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PHOTOCATALYTIC DEGRADATION OF CARCINOGENIC RHODAMINE 6G DYE BY STRONTIUM AND TIN DOPED CADMIUM SULPHIDE NANOPARTICLES

MADHURI M. BHAGAT
Department of Chemistry, Dr.Babasaheb Ambedkar Technological University, Lonere, Raigad, India,
madhurisd16@gmail.com

DR. P. B. LOKHANDE
Department of Chemistry, Dr.Babasaheb Ambedkar Technological University, Lonere, Raigad, India
pblokhande@dbatu.ac.in

DR. H. A. MUJAWAR
Department of Chemistry, Dr.Babasaheb Ambedkar, Technological University, Lonere, Raigad, India
hamujawar@dbatu.ac.in

Abstract:

Pure, Sn and Sr doped Cadmium Sulphide photocatalysts were prepared by chemical coprecipitation method with different proportion of dopant ($Cd_xSr_ySn_{1-x+y}S$). The prepared samples were characterised by SEM (Scanning Electron Microscopy), EDX (Energy Dispersive X-Ray Diffraction, and XRD (X-Ray diffraction) spectroscopy. Structural and optical study reveals, the size and band gap was reduced than pure CdS. Photocatalytic degradation experiments were carried out in UV-Photo reactor for degradation study and in sunlight. The photocatalytic activity of Sr and Sn doped Cadmium Sulphide was studied by changing the factors pH, light intensity, catalyst loading and reuse of photocatalyst were studied by the degradation of R6G dye. The photocatalytic activity doped CdS and undoped CdS was compared by means of oxidative photocatalytic degradation of R6G dye. Doped Cadmium Sulphide photocatalyst was observed more effective and efficient than undoped Cadmium Sulphide.

Keywords: photodegradation; nanoparticles; coprecipitation method; photocatalysis; R6G.

I. INTRODUCTION :

Reddish purple colored Rhodamine 6G dye is used as laser medium to enhance the efficiency of dye lasers. [1]. It is mostly used in textile industries as colorant. When discharge in water it can cause serious water pollution problem due to its high toxic nature and water soluble property. The textile industry is one of the main `sources, for the discharge of large amounts of industrial waste water [2]. It has been medically proven that drinking water contaminated with Rhodamine dyes could lead to subcutaneous tissue borne sarcoma which is highly carcinogenic [2]. In addition, others kinds of toxicity such as reproductive and neurotoxicity have been widely and intensively investigated and proved as well by exposure to these dyes [2]. Gaint macromolecular structure of Rhogamine 6G (fig.1)non biodegradable and hazardous to environment.

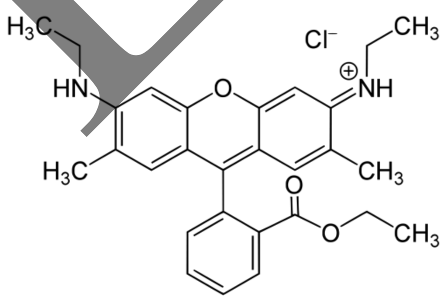


Fig.1. Structure of Rhodamine 6G dye

Now a days many advance methods have been used for abatement of dangerous carcinogenic, recalcitrant organic waste from water. These methods like reverse osmosis ozonization biological treatment etc. has its own disadvantages and limitations. A new trend is now investigated for the successful removal of organic compound from the waste water. Since the last decade, Semiconducting nanomaterials have been extensively used due to their unique properties and application in diverse area [3]. Commonly used semiconductors are ZnO, ZnS, TiO_2, Fe_2O_3, CuS, CdS etc. Semiconductors can act as sensitizers for light-reduced redox processes due to their electronic structure, which is characterized by a filled valence band and an empty conduction band [4].

Photocatalytic activity is the surface activity of compound, which acts as catatalyst in presence of light. This reaction is called photocatalysis. Now a day various semiconducting materials of nano sized particles having large surface area have been used for the purpose of photocatalytic reaction. The harmful dyes and other toxic material can be removed from the waste water by applying photocatalytic degradation. The process of photocatalysis includes generation of hydroxyl radical by the electron and hole in the process of redox reaction on the surface of the photocatalyst. These radicals are then responsible for the oxidation of organic pollutants [5].

