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Preparation of ZnS nanocrystal and investigation of its photocatalytic activity in removal of C.I. acid blue 9 from contaminated water

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ABSTRACT

Zinc sulfide (ZnS) nanocrystals in the cubic structure with the mean diameter size of 6 nm were prepared via precipitation method and examined as a photocatalyst for the UV-induced removal of C.I. Acid Blue 9 (AB9) from contaminated water as a deputy of organic pollutants. The effects of various parameters, such as UV light intensity, effect of addition of peroxydisulfate ($S_2O_8^{2-}$) and periodat (IO_4^-) on the photo catalytic decolorization of AB9 were investigated. The results showed that the removal efficiency of AB9 through UV/ZnS process increased with increasing illumination intensity, $S_2O_8^{2-}$ and IO_4^- concentrations.

Keywords: Advanced Oxidation Processes (AOPs); Inorganic oxidant; Nanoparticles, Photocatalysis; Wastewater; Zinc sulfide

1. Introduction

Synthetic dyes are commonly used in dying processes and are in general the greatest pollutants found in wastewaters [1]. The adverse effects of these synthetic dyes on the environment include an increase of the color and toxicity of the waters, death of fishes and zooplanktons, general affectation of ecosystems, and widespread aesthetic damage [2]. For the treatment of these dyes biological processes are ineffective. Also common treatment processes, such asdsorption on activated carbon, flocculation and electrocoagulation are not efficient methods because in these processes pollutants are appeared in solid wastes, thus creating other environmental problems requiring further treatment. However, the recent developments in chemical treatment of wastewaters improve catalytic and oxidative degradation of organic compounds dissolved in aqueous media. These are generally referred to as "advanced oxidation processes" (AOPs) [3]. Semiconductor photocatalysis is a newly developed AOP, which can be conveniently applied for the degradation of dye pollutants. The proposed mechanism for dye degradation using photocatalysts (PC) was suggested as follows [4,5]:

$$PC + h\upsilon \rightarrow h^+_{VB} + e^-_{CB} \quad (1)$$

$$OH^- + h^+_{VB} \rightarrow OH^\bullet \quad (2)$$

$$H_2O + h^+_{VB} \rightarrow OH^\bullet + H^+ \quad (3)$$

$$O_2 + e^-_{CB} \rightarrow O_2^{\bullet -} \quad (4)$$

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

$$2O_2^{\bullet -} + 2H^+ \rightarrow O_2 + H_2O_2 \quad (6)$$

$$H_2O_2 + e^-_{CB} \rightarrow OH^- + OH^\bullet \quad (7)$$

$$Dye + h^+_{VB} \rightarrow Dye^{\bullet +} \rightarrow \text{Final species} \quad (8)$$

$$Dye + OH^\bullet \rightarrow Dye^\bullet \rightarrow \text{Final species} \quad (9)$$

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Recently, transition-metal sulfides, in particular ZnS and CdS, have been intensively studied because of their unique catalytic functions compared to those of TiO_2. ZnS nanocrystals are good photocatalysts as a result of the rapid generation of electron–hole pairs by photoexcitation and the highly negative reduction potentials of excited electrons. The notable finding in ZnS photocatalysis is an irreversible two-electron-transfer photoreduction of organic substrates [6]. ZnS is a wide band gap semiconductor with a band gap energy of 3.68 eV for the cubic phase and 3.80 eV for the hexagonal wurtzite phase at room temperature. To fully achieve the photocatalysis properties of ZnS, well-defined structure is desirable. Generally, as is known, the photoactivity of semiconductor materials can be intensively influenced by their structure and particle size, in which particle size is a particularly important factor [7]. Some of the methods that have been used to synthesize ZnS nanocrystal include colloidal synthesis [8], microwave thermolysis [9], solvothermal [10], micro emulsion [6] and precipitation method in the presence of a complexing agent that produce a complex with one of the precursors and inhibits the direct reaction between precursors. As we know, in the liquid synthesis, kinetically controlling the nucleation and growth rate could conceivably modulate the size and shape of the crystals. Sometimes, a special coordinating reagent is used to tailor the crystal growth. Some of the complexing agents that were used in the synthesis of ZnS nano particles include cysteine, thioglycerol, thioglycolic acid (TGA), etc. [11,12]. It is well-known that some compounds such as amines are able to coordinate with metal ions, especially transition metal ions [10]. An EDTA molecule contains two N atoms, so it is a good chelating ligand and can be used as a structure-directing reagent in synthesizing some semiconductors.

