314
60.0	0.305	0.4843
70.0	0.265	0.4232
80.0	0.241	0.3820
90.0	0.215	0.3324
100.0	0.198	0.2966

Rate constant (k) with CdS = 1.56×10^{-4} sec^{-1}
Rate constant (k) with ZnO = 1.44×10^{-4} sec^{-1}
Rate constant (k) with CdS-ZnO = 1.68×10^{-4} sec^{-1}

Effect of pH

The pH of the solution was increased from 5.0 to 10.0, and the observed results are reported in Table 3. It has been observed that the rate of degradation of azure A increases with increase in pH and maximum efficiency was exhibited at pH 8.5. This behavior may be explained on the basis that on increasing pH, there was higher probability for the genration of oxygen anion radical ($O_2^{-\bullet}$), which are produced from the reaction between O_2 molecule and electron (e^-) of the semiconductor. When pH was increased above 8.5, the rate of the reaction was found to decrease, which may be due to the fact that cationic form of azure A is converted to its neutral form, which faces no attraction towards the negatively charged semiconductor surface due to the absorption of OH^- ions.

Table 3: Effect of pH

[Azure A] = 3.00 x 10^{-5} M Light intensity = 50.0 mWcm^{-2}

Amount of composite = 0.10 g

pH	Rate constant (k) × 10^4 (sec^{-1})
5.0	0.26
5.5	0.29
6.0	0.35
6.5	0.47
7.0	0.58
7.5	0.75
8.0	1.10
8.5	**1.60**
9.0	1.41
9.5	1.29
10.0	0.88

Effect of dye concentration

The effect of dye concentration on the photocatalytic degradation of azure A was observed in the range of 2.4×10^{-5} to 4.2×10^{-5} M and results are reported in the Table 4. As the concentration of the dye was increased, it was observed that the dye degradation efficiency increases but after 3.00 × 10^{-5} M (optimum condition), the efficiency of the photocatalytic degradation showed a declining behavior. Here, dye will start acting as an internal filter and it will not allow the desired light intensity to reach the surface of the semiconductor present at the bottom of the reaction vessel.

Table 4: Effect of dye concentration

Amount of composite = 0.10 g

pH = 8.5
Light intensity = 50.0 $mWcm^{-2}$

[Azure A] × 10^5 M	**Rate constant (k) × 10^4 (sec^{-1})**
2.4	1.09
2.6	1.31
2.8	1.43
3.0	**1.68**
3.2	1.48
3.4	1.20
3.6	1.08
3.8	0.97
4.0	0.95
4.2	0.90

Effect of amount of composite

The amount of semiconductor is also likely to affect the degradation of dye and therefore, different amounts of semiconductor were used. The results are reported in Table 5. When the semiconductor amount was kept low, the rate of degradation of dye was also less. It was observed that as the amount of photocatalyst was increased, the rate of photocatalytic activity increases. The rate of degradation was optimum at 0.10 g of the semiconductor. Beyond 0.10 g, the rate constant decreases slightly. Because after this value (0.10 g), an increase in the amount of photocatalyst will only increase the thickness of the photocatalyst layer and not the exposed the surface area. This was confirmed by taking reaction vessels of different dimensions. This slight decline may be due to the fact that excessive amount of photocatalyst may create hindrance and blocks light penetration.

Table 5: Effect of composite photocatalyst

[Azure A] = 3.00 x 10^{-5} M pH = 8.5
Light intensity = 50.0 mWcm^{-2}

Amount of composite (g)	Rate constant (k) × 10^4 (sec^{-1})
0.02	0.88
0.04	1.9
0.06	1.42
0.08	1.51
0.10	**1.68**
0.12	1.56
0.14	1.51

Effect of light intensity

The distance between the light source and exposed surface area of photocatalyst was varied to determine the effect of light intensity on the photocatalytic degradation of azure A. The results are summarized in Table 6. The results show that photocatalytic degradation of azure A was more on increasing the intensity of light as this increases the number of photons striking per unit area of photocatalyst surface per unit time. The maximum rate was observed at 50.0 mWcm^{-2} for degradation of azure A. Further increasing the intensity above 50.0 mWcm^{-2}, there was a slight decrease in the rate of photodegradation. This may be due to some thermal effects or side reactions.

Table 6: Effect of light intensity

[Azure A] = 3.00 x 10^{-5} M pH = 0.10 g
Amount of composite = 0.10 g

Light intensity (mW cm^{-2})	Rate constant (k) × 10^4 (sec^{-1})
20.0	0.61
30.0	0.74
40.0	1.19
50.0	**1.68**
60.0	1.51
70.0	1.45

Mechanism

On the basis of all these observations, a tentative mechanism for degradation of dye is proposed as follows:

$$ {}^{1}AA_0 \xrightarrow{h\nu} {}^{1}AA_1 \qquad \ldots(3)$$

$$ {}^{1}AA_1 \xrightarrow{ISC} {}^{3}AA_1 \qquad \ldots(4)$$

$$ SC \xrightarrow{h\nu} e^{-}(CB) + h^{+}(VB) \qquad \ldots(5)$$

$$ e^{-} + O_2 \longrightarrow O_2^{-\bullet} \qquad \ldots(6)$$

$$ O_2^{-\bullet} + {}^{3}AA_1 \longrightarrow \text{Leuco AA} \qquad \ldots(7)$$

$$ \text{Leuco AA} \longrightarrow \text{Products} \qquad \ldots(8)$$

Azure A dye (AA) absorbs suitable wavelength and gives its first excited singlet state. Then it undergoes intersystem crossing (ISC) to give the triplet state of the dye. On the other hand, the semiconducting composite CdS-ZnO also uses the radiant energy to excite its electron from valence band to the conduction band. This electron will be abstracted by oxygen molecule (dissolved oxygen) generating superoxide anion radical ($O_2^{-\bullet}$). This anion radical will convert the dye to its leuco form, which is degraded in products. $^{\bullet}$OH radical does not participate as an active oxidizing species in this degradation reaction. This was confirmed by the fact that the rate of photodegradation was not affected appreciably in presence of hydroxyl radical scavenger, isopropanol

A comparative study has been carried out between photocatalytic activity of pure CdS, ZnO and their composite. Azure A dye has been used as a model system to compare their photocatalytic performances. The rate constants for photocatalytic degradation of azure A using CdS, ZnO and CdS-ZnO were 1.56×10^{-4} sec^{-1}, 1.44×10^{-4} sec^{-1}, 1.68×10^{-4} sec^{-1}, respectively. These results clearly indicates that the composite CdS-ZnO has shown better results as compared to CdS and ZnO alone. The observation of present work will explore the use of composites for better photocatalytic performance.

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