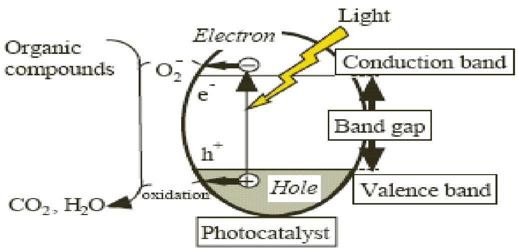


Fig. 2. Mechanism of Photocatalytic activity of photocatalyst

Among the above mentioned semiconductors, Cadmium Sulphide is an important semiconductor which is applicable in various field because of its special physical, chemical and optoelectronic properties. It is a chalcogenide having a band gap of 2.42 eV which can be adjusted by adding impurities like metals and naonmetals etc. These intentionally added impurities called dopent. Although CdS is a good candidate for photocatalytic water reduction and pollutant oxidation, it has the fatal photo corrosion problem due to the oxidation of itself by the photogenerated hole [8]. In present work Cadmium Sulphide is doped with different concentrations of Strontium and Tin. Several methods are now investigated for the preparation of the cadmium sulphide nanoparticles. In present study Cadmium Sulphide doped with Strontium and Tin were prepared by Chemical coprecipitation method. The reason behind choosing this method is formation of highly crystalline nanosized semiconducting material, easy handling and requirement of less atmospheric conditions.

II. EXPERIMENTAL :

A. SYNTHESIS OF SR AND SN DOPED CDS:

Cadmium sulphide nanoparticles doped with Strontium (Sr) and Tin (Sn) were prepared by Chemical co-precipitation method. All the chemicals used were of AR grade. Four samples (A,B,C,D) of different concentrations of Srontium (Sr) and Tin (Sn) were prepared by varying concentrations of Sr and Sn from 0.02M to 0.08M by using the formula ($Cd_xSr_ySn_{1-x+y}S$). These samples were prepared by taking an appropriate proportion of Strontium Nitrate $Sr(NO_3)_2$, Stannous Chloride dihydrate $SnCl_2.2H_2O$, Cadmium acetate $Cd(CH_3COO)_2$ dihydrate, and Thiourea CS $(NH_2)_2$were used for the synthesis of doped photocatalyst . Pure Cadmium Sulphide was also prepared by taking molar proportions of Cadmium Acetate and Thiourea.

Calculated quantity of all the reactants were dissolved in 100ml distilled water and then the mixture of Cadmium acetate , stannous chloride and strontium nitrate was stirred for 10 minutes on magnetic stirrer. After10 minutes the Thiourea solution was added drop wise to this mixture in to this mixture and the pH of solution was adjusted to 11 by ammonia solution. This mixture was stirred for 1 hour at the temperature 70^{o}C for the synthesis of nanomaterials. Initially faint yellow precipitate was formed which gets darken after one hour. The yellow colored precipitate was then filtered, washed with water and ethanol several times and dried in oven.

Same procedure was repeated for the preparation of pure cadmium sulphide by using Cadmium acetate dihydrate and Thiourea. The reactions are as follow

$Cd(CH_3COO)_2+CS(NH_2)_2 \rightarrow Cd(CS(NH_2)_2)_2(CH_3COO)_2$....(1)

$Cd(CS(NH_2)_2)_2(CH_3COO)_2 \rightarrow$

$dS+NH_3+HCNS+CH_3COCH_3+CH_2CO$.. (2)

Though the yellow color is the initial confirmation for the successful synthesis of cadmium sulphide but for final conformation and validation, the characterization of synthesized material was carried out by different analytical methods..

B. CHARACTERISATION OF SAMPLE:

The five samples of pure and Sr, Sn doped Cadmium sulphide prepared by co-precipitation method were characterized by SEM(Scanning Electron Microscopy), EDX (Energy Dispersive X –Ray Spectroscopy) and XRD (X- Ray diffraction Spectroscopy). and UV-Visible Spectroscopy. Wavelength maxima (λ Max) for prepared samples were recorded on UV-Visible spectrophotometer (model no. DR 5000 Hach).

