International Research Journal of Engineering and Technology (IRJET) e-ISSN: 2395 -0056
Volume: 03 Issue: 04 | Apr-2016 www.irjet.net p-ISSN: 2395-0072

Photo Catalytic Degradation of Methyl Orange by Using CdS Semiconductor Nanoparticles Photo catalyst

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Abstract - *Using CdS semiconductor Nanoparticles Photo catalyst, kinetics of photo degradation of Methyl Orange has been studied at different intensities of radiation in the visible range. Photo degradation of studied dye follows the first order kinetics. The observed reaction rate constant (K) data reveals that the rate of photo degradation on dye increases with the increase in the intensity of radiations, however the reaction rate decreases with the increase of [H_2O]/[surfactant] = (W) values in the micro emulsion used for the synthesis of Nanoparticles. The CdS nanoparticles are synthesized in water-in-oil micro emulsion using different [H_2O]/[surfactant] = (W) ratio. The synthesized nanoparticles have been characterized by their XRD and TEM images.*

Key Words: **Semiconductors, Nanoparticles, Photo catalyst, Photo degradation, Methyl Orange**

1.INTRODUCTION

Organic pollutants present in water near industrial areas are a major problem for present world. During dye production and textile manufacturing processes, a large quantity of waste water containing dye stuffs with intensive color and toxicity are introduced into the aquatic system. These dyes do not decompose rapidly through natural processes and are resistant to aerobic degradation. It is necessary to find an effective method of waste water treatment in order to remove color from effluents. A number of physical and chemical techniques have been reported for the removal of dye compounds such as adsorption, an activated carbon, bio-degradation, ozonation and advanced oxidation processes such as Fenton and photo Fenton catalytic reaction, H2O2/UV processes and semiconductor photo catalysis. But now a day's photo catalytic degradation of organic pollutants present in water by using semiconductor nanoparticles is emerged as a new and advanced technique for purification of water. It is a low temperature and non-energy intensive approach for chemical waste remediation.

The basic principles under semiconductor photo catalysis involves photo generated electrons (e-) and holes (h+) migrating to the surface of the photo catalyst and serving as redox sources that react with adsorbed organic pollutants and leading to their degradation. A general procedure for photo oxidation of dye using semiconductor photo catalyst is shown in following figure.

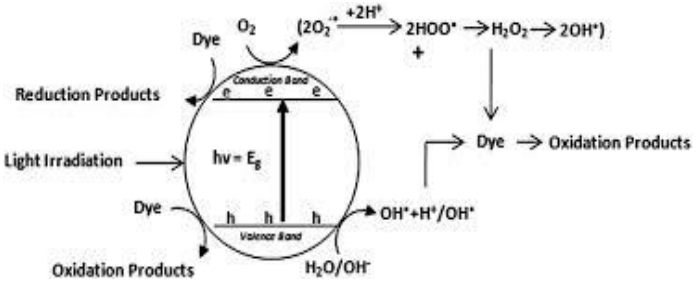

Figure 1 : Photooxidation of dye using semiconductor photo catalyst.

In photo catalytic process using semiconductor photo catalyst photons of ultra band gap energy is absorbed by the catalyst and an electron (e-) – hole (h+) pair is generated in the bulk. These electrons (e-) – hole (h+) pairs then move towards the surface via diffusion where they react with an adsorbed hydroxyl ion to produce an adsorbed hydroxyl radical which can then oxidize the organic substrate. A general semiconductor photo sensitized reaction can be represented as:

$$\text{Organic dye} + 2\ H2O \xrightarrow[h\nu \geq Ebg]{semiconductor} > Co2 + 2H2$$

The aim of present work is to access the photo catalytic degradation of mono azo dye (Methyl Orange) , selected due to its toxicity as well as its presence in water of several industries. Further kinetics of photo degradation of Methyl Orange was studied by using CdS semiconductor nanoparticles photo catalyst at different intensities of radiation in the visible range. In the present investigation semiconductor nanoparticles of CdS have been prepared by carrying out the reaction between Cd (NO3)2 with H2S gas in water-in-oil micro emulsion containing cyclohexane, polyoxyethylene t-octyl phenol(Triton X-100) and water using different [H2O]/[surfactant] = (W) ratio. The synthesized nanoparticles have been characterized by their XRD spectra and TEM images.