C.I. Acid Blue 9 (AB9) which belongs to acidic dyes group is soluble in cold water and methanol. It can be found in thousands of textile (as a dye for wool and silk), foodstuff and pharmaceutical wastewaters. In addition, C.I. Acid Blue 9 is one of the components of Aquashade which can be used as an aquatic algaecide/herbicide, in natural or manmade ponds, lakes, fountains, fish farms, and fish hatcheries, and may be applied by both professional applicators and homeowners. It is hazardous in case of ingestion, of skin contact (irritant), of eye contact (irritant) and inhalation [13].

Herein, we chose EDTA as a suitable coordinating agent and inexpensive material to synthesize ZnS nanocrystals via precipitation method and then, the prepared ZnS nanocrystals were tested as a photocatalyst for the UV-induced decolorization of dye solution containing AB9 as a deputy of organic pollutants in aqueous solutions.

2. Materials and methods

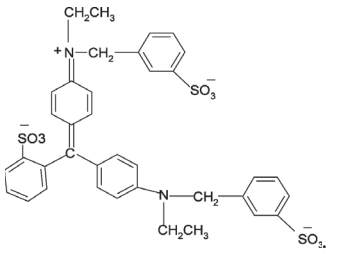
2.1. Materials

C.I. Acid Blue 9 (AB9) was obtained from Shimi Keshavarz Company, Iran. Its structure and characteristics is given in Table 1. $Zn(CH_3COO)_2.2H_2O$, NaOH, H_2SO_4 and EDTA are all analytical reagents and were obtained from Merck Co., Germany. And Na_2S with 60% purity were obtained from Fluka Co.

2.2. Preparation of ZnS nanocrystals

Nanocrystalline ZnS was prepared using the precipitation method in the presence of EDTA. $Zn(CH_3COO)_2$ and Na_2S were usedin equal molar as $Zn^{2+}$and S^{2-} sources and EDTA were used to produce a complex with Zn^{2+} to inhibit the direct reaction between $Zn^{2+}$and S^{2-}. The average crystallite size (D in nm) of prepared ZnS nanopowder were determined from XRD patterns (Fig. 1).

Table 1
Structure and characteristics of C.I. Acid Blue 9

Chemical formula	$C_{37}H_{34}N_2Na_2O_9S_3$
Chemical class	Triphenyl Methane
Color index number	CI 42090
Cass number	3844-45-9
M_W (g mol^{-1})	792.86
λ_{max}(nm)	637
Structure	

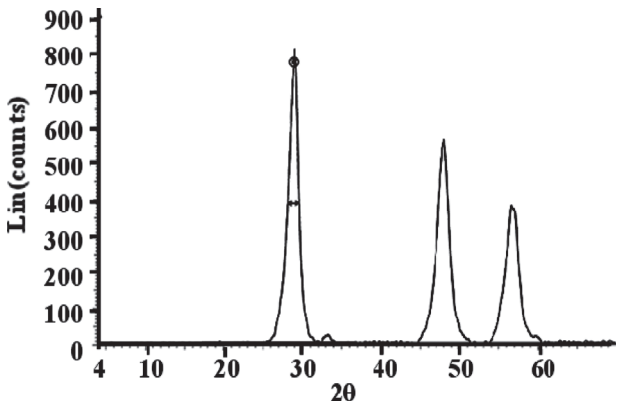


Fig. 1. XRD pattern of prepared ZnS nanocrystals.

The average crystalline size of the samples was calculated according to Debye–Scherrer formula:

$$D \approx \frac{0.9\lambda}{\beta \cos(\theta)} \quad (10)$$

where D is the average crystallite size (nm), λ is the wavelength of the X-ray radiation (Cu K_α = 0.154178 nm), β is the width at half of maximum intensity of the peak and θ is the diffraction angle. The mean particle size of ZnS nanopowders was calculated about 6 nm. as a show in Fig. 1 synthesized nanocrysals were pure.

