Scientific paper

Photodegradation of Organic Dyes using Nanoparticles of Cadmium Sulfide Doped with Manganese, Nickel and Copper as Nanophotocatalyst

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Received: 23-08-2008

Abstract

Photoreactivity of cadmium sulfide nanoparticles as undoped and doped with manganese, nickel and copper were studied in the decolorization of methylene blue and safranin under UV and Vis irradiations. The dopant, mole fraction of dopant to cadmium ion, pH of solution, dosage of photocatalyst and concentration of dye are variables that influence on the photoreactivity of nanocatalysts. In among of photocatalysts, the prepared nanoparticles CdS, $Cd_{0.98}Mn_{0.02}S$, $Cd_{0.96}Ni_{0.04}S$ and $Cd_{0.90}Cu_{0.10}S$ show the most degradation efficiency in order: $Cd_{0.90}Cu_{0.10}S > Cd_{0.96}Ni_{0.04}S > Cd_{0.98}Mn_{0.02}S \cong CdS$. The optimum dosage of photocatalyst was obtained 120.0 mg/L. The effect of pH was studied in pH amplitude of 2–12 and the most degradation efficiency was obtained in alkaline pH of 11.0. Degradation efficiency was decreased with increasing the concentration of dye more than 5.0 mg/L. In the optimized conditions, the degradation efficiency was obtained 91–98 and 86–95 for methylene blue and safranin, respectively, in irradiation time of 120 min.

Keywords*:* Nanoparticles, cadmium sulfide, decolorization, photodegradation, methylene blue, safranin

1. Introduction

Nano-scale semiconductor particles possess higher surface area-to-volume ratio than their bulk counterparts, and thus allow for greater photon absorption on the photocatalyst surface. Moreover, recombination of the electron-hole pair within the semiconductor particle is drastically reduced as particle size decreases. With decreasing particles size of semiconductor to nanometer-scale, the band-gap energy greatly increased, which in turn led to higher redox potentials in the system. Therefore, the nano-scale semiconductor is expected to have higher photocatalytic activity than its bulk.[1–3]

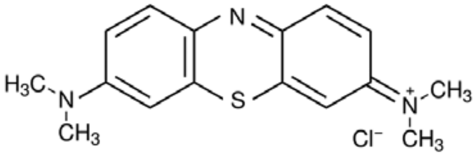
Textiles industries produce large volume of colored dye effluents which are toxic and non-biodegradable. These dyes create severe environmental pollution problems by releasing toxic and potential carcinogenic substances into the aqueous phase. Various chemical and physical processes such as precipitation, adsorption, air stripping, flocculation, reverse osmosis and ultrafiltration can be used for color removal from textile effluents.[4–8]

Among various physical, chemical and biological techniques for treatment of wastewaters, heterogeneous photocatalysis has been considered as a cost-effective alternative for water remediation. Photocatalytic degradation has been shown to be one of the most promising processes for the wastewater treatment due to its advantages over the traditional techniques, such as quick oxidation, no formation of polycyclic products, oxidation of pollutants in the ppb range, etc.[9–12] The primary mechanism of photodegradation is the generation of hydroxyl radicals obtained by the reaction of holes with surface hydroxyls or water and their attachment to organic compounds.[13]

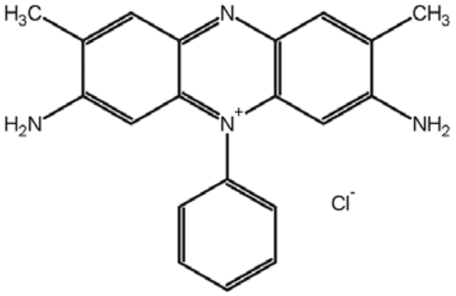
In recent years, metal chalcogenides have attracted considerable attention due to their proven and potential applications in electronic, optical and superconductor devices. Cadmium sulfide as a semiconductor was applied in solar cells, photoelectronic devices and photocatalyst degradation.[14,15] The photocatalytic treatment of wastes containing dyes using TiO_2 has also been widely reported in the literatures. Whereas, the other semiconductors such as cadmium sulfide as doped have been restrictedly used in the dimensions of nano-scale.[16,17]

This paper reports a simple route for the preparation nanoparticles of cadmium sulfide as undoped and doped with Mn, Ni and Cu via co-precipitation method in the presence of mercaptoethanol as capping agent. The prepared nanoparticles are used as photocatalyst in degradation of methylene blue and safranin as organic dyes.

Methylene blue is a heterocyclic aromatic chemical compound with molecular formula $C_{16}H_{18}ClN_3S$. It has many uses in a range of different fields, such as biology or chemistry. This dye is stable, incompatible with bases, reducing agents and strong oxidizing agents. It is harmful if swallowed and may be harmful if inhaled and in contact with skin. It causes severe eye irritation and investigated as a mutagen. Safranines are the azonium compounds of symmetrical 2,8-dimethyl-3,7-diamino-phenazine. This compound has effect on the lungs, thorax or respiration affected. It may be harmful by ingestion, causes eye irritation, may be harmful by skin absorption, causes skin irritation and may be harmful by inhalation.



Methylene blue (3,7-Bis(dimethylamino)phenothiazin-5-iumchloride)



Safranin (3,7-Diamino-2,8-dimethyl-phenylphenazinium chloride)

Figure 1. Structure of methylene blue and safranin

2. Experimental

2. 1. Materials

The dyes (Fig. 1) of methylene blue (C.I name: Basic Blue 9, $C_{16}H_{18}N_3ClS3H_2O$) and safranin O (C.I name: Basic Red 2, $C_{20}H_{19}ClN_4$) were purchased from Fluka Company. The chloride salts of cadmium, manganese, nickel and copper, ($CdCl_2 \cdot H_2O$, $MnCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$), all from Merck, were used as source of metal ions and Na_2S9H_2O (Merck) was used as source of sulfide ion. 2-Mercaptoethanol (2-hydroxyethanthiol, $HOCH_2CH_2SH$) and isopropyl alcohol were procured from Merck Company and used as received. The p-H of solution samples has been changed using hydrochloric acid and sodium hydroxide (Merck). Double-distilled water was used for preparation of solutions.