2. EXPERIMENTAL

2.1 MATERIAL:

Triton X-100(S.D.S),Cd(NO3)2(E-marck),Methyl Orange (BDH fine chemicals) and cyclohexane were used as such.

Double distilled water (specific conductivity 0.5 x 10 -5 S.cm-1) was used for preparing different dye solution.

2.2 METHOD:

2.2.1 PREPARATION OF CdS NANOPARTICLES :

Water-in-oil micro emulsion was prepared by a thorough mixing of cyclohexane, surfactant(Triton X-100)and aqueous solution of cadmium nitrate(Cd(NO3)2) = 10-2M, [H2O]/[surfactant] = W (5 or 10). H2S gas was passed through the above clear solution for about 5 minutes and the excess of H2S was boiled off. The product was filtered through the Watmann No. 1 filter paper to reject any suspended material. The colloidal filtrate was transferred to a one liter size beaker. Excess of solvent was evaporated to dryness and then heated at 150^0 C for 2 hours. The CdS nanoparticles were firmly adhered at the bottom of the beaker. The prepared CdS crystals are characterized by their XRD spectra and TEM images.

2.2.2 PHOTO CHEMICAL DEGRADATION :

100 ml of 10-4 dye solution was added to the above beaker and the same was irradiated by placing 30 cm below lightening electric bulbs of 100W and 200W. 5 ml of sample was drawn out each time from the reaction vessel at one hour interval. The absorbance of the sample was measured using a colorimeter. The rate of the reaction was then studied at different intensities by measuring the absorbance as a function of time.

3. RESULTS AND DISCUSSIONS:

3.1 TEM STUDY:

Transmission electron microscope (TEM) images of synthesized CdS nanoparticles are given in figure. It is evident that the size of nanoparticles increases with the increase of [H2O]/[surfactant] = W ratio in the micro emulsion in the synthesis of CdS nanoparticles. On increasing the [H2O]/[surfactant] = W ratio, the micellar core size of water-in-oil micro emulsion becomes larger which can accommodate more molecules of the CdS molecules leading to the larger size of nanoparticles. A synthesized CdS nanoparticle varies from 6 to 10 nm.

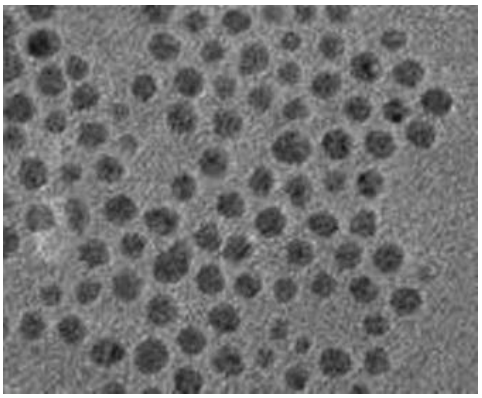

Figure 2. : Transmission electron microscope (TEM) images of CdS nanoparticles synthesized in micro emulsion [H2O]/[Trition-X-100] (w) = 5

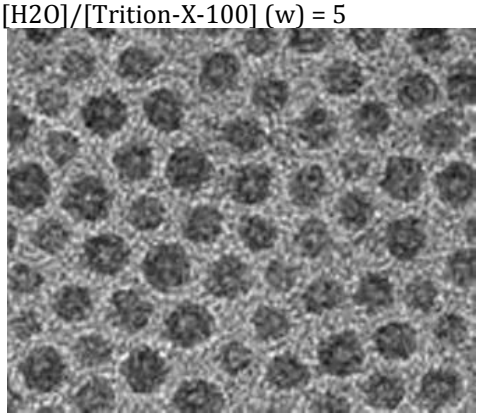

Figure 3. : Transmission electron microscope (TEM) images of CdS nanoparticles synthesized in micro emulsion [H2O]/[Trition-X-100] (w) = 10

3.2 XRD SPECTRA:

X-ray diffraction (XRD) spectra of synthesized CdS nanoparticles dispersed in cyclo hexane were obtained using copper K radiation (λ =1.542 ^{0}A). The observed XRD spectra is given in figure

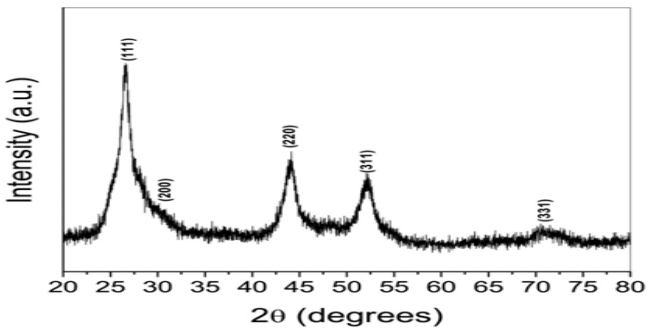

Figure 4. : X-Ray Diffraction (XRD) spectra of synthesized CdS nano particles dispersed in cyclo hexane.
The principal diffraction peaks for CdS appears at 2θ = 26^0, 44^0 and 52^0 Which corresponds to Miller indices (111),(220)

and (311) respectively, Suggesting cubic crystal structure of CdS. Particle size of the synthesized nanomaterial was obtained using Scherrer equation.

$\beta = \lambda / L \cos\theta$

where β = breadth of peak in XRD spectra , λ = wavelength of radiation used and L = diameter of the particle.

4. KINETICS OF PHOTO DEGRADATION STUDY:

4.1Determination of λ_{max}

For obtaining λ max plots of absorbance versus wavelength (nm) for Methyl Orange (10-4M) were drawn. The value of λ max corresponds to the maximum was obtained at 470 nm for methyl orange.

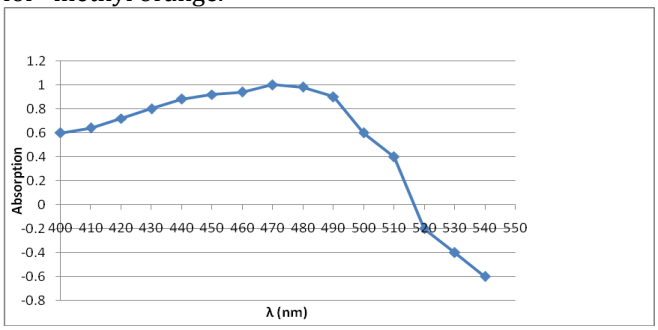

Figure 5. : Plot of absorbance as a function of wavelength (nm) for methyl orange [10-4] (λ max =470 nm)

4.2 PHOTO DEGRADATION STUDY

The value of absorbance and concentration of methyl orange as a function of time at different intensity of radiation is given in table 1. The value of absorbance of methyl orange at different intensities as a function of time at different [H2O]/[surfactant] = W ratio are given in table 2 and table 3. The values of reaction rate constant (K) data are given in table 4. and the percentage degradation values of dye after 8 hours are given in table 5.

The rate constant of photo degradation increases with intensity of radiation due to increase in the number of photons per unit time interacting with substrate molecules. The rate of absorbance decreases with increase in the intensity of light. The rate of absorption also decreases by increasing the irradiation time because of the decrease in amount of absorbing reactant molecules with increasing time as more and more dye molecules were getting degraded with passing time and by increasing the intensity of irradiation, Hence the rate of absorption decreases. However on increasing [H2O]/[surfactant] = W ratio in the micro emulsion, the photo degradation rate constant decreases. It is because on increasing the value of w, the core size of the micelle in micro emulsions increases resulting in the large particle size of the semiconductor CdS nanoparticles. This lead to decrease in the specific area of nanoparticles and hence the decrease occur in the reaction rate of photo degradation of dye.

Table 1. : Values of absorbance and concentration of methyl orange as a function of time at different intensity of irradiation.

	Intensity 100 W		Intensity 200 W	
Time (Hr.)	Absor bance	Concentration [methyl orange] x 10-4	Absor bance	Concentration [methyl orange] x 10-4
0	0.998	0.650	0.998	0.648
2	0.945	0.614	0.886	0.574
4	0.884	0.576	0.804	0.525
6	0.850	0.551	0.705	0.458
8	0.786	0.524	0.593	0.385

Table 2. : Value of absorbance and concentration of methyl orange as a function of time at different [H2O]/[surfactant] ratio at a intensity of 100 W.

Intensity = 100 W				
	[H2O]/[surfactant] = 5		[H2O]/[surfactant] = 10	
Time (Hr.)	Absor-bance	Concentration [methyl orange]x10-4	Absor-bance	Concentration [methyl orange]x 10-4
0	0.998	0.650	0.998	0.648
2	0.943	0.604	0.970	0.630
4	0.887	0.570	0.938	0.610
6	0.845	0.545	0.909	0.591
8	0.780	0.520	0.866	0.564

Table 3. : Value of absorbance and concentration of methyl orange as a function of time at different [H2O]/[surfactant] ratio at a intensity of 200 W.

Intensity = 200 W				
	[H2O]/[surfactant] = 5		[H2O]/[surfactant] = 10	
Time (Hr.)	Absor bance	Concentration [methyl orange]x 10-4	Absorb ance	Concentration [methyl orange]x 10-4
0	0.998	0.648	0.998	0.648
2	0.880	0.571	0.932	0.609
4	0.801	0.520	0.825	0.535
6	0.710	0.462	0.785	0.512
8	0.590	0.382	0.704	0.452

Table 4. : Value of photo degradation rate constant K at varying intensity of radiation and [H2O]/[surfactant] ratio.

[H2O]/[trition-X-100] = w	Intensity(watt)	Rate constant (K)
5	100	0.0267
5	200	0.0576
10	100	0.0177
10	200	0.0415

Table 5. : Value of percentage degradation at varying intensity of radiation and [H2O]/[surfactant] ratio.

[H2O]/[surfactant] = w	Intensity(watt)	Percentage degradation of methyl orange
5	100	21.39
5	200	30.50
10	100	13.10
10	200	25.50

5. CONCLUSION

From the present study it has been concluded that nanosize materials have promising applications in many areas such as microelectronic devices and in various chemical processes. Photo degradation of dye using semiconductor photo catalyst is an advanced, low cost, more effective and non energy consuming process. A semiconductor has a manifold electronic energy levels filled with electrons- the valence band (VB) and also a manifold higher energy levels that are largely vacant-the conduction band (CB). The energy difference between these two bands is termed as band-gap energy (Ebg) which can be absorbed by the semiconductor from the solar radiation.

In present investigation semiconductor nanoparticles of CdS have been prepared by carrying out the reaction between cadmium nitrate (Cd (NO3)2) with H2S gas in water-in-oil micro emulsion by varying [H2O]/[surfactant] ratio. It has been observed that the size of nano particles increases with the increase of [H2O]/[surfactant] ratio in the micro emulsion in the synthesis of CdS nanoparticles. On increasing [H2O]/[surfactant] ratio, the micellar core size of water-in-oil micro emulsion becomes larger which can accommodate more molecules of CdS molecules leading to larger size of nano particles so that the rate of photo absorption decreases and hence the rate of photo degradation of dye also decreases.

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