2.3. Photoreactor and procedure

All the experiments were carried out in a batch photoreactor. The radiation source was a UV lamp (30 W, UV-C, λ_{max} = 253.7 nm, Philips, The Netherlands), which placed above photoreactor. For the photodecolorization of AB9, a solution containing known concentration of the AB9 and ZnS nanopowder was prepared and it was allowed to equilibrate for 30 min in the darkness, then 100 ml of the prepared suspension was transferred to a 100 ml glass reactor, then the lamp was switched on to initiate the reaction. During irradiation, the glass reactor mounted on a magnetic stirrer to keep the suspension homogenous and the suspension was sampled after appropriate illumination times. Before determination of concentration of the AB9, samples was filtered through filter disks with 0.2 μm diameter to remove ZnS particles. The concentration of the AB9 in each sample was determined using a spectrophotometer (UV/Vis Spectrophotometer, Perkin-Elmer 550 SE, England) at λ_{max}= 637 nm and a calibration curve. By this method conversion percent of AB9 can be obtained in different time. Then the degree of photodegradation (X: $X = (C_0 - C_t)/C_0$) were calculated as functions of irradiation time.

3. Results and discussion

3.1. Effect of UV light intensity on the decolorization of AB9

The effect of UV light intensity on the removal efficiency of AB9 has been examined by changing the distance between UV light source and reactor at constant dye concentration (20 mg l^{-1}) and catalyst loading (150 mg l^{-1}). It is evident that the degree of decolorization increases with increasing the light intensity as shown in Fig. 2. The UV irradiation generates the photons that are required for the electron transfer from the valence band to the conduction band of a semiconductor photocatalyst and the overall energy input to a photocatalytic process is dependent on the light intensity.

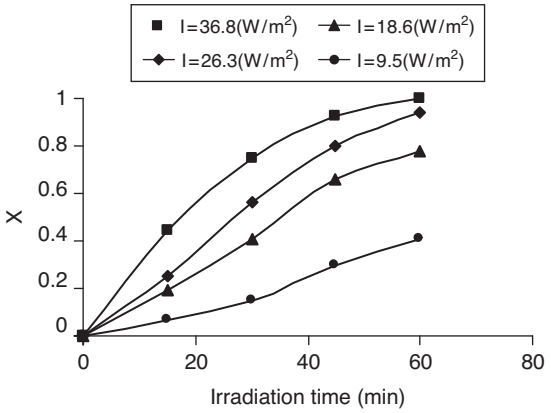


Fig. 2. Effect of UV light intensity on photocatalytic decolorization of AB9 $[AB9]_0$ = 20 mg l^{-1}; [ZnS] = 150 mg l^{-1}; pH = 6.3.

There for, the efficiency of decolorization increases when more radiation falls on the catalyst surface and hence more hydroxyl radicals are produced [14].

3.2. Effect of addition of $S_2O_8^{2-}$ to UV/ZnS process on the decolorization of AB9

The effect of addition of $S_2O_8^{2-}$ on the photocatalytic decolorization of AB9 has been investigated by varying the amount of $(NH_4)_2S_2O_8$ from 0 to 100 mg l^{-1}. The results are shown in Fig. 3. It can be seen that increasing of persulfate concentration cause the increasing of removal efficiency of AB9. Addition of persulphate to photocatalytic processes enhances the decolorization rate by two ways [15].

(i) Persulphate ion scavenges the conduction band electron and promotes the charge separation and production of other oxidizing species namely sulphate radical anion (Eq. 11).

