



## Nanoparticles of zinc sulfide doped with manganese, nickel and copper as nanophotocatalyst in the degradation of organic dyes

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### ABSTRACT

Nanoparticles of zinc sulfide as undoped and doped with manganese, nickel and copper were used as photocatalyst in the photodegradation of methylene blue and safranin as color pollutants. Photoreactivity of doped zinc sulfide was varied with dopant, mole fraction of dopant to zinc ion, pH of solution, dosage of photocatalyst and concentration of dye. The characterization of nanoparticles was studied using X-ray powder diffraction (XRD) patterns and UV–vis spectra. The maximum degradation efficiency was obtained in the presence of  $Zn_{0.98}Mn_{0.02}S$ ,  $Zn_{0.94}Ni_{0.06}S$  and  $Zn_{0.90}Cu_{0.10}S$  as nanophotocatalyst. The effect of dosage of photocatalyst was studied in the range of 20–250 mg/L. It was seen that 150.0 mg/L of photocatalyst is an optimum value for the dosage of photocatalyst. The most degradation efficiency was obtained in alkaline pH of 11.0 with study of photodegradation in pH amplitude of 2–12. The degradation efficiency was decreased in dye concentrations above of 5.0 mg/L for methylene blue and safranin dyes. In the best conditions, the degradation efficiency was obtained 87.3–95.6 and 85.4–93.2 for methylene blue and safranin, respectively.

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### 1. Introduction

Environmental problems associated with hazardous wastes and toxic water pollutants have been attracted much attention. Among them, organic dyes are one of the major groups of pollutants in wastewaters produced from textile and other industrial processes [1–4]. Among various physical, chemical and biological techniques for treatment of wastewaters, heterogeneous photocatalysis has been considered as a cost-effective alternative for water remediation [5]. The superiority of photocatalytic technique in wastewater treatment is due to its advantages over the traditional techniques, such as quick oxidation, no formation of polycyclic products, oxidation of pollutants in the ppb range. Photocatalysis is a process by which a semiconductor materials absorbs light of energy more than or equal to its band-gap, thereby generating electrons and holes, which can further generate free-radicals in the system to oxidize the substrate. The resulting free-radicals are very efficient oxidizers of organic mater [6,7].

The photocatalytic treatment of wastes containing dyes has also been widely reported in the literature. In most cases,  $TiO_2$  was used as a famous photocatalyst, whereas, the other semiconductors such as metal sulfides were lesser used especially in the dimensions of nano-scale [8–14].

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 [5,9,13]. Moreover, recombination of the electron-hole pair within the semiconductor particle is drastically reduced as particle size decreases. With decreasing the particle size of semiconductor to nanometer-size scale, the band-gap energy increased greatly, 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.

One of the attractive research fields in recent years is synthesis of various sizes and shapes of semiconductor materials nanoparticles. The goal of these activities is improving the performance and utilization of nanoparticles in various applications from sensing devices to photonic materials in molecular electronics and to advanced oxidation techniques (AOTs). The size and shape dependent optical and electronic properties of these nanoparticles make an interesting case for exploiting them in light induced chemical

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reactions. Of particular emphasis in this review is their application in advanced oxidation processes. In this context, nanoparticles are commonly employed as photocatalysts [15].

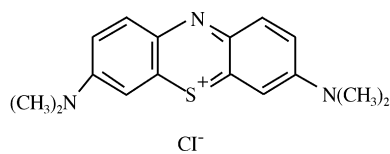
This paper reports a simple route for the preparation of nanoparticles of zinc sulfide as undoped and doped with Mn, Ni and Cu via co-precipitation method in the presence of mercaptoethanol as capping agent. The prepared nanoparticles are used as photocatalyst in degradation of methylene blue and safranin as organic dyes. The influences of parameters are studied to achieve to degradation efficiency of dyes near 100%.

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. It appears as a solid, odorless, dark green powder that yields a blue solution when dissolved in water at room temperature. This dye is stable, incompatible with bases, reducing agents and strong oxidizing agents. It is harmful if swallowed. It may be harmful if inhaled and in contact with skin as well as 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. May be harmful by ingestion, causes eye irritation, may be harmful by skin absorption, causes skin irritation and may be harmful by inhalation.

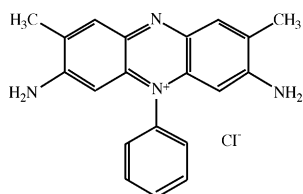
## 2. Experimental

### 2.1. Materials

The chloride salts of zinc, manganese, nickel and copper ( $ZnCl_2$ ,  $MnCl_2 \cdot 2H_2O$ ,  $NiCl_2 \cdot 6H_2O$ ,  $CuCl_2 \cdot 2H_2O$ ), all from Merck, were used as source of metal ions and  $Na_2S \cdot 9H_2O$  (Merck) was used as source of sulfide ion. 2-Mercaptoethanol (2-hydroxyethanethiol,  $HOCH_2CH_2SH$ ) and isopropyl alcohol were prepared from Merck Company and used as received. Hydrochloric acid and sodium hydroxide were applied for variation of pH of sample solutions. The dyes of methylene blue (C.I. name: Basic Blue 9,  $C_{16}H_{18}N_3ClS \cdot 3H_2O$ ) and safranin O (C.I. name: Basic Red 2,  $C_{20}H_{19}ClN_4$ ) were purchased from Fluka Company. Double-distilled water was used for preparation of solutions.



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



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

### 2.2. Catalyst preparation

The nanoparticles of  $Zn_{1-x}S:M_x$  (M: Mn, Ni, Cu and  $x=0, 0.02, 0.04, 0.06, 0.08$  and  $0.10$ ) were purchased using controlled precipitation and co-precipitation methods. Initial, 50 mL homogeneous solutions 0.01 M of  $ZnCl_2$  and  $MCl_2$  (M: Mn, Ni or Cu) as mole ratio of

$[M^{2+}]/[Zn^{2+}] = X$  and 50 mL solution of 0.1 M mercaptoethanol were added in a balloon (three-vent) on a magnetic stirrer. Then, 50 mL solution of 0.01 M sodium sulfide was added drop by drop using a decanter vessel (each 6–8 s, one drop) under nitrogen atmosphere while the mixture was stirred vigorously at room temperature. The precipitated nanoparticles of  $Zn_{1-x}M_xS$  were then centrifuged at 4000 rpm, washed three times with water to eliminate unreacted ions, and finally washed three times with isopropyl alcohol. The cleaned powders were dried for about 10 h at  $80^\circ C$  until complete evaporation of the solvent was achieved. To this way, the nanoparticles of ZnS, ZnS:Mn, ZnS:Ni and ZnS:Cu with percentages of 2, 4, 6, 8 and 10% of doped ion were purchased.

### 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 solutions of nanoparticles were recorded by using an UV–vis spectrophotometer PerkinElmer Lambda 2 at room temperature. X-ray powder diffraction (XRD) patterns were recorded on a Siemens D-5005 diffractometer using  $Cu K\alpha$  irradiation ( $\lambda = 1.5418 \text{ \AA}$ ). Zeta ( $\zeta$ ) 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  $1.0 \times 10^{-3} M$  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  $1.0 \times 10^{-2}$  were used to adjust pH to the desired values.

### 2.4. Photodegradation experiments

Photodegradation experiments were performed with a photocatalytic reactor system. 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 was placed in a 5 cm diameter quartz tube with one end tightly sealed by a Teflon stopper. 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 3.0–15.0 mg/L of dyes as pollutant and 20.0–250.0 mg/L of nanoparticles as nanophotocatalyst. The whole reactor was cooled with a water-cooled jacket on its outside and the temperature was kept at  $25^\circ C$ . All reactants in the reactions were stirred using a magnetic stirrer to ensure that the suspension of the catalyst was uniform during the course of the reaction. To determine the percent of destruction of dyes, the samples were collected at regular intervals, filtered through Millipore membrane filters, and centrifuged to remove the nanocatalyst particles that exist as undissolved particles in the samples.

A 500-W halogen lamp as the visible light source was used for investigation of activity of nanocatalysts under the similar conditions with experiments in the UV region. A cutoff filter was applied to remove wavelengths below 420 nm to ensure irradiation completely by visible light.

The wavelengths of absorbance maximum ( $\lambda_{max}$ ) of methylene blue and safranin are 661 and 519 nm, respectively. Therefore, photometric analysis of samples before and after of irradiation can be used for measurement of %D (Degradation efficiency of dye). The absorbance of samples was measured by a UV–vis spectrophotometer PerkinElmer Lambda 2 using a paired 1.0 cm quartz cell. The decrease of absorbance value of samples at  $\lambda_{max}$  of dyes after irradiation in a certain time interval will be shown the rate of decolorization and therefore, photodegradation efficiency of the dyes as well as the activity of nanoparticles as photocatalyst. The decol-

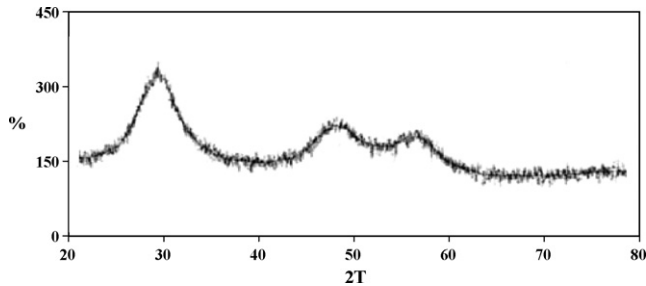


Fig. 1. X-ray diffraction patterns of pure ZnS nanocrystals.

orization and degradation efficiency have been calculated as:

$$\%D = 100 \times \left[ \frac{C_0 - C}{C_0} \right]$$

where  $C_0$  is the initial concentration of dye and  $C$  is the concentration of dye after irradiation in selected time interval.

In order to obtain maximum degradation efficiency, pH, concentration of dye and amount of photocatalyst were studied in amplitudes of 2.0–12.0, 3.0–15.0 and 20–250.0 mg/L, respectively. The experiments were carried out in the presence of nanoparticles of ZnS, ZnS:Mn, ZnS:Ni and ZnS:Cu with percentages of 2, 4, 6, 8 and 10% of doped ion and for two selected dyes.

### 3. Results and discussion

#### 3.1. Characterization of nanoparticles

The UV–vis spectra and XRD patterns were used for evaluation of approximately size of prepared nanoparticles includes ZnS, ZnS:Mn(2–10%), ZnS:Ni(2–10%) and ZnS:Cu(2–10%). The XRD patterns of pure ZnS and ZnS doped with 10% Cu as two samples are shown in Figs. 1 and 2. They reveal that the particles exhibit a zinc-blend crystal structure. The three diffraction peaks correspond to (1 1 1), (2 2 0) and (3 1 1) planes of the cubic crystalline ZnS [16–18]. The average size particles of the all of undoped and doped zinc sulfide was obtained about 2.0–10.0 nm using Debye–Scheerer formula and based on the full width half maxima (FWHM) of X-ray diffraction pattern.

The UV absorption analysis of the sample provides the information relating to the size of particles. Fig. 3 shows the absorption spectra of ZnS, ZnS:Mn(2%), ZnS:Ni(6%) and ZnS:Cu(10%) nanoparticles in isopropyl alcohol solvent. Their absorption spectra shoulder is shown about 305–310 nm. While, the absorption shoulder for macrocrystalline ZnS is seen at about 350 nm. 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 [19,20].

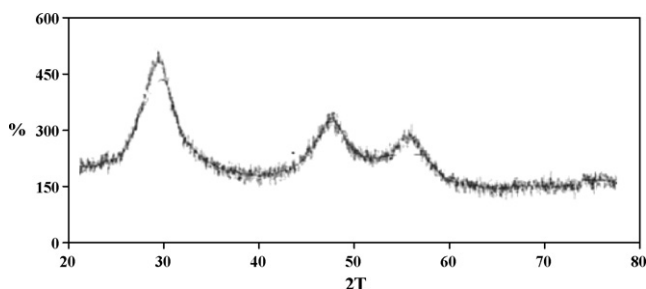


Fig. 2. X-ray diffraction patterns of ZnS:Cu(10%) nanocrystals.

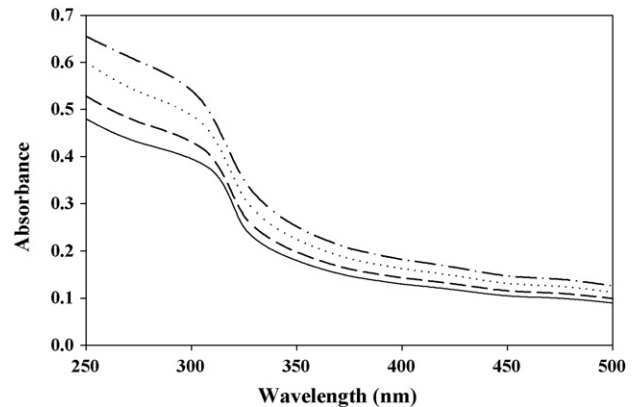


Fig. 3. UV–vis spectra of nanocrystals of ZnS, Zn<sub>0.98</sub>Mn<sub>0.02</sub>S, Zn<sub>0.94</sub>Ni<sub>0.06</sub>S and Zn<sub>0.90</sub>Cu<sub>0.10</sub>S in isopropyl solution from bottom to top.

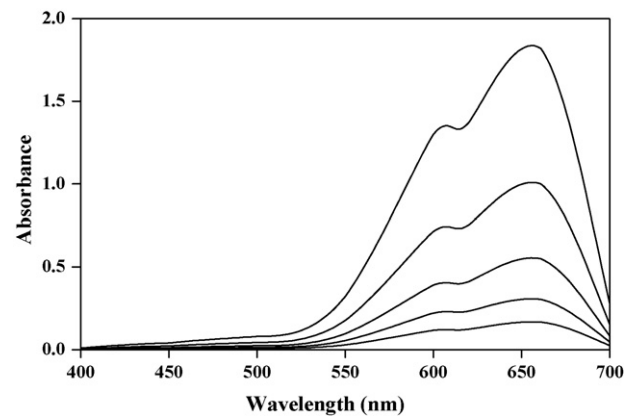


Fig. 4. Decrease absorption spectra of methylene blue (5.0 mg/L) in the presence of ZnS nanoparticles (100.0 mg/L) in irradiation times 0, 30, 60, 90 and 120 min.

#### 3.2. Photodegradation of dyes using nanophotocatalysts

Figs. 4 and 5 show the degradation of dyes (5.0 mg/L) under irradiation in time interval of 30 min and in the presence of nanoparticles of ZnS (100.0 mg/L) as photocatalyst. The decrease of absorption spectra and therefore absorbance of samples at  $\lambda_{\max}$  of dyes (661 and 519 nm for methylene blue and safranin, respectively) is indicated by degradation of dyes in the applied conditions. As a consequence, the decrease of samples absorbance due to decrease

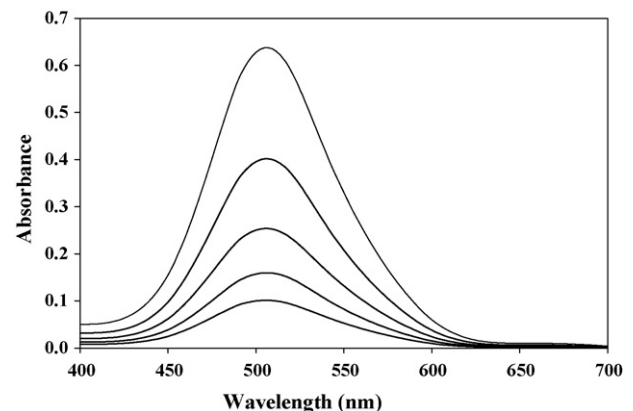
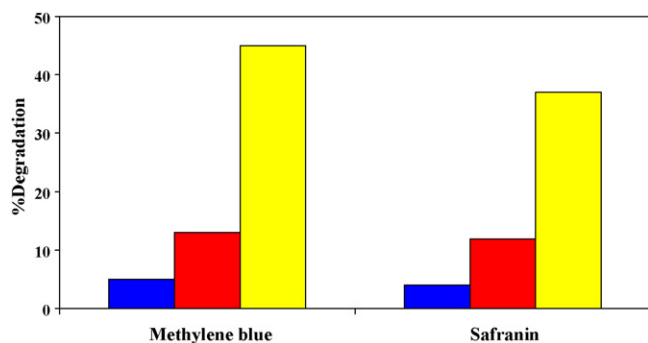


Fig. 5. Decrease absorption spectra of safranin (5.0 mg/L) in the presence of ZnS nanoparticles (100.0 mg/L) in irradiation times 0, 30, 60, 90 and 120 min.



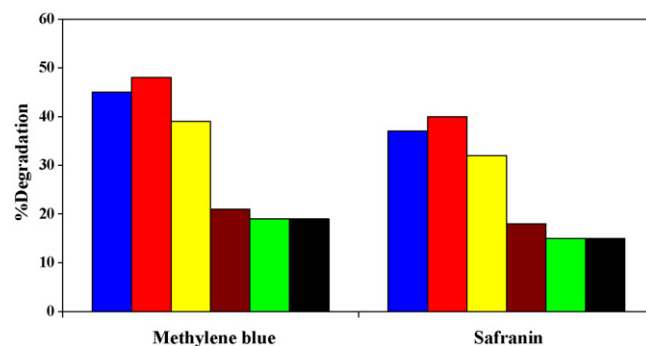
**Fig. 6.** Photodegradation of dyes in the absence (blue) and in the presence of macrocrystalline (red) and nanocrystalline (yellow) of ZnS (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

of dyes concentration is recorded for measurement of decolorization rate.

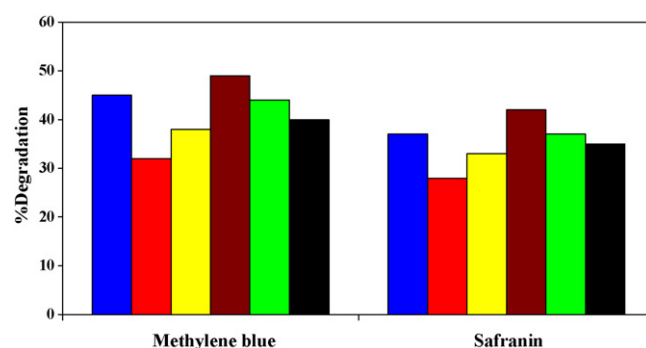
In Fig. 6, comparison of photodegradation of dyes with concentration of 5.0 mg/L is shown in the absence, macrocrystalline and nanocrystalline of ZnS with dosage 100.0 mg/L in time interval 30 min. The order photodegradation efficiency for both dyes is obtained: without ZnS < macrocrystalline ZnS < nanocrystalline ZnS. Photocatalyst effect of zinc sulfide on the decolorization process of dyes is observed with increasing the degradation efficiency in the presence of ZnS. Also, comparison of %D in the presence of ZnS macrocrystalline and nanocrystalline is shown that the %D is increased with decreasing of particles size of photocatalyst. ZnS 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 ZnS 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 hydroxide reactive radicals ( $\text{OH}^\bullet$ ) were formed from combination of holes with water molecules and/or hydroxide anions. The radical hydroxide with  $E^\circ = +3.06\text{ V}$  is a strong oxidative and oxidize dyes as non-selective to mineral species as partial or complete [21,22].

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 [23]. This pointer and increasing of accessible surface of photocatalysts as nanoparticles [24] lead to increasing of photodegradation rate of dyes.

As mentioned, the number and the lifetime of free carriers (electrons/holes) are particle size- and dopant-dependent. In order to investigation of effect of dopant, the photodegradation efficiency of dyes (5.0 mg/L) were studied in the presence of ZnS:Mn(2–10%), ZnS:Ni(2–10%) and ZnS:Cu(2–10%) nanoparticles (100.0 mg/L) in irradiation time of 30 min. The obtained results are given in Figs. 7–9 for ZnS:Mn, ZnS:Ni and ZnS:Cu, respectively. As seen, the maximum photodegradation efficiency were obtained in the presence of ZnS:Mn(2%), ZnS:Ni(6%) and ZnS:Cu(10%). On the other hand, the most decolorization for both dyes was occurred using  $\text{Zn}_{0.98}\text{Mn}_{0.02}\text{S}$ ,  $\text{Zn}_{0.94}\text{Ni}_{0.06}\text{S}$  and  $\text{Zn}_{0.90}\text{Cu}_{0.10}\text{S}$  as photocatalyst in among of prepared nanoparticles. Doping of ZnS 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



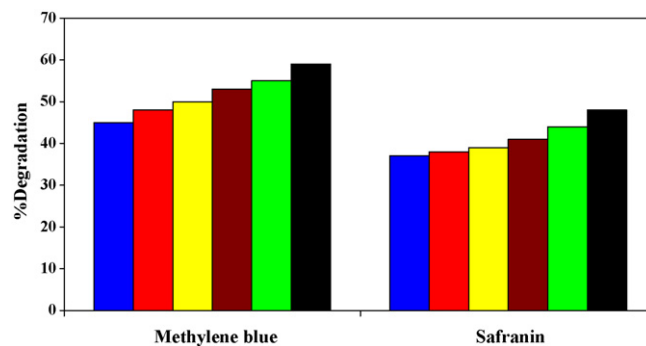
**Fig. 7.** Photodegradation of dyes in the presence of nanophotocatalysts of ZnS (blue),  $\text{Zn}_{0.98}\text{Mn}_{0.02}\text{S}$  (red),  $\text{Zn}_{0.96}\text{Mn}_{0.04}\text{S}$  (yellow),  $\text{Zn}_{0.94}\text{Mn}_{0.06}\text{S}$  (brown),  $\text{Zn}_{0.92}\text{Mn}_{0.08}\text{S}$  (green) and  $\text{Zn}_{0.98}\text{Mn}_{0.02}\text{S}$  (black) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).



**Fig. 8.** Photodegradation of dyes in the presence of nanophotocatalysts of ZnS (blue),  $\text{Zn}_{0.98}\text{Ni}_{0.02}\text{S}$  (red),  $\text{Zn}_{0.96}\text{Ni}_{0.04}\text{S}$  (yellow),  $\text{Zn}_{0.94}\text{Ni}_{0.06}\text{S}$  (brown),  $\text{Zn}_{0.92}\text{Ni}_{0.08}\text{S}$  (green) and  $\text{Zn}_{0.98}\text{Ni}_{0.02}\text{S}$  (black) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

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 [24,25].

Among dopants, the  $\text{Cu}^{2+}$  ion leads to the most decolorization and degradation efficiency 59 and 48% was obtained for methylene blue and safranin, respectively, in the time irradiation of 30 min and in the presence of  $\text{Zn}_{0.90}\text{Cu}_{0.10}\text{S}$  photocatalyst. The  $\text{Cu}^{2+}$  ion can be reduced to  $\text{Cu}^+$  ion by a hole produced with semiconductor. The resulting ion ( $\text{Cu}^+$ ) is a strong oxidative and hence it can be an oxi-



**Fig. 9.** Photodegradation of dyes in the presence of nanophotocatalysts of ZnS (blue),  $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{S}$  (red),  $\text{Zn}_{0.96}\text{Cu}_{0.04}\text{S}$  (yellow),  $\text{Zn}_{0.94}\text{Cu}_{0.06}\text{S}$  (brown),  $\text{Zn}_{0.92}\text{Cu}_{0.08}\text{S}$  (green) and  $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{S}$  (black) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

**Table 1**

Apparent degradation rate constant ( $k$ ) and standard deviation ( $n=3$ ) of dyes with initial concentrations of 5.0 mg/L under UV irradiation

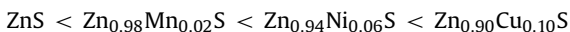
Photocatalyst	Methylene blue	Safranin
ZnS macrocrystalline	$5.88 \pm 0.14 \times 10^{-3} \text{ min}^{-1}$	$5.26 \pm 0.21 \times 10^{-3} \text{ min}^{-1}$
ZnS nanocrystalline	$19.93 \pm 0.22 \times 10^{-3} \text{ min}^{-1}$	$16.40 \pm 0.26 \times 10^{-3} \text{ min}^{-1}$
Zn <sub>0.98</sub> Mn <sub>0.02</sub> S	$20.87 \pm 0.19 \times 10^{-3} \text{ min}^{-1}$	$17.71 \pm 0.25 \times 10^{-3} \text{ min}^{-1}$
Zn <sub>0.94</sub> Ni <sub>0.06</sub> S	$22.45 \pm 0.25 \times 10^{-3} \text{ min}^{-1}$	$18.58 \pm 0.20 \times 10^{-3} \text{ min}^{-1}$
Zn <sub>0.90</sub> Cu <sub>0.10</sub> S	$26.61 \pm 0.23 \times 10^{-3} \text{ min}^{-1}$	$21.32 \pm 0.21 \times 10^{-3} \text{ min}^{-1}$

dizing agent for dyes. As a result, in these conditions, in beside of holes and hydroxyl radicals, Cu<sup>+</sup> ions, also, act as an oxidizing agent and therefore, the rate of decolorization was increased. It is reminding, increasing of mole fraction of Cu<sup>2+</sup> and use of Zn<sub>0.85</sub>Cu<sub>0.15</sub>S as photocatalyst leads to decreasing of degradation efficiency of methylene blue and safranin to 53 and 40%, respectively. As a result, the maximum activity was obtained with using mole fraction 0.1 for Cu<sup>2+</sup> ion in Zn<sub>1-x</sub>Cu<sub>x</sub>S nanoparticles.

Many authors have reported that the kinetic behaviour of photocatalytic reaction can be described by a modified Langmuir–Hinshelwood model [26,27].

$$\frac{1}{r_o} = \frac{1}{k} + \frac{1}{kKC_o}$$

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 indicated 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 of dyes were calculated and collected in Table 1. The photoreactivity of nanocatalysts were obtained as:



The degradation of dyes was studied in the presence of Zn<sub>0.98</sub>Mn<sub>0.02</sub>S, Zn<sub>0.94</sub>Ni<sub>0.06</sub>S and Zn<sub>0.90</sub>Cu<sub>0.10</sub>S nanoparticles as photocatalyst under irradiation in the visible region in order to compare activity of nanocatalysts under UV and VIS irradiation. In Table 2, the apparent degradation rate constant ( $k$ ) of dyes were calculated under these conditions. As seen from Tables 1 and 2, under VIS irradiation, the apparent degradation rate constants of dyes were decreased about 20–40% in comparison UV irradiation. Therefore, the reactivity of investigated photocatalysts under VIS irradiation is less than UV irradiation.

The proposed mechanism for dye degradation using photocatalysts (PC) was suggested as follows [6]:

**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
Zn <sub>0.98</sub> Mn <sub>0.02</sub> S	$13.56 \pm 0.22 \times 10^{-3} \text{ min}^{-1}$	$11.00 \pm 0.20 \times 10^{-3} \text{ min}^{-1}$
Zn <sub>0.94</sub> Ni <sub>0.06</sub> S	$16.84 \pm 0.21 \times 10^{-3} \text{ min}^{-1}$	$13.38 \pm 0.25 \times 10^{-3} \text{ min}^{-1}$
Zn <sub>0.90</sub> Cu <sub>0.10</sub> S	$22.32 \pm 0.19 \times 10^{-3} \text{ min}^{-1}$	$17.06 \pm 0.24 \times 10^{-3} \text{ min}^{-1}$

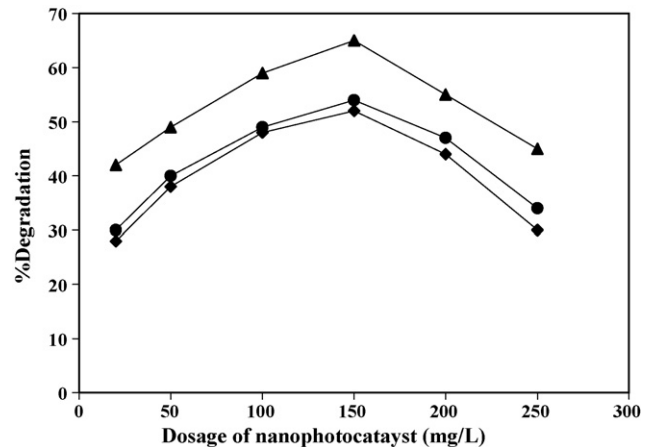


Fig. 10. Effect of dosage of photocatalysts on the photodegradation efficiency of methylene blue dye: (♦)Zn<sub>0.98</sub>Mn<sub>0.02</sub>S, (●)Zn<sub>0.94</sub>Ni<sub>0.06</sub>S and (▲)Zn<sub>0.90</sub>Cu<sub>0.10</sub>S.



### 3.3. Effect of variables influence on degradation efficiency

#### 3.3.1. Effect of dosage of nanophotocatalyst

The initial rate of photocatalytic degradation of many pollutants is a function of the photocatalyst dosage [28,29]. Figs. 10 and 11 illustrate photodegradation of methylene blue and safranin, respectively, in the different dosage of nanocatalysts Zn<sub>0.98</sub>Mn<sub>0.02</sub>S, Zn<sub>0.94</sub>Ni<sub>0.06</sub>S and Zn<sub>0.90</sub>Cu<sub>0.10</sub>S with irradiation time of 30 min. Because increasing in active sites, the rate decolorization is increased to maximum degradation efficiency in the presence 150.0 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.

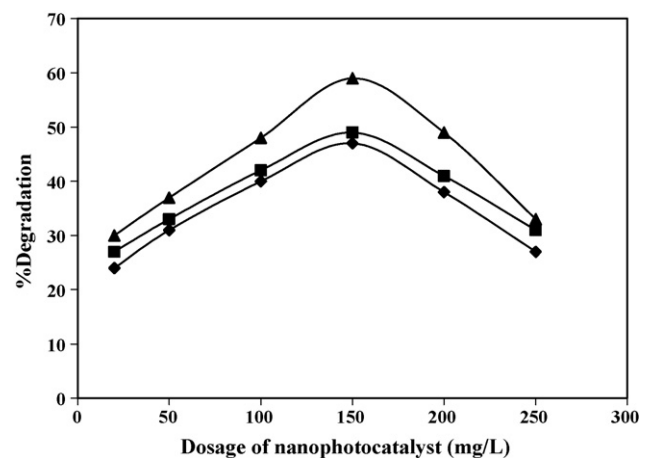


Fig. 11. Effect of dosage of photocatalysts on the photodegradation efficiency of safranin dye: (♦)Zn<sub>0.98</sub>Mn<sub>0.02</sub>S, (●)Zn<sub>0.94</sub>Ni<sub>0.06</sub>S and (▲)Zn<sub>0.90</sub>Cu<sub>0.10</sub>S.

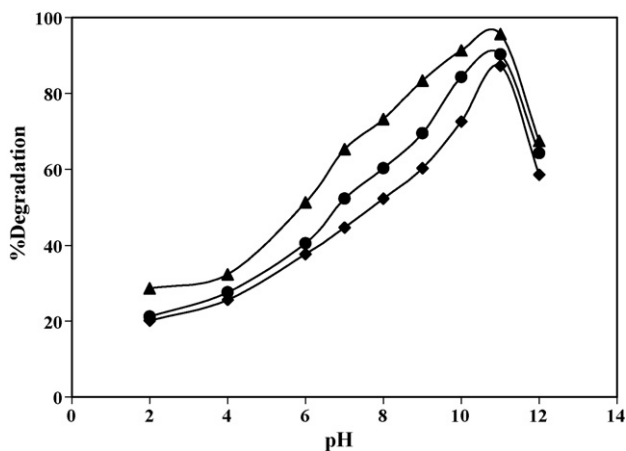


Fig. 12. Effect of pH of solution on the photodegradation efficiency of methylene blue dye: (◆)  $Zn_{0.98}Mn_{0.02}S$ ; (●)  $Zn_{0.94}Ni_{0.06}S$  and (▲)  $Zn_{0.90}Cu_{0.10}S$ .

### 3.3.2. Effect of pH

Photodegradation of dyes (5.0 mg/L) was studied in amplitude pH of 2.0–12.0 in the presence of nanocatalysts  $Zn_{0.98}Mn_{0.02}S$ ,  $Zn_{0.94}Ni_{0.06}S$  and  $Zn_{0.90}Cu_{0.10}S$  (150.0 mg/L). The results for irradiation time of 30 min are shown in Figs. 12 and 13. In all cases, the maximum degradation efficiency was obtained in alkaline pH 11 for both dyes. In the presence of  $Zn_{0.98}Mn_{0.02}S$ ,  $Zn_{0.94}Ni_{0.06}S$  and  $Zn_{0.90}Cu_{0.10}S$  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  $Zn_{0.98}Mn_{0.02}S$ ,  $Zn_{0.94}Ni_{0.06}S$  and  $Zn_{0.90}Cu_{0.10}S$ , respectively. The zeta ( $\zeta$ ) potential data for nanocatalysts of  $Zn_{0.98}Mn_{0.02}S$ ,  $Zn_{0.94}Ni_{0.06}S$  and  $Zn_{0.90}Cu_{0.10}S$  is shown in Fig. 14. 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 molecules (with positive charge) on the surface of photocatalysts in alkaline solutions and thus the increasing of degradation efficiency of dyes [30].

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

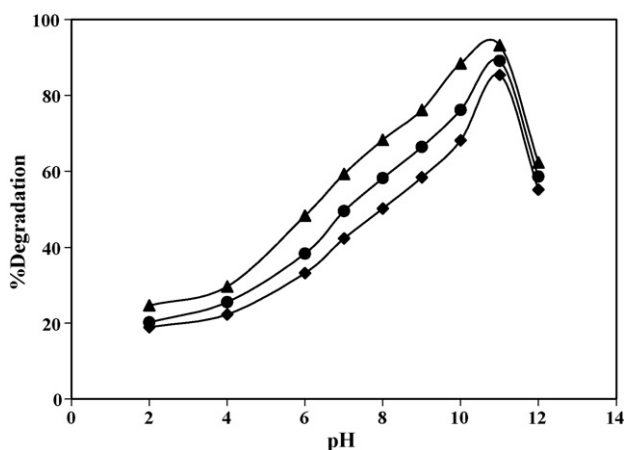


Fig. 13. Effect of pH of solution on the photodegradation efficiency of safranin dye: (◆)  $Zn_{0.98}Mn_{0.02}S$ ; (●)  $Zn_{0.94}Ni_{0.06}S$  and (▲)  $Zn_{0.90}Cu_{0.10}S$ .

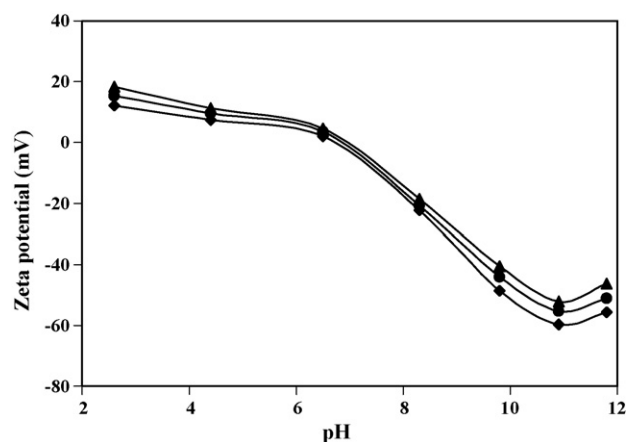


Fig. 14. Zeta potential of (▲)  $Zn_{0.98}Mn_{0.02}S$ , (●)  $Zn_{0.94}Ni_{0.06}S$  and (◆)  $Zn_{0.90}Cu_{0.10}S$  nanocatalysts as a function of pH value.

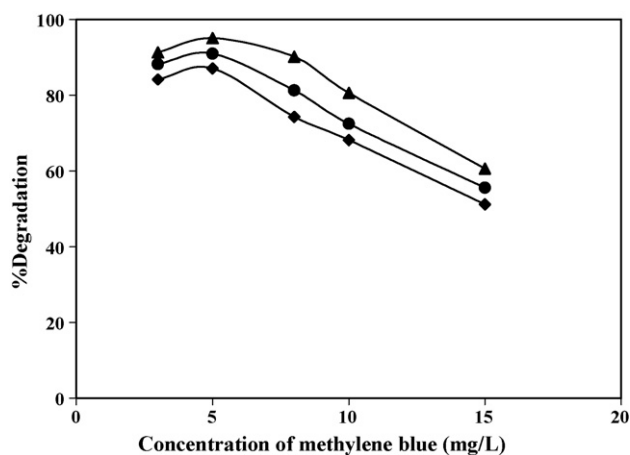


Fig. 15. Effect of concentration of dye on the photodegradation efficiency of methylene blue: (◆)  $Zn_{0.98}Mn_{0.02}S$ , (●)  $Zn_{0.94}Ni_{0.06}S$  and (▲)  $Zn_{0.90}Cu_{0.10}S$ .

when the pH value is so high (pH >12) because the hydroxyl ions compete with dyes molecules in adsorption on the surface of photocatalysts [31].