C. PHOTOCATALYTIC DEGRADATION EXPERIMENTS:

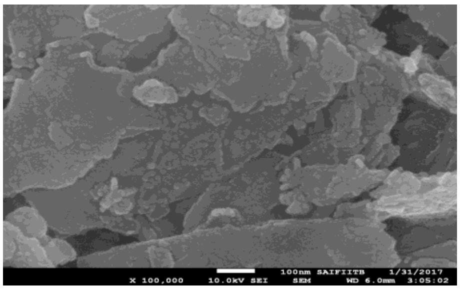
Photocatalytic degradation study was carried out in the presence of UV radiation and in Solar radiation. For all the phtocatalytic degradation study 100ml of 20 ppm Rhodamine 6G dye sample was taken in 250 ml reaction vessel. For the study of effect of catalyst loading on the degradation of R6G dye, 50-200 mg of photocatalyst was added in reaction vessel. Degradation of R6G dye was observed by measuring the initial absorbance and absorbance at one hour time interval on UV-visible spectrophotometer.

III RESULTS AND DISCUSSION:

A. CHARACTERIZATION STUDY:

1. SCANNING ELECTRON MICROSCOPY (SEM) ANALYSIS:

SEM is valuable analytical tool that allows for a non destructive examinations of various types of materials. The morphology of prepared doped Cadmium Sulphide was studied by Scanning Electron Microscopy (SEM). **Fig. 3** 1a, 1b, 1c, 1d and 1e are the SEM images for sample A, B, C, D, and E respectively.



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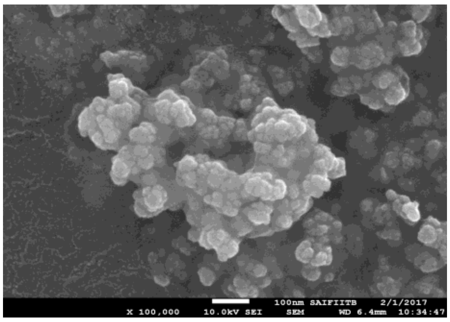

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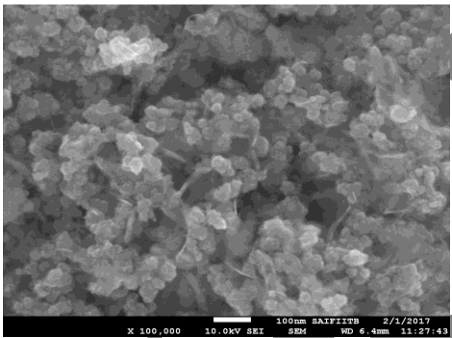

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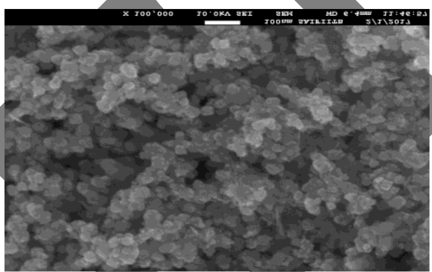

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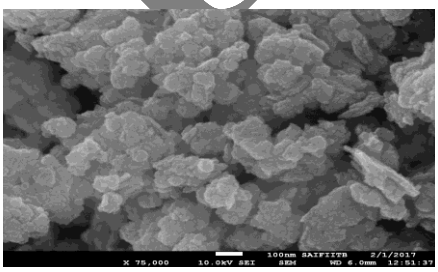


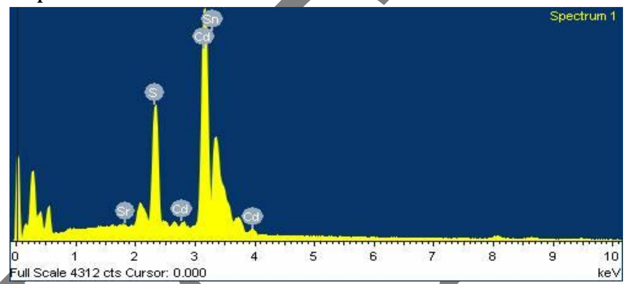
1 e.

Fig. 3 1a, 1b, 1c, 1d and 1e are the SEM images for sample A, B, C, D, and E respectively.

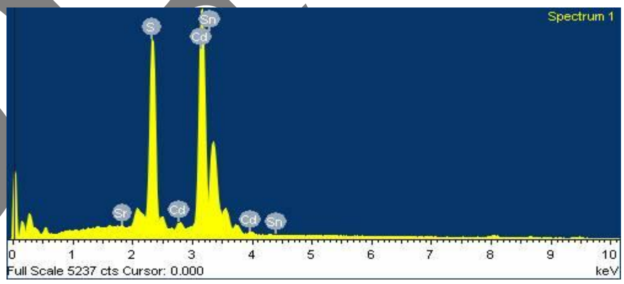
The above SEM images showed the agglomeration of prepared pure and doped cadmium sulphide nanoparticles. The data also reveals the nano particles are spherical in shape and sponge like structure.

2. ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDX) ANALYSIS:

EDX is an analytical technique used for elemental analysis or composition of samples. Following are the EDX images of prepared pure and doped Cadmium sulphide nanoparticles.



a.



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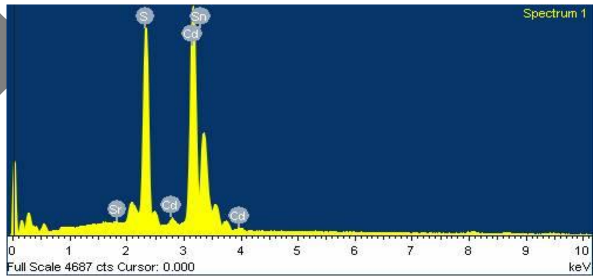

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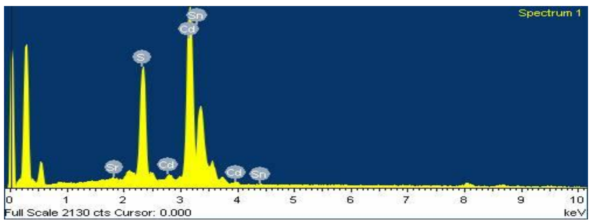

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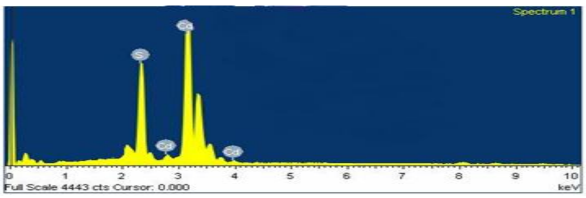


e.

Fig.4. a, b, c, d and e are the EDX images for the samples A,B, C,D,and E repectively.

The EDX images of samples A, B, C, D and E are shown in Fig no.4.The EDX data reveals the successful incorporation of Strontium and Tin in Cadmium Sulphide crystal.

3. X-RAY DIFFRACTION (XRD) ANALYSIS:

XRD is a rapid analytical technique used for phase identification of crystalline material and provide information about unit cell dimensions. The size of prepared Sr and Sn doped Cadmium Sulphide nanoparticles were found with the help of X-Ray diffraction study.

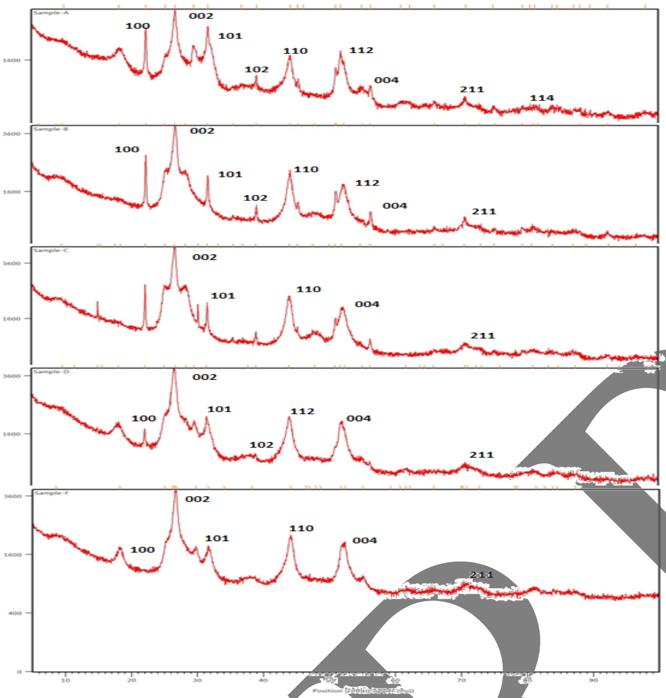


Fig. 5. XRD images for sample A, B, C, D and E respectively.

All the diffraction peaks in the XRD patterns of CdS nanoparticless shows good agreement with standard hexagonal wurtzite structure of CdS.The XRD images shows the prepared nanoparticles are highly crystalline. The planes (100), (102), (002), (112), (004), (211) are the planes for hexagonal structure for doped Cadmium Sulphide nanoparticles. The calculated particle sizes by the Debey Sherrer Equation.

$$d = \frac{n\lambda}{\beta\cos\theta}$$

Table 1 Particle size for pure and doped cadmium sulphide.

Sr no.	Samples	Composition of PC	d
1	A	0.02M Sr,0.08M Sn CdS	46.3nm
2	B	0.04M Sr,0.06M Sn CdS	46.3nm
3	C	0.06M Sr,0.04M Sn CdS	46.3nm
4	D	0.08M Sr,0.02M Sn CdS	46.3nm
5	E	CdS	84.2 nm

d-particle size for samples A,B,C,D and E respectively in nm

Particle size, calculated from XRD data of pure Cadmium Sulphide prepared by chemical coprecipitation method is 84.2 nm. On doping with Sr and Sn it decreases to 46.3 nm providing large surface area and ultimately enhanced photocatalytic activity of Photocatalyst.

4. UV-VISIBLE SPECTROSCOPY:

The λ_{max} of prepared samples was determine by using UV-Visible spectrophotometer. The band gap for each sample is calculated from the λ_{max} value.

Table 2. λ max and Band gap for pure and doped cadmium sulphide

Samples	λ_{max}	Band Gap eV
0.02Sr,0.08 Sn CdS	508 nm	2.370
0.04Sr,0.06 Sn CdS	536 nm	2.310
0.06Sr,0.04 Sn CdS	542 nm	2.287
0.08Sr,0.02 Sn CdS	571 nm	2.171
CdS	498 nm	2.489

λ max- wavelength maximum in nm and band gap in eV

It is observed from the data, the band gap of pure CdS is 2.4 eV. There is decrease in band gap of Cadmium Sulphide by doping impurities of Strontium and Tin. The band gap of 0.04 Sr and 0.06 Sn doped Cadmium Sulphide decreased up to 2.1 eV, which is smallest among the rest of the samples. If there is decrease in band gap, less energy will required for the formation of electron and hole which are responsible degradation of organic compound.

B. PHOTODEGRADATION EXPERIMENT:

The photocatalytic degradation experiment in UV light was carried out in special UV-light chamber called UV-photoreactor. The temperature of the reaction mixture was maintained below 25°C to avoid photodecomposition of dye. The light intensity produced by 13 watt UV lamp was measured by lux meter and found to be 4210 lux. The Pure and doped Cadmium Sulphide with different proportion of Strontium and Tin shows almost similar degradation of Rhodamine 6G dye after 6 hours. UV light is slightly better choice for degradation of R6G as it shows more degradation in UV light.

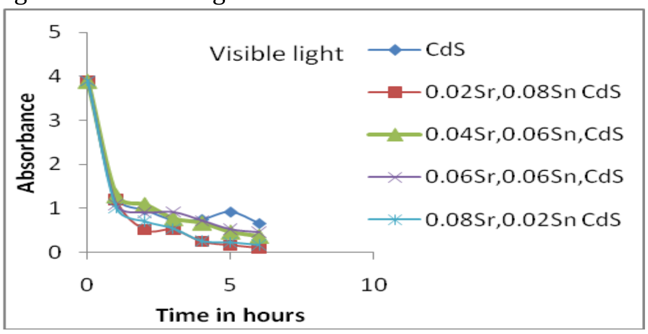


Fig. 6 a. Photocatalytic activity of Sr and Sn doped and pure CdS in Visible light

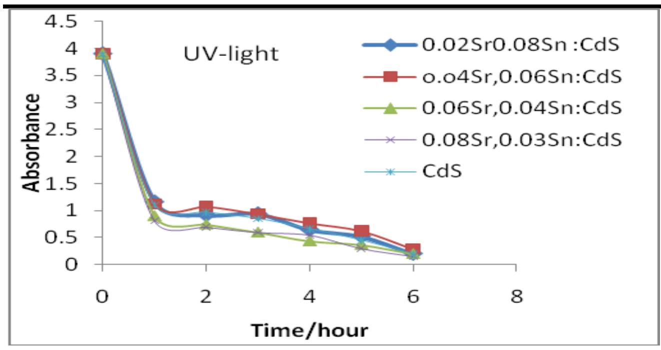


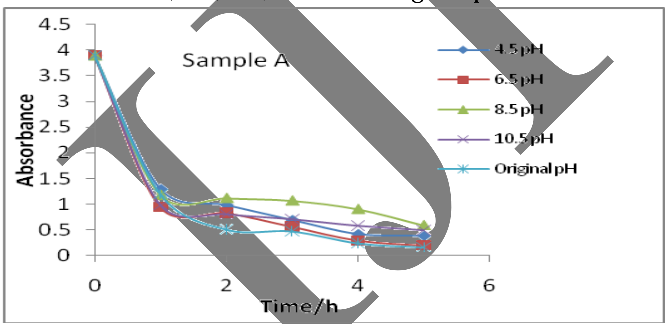
Fig. 6 b. Photocatalytic activity of Sr and Sn doped and pure CdS in UV light

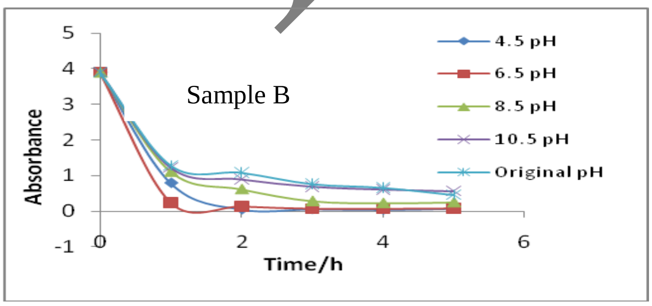
Pure CdS shows good degradation in UV light rather than visible light. Doped compounds shows enhance Photodegradation in both UV light and Visible light. In visible light 0.02 Sr, 0.08Sn doped cadmium Sulphide showed highest degradation among five samples. But in UV light 0.06Sr, 0.04Sn doped cadmium Sulphide has been found better photocatalyst than other four samples.

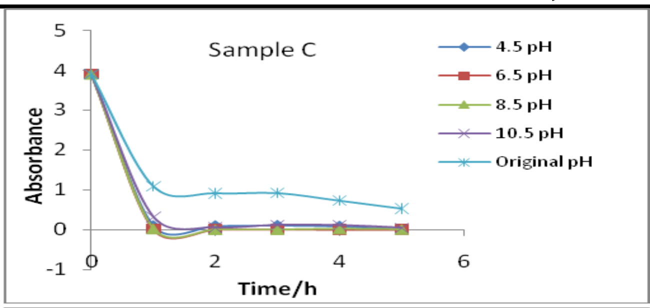
1. EFFECT OF PH:

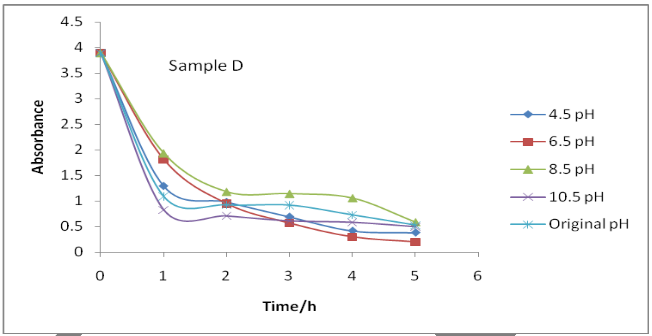
The effect of pH was studied at ordinary pH, at pH 4.4, 6.5, 8.5, and 10.5 pH. The ordinary pH of the Rhodamine 6G dye and catalyst solution was 7.5. For the experiment 100 mg of photocatalyst were taken per 100 ml of Rhodamine 6G dye. The pH was adjusted with HCl and NH_4OH solution and the solutions were stirred in solar light for five hours. Change in concentration for each hour was recorded on UV-Visible spectrophotometer.

PCD rate is slightly depends on the pH of the reaction solution when CdS used as photocatalyst. The graph were plotted for each sample time Vs Absorbance at 1 hour time interval for 4.5, 6.5, 8.5, 10.5 and original pH.









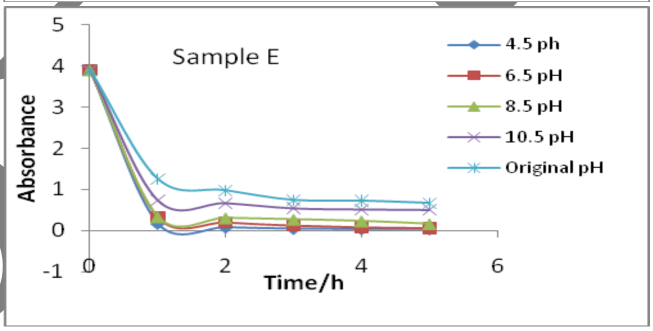


Fig.**7** Graph showing the effect of pH on degradation of R6G for pure and doped cadmium sulphide.

The original pH of solution is 7.5. The all five samples shows better result at pH=6.5.The above data revealed that neither acidic 4.5 nor basic 8.5 and 10.5 pH is suitable for degradation of R6G dye. The optimum pH for the degradation of R6G dye by CdS is 6.5pH. This pH favours the adsorption of dye on the surface of photocatalyst and thereby production of OH radicals. The point of intersection of the resulting null pH (pH= 7.5)corresponds to the zero point charge, pH ZPC, at this point the surface charge on hydrous CdS is neutral. As the pH is lowered the surface of the cadmium sulphide gets protonated and become positively charged. This positively charged surface then attracts anions (OH) towards itself which increases degradation efficiency of photocatalyst.[15].

Table3. Degradation efficiency of Pure and doped CdS samples.

Sr. no	Samples	η % For optimum 6.5 pH	η % for catalyst loading 100mg/ 100ml R6G
1	A	90%	97%
2	B	97%	91%
3	C	99%	88%
4	D	95%	95%
5	E	98%	82%

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At an optimum pH of 6.5 the sample C has highest degration efficiency of R6G dye. It shows 99% degradation of Rhodamine 6G dye.

2. EFFECT OF CATALYST CONCENTRATION

For the study of effect of photocatalyst loading 50mg, 100mg, 150mg and 200mg of photocatalyst were taken per 100ml of R6G dye. The above Five samples are irradiate with sunlight for 6 Hours. The samples were taken at each hour time interval and absorbance were recorded

The Pure CdS and 0.02M Sr, 0.08M Sn doped CdS, 0.04M Sr, 0.06M Sn doped CdS snows the good degradation result at 100mg of catalyst concentration but 0.06M Sr, 0.04M Sn doped CdS and 0.08M Sr, 0.02M Sn doped CdS gave good result for degradation of R6G dye as it exposes a large surface area and rays of sunlight that activated the proper energy for the formation of electron and hole. At the higher concentration of photocatalyst the rays of light cannot penetrate by the crowed of surface hence shows low degradation rate.

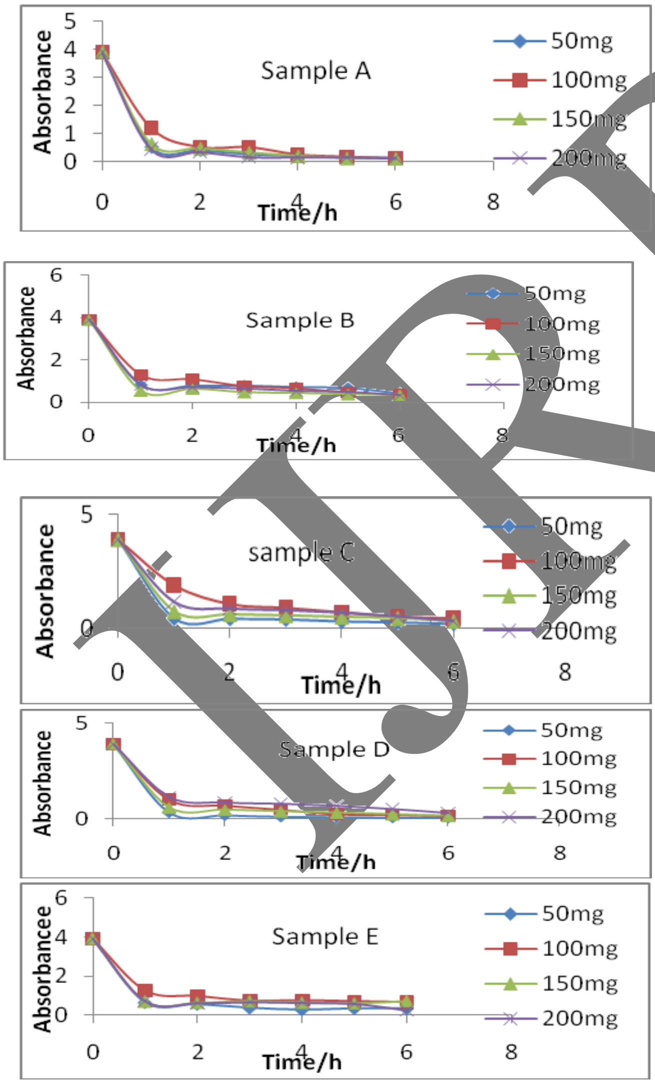

Fig.8 Graph showing the effect of catalyst concentration on degradation of R6G for pure and doped cadmium sulphide

3. EFFECT OF INTENSITY OF LIGHT:

Intensity effect was studied by taking the 100 ml solution of Rhodamine 6G dye loaded with 100mg of sample photocatalyst and irradiating it with sunlight for 6 hours with continuous stirring. The intensity was measured at the starting of the experiment and at each hour time interval on Lux meter .Initial absorbance and absorbance at each time interval was checked on UV-Visible spectrophotometer for all five samples. Intensity shows the tremendous effect on the photocatalytic activity of photocatalyst. More intensity favours the high degradation rate.

From the table it is clear that, at very first hour, in case of all five samples degradation rate is very high i.e. nearly half of the initial concentration due to the very high intensity. From From the table it is clear that, at very first hour, in case of all five samples degradation rate is very high i.e. nearly half of the initial concentration due to the very high intensity. From the second to third hour there is again half reduction in concentration. From third hour as the intensity lowers degradation rate is also lowered. So the light plays an important role in photocatalytic degradation.

4. REUSE OF PHOTOCATALYST:

For the study of reuse of photocatalyst, the efficiency of used catalysts was checked. The used catalysts were collected, washed with water, centrifuged and dried in electric oven at 100^{0}C. Then the photocatalytic activity of these catalysts was checked by irradiating the sunlight to the Rhodamine 6G dye for about 4 hours. The initial and final absorbance was noted. It was observed that stability, activity and efficiency of the photo-catalysts were remains same. This makes the photocatalyst most effective and cost effective

Table 4 Effect of light intensity on photocatalytic degradation efficiency of pure and doped cadmium sulphide.

	Int. in Lux	Sample A		Sample B		Sample C		Sample D		Sample E	
		Abs	η %	Abs	η %	Abs	η %	Abs	η %	AbS	η %
0	104000	3.898		3.898		3.898		3.898		3.898	
1	100800	1.199	69	1.289	67	1.086	72	1.014	74	1.253	68
2	103700	0.593	85	1.088	72	0.916	77	0.707	82	0.976	75
3	88500	0.579	87	0.767	80	0.912	77	0.545	86	0.743	80
4	70500	0.246	94	0.664	83	0.735	81	0.260	93	0.739	80
5	49500	0.166	96	0.465	89	0.526	86	0.232	94	0.728	81
6	20200	0.103	97	0.346	91	0.460	88	0.173	95	0.668	83S

Abs = absorbance at time t, η = photocatalytic degradation efficiency, Int.= Intensity of sunlight, photocatalyst = 100mg/100ml of R6G dye,
Initial pH of the suspension = 7.56

IV. CONCLUSIONS:

The pure and doped cadmium sulphide with Strontium and tin prepared by chemical coprecipitation method are highly crystalline and nanosized. The band gap of pure cadmium sulphide was narrowed by adding Strontium and Tin. The 6.5 pH is optimum pH for the photocatalytic activity of cadmium sulphide. The catalyst concentration affects the degradation rate. High intensity of light increases the reaction rate of photocatalysis. There is no change in properties, stability and efficiency of photocatalyst on reusing it. Sn and Sr doped cadmium sulphide can be a good choice for the removal of Rhodamine 6G dye from the water effluents.

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