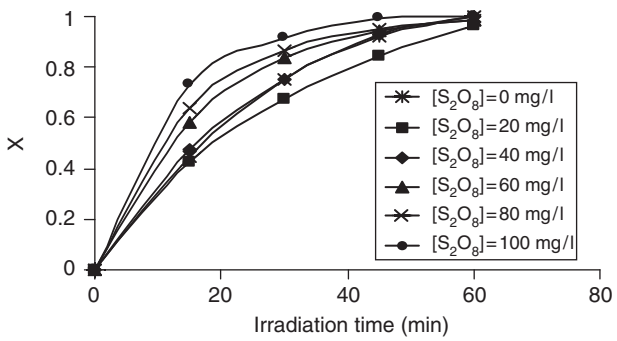


Fig. 3. Effect of addition of $S_2O_8^{2-}$ on photocatalytic decolorization of AB9 $[AB9]_0$ = 20 mg l^{-1}; [ZnS] = 150 mg l^{-1}; pH = 6.3.

$$S_2O_8^{2-} + e^-_{(CB)} \rightarrow SO_4^{\bullet -} + SO_4^{2-} \quad (11)$$

(ii) $S_2O_8^{2-}$ can generate sulphate radical anion ($SO_4^{\bullet -}$) both thermally and photocatalytically in aqueous solution. This radical anion is a strong oxidant and participates in the degradation processes by the following pathways (Eq. 12–15):

$$SO_4^{\bullet -} + e^-_{(CB)} \rightarrow SO_4^{2-} \quad (12)$$

$$SO_4^{\bullet -} + H_2O_2 \rightarrow {}^{\bullet}OH + SO_4^{2-} + H^+ \quad (13)$$

$$SO_4^{\bullet -} + \text{Dye} \rightarrow \text{Dye intermediate} + SO_4^{2-} \quad (14)$$

$$SO_4^{\bullet -} + \text{Dye intermediate} \rightarrow \text{mineralization} \quad (15)$$

3.3. Effect of addition of IO_4^- to UV/ZnS process on the decolorization of AB9

The effect of addition of IO_4^- on the photocatalytic decolorization of AB9 has been investigated by varying the amount of $NaIO_4$ from 0 to 100 mg l^{-1}. The results are shown in Fig. 4. It can be seen that increasing of periodate concentrations increases the removal efficiency of AB9. IO_4^- increases the decolorization of AB9 by capturing the electrons ejected from ZnS so that the probability of recombination of electrons and holes will decrease, i.e. the available number and the survival time of holes will be higher and thus react effectively with adsorbed water molecules to produce more hydroxyl radicals [16,17].

$$IO_4^- + 8e^-_{(cb)} + 8H^+ \rightarrow 4H_2O + I^- \quad (16)$$

Also the photocatalytic decolorization of periodate under UV irradiation (254 nm) involves the formation

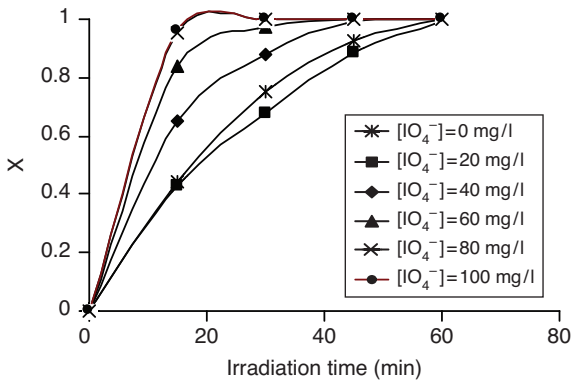


Fig. 4. Effect of addition of IO_4^- on photocatalytic decolorization of AB9 $[AB9]_0$ = 20 mg l^{-1}; [ZnS] = 150 mg l^{-1}; pH = 6.3.

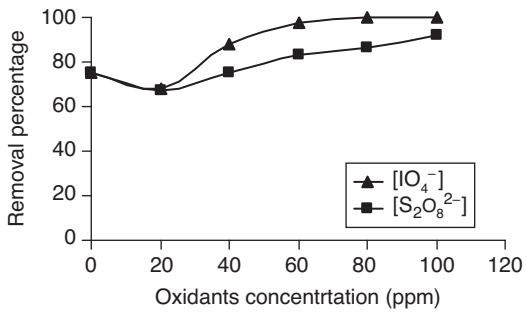


Fig. 5. Comparison the effect of addition of IO_4^- and $S_2O_8^{2-}$ on photocatalytic decolorization of AB9 $[AB9]_0$ = 20 mg l^{-1}; [ZnS] = 150 mg l^{-1}; pH = 6.3; time = 30 min.

of a number of highly reactive radical and non-radical intermediates as follows:

$$IