Synthesis, Size Characterization and Photocatalytic Activities of Copper Sulfide (Cus) and Cadmium Sulfide (Cds) Nanoparticles using Oxidative Degradations of Meldola's Blue, Crystal Violet and Alizarin Red in Aqueous Medium at 25°C

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Abstract — **Metal sulfide nanoparticles show significant catalytic properties similar to metal oxide nanoparticles. Metal sulfides are cheap, cost-effective, present in abundance, stable and easily recyclable. In the current work, nanoparticles of CuS and CdS are synthesized using poly-N-vinylpyrrolidone (PVP) as the capping agent and excess aqueous H2S at 25°C. The black and yellow residues from CuS and CdS systems are ultra centrifuged, washed and dried. The size characterizations are determined using the UV-DRS, PXRD, FESEM, EDAX and HRTEM measurements. Adopting pseudo first order experimental condition, 1.0mM, aqueous dye solution of Meldola's Blue (MB), Crystal Violet (CV) and Alizarin Red (AR) are used separately to follow the oxidative degradation kinetics under UV irradiation at 300 nm. Absorbance variation with time are measured at constant λmax equals to 430nm, 550nm and 550nm corresponding to AR, MB and CV dye systems respectively. Effects of catalyst loadings and substrate concentrations are followed. Among the catalysts effect, CdS nanoparticles proved as a better catalyst than the CuS nanoparticles system. The overall rate co-efficient values are found to be 9×10-4s-1, 4×10-4 s-1, and 2×10-4 s-1 for MB, CV and AR dye degradations respectively. The trend witnessed in the dye degradation capacity catalyzed by CdS NPs is CV>MLB>AR, while in CuS NPs catalysis AR>MLB>CV has been observed. In order to ascertain complete degradation, H_2O_2 effect was included for AR dye. Herein also CdS nanoparticles produced higher rate constant value than CuS for the dye degradations.**

I. 1.INTRODUCTION

Metal sulfides in the form of nanoparticles exhibit photocatalytic activity similar to the nanoparticles of metal oxides and other inorganic compounds [1, 2]. Nanoparticles of transition metal compounds are proved to possess enhanced physical properties, such as optical, magnetic, semiconducting, electrical and catalytic properties compared to the bulk materials [3, 4]. Therefore, synthesis, size characterization and the photocatalytic activity of popular and well-used materials such as CuS and CdS are chosen for the present investigation. These materials in the nano sizes can act as substitute to noble and costlier metals in terms of imparting abundance, cost effectiveness, and stability. Photocatalysis is a greener pathway that can be adopted for the oxidative degradation of organic matter without involving corrosive solvents. The present work is devoted to utilize the photocatalytic properties of CuS NPs and CdS NPs for the oxidative degradation of aqueous source pollutants and intensely colored dyes such as Crystal violet (CV), Meldola's blue (MLB) and Alizarin red (AR) at 25°C. Upon irradiation with UV or light photons, the dye solutions having nanoparticle catalysts produce a hole [H+] and an electron (e-) pair, which can recombine or dissociate at the surface of catalyst particle [5-7]. These interact with the dye substrates causing dye degradation. Effects of composition of dye and catalysts, and their nature are studied. The trend in the photocatalytic activity observed shows that CdS NPs are more efficient than CuS NPs. Implication of the results are discussed.

II. EXPERIMENTAL

A. Chemicals and reagents

Cadmium Nitrate, Copper Nitrate, Sodium Sulfide, Poly-n-Vinyl Pyrrolidone (PVP) and Ethanol were purchased from Merck India, with 99.9% purity. The chemicals were used as such, without further purifications. Triple distilled was used in all solution preparations.

B. Synthesis of CdS NPs and CuS NPs

Nitrate salts of copper and cadmium were used as the starting materials. 50ml of 0.1M aqueous solution of CdNO3.3H2O and 50ml of 1.5M sodium sulfide were added drop wise in a round bottomed flask kept under stirring. 5 mL of 2 Wt% of PVP solution was added to the mixture and vigorously stirred for 5 hours at room

temperature. Similar procedure was adopted for CuS NPs using copper nitrate as the precursor. The color of the CdS NPs and CuS NPs suspensions appeared as bright yellow and shiny black respectively. The powders were washed and filtered with ethanol and distilled water several times to remove the excess organic residue. The collected sample were dried and stored in the desiccator at 25^{o}C.

C. Size Characterization

The FESEM, EDAX, and HRTEM measurements of the CuS NPs and CdS NPs are given in fig.1. FESEM and HRTEM were measured using SU6600 HITACHI model operating at an accelerating voltage of 100kv and FEI-TECNAIG and model-30-Swin operating at an accelerating voltage of 300kv instruments respectively. Applying particle size distribution analysis, it was found that CdS NPs existed as 6±1nm size and CuS NPs existed as 20±1nm size.

D. Photocatalysis

Photocatalytic activity of CuS NPs and CdS NPs were studied by using UV irradiation and degradation of Crystal violet (CV), Meldola's blue (MLB) and Alizarin red (AR) dyes in aqueous solution. UV-lamp with 300nm wavelength source was used. Vertical and top view irradiation setup was maintained. The content in the quartz was continuously stirred. The distance between the UV source and surface of solution was maintained at 15 cm. The absorbance of the aliquots was measured at various intervals of time. The kinetics of dye degradation was followed from absorbance variation with time data and generating the pseudo first order plot by plotting log (OD0/ODt) versus time, passing through origin. The mean slopes were multiplied with 2.303 constant to get in the rate coefficient values. The same procedure was adopted with various catalyst feed loadings and with various dye concentrations.

III. RESULTS AND DISCUSSION

A. Size of the CdSNPs and CuS NPs

In fig.1 HRTEM and FESEM with EDAX are given. The mean value of CdS NPs was found to be 6±1 nm, while that of CuS NPs was found to be 20±1nm. Under similar experimental conditions used in the preparation, CuS NPs are found to be bigger in size than the CdS NPs. This may be due to higher inter particle attraction forces in the case of CuS NPs compared to CdS NPs. Therefore, the photocatalytic activity shall be different between the two metal sulfide nanoparticles.

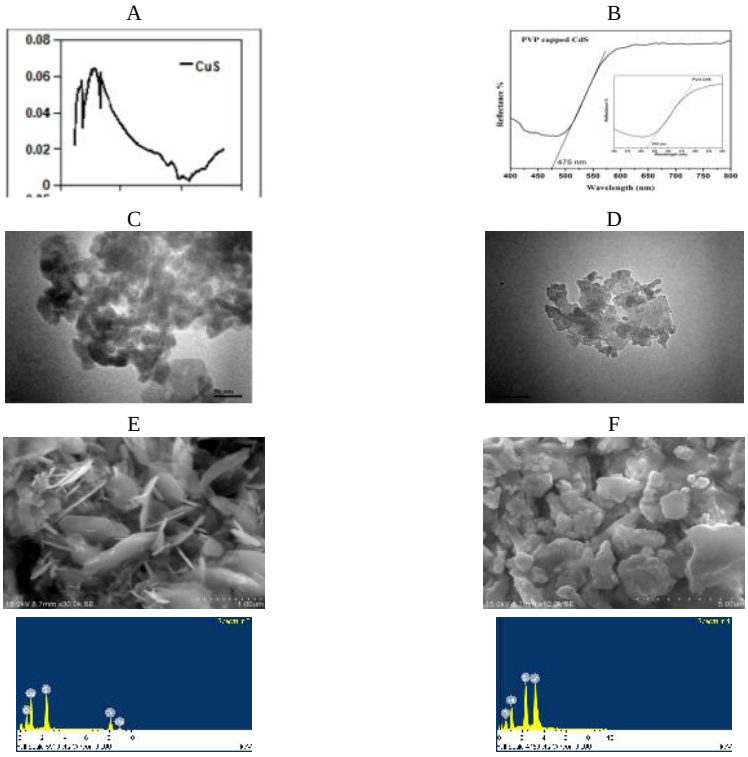

Fig.1 UV-DRS(A, B), HRTEM photos (C, D) and FESEM with EDX (E, F) of CuS NPs and CdS NPs in the synthesized samples

B. Photocatalysis studies

Due to the strong absorbance in the visible region, all the dyes are intensely colored at neutral pH in water. Upon UV-irradiation in the presence of photo catalyst, the degradation of the dye dissolved in water gets initiated, which is indicated by decolourization of the solution. The absorbance variations with time measured separately

for the three dye solutions in the presence of a catalyst are shown in fig.2. These measurements are used to determine the rate constant values of the dye degradations under pseudo first order conditions. In fig.3, separate kinetic plots generated in the presence of CuS NPs and CdS NPs are given for the three dye systems. Best fit linear plots for the pseudo first order condition are observed. The slopes of the plots are used to determine the rate coefficient values, and the same are presented in Table.1

TABLE I. PSEUDO FIRST ORDER RATE COEFFICIENT VALUES FOR THE DYE DEGRADATION WITH CUS NPS AND CDS NPS , DCATALYST AND DYE COMPOSITION EFFECTS

Catalyst	**CuS NPs**			**CdS NPs**		
Dyes+catalyst	***CV(×10-5 s-1)***	***MLB(×10-5 s-1)***	***AR(×10-5 s-1)***	***CV(×10-5 s-1)***	***MLB(×10-5 s-1)***	***AR(×10-5 s-1)***
0.02mM+1mg	4.2	3.3	9.3	7.2	4.4	2.2
0.03mM+2mg	3.3	2.2	8.2	6.3	5.2	1.3
0.01mM+1mg	3.5	2.5	10.3	6.3	5.1	4.4
0.01mM+1mg	5.2	3.5	12.2	8.3	7.3	3.2

C. Catalyst and dye composition variation

Effects of variation in catalyst loadings and dye concentrations on the rate constant values are studied to optimize the degradation conditions. In fig.3, the kinetic plots obtained for the catalyst feed loading of 1mg/20mL and 2mg/20mL are given. For both catalyst systems, CuS NPs and CdS NPs, the increase in catalyst amount increases the degradation rates for all the three dye systems. Regarding the effect of dye concentration variation, keeping the catalyst concentration constant, the kinetic plots generated are shown in fig.3. It reveals that the rate constant values decrease with decrease in the dye concentration. The effect of catalyst and dye compositions on the rate coefficient value can be analyzed from the data in Table.1.

Regarding the variation in the photocatalytic activity, the band gap energies of CuS NPs and CdS NPs are analyzed based on the values determined from the UV-DRS in fig .1. 2.42 ev and 2.2 ev are the measured band gap values for CdS NPs and CuS NPs respectively. It can be seen that the CdS NPs with size 6±1nm possess 2.42ev as the band gap energy, while 20±1nm can posses 2.2 ev band gap energy. In all, CdS NPs catalyzed systems show higher rate constants of dye degradations compared to CuS nano catalyzed systems. Additionally, a smaller sized nanoparticle catalyzed dye system exhibit higher photocatalytic degradation than the larger size nanoparticle catalyzed systems.