2. 2. Catalyst Preparation

The nanoparticles of $Cd_{1-X}S:M_X$ (M: Mn, Ni, Cu and X = 0, 0.02, 0.04, 0.06, 0.08 and 0.10) were prepared with 50 mL homogeneous solutions 0.01 M of $CdCl_2$ and MCl_2 (M: Mn, Ni or Cu) as mole ratio of $[M^{2+}]/[Cd^{2+}] = X$ and 50 mL solution of 0.1 M mercaptoethanol. Then, 50 mL solution of 0.01 M sodium sulfide was added drop by drop (each 6–8 s, one drop) under nitrogen atmosphere at room temperature while the mixture was stirred vigorously. As precipitated $Cd_{1-X}M_XS$ nanoparticles were then centrifuged at 4000 rpm, washed three times with water to eliminated unreacted ions, and finally washed three times with isopropyl alcohol. The cleaned powders were dried for about 10 h at 80 °C until complete evaporation of the solvent was achieved. To this way, the nanoparticles of CdS, CdS:Mn, CdS:Ni and CdS:Cu with percentages of 2, 4, 6, 8 and 10% of doped ion were prepared.

2. 3. Catalyst Characterization

The sol transparent samples of nanoparticles were prepared with dispersing of them in isopropyl alcohol. The UV-Vis absorption spectra of 10 mM transparence solutions of nanoparticles were recorded by using an UV-Vis spectrophotometer Perkin-Elmer Lambda 2 at room temperature. X-ray powder diffraction (XRD) patterns were recorded on a diffractometer D8ADVANCE model of BRUKER Company using Cu K_α irradiation (λ=1.5418 A°). Transmission electron micrographs (TEMs) of the nanoparticles were taken by a JEOL JEM-1200EXII electron microscope operating at 120kV. The supporting grids were formvar-covered, carbon-coated, 200-mesh copper grids.

Zeta (ζ) potential measurements were carried out to characterize the surface charge of nanoparticles using a Zeta-Meter System 3.0+ Model zetameter. Samples were prepared with 0.5 wt. % of nanocatalyst and 1.0×10^{-3} M NaCl electrolyte, and dispersed for 15 min using an ultrasonic probe. After dispersing, the solution was allowed to sediment for 30 min and the agglomerates were removed. The HCl and NaOH with concentrations of 1.0×10^{-2} were used to adjust pH to the desired values.

2. 4. Photodegradation Experiments

A photocatalytic reactor system was used for photodegradation experiments. This bench-scale system consisted of a cylindrical Pyrex-glass cell with 1.0 L capacity, 10 cm inside diameter and 15 cm height. A 100 W mercury lamp (4 mW/cm^2) and a 500-W halogen lamp (10 mW/cm^2) as the sources of UV and VIS light, respectively, were placed in a 5 cm diameter quartz tube with one end tightly sealed by a Teflon stopper. A cutoff filter was applied to remove wavelengths below 420 nm to ensure irradiation completely by visible light. The lamp and the tube were then immersed in the photoreactor cell with a light path of 3.0 cm. The photoreactor was filled with 0.5 L of 5.0 mg/L of dyes as pollutant and 50.0–150.0 mg/L of nanoparticles as nanophotocatalyst. The temperature of whole reactor was kept at 25 °C using a water-cooled jacket on its outside. All reactions were stirred using a magnetic stirrer to ensure that the suspension of catalyst was uniform during the course of the reaction. In fixed time intervals, the samples were collected for determine degradation efficiency, filtered through Millipore membrane filters, and centrifuged to remove the nanocatalyst.

Photometric analysis of samples before and after of irradiation can be used for measurement of degradation efficiency, %D.

$$\%D = 100 \times [(A_o–A)/A_o] = 100 \times [(C_o–C)/C_o]$$

where A_o, A, C_o and C are initial absorbance and absorbance after irradiation time, initial concentration of dye solution and concentration of dye after irradiation time, respectively. The concentration of dye after irradiation time, C, is calculated using Beer,s-Lambert equation and absorption measurement at λ_{max} of dye solution. The wavelengths of absorbance maximum (λ_{max}) of methylene blue and safranine are 661 and 519 nm, respectively. The absorbance of samples was measured by a UV-Vis spectrophotometer Perkin-Elmer Lambda 2 using a paired 1.0 cm quartz cell. The decrease of absorbance value of samples at λ_{max} after irradiation in a certain time interval will be showed the rate of decolorization and therefore, photodegradation efficiency of the dyes as well as the activity of nanoparticles as photocatalyst.

3. Results and Discussion

3. 1. Characterization of Nanoparticles

The UV-Vis spectra, XRD patterns and TEM graphs were used for evaluation of prepared nanoparticles includes CdS, CdS:Mn(2–10%), CdS:Ni(2–10%) and CdS:Cu(2–10%). The UV-Vis absorption analysis of the sample provides the information relating to the size of particles. Fig. 2 shows the absorption spectra of CdS, CdS:Mn(2%), CdS:Ni(4%) and CdS:Cu(10%) nanoparticles in isopropyl alcohol solvent. Their absorption spectra shoulder is shown about 370–380 nm. While, the absorption shoulder for macrocrystalline CdS is seen at about 510 nm with band-gap energy of 2.4 eV.[18,19] Therefore, this blue shift and correlation between band edge and quantum dot size indicates that the size of prepared particles is less than 10.0 nm.[20,21]

