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Effective removal of non-biodegradable methyl orange dye by using CdS/activated carbon nanocomposite as a photocatalyst

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ABSTRACT

In this study, CdS combined activated carbon (AC) nanocomposite was prepared by a simple method similar to chemical bath deposition method of thin film deposition. This prepared composite was characterized by X-ray diffraction and scanning electron microscopy. The photocatalytic activities of CdS/AC nanocomposite were examined by the degradation of methyl orange (MeO) under visible light irradiation. The photodegradation rate of MeO under visible light irradiation reached 78.92%. The effect of operational parameters i.e. pH of the solution, dye concentration, irradiation time, solar irradiation, and reusability of photocatalyst on the degradation rate of non-biodegradable azo dye in aqueous solution were examined. The best conditions for maximum photocatalytic degradation of MeO were found to be acidic pH, solar irradiation, and 40 ppm initial dye concentration. The CdS/AC nanocomposite showed the best photocatalytic activity, which may be due to an increase in the photo-absorption effect of AC and the cooperative effect of CdS.

Keywords: Activated carbon photocatalysis; CdS; Methyl orange

1. Introduction

The removal of non-biodegradable organic chemicals is a crucial ecological problem. Dyes are one of the important class of synthetic organic compounds used in the textile industry and are common industrial pollutants. Due to the stability of dyes, conventional biological treatment methods for industrial wastewater treatment are ineffective resulting often in an intensively colored discharge from the treatment facilities [1].

Azo dyes are the most important class of synthetic organic dyes used in the textile industry and are common industrial pollutants [2–7]. Large amount of azo dyes are produced and enter the environment during the production and manufacturing processes. Due to their stability, conventional biological treatment methods for industrial wastewater treatment are ineffective, frequently resulting in an intensely colored discharge from the treatment plants. Further, these azo dyes are readily reduced under anaerobic conditions to potentially hazardous aromatic amines. Thus, it is important to develop new treatment methods that are more efficient in eliminating dyes from the wastewater [8,9].

Advanced oxidation processes particularly based on the photocatalytic degradation are of ample interest for the degradation of organics by oxidation of a variety of organics and dyes [10–14]. The ability of the photocatalytic technique to completely degrade organics into water and CO_2 without generating any harmful by-products, has popularized its role as a wastewater purifier. The technique has been widely

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employed for the photomineralization of many dyes such as methylene blue, acid dyes, azo dyes, and reactive black [12]. Most of the photocatalytic studies use either synthetic or commercial TiO_2 as the photocatalyst [13,14].

Heterogeneous photocatalysis has been envisaged as an efficient technique not only for decolorization, but also for detoxification for treatment of colored wastewater, that compose the most predominant source of environmental contaminations [15]. Among the various semiconductor photocatalysts, titania (TiO_2) possessesmerits of low cost, nontoxicity, chemical inertness, and high efficiency. It is therefore widely used to assist photodegradation of organic pollutants in water and the atmosphere [16–18]. In addition, using titania in the form of films rather than slurry is preferable in the industry because the former avoids the nuisance recovery procedure for the nanoparticles.

Activated carbon (AC) is widely used as a support in gas and water remediation because of its good adsorption capacity, and supported semiconductor with AC exhibits a synergies that has marked effects on the kinetics of disappearance of pollutants, each pollutant being more rapidly photodegraded [19–22].

In this general context of environmental problems caused by different kinds of pollutants, wastewater coming from the textile industry has been discussed in this regard. Textile wastewater processing is one of the most important industries in the world and it employs a variety of chemical compounds, depending on the nature of the raw material and product. Main pollution in textile wastewater came from dyeing and finishing processes. All these processes need the input of wide range of chemicals and dyestuffs, which is generally an organic compound of complex structure. As all of them are not contained in the product, they became waste and caused disposal problems. Major pollutants in textile wastewaters are high-suspended solids, chemical oxygen demand, color, acidity, and other soluble substances. The removal of color from textile industry and dyestuff manufacturing industry wastewaters represents a major environmental concern. In addition, only 47% of 87 of dyestuff are biodegradable [23]. It has been documented that residual color is usually attributed to insoluble dyes which have low biodegradability [24].

Herein, CdS/AC nanocomposite was prepared by the simple chemical method. Photocatalytic activity of CdS/AC nanocomposite was evaluated by the degradation of a typical kind of azo dye methyl orange (MeO), whose structure is shown in Fig. 1. The effects of various parameters on the photocatalytic activity of CdS/AC were studied and the kinetics of MeO degradation were also analyzed.

2. Experimental

2.1. Materials and methods

MeO was obtained from LOBA Chemie and used without further purification. The nano-sized photocatalyst used in this work was synthesized from $CdCl_2$, thiourea and AC. All chemicals were of analytical grade. MeO ($C_{14}H_{14}N_3SO_3Na$) structure is shown in Fig. 1, and has sulphonic groups, which are responsible for the high solubility of these dyes in water. Different concentrations of MeO dye (10, 20, 30, 40, 60, 70, 80, 90 and 100 ppm) were prepared using deionzed water.

2.2. Preparation of CdS/AC nanocomposite composite photocatalysts

In the present work, the noncrystalline CdS/AC composite has been synthesized by a simple chemical method similar to chemical bath deposition technique. Analytical grade reagents were used without further

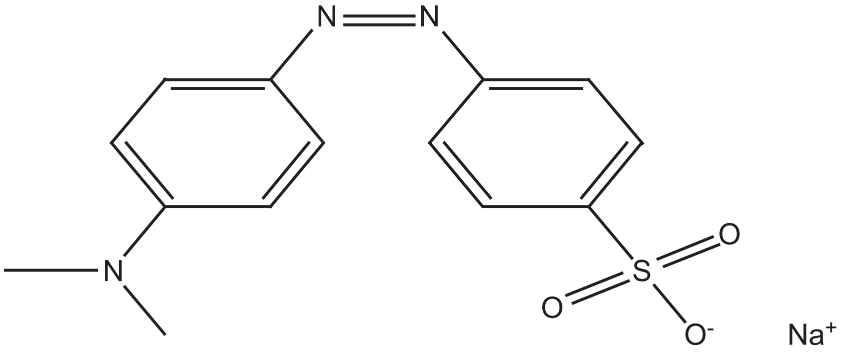

Fig. 1. Stucture of MeO dye.

purification. The synthesis of nanocomposite was carried out by using aqueous solution of cadmium chloride and thiourea as a main precursor of Cd and S, respectively. For the preparation of CdS/AC, first 50 ml of 0.1 M cadmium chloride and thiourea solution has been prepared. After complete dissolution of cadmium choloride the pH of the solution was maintained at > 9 by addition of ammonia and addition is continued till the clear solution is obtained, then 0.04 gm AC was added to the above solution and stirred for 30 min, then after 50 ml equimolar solution of thiourea was added to the cadmium chloride-AC solution and the temperature of the solution was maintained at 85°C, for 120 min. After sometime, solution becomes yellowish and the process of formation of CdS/AC composite started. After the complete formation, the nanocomposite was ultrasonically cleaned in deionized water using ultrasonic water bath (Systronics 6.5L 200, India Ltd., Mumbai) and dried in air.

2.2.1. Characterization of catalyst

The X-ray diffractogram was recorded from the department of earth science IIT, Mumbai with Cu-Kα at room temperature. The morphological study of the thin film was done using scanning electron microscopy (SEM). Then obtained noncrystalline composite was employed in photocatalytic experiments.

2.3. Photocatalytic activity measurements

MeO solution was used as a model wastewater to investigate the photocatalytic activity of CdS/AC from its decolorization (10 ppm initial concentration in 50 ml aqueous suspension containing certain samples). The reactions were carried out in a glass vessel, and the reactor was irradiated by UV light (220–400 nm) from mercury vapor lamp (Champion 250V–450W) located directly above the vessel at a distance of 50 cm from the liquid surface. The concentration of aqueous MeO during degradation and treatment was determined with UV-Vis double beam spectrophotometer (Systronics-2203, India) by measuring the absorbance at λ_{Max} 465 nm.

2.3.1. Absorbance measurement

The absorbances of dye solutions before and after treatment were measured at different time interval in same irradiation source. Measurements were carried out using Systronics-2203 double beam UV-Vis spectrophotometer at maximum wavelength (λ_{Max}) 465 nm and with aid of glass cells (10 mm optical path length). The percentage of degradation of dye was calculated by using Eq. (1):

$$\text{Degradation}\,\% = \frac{C_0 - C_t}{C_t} \times 100 \tag{1}$$

Where C_0 is the initial concentration of dye before treatment and C_t is the concentration of the dye after time t.

3. Discussion of results

3.1. Characterizations of CdS/AC nanocomposite

3.1.1. X-ray diffraction (XRD) analysis

In general, CdS exist in two crystal structures cubic and hexagonal. CdS/AC crystals show three diffraction peaks at two theta 26.82, 44.12, and 52.44 which are associated with the (111), (220), and (311) reflections of the cubic structure.It is mentionable that the identification and assignments of the observed diffraction patterns were made using the JCPDS data for which results are shown in Table 1.

The XRD graph of CdS/AC nanocomposite prepared using $CdCl_2$ and thiourea is shown in Fig. 2. It is observed that XRD pattern shows the preferred orientation along (111) plane. The grain size was calculated using Scherer [25] formula (see Eq. (2)).

$$D = k\lambda/\beta cos\theta \tag{2}$$

Where D is grain size, k is a constant taken to be 0.94, B is the full width at half maximum(FWHM), and λ is wavelength of X-ray. The grain size calculated using the formula is found 80.13 nm and it confirms the formation of nano-sized grains in CdS/AC composite.

3.2. SEM

The surface morphology of CdS/AC nanocomposite was investigated using SEM technique and SEM image is shown in Fig. 3. SEM has been proved to be an unique, convenient, and versatile method to analyze

Table 1
Comparison of XRD pattern with JCPDS data

JCPDS Card no. 10-0454 2 Theta (θ)		Intensity		$h\ k\ l$ plane cubic CdS
Standard	Observed	Standard	Observed	
26.505	26.82	100	100	1 1 1
43.959	44.12	80	40	2 2 0
52.130	52.44	60	32	3 1 1

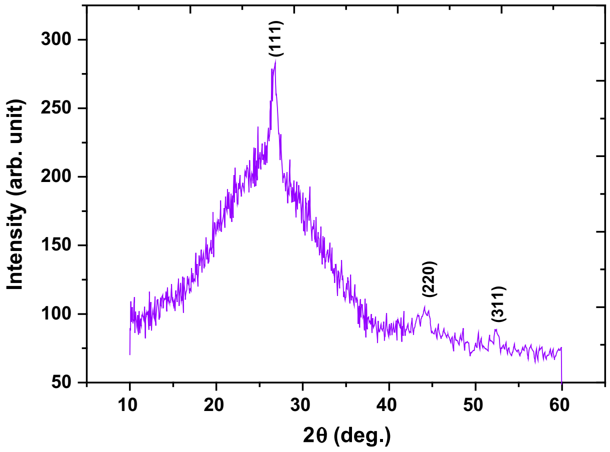

Fig. 2. XRD pattern of CdS/AC nanocomposite.

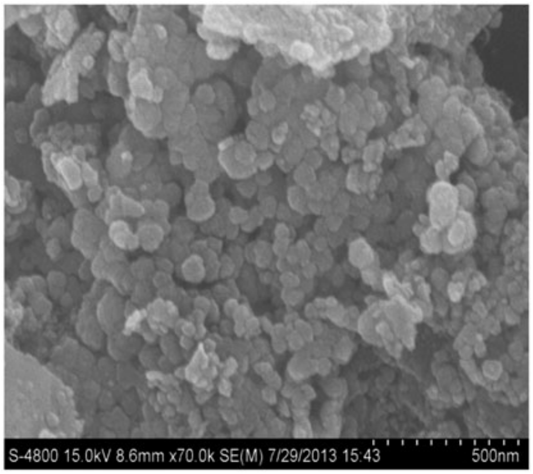

Fig. 3. SEM micrograph of CdS/AC nanocomposite.

surface morphology of thin film and to determine the grain size. The SEM photograph depict the surface texture and porosity, of CdS/AC photocatalysts, it is clear that CdS/AC has the rough surface with heterogeneous porous nature. It indicates that there is good possibility for removal of dye by using CdS/AC nanocomposite.

3.3. Photocatalytic behavior

To optimize the reaction conditions, photocatalytic removal of MeO was studied at λ_{Max} 465 nm, to achieve maximum degradation of dye. The results obtained during this study are being presented in Figs. 4–9. The study of different operational parameters are given as below:

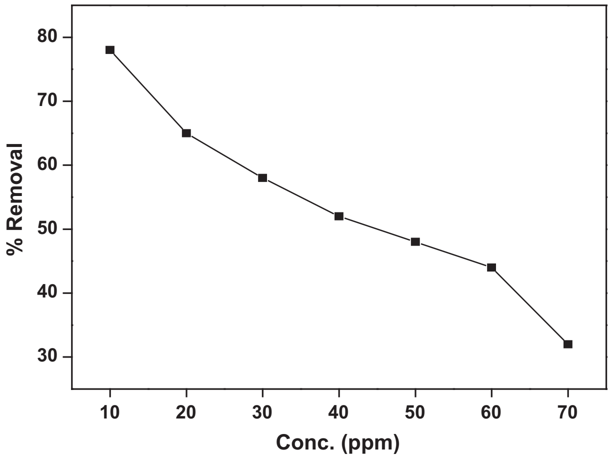

Fig. 4. Effect of Initial concentration on percentage removal of MeO dye by using CdS/AC nanocomposite.

3.3.1. Effect of initial concentration

We studied the effect of change in substrate (dye) concentration on photocatalytic degradation by varying concentration of dye from 10 to 70 ppm and found out that as concentration of dye increases, the rate of degradation decreases. Results obtained are shown in Fig. 4. This effect can be observed due to following reasons: it is generally noted that the degradation rate decreases with the increase of dye concentration. The decrease in dye degradation as the dye concentration increases is a result of generation of OH radicals on the catalyst surface which is reduced since the active sites are covered by dye ions. Irradiation of MeO dye by using UV source, the degradation of the dye decreases 34.1% as the dye concentration increase. Also penetration of UV light becomes difficult due to increased color of the solution, hence sufficient light does not reach to the catalyst.

3.3.2. Effect of catalyst loading

The effect of photocatalyst amount on the degradation rate of MeO dye was investigated by employing different catalyst dose (i.e. 1–9 g/L) of CdS/AC composite with UV light varying from 1 to 9 gm/L at initial dye concentration 40 ppm and at pH 10. It is observed that the initial rate increases with the increase in catalyst concentration, and becomes maximum as shown in Fig. 5. The optimum catalyst concentration for the degradation of MeO dye is 9 g/L^{-1}. The number of photons absorbed and the number of dye molecules adsorbed are increased with the increase in catalyst concentration, thereby enhancing the rate of degradation. But above a certain level the number of

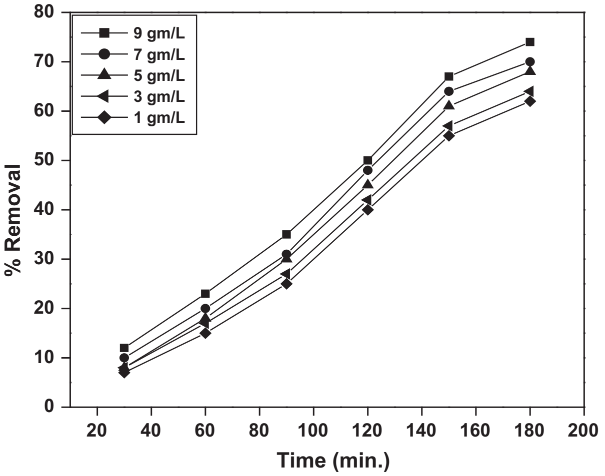

Fig. 5. Effect of catalyst loading on percentage removal of MeO dye by using CdS/AC nanocomposite.

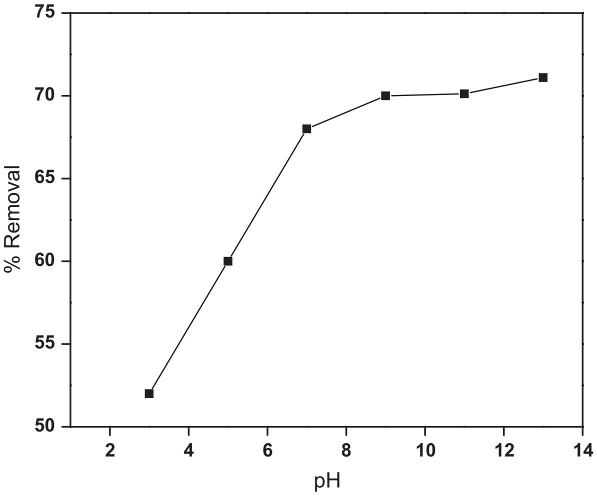

Fig. 6. Effect of pH on percentage removal of MeO dye by using CdS/AC nanocomposite.

substrate molecules are not sufficient to fill the surface active sites of CdS/AC. Hence, further addition of catalyst does not lead to the enhancement of the degradation rate. The degradation rate may also decrease due to the aggregation of CdS/AC composite particles at higher concentrations. Increase in the degradation of MeO with increase in amount of catalyst dose may be due to increase in catalyst surface area for absorption of quanta and interaction of molecules of reaction mixture with catalyst, result is that number of holes (h+), hydroxyl radicals, and supra oxide ions (O^{-}) are increased, these are principal oxidizing intermediate in advance oxidation process and increases the rate of degradation.

3.3.3. *Effect of pH*

The wastewater from textile industries usually have a wide range of pH values. Further, the generation of hydroxyl radicals is also a function of pH. Thus, pH plays an important role both in the characteristics of textile wastes and generation of hydroxyl radicals. Hence, attempts have been made to study the influence of pH in the degradation of dyes in the UV light irradiation. Photocatalytic degradation process was examined at pH values ranging from 3 to 13 for MeO dye. In all the experiments, pH was adjusted by adding appropriate amount of 0.02 N H_2SO_4 or 0.02 N NaOH solution. The effect of pH on the degradation of MeO is shown in Fig. 6. At optimum concentration of dyes in both acidic and alkaline pH, it seems to decrease the percentage removal of the dyes. The inhibitory effect seems to be more pronounced in the alkaline range (pH 11–13). At high pH values the hydroxyl radicals are so rapidly scavenged that they do not have the opportunity to react with dyes. The pH not only affects the surface properties of CdS/AC, but also the dissociation of dyes and formation of hydroxyl radicals. The interpretation of pH effect on the efficiency of the photodegradation process is a very difficult process, because three possible reaction mechanisms can contribute to dye degradation, namely, attack of hydroxyl radical, direct oxidation by the positive hole, and direct reduction by the electron in the conducting band. The importance of each one suggests that as the initial concentration of the dye increases, the need of catalyst surface needed for the degradation also increases. Since illumination time and amount of catalyst are constant, the OH radical (primary oxidant) formed on the surface of CdS/AC is also constant. So that the relative number of free radicals attacking the dye molecules decreases with increasing amount of the catalyst [25].

3.3.4. *Effect of illumination time*

The fixed amount of CdS/AC nanocomposite was 9.0 gm/L. Initial concentration of MeO was 40 ppm. The relationships between photocatalytic degradation of MeO dye and the illumination time (Contact time) were investigated. The results are shown in Fig. 7, it can be seen that the degradation of MeO increases with the increase in the illumination time.