As the other words, at low pH, the adsorption of cationic dyes on the surface of photocatalysts decreased because the photocata-

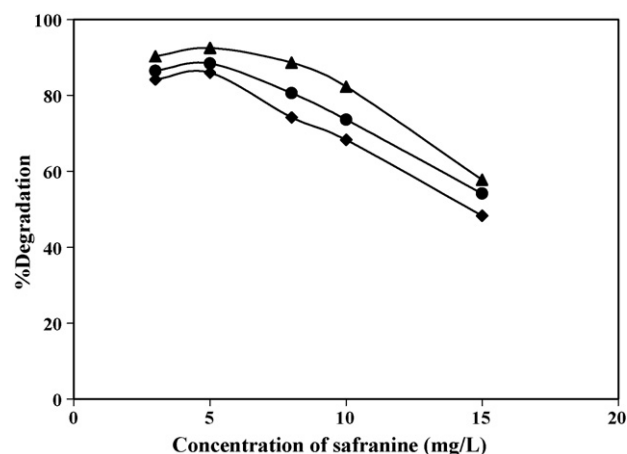


Fig. 16. Effect of concentration of dye on the photodegradation efficiency of safranin: (◆)  $Zn_{0.98}Mn_{0.02}S$ , (●)  $Zn_{0.94}Ni_{0.06}S$  and (▲)  $Zn_{0.90}Cu_{0.10}S$ .

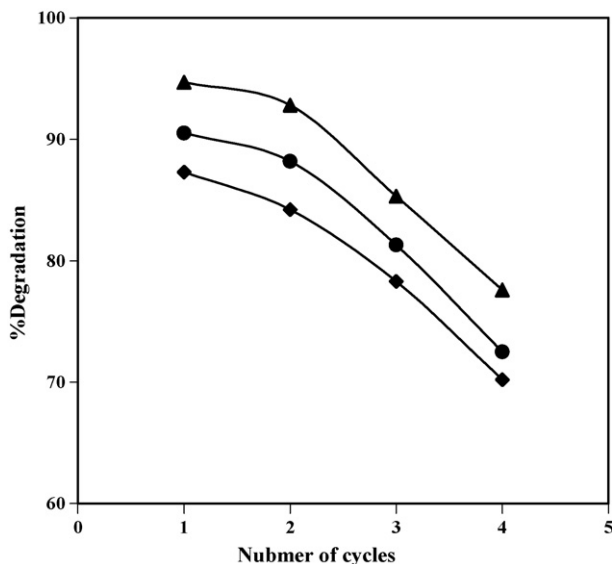


Fig. 17. Reproducibility of the nanocatalysts for methylene blue photodegradation: (♦) Zn<sub>0.98</sub>Mn<sub>0.02</sub>S, (●) Zn<sub>0.94</sub>Ni<sub>0.06</sub>S and (▲) Zn<sub>0.90</sub>Cu<sub>0.10</sub>S.

lysts surface will be positively charged and repulsive forces is due to decreasing adsorption. Thus, the degradation efficiency will be decreased in acidic pH.

### 3.3.3. Effect of concentration of dyes

The degradation efficiency of dyes (irradiation time of 30 min) decreased with increasing the initial concentration of dyes to more than 5.0 mg/L. The results are shown in Figs. 15 and 16. The decrease of %D with increasing of concentration of dyes 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 occupied space 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

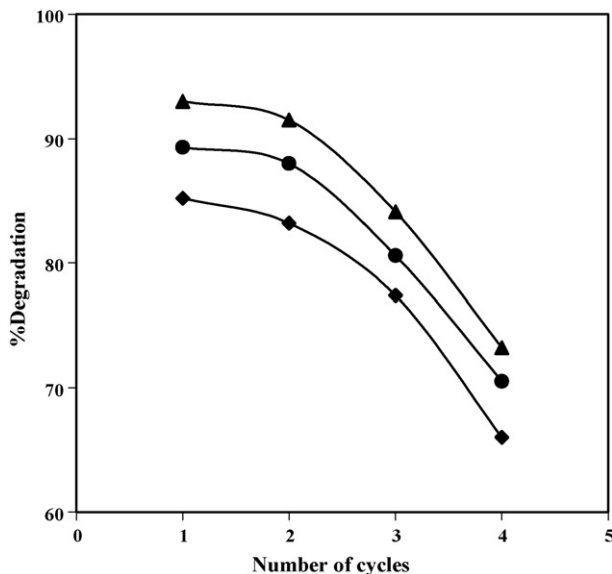


Fig. 18. Reproducibility of the nanocatalysts for safranin photodegradation: (♦) Zn<sub>0.98</sub>Mn<sub>0.02</sub>S, (●) Zn<sub>0.94</sub>Ni<sub>0.06</sub>S and (▲) Zn<sub>0.90</sub>Cu<sub>0.10</sub>S.

molecules of dyes and the excitation of photocatalyst particles by photons will be reduced. Thus, photodegradation efficiency diminished [32].

### 3.3.4. Reproducibility of the photocatalysts

Figs. 17 and 18 show the reproducibility of Zn<sub>0.98</sub>Mn<sub>0.02</sub>S, Zn<sub>0.94</sub>Ni<sub>0.06</sub>S and Zn<sub>0.90</sub>Cu<sub>0.10</sub>S as nanocatalysts for methylene blue and safranin photodegradation, respectively, during a four cycles experiment. Each experiment was carried out under identical conditions of 5.0 mg/L of dyes, 150.0 mg/L of nanocatalyst, pH 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. As seen from Figs. 17 and 18, 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

Semiconductor of zinc sulfide as undoped and doped with manganese, nickel and copper can be used as a photocatalyst in the process of photodegradation of color pollutants. In the presence of nanophotocatalysts, the degradation efficiency is increased due to increase of applicable surface of photocatalyst as well as accelerate migration rate of electron/hole to the surface of the nanoparticles. The photodegradation efficiency is proved with increasing the concentration of hydroxide ion and therefore increasing hydroxyl reactive radical in alkaline medium.

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