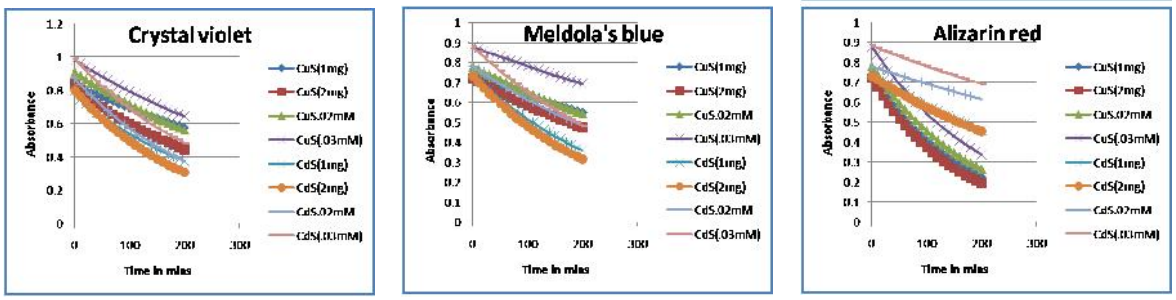

Fig.2 The absorbance variation with time plots of CV, MLB, AR dyes in the presence of CuS NPs and CdS NPs

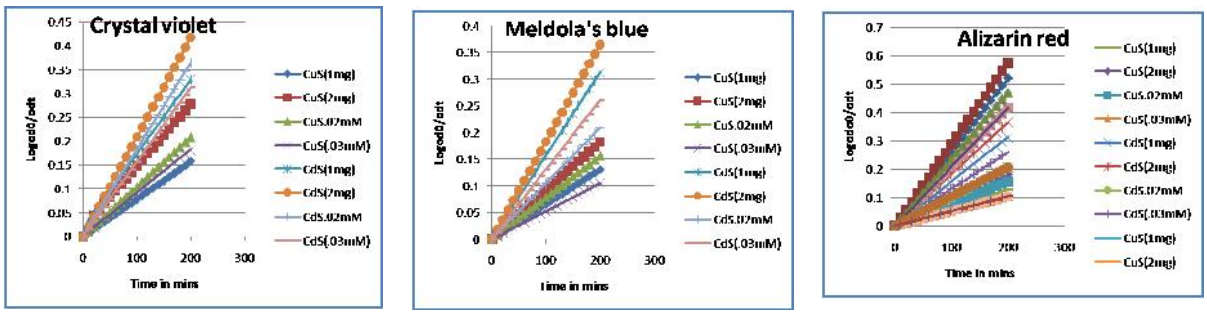

Fig.3 The kinetic plots of log (OD0/ODt versus time for CV, MLB, AR in the presence of CdS NPs and Cus catalyst amount variation 1)1mg/20mL, 2) 2mg/20mL and dye concentration variation 3) 0.02mM 4) 0.03mM

The photo degradability of three dyes can be analyzed based on the rate constant values. Keeping the dye concentrations constant, it is found that CuS NPs and CdS NPs show different trends on the three dye systems. In the case of CdS NPs-catalyzed dye degradation, the trend observed is CV>MLB>AR. In the case of CuS NPs-catalyzed system, AR>MLB>CV gradation is observed. Due to the differences in the surface interaction of the catalyst at various functional groups of the dye systems, such variations are detected. Due to the poor photo

degradability rate, constant values obtained for AR in the presence of CdS NPs are low. Therefore, H_2O_2 was incorporated, and repeated the photocatalysis. Under this condition, complete decolorization was seen, and the trend observed among the three dyes in the presence of H_2O_2 remained the same as in the absence of H_2O_2.

IV. CONCLUSIONS

CdS NPs and CuS NPs are synthesized using PVP as the capping agent, resulting in 6±1nm and 20±1nm, respectively, as the mean particle sizes. Intensely colored dyes such Crystal violet (CV), Meldola's blue (MLB) and Alizarin red (AR) are chosen for the degradations catalyzed by CdS NPs and CuS NPs in the presence of 300 nm UV-irradiation. The degradation kinetics was followed by measuring absorbance versus time data, based on which the rate coefficient values are determined. The trend observed regarding photocatalytic activity among the two catalyst systems it that CdS NPs exhibited increase in photocatalytic activity than that of CuS NPs for constant catalyst composition conditions. The trend observed regarding photo degradability of three dye is CV>MLB>AR for the CdS NPs catalysis and AR>MLB>CV for the CuS NPs catalysis.

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