3.3.5. *Effect of solar light intensity*

Light intensity is a major factor in photocatalytic degradation because electron–hole pairs are produced by light energy. Augugliaro [26] reported that the

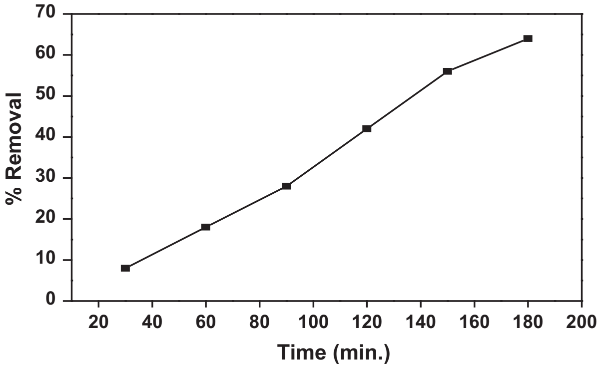

Fig. 7. Effect of contact time on percentage removal of MeO dye by using CdS/AC nanocomposite.

heterogeneous photocatalytic method can be successfully used not only for the color abatement, but also for the complete degradation of MeO from wastewater. The percentage degradation of dye increases with increasing solar light intensity. Under the higher intensity of light irradiation, the enhancement was considerably higher, because the electron–hole formation is predominant and, hence electron–hole recombination is negligible. However, if the light intensity is lower, electron–hole pair separation competes with recombination which in turn lowers the formation of free radicals, thereby causing less effect on the percentage removal of the dye. In the case of MeO, 78.92% decolorization efficiency was observed at 180 min irradiation time under solar light. At increased light intensity electron–hole pair separation competes with recombination, thereby causing effect on the reaction rate. In our study, the enhancement of the rate of decolorization as the light intensity increased was also observed and agreed with the other studies [27].

3.3.6. Effect of UV light and catalyst

It can be seen from Fig. 8. that in the presence of both CdS/AC nanocomposite and UV light 78% of dye degraded in the time of 180 min. This was contrasted with 26.11% degradation for the same experiments performed in the absence of UV light and negligible degradation 2% was observed when the reaction is allowed to occur in the presence of UV light and in the absence of CdS/AC nanocomposite. These observations clearly show that both UV radiation and a photocatalyst are needed for the effective destruction of MeO.

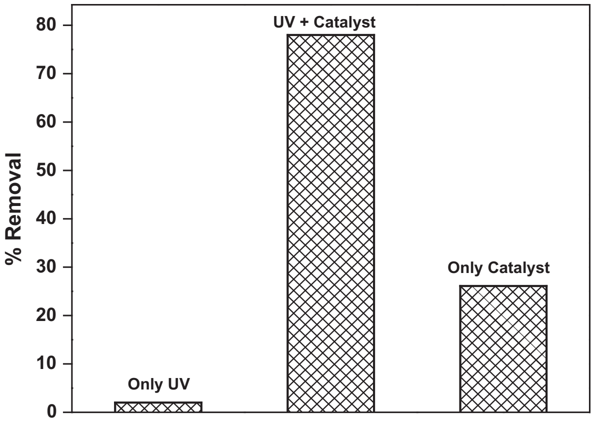

Fig. 8. Effect of UV light and catalyst on percentage removal of MeO dye by using CdS/AC nanocomposite.

3.3.7. Reusability

The reusability of photocatalyst CdS/AC was investigated to observe the stability and degree of photodegredation of MeO. While studying reuse of photocatalyst, all parameters including, initial concentration, irradiation time, pH, and amount of CdS/AC nanocomposite were kept constant. The mixture of photocatalytic batch experiment was filtered, and washed four times with double-distilled water, and then dried at 94˚C in oven. Recovered photocatalyst then reused and applied four times as in the previous degradation process. Results show (Fig. 9) no significant reduction in photocatalytic efficiency in photodegradation of MeO observed, this indicates the stability of CdS/AC as a photocatalyst.

3.3.8. Kinetics

It is see that $\ln(A_0/A_t)$ is directly proportional to irradiation time. The absorbance of MeO solution is directly proportional to concentration. So we can conclude that the photocatalytic degradation is the first-order reaction.

The apparent first-order kinetic equation $\ln(C_0/C_t) = kt$ was used to fit experimental data, where k is apparent rate constant, C_0 is the initial solution concentration of MeO, and C_t is the concentration of Meo at time t. The linear transforms in $\ln(C_0/C_t)$ as a function of irradiation time given in Fig. 8 confirm that the kinetic curves were of apparent first-order. The slope of the $\ln C_0/C_t$ Vs time plot gives the value for the rate constant k in min^{-1}.

The photocatalytic activity can be compared by k value. The k values, which are obtained by linear fitting from Fig. 10, are 0.004812, 0.003466, and

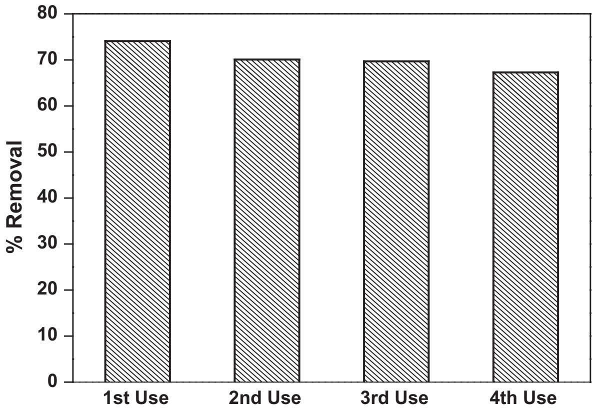

Fig. 9. Effect of reusability on percentage removal of MeO dye by using CdS/AC nanocomposite.

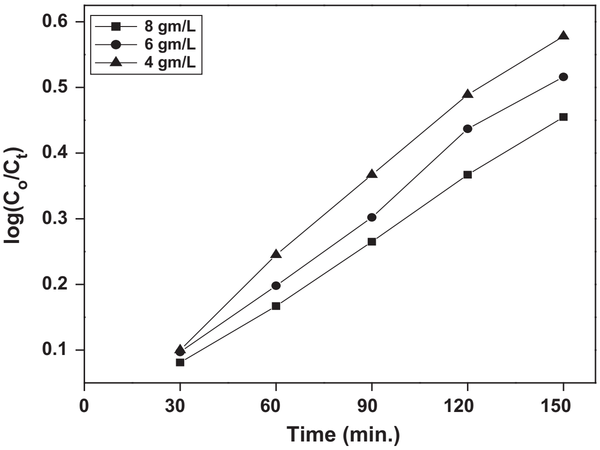

Fig. 10. Comparison of kinetic degradation of MeO dye by using CdS/AC nanocomposite.

0.002811 for the CdS/AC catalyst dose of 4, 6, and 8 gm/L, respectively. The degradation rate increases with increasing catalyst dose of CdS/AC catalyst. The wavelength of the maximum absorbance of MeO solution is 465 nm and the absorbance of the solution is directly proportional to its concentration.

4. Conclusions

This study focused on the removal of non-biodegradable MeO dye by means of a novel photocatalyst CdS/AC synthesized by simple chemical method similar to chemical bath deposition technique.

We observe the following results given in order:

- XRD analysis: XRD pattern shows the formation of nano-sized grains of CdS/AC composite with cubic structure.
- SEM: SEM also confirmes the formation of nano-sized grains of the composite
- Effect of variation in dye concentration: as concentration of dye increases the rate of degradation of dye decreases.
- Effect of catalyst dose: as concentration of catalyst increases the rate of degradation of dye molecules also increases.
- Variation in pH: in acidic range of pH the rate of degradation is very less as pH increases rate of degradation also increases, and between pH ranges 7.5–9 rate of degradation is faster on further increase in pH the rate of degradation decreases.
- Effect of light intensity: on increasing light intensity the rate of degradation of dye molecules increases up to certain limit until there is no further changes in the rate of degradation.
- Effect of illumination time: rate of degradation increases with increase in illumination time.
- Effect of UV light and catalyst: in presence of UV light only 1% removal of MeO by CdS/AC is observed, in the presence of catalyst only 26.11% removal was measured, while in the presence of both UV light and catalyst 78% removal is obtained.
- Reusability: CdS/AC composite shows small decrease i.e. 3–5% in percent removal of MeO up to the four time use.
- Kinetics: the photocatalytic reaction for removal of MeO in the presence of CdS/AC nanocomposite found to follow pseudo-first-order kinetics.

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