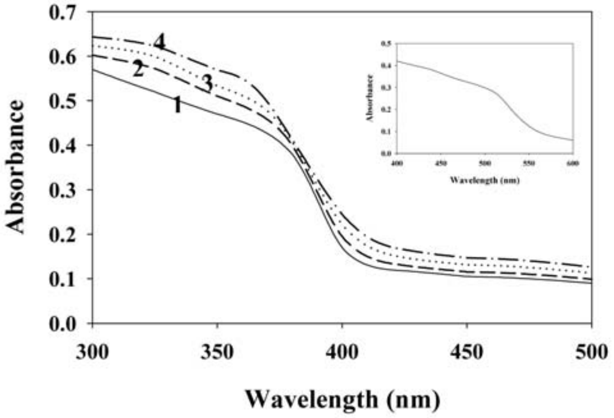


Figure 2. UV-Vis spectra of nanocrystals of 1; CdS, 2; $Cd_{0.98}Mn_{0.02}S$, 3; $Cd_{0.96}Ni_{0.04}S$ and 4; $Cd_{0.90}Cu_{0.10}S$ in isopropyl solution. The inset of the figure shows the absorption spectra of macrocrystalline CdS.

The band gap of the semiconductor becomes larger with decreasing particle size, and is indicated by an absorption shift to shorter wavelengths. The levels of the valence band are moderately shifted to lower energies, while those of the conduction band are strongly shifted to higher energies.[22]

The XRD pattern of CdS nanoparticles is shown in Fig. 3A. Three broad peaks with 2θ vales 26.5, 44.0 and 52.0° corresponding to the (111), (220) and (311) plans of CdS, respectively, therefore the powders are pure cubic CdS phase. In Fig. 3B, the XRD pattern of the reference of CdS is shown for comparison. Due to the size effect, the XRD peaks are broadened as the particles become

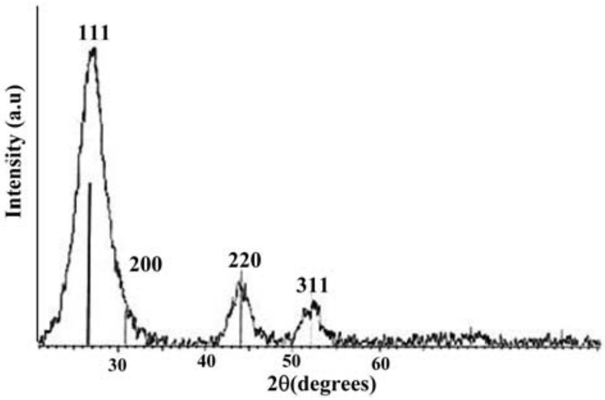


Figure 3A. X-ray diffraction patterns of pure CdS nanocrystals

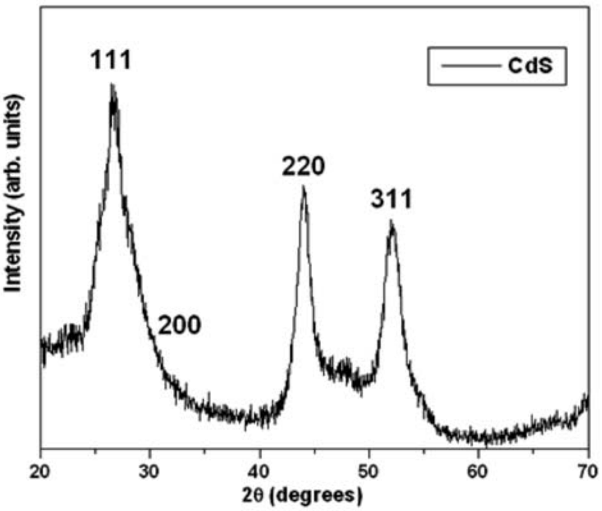


Figure 3B. X-ray diffraction patterns of the reference of CdS nanocrystals.[18]

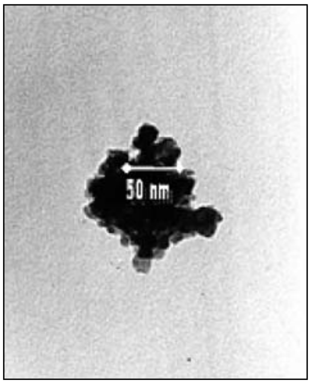


Figure 4. TEM image of nanoparticles of CdS:Cu(10%).

smaller. The diameter of CdS nanoparticles estimated from Scherrer formula is <5.0 nm.[21,23] Also, transmission electron micrographs (TEM) images confirmed the formation of CdS:Cu (10%) nanoparticles with diameters of 6.0 ± 1.0 nm (Fig. 4).

3. 2. Photodegradation of Methylene Blue and Safranin Using Nanophotocatalysts

The degradation of methylene blue and safranin (5.0 mg/L) under UV irradiation in time intervals of 30, 60, 90 and 120 min and in the presence of nanoparticles of CdS (100.0 mg/L) as photocatalyst are shown in Figs. 5 and 6, respectively. The decrease of absorption spectra and therefore absorbance of methylene blue and safranine at λ_{max} of 661 and 519 nm, respectively, show decolorization of dyes in the applied conditions. As a consequence, the decrease of samples absorbance due to decrease of dyes concentration is recorded for measurement of decolorization rate and therefore degradation efficiency (%D).

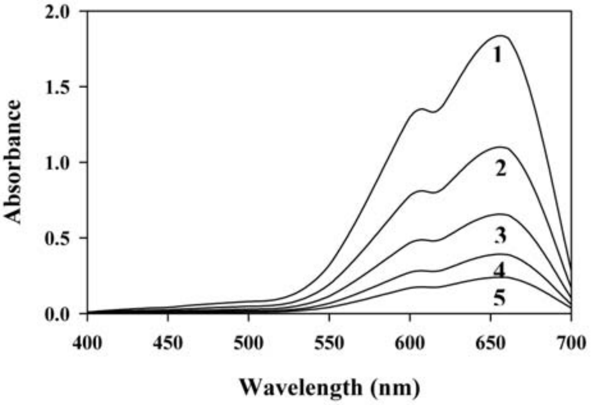


Figure 5. Decrease absorption spectra of methylene blue (5.0 mg/L) in the presence of CdS nanoparticles (100.0 mg/L) in irradiation times of 1; 0, 2; 30, 3; 60, 4; 90 and 5; 120 min.

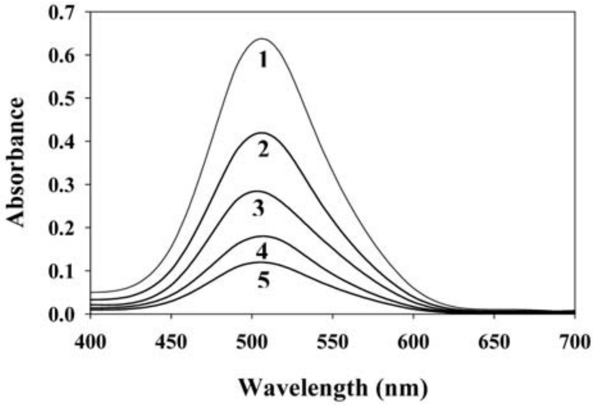


Figure 6. Decrease absorption spectra of safranin (5.0 mg/L) in the presence of CdS nanoparticles (100.0 mg/L) in irradiation times of 1; 0, 2; 30, 3; 60, 4; 90 and 5; 120 min.

Many authors have reported that the kinetic behavior of photocatalytic reaction can be described by a modified Langmuir-Hinshelwood model.[24,25]

$$1/r_o = 1/k + 1/kKC_o$$

At high substrate concentration, adsorbed reactant molecules may occupy all the catalytic sites on the catalyst surface and this leads to zero-order kinetics. At low concentration, the number of catalytic sites will not be limiting factor and the rate of degradation is proportional to the substrate concentration, in accordance with apparent first-order kinetics. In order to confirm the speculation, $\ln(C_o/C)$ was plotted as a function of the irradiation time. The calculated results indicate that the first-order model gives a better fit. The apparent degradation rate constant (k) of dyes with initial concentrations of 5.0 mg/L were calculated and collected in Table 1.

In Figs. 7 and 8, photodegradation of methylene blue and safranin, respectively, with initial concentration of 5.0 mg/L are shown in the absence, macrocrystalline and nanocrystalline of CdS with dosage 100.0 mg/L in time inter-

Table 1: Apparent degradation rate constant (k) and standard deviation (n = 3) of methylene blue and safranin with initial concentrations of 5.0 mg/L.

Photocatalyst	Methylene blue	Safranin
	5.23 ± 0.1410^{-3} min^{-1}	2.68 ± 0.1710^{-3} min^{-1}
CdS macrocrystaline	14.52 ± 0.2010^{-3} min^{-1}	11.26 ± 0.2910^{-3} min^{-1}
CdS nanocrystaline	17.13 ± 0.2210^{-3} min^{-1}	14.00 ± 0.2210^{-3} min^{-1}
$Cd_{0.98}Mn_{0.02}S$	17.14 ± 0.2610^{-3} min^{-1}	14.12 ± 0.2110^{-3} min^{-1}
$Cd_{0.96}Ni_{0.04}S$	19.52 ± 0.1910^{-3} min^{-1}	16.11 ± 0.1710^{-3} min^{-1}
$Cd_{0.90}Cu_{0.10}S$	23.05 ± 0.1310^{-3} min^{-1}	19.32 ± 0.2710^{-3} min^{-1}

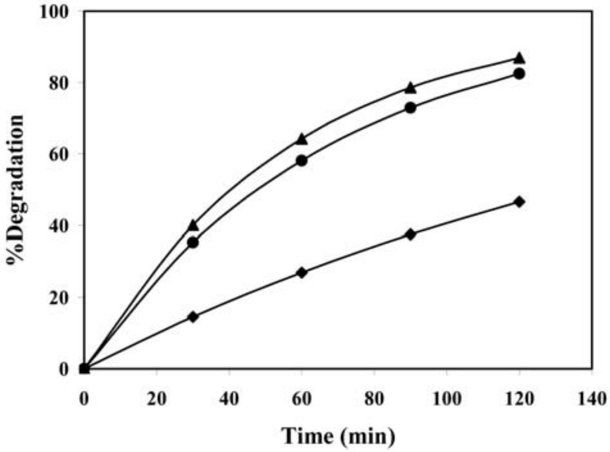


Figure 7. Photodegradation of methylene blue in the absence (◆) and presence of macrocrytaline (●) and nanocrystaline (▲) of CdS.

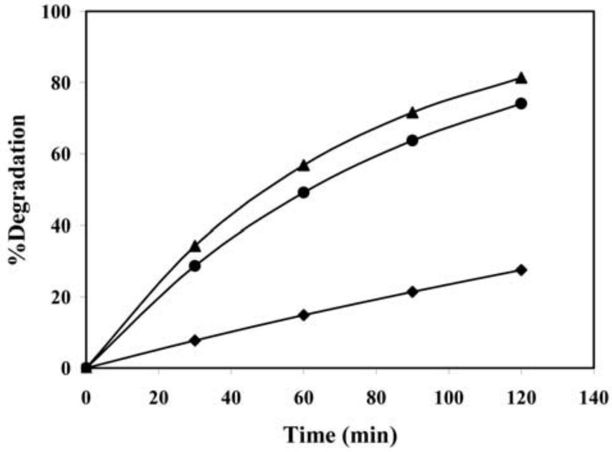


Figure 8: Photodegradation of safranin in the absence (◆) and presence of macrocrytaline (●) and nanocrystaline (▲) of CdS.

vals 30, 60, 90 and 120 min. The obtained apparent degradation rate constants (Table 1) and Figs. 7 and 8 show that semiconductor CdS is a photocatalyst in decolorization of dyes. CdS is a semiconductor and photodegradation of a dye is initiated by the photoexcitation of the semiconductor. The electron/hole pair is obtained from photoexcitation of CdS and the high oxidative potential of holes can be lead to direct and indirect oxidation of dyes. In the indirect oxidation process of dyes, the hydroxyl reactive radicals (OH$^{)}$ were formed from combination of holes with water molecules and/or hydroxide anions. The radical hydroxyl with $E^o = +3.06$ V is a strong oxidative and oxidize dyes as non-selective to mineral species as partial or complete.[26,27] The proposed mechanism for dye degradation using photocatalysts (PC) was suggested as follows:[28]

$$PC + h \rightarrow h^+_{VB} + e^-_{CB} \tag{1}$$

$$OH^- + h^+_{VB} \rightarrow OH^\bullet \tag{2}$$

$$H_2O + h^+_{VB} \rightarrow OH^\bullet + H^+ \tag{3}$$

$$O_2 + e^-_{CB} \rightarrow O_2^{-\bullet} \tag{4}$$

$$O_2^{-\bullet} + e^-_{CB} + 2H^+ \rightarrow H_2O_2 \tag{5}$$

$$2O_2^{-\bullet} + 2H^+ \rightarrow O_2 + H_2O_2 \tag{6}$$

$$H_2O_2 + e^-_{CB} \rightarrow OH^- + OH^\bullet \tag{7}$$

$$\text{Dye} + h^+_{VB} \rightarrow \text{Dye}^{+\bullet} \rightarrow \text{Final specie} \tag{8}$$

$$\text{Dye} + OH \rightarrow \text{Dye}^{\prime\bullet} \rightarrow \text{Final species} \tag{9}$$

Increasing of apparent degradation rate constants from 14.52×10^{-3} to 17.13×10^{-3} min^{-1} (methylene blue) and 11.26×10^{-3} to 14.00×10^{-3} min^{-1} (safranin) in the presence of macrocrystalline and nanocrystalline of CdS, respectively, show the effect of particles size of photocatalyst. In photocatalysis process, the total number of free carriers (electron/hole) on the surface of photocatalyst determines the efficiency of catalyst. For large particles, the volume recombination of electrons and holes dominates. This condition largely reduces the number of free charges on the surface and deteriorates the photocatalytic activity. For nanoparticles, the transportation length of electron/hole from crystal interface to the surface is short, which helps to accelerate the migration rate of electron/hole to the surface of the nanoparticle to participate the reaction process[29] This pointer and increasing of accessible surface of photocatalysts as nanoparticles lead to increasing of photodegradation rate of dyes.[30]

As mentioned, the number and the lifetime of free carriers (electrons/holes) are particle size- and dopant-dependent. In order to investigation of dopant effect, the photodegradation efficiency of methylene blue and safranin (5.0 mg/L) were studied in the presence of CdS:Mn(2–10%), CdS:Ni(2–10%) and CdS:Cu(2–10%) nanoparticles (100.0 mg/L) in irradiation time of 120 min. The obtained results are shown in Figs. 9–11 for CdS:Mn, CdS:Ni and CdS:Cu, respectively. As seen, the maximum photodegradation efficiency were obtained in the presence of CdS:Mn(2%), CdS:Ni(4%) and CdS:Cu(10%). On the other hand, the most decolorization was occurred using $Cd_{0.98}Mn_{0.02}S$, $Cd_{0.96}Ni_{0.04}S$ and $Cd_{0.90}Cu_{0.10}S$ as photocatalyst in among of prepared nanoparticles. Apparent degradation rate constants do not show any improvements with doping manganese in CdS nanoparticles. Doping of CdS with other transition metal ions offers a way to trap charge carriers and extend the lifetime of one or both of the charge carriers. Consequently, dopants enhance the efficiency of the photocatalyst. Different dopants may not have the same effect on trapping electrons and/or holes on the surface or during interface charge transfer because of the different positions of the dopant in the host lattice. Consequently, the photocatalytic efficiency would be different for different types of dopants.[31]

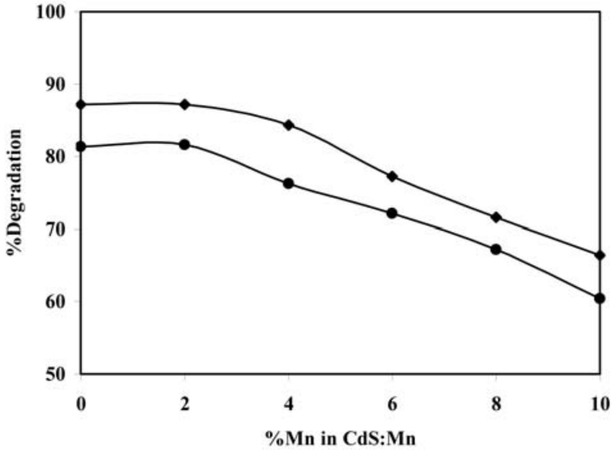


Figure 9. Photodegradation of methylene blue (◆) and safranin (●) in irradiation time of 120 min in the presence of nanophotocatalysts of CdS:Mn.

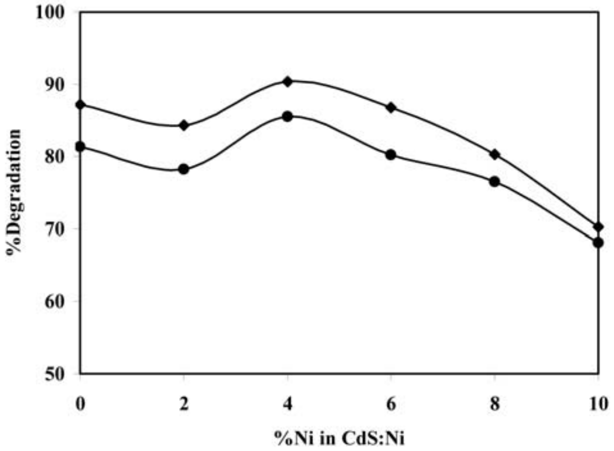


Figure 10. Photodegradation of methylene blue (◆) and safranin (●) in irradiation time of 120 min in the presence of nanophotocatalysts of CdS:Ni.

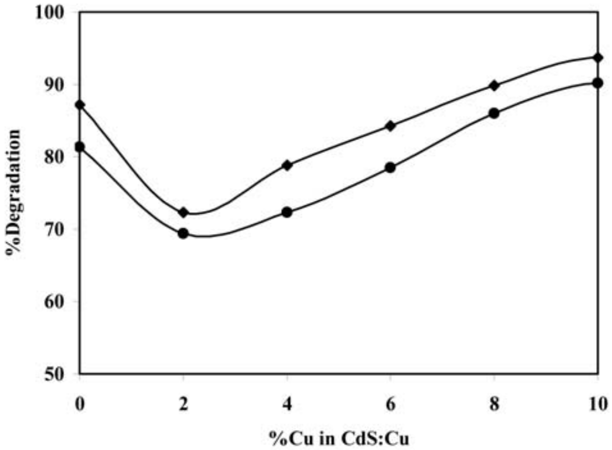


Figure 11. Photodegradation of methylene blue (◆) and safranin (●) in irradiation time of 120 min in the presence of nanophotocatalysts of CdS:Cu.

The most degradation efficiencies were obtained using Cu^{2+} ions as dopant in CdS nanoparticles ($Cd_{0.90}Cu_{0.10}S$). The Cu^{2+} ion can be reduced to Cu^+ ion by a hole produced by semiconductor. The resulting ion (Cu^+) is a strong oxidative and hence it can be an oxidizing agent for decolorization of methylene blue and safranin. The degradation efficiency was decreased with increasing of mole fraction of Cu^{2+} more than 0.10.

3. 3. Study of Variables Influence on Degradation Efficiency

The initial rate of photocatalytic degradation of many pollutants is a function of the photocatalyst dosage.[32,33] Figs. 12 and 13 illustrate photodegradation of methyelne blue and safranin, respectively, in the different dosage of nanocatalysts $Cd_{0.98}Mn_{0.02}S$, $Cd_{0.96}Ni_{0.04}S$ and $Cd_{0.90}Cu_{0.10}S$ with irradiation times of 120 min. Because increasing in active sites, the rate decolorization is increased to maximum degradation efficiency in the presence amounts of 120.0 mg/L of nanophotocatalyst. However, as the loading was increased beyond the optimum amount, the decolorization rate decreased due to increasing the opacity of the suspension samples and therefore increasing the light scattering. In these conditions, the penetration depth of the photons is decreased and less catalysts nanoparticles could be activated. Also, addition of a high dose of the semiconductor decreases the light penetration by the photocatalyst suspension and reduces the degradation rate.

Photodegradation of dyes (5.0 mg/L) was studied in amplitude pH of 2.0–12.0 in the presence of nanocatalysts

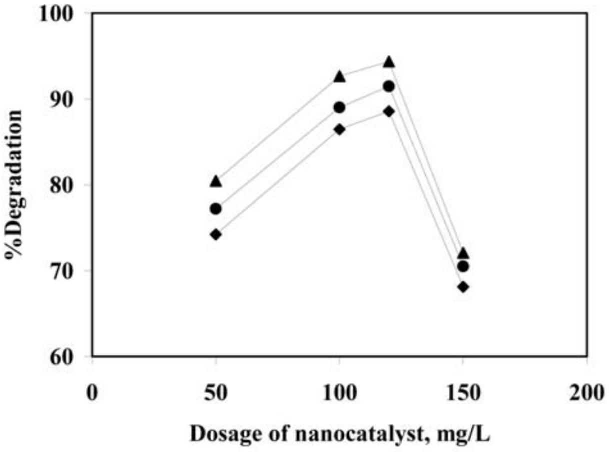


Figure 12. Effect of dosage of nanocatalysts on the photodegradation efficiency of methylene blue dye, (◆)$Cd_{0.98}Mn_{0.02}S$, (●)$Cd_{0.96}Ni_{0.04}S$ and (▲)$Cd_{0.90}Cu_{0.10}S$.

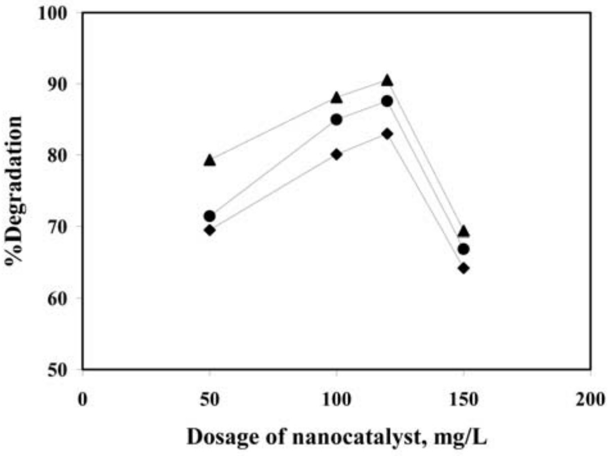


Figure 13. Effect of dosage of nanocatalysts on the photodegradation efficiency of safranin dye, (◆)$Cd_{0.98}Mn_{0.02}S$, (●)$Cd_{0.96}Ni_{0.04}S$ and (▲)$Cd_{0.90}Cu_{0.10}S$.

$Cd_{0.98}Mn_{0.02}S$, $Cd_{0.96}Ni_{0.04}S$ and $Cd_{0.90}Cu_{0.10}S$ (120.0 mg/L). The results for irradiation time of 120 min are shown in Figs. 14 and 15. In all cases, the maximum degradation efficiency was obtained in alkaline pH 11 for both dyes. In the presence of $Cd_{0.98}Mn_{0.02}S$, $Cd_{0.96}Ni_{0.04}S$ and $Cd_{0.90}Cu_{0.10}S$ and in pH 11, degradation efficiency 87.3, 90.3 and 95.6% for methylene blue is obtained, respectively. Also, in pH 11, the degradation efficiency of safranin is arrived 85.4, 89.1 and 93.2% using $Cd_{0.98}Mn_{0.02}S$, $Cd_{0.96}Ni_{0.04}S$ and $Cd_{0.90}Cu_{0.10}S$, respectively. The zeta (ζ) potential data for nanocatalysts of $Cd_{0.98}Mn_{0.02}S$, $Cd_{0.96}Ni_{0.04}S$ and $Cd_{0.90}Cu_{0.10}S$ is shown in Fig. 16. The results show isoelectric points (IEP) in amplitude pH of 7.0–7.5. Therefore, the surfaces of photocatalysts are positively charged in acidic solutions and negatively charged in alkaline solutions. As a result, it is not surprise the increasing of the adsorption of dyes molecu-

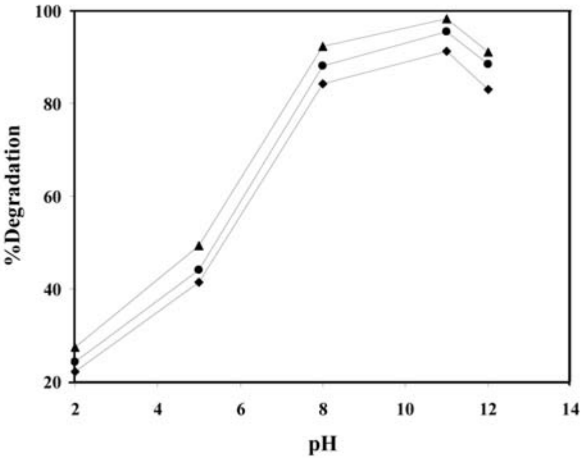


Figure 14. Effect of pH of solution on the photodegradation efficiency of methylene blue dye, (◆)$Cd_{0.98}Mn_{0.02}S$, (●)$Cd_{0.96}Ni_{0.04}S$ and (▲)$Cd_{0.90}Cu_{0.10}S$.

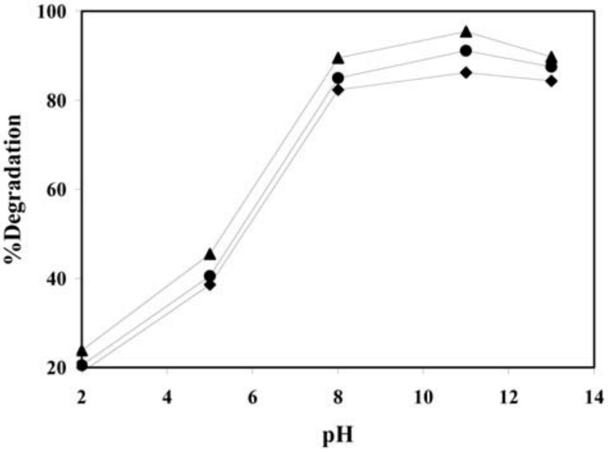


Figure 15. Effect of pH of solution on the photodegradation efficiency of safranin dye, (◆)$Cd_{0.98}Mn_{0.02}S$, (●)$Cd_{0.96}Ni_{0.04}S$ and (▲)$Cd_{0.90}Cu_{0.10}S$.

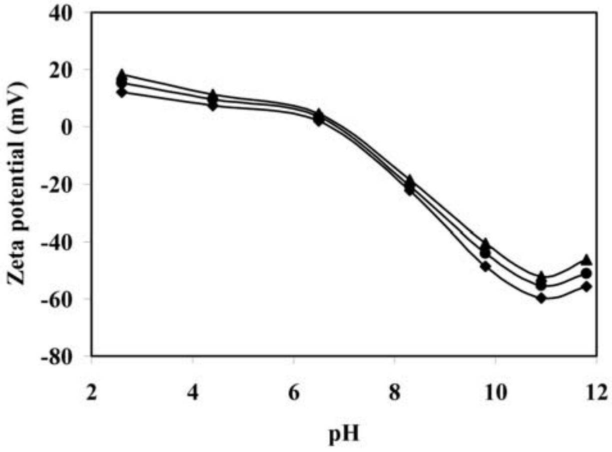


Figure 16. Zeta potential of (▲)$Cd_{0.98}Mn_{0.02}S$, (●)$Cd_{0.96}Ni_{0.04}S$ and (◆)$Cd_{0.90}Cu_{0.10}S$ nanocatalysts as a function of pH value.

les (with positive charge) on the surface of photocatalysts in alkaline solutions and thus the increasing of degradation efficiency of dyes.[34,35]

A low pH is associated with a positively charged surface which cannot provide hydroxyl group which are needed for hydroxyl radical formation. On the other hand, higher pH value can provide higher concentration of hydroxyl ions to react with the holes to form hydroxyl radicals.[24] But, the degradation of dyes is inhibited when the pH value is so high (pH > 11) because the hydroxyl ions compete with dyes molecules in adsorption on the surface of photocatalysts.[36] As the other words, at low pH, the adsorption of cationic dyes on the surface of photocatalysts decreased because the photocatalysts surface will be positively charged and repulsive forces is due to decreasing adsorption. Thus, the degradation efficiency will be decreased in acidic pH.

The degradation efficiency of methylene blue and safranin decreased with increasing the initial concentration of dyes to more than 5.0 mg/L. In the presence photocatalyst of $Cd_{0.98}Mn_{0.02}S$, $Cd_{0.96}Ni_{0.04}S$ and $Cd_{0.90}Cu_{0.10}S$ and initial concentration of dyes 10.0 mg/L, the degradation efficiency decreased to 87.12, 91.56 and 93.50 for methylene blue, respectively, and 84.25, 88.42 and 92.24% for safranin, respectively. The decrease of %D with increasing of dyes concentration can be due to two reasons. With increasing the amounts of dye, the more of dye molecules will be adsorbed on the surface of the photocatalysts and the active sites of the catalysts will be reduced. Therefore, with increasing occupy of catalyst surface, the generation of hydroxyl radicals will be decreased. Also, increasing concentration of dyes can be lead to decreasing the number of photons that is arrived to the surface of catalysts. The more light are adsorbed by molecules of dyes and the excitation of photocatalyst particles by photons will be reduced. Thus, photodegradation efficiency diminished.[37]

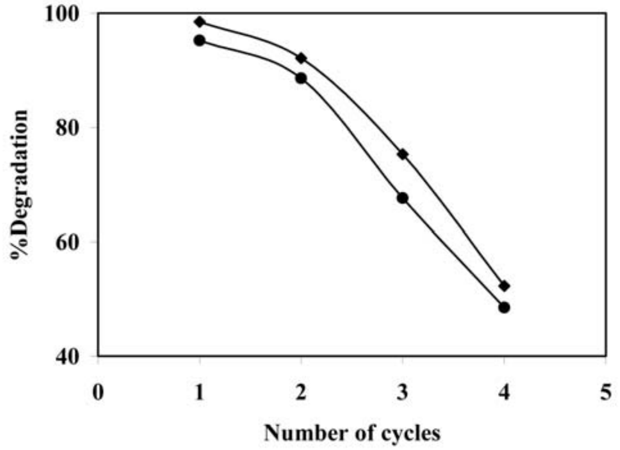


Figure 17. Reproducibility of the nanocatalysts of $Cd_{0.90}Cu_{0.10}S$ for photodegradation of (◆) methylene blue and (●)safranin.

3. 4. Photodegradation of Dye Under VIS Irradiation

In order to compare activity of nanocatalysts under UV and VIS irradiation, the degradation of dyes was studied in the presence of $Cd_{0.98}Mn_{0.02}S$, $Cd_{0.96}Ni_{0.04}S$ and $Cd_{0.90}Cu_{0.10}S$ nanoparticles as photocatalyst. The apparent degradation rate constant (k) of dyes under VIS irradiation are collected in Table 2. With comparison results of Tables 1 and 2, are seen that the photoreactivity of nanocatalysts are decreased under VIS irradiation.

3. 5. Reproducibility of the Photocatalysts

Four cycles experiment were performed for obtaining reproducibility of the photocatalysts of $Cd_{0.90}Cu_{0.10}S$. Each experiment was carried out under identical conditions of 5.0 mg/L of dyes, 150.0 mg/L of nanocatalyst, p-H of 11, irradiation time of 30 min and at room temperature. After each degradation experiment, the concentration of dyes was adjusted back to its initial value of 5.0 mg/L. Fig. 17 show the reproducibility of nanocatalyst for photodegradation of methylene blue and safranin. A small and gradual decrease in the activity of nanocatalysts was observed at the first two cycles. But, decreasing of the activity was seen intense after the first and second cycles.

4. Conclusions

Cadmium sulfide as undoped and doped with manganese, nickel and copper as semiconductor material in nanometer-size scale can be used as a photocatalyst in the process of decolorization of organic dyes. The increasing of applicable surface of photocatalyst as well as accelerate migration rate of electron/hole to the surface of the nanoparticles due to increasing degradation efficiency. Also, the photodegradation efficiency were increased with increasing the concentration of hydroxide ion and therefore increasing of hydroxyl reactive radical in pH > 7.

Table 2: Apparent degradation rate constant (k) and standard deviation (n=3) of dyes with initial concentrations of 5.0 mg/L under VIS irradiation.

Photocatalyst	Methylene blue	Safranin
$Cd_{0.98}Mn_{0.02}S$	12.86 ± 0.2010^{-3} min^{-1}	10.05 ± 0.2210^{-3} min^{-1}
$Cd_{0.96}Ni_{0.04}S$	14.94 ± 0.2510^{-3} min^{-1}	12.58 ± 0.3010^{-3} min^{-1}
$Cd_{0.90}Cu_{0.10}S$	19.32 ± 0.2910^{-3} min^{-1}	15.16 ± 0.2010^{-3} min^{-1}

5. References

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Povzetek

Fotoreaktivnost nanodelcev kadmijevega sulfata (nedopiranega in dopiranega z manganom, nikljem in bakrom) smo raziskovali z razbarvanjem (degradacijo) metilen modrega in safranina pod vplivom UV in VIS svetlobe. Proučevali smo vpliv dopirane snovi, molski delež le te napram kadmijevemu ionu, pH raztopine, količine fotokatalizatorja in koncentracijo barvila na fotoreaktivnost nanokatalizatorja. Pripravili smo vrsto fotokatalizatorjev, katerih učinkovitost degradacije pada v smeri $Cd_{0.90}Cu_{0.10}S > Cd_{0.96}Ni_{0.04}S > Cd_{0.98}Mn_{0.02}S \cong CdS$. Izkazalo se je, da optimalna koncentracija fotokatalizatorja znaša 120.0 mg/L pri pH = 11.0. Z naraščajočo koncentracijo barvila stopnja degradacije pada. V optimalnih pogojih je degradacija 91–98 % za metilen modro ter 86–95 % za safranin po 120 minutah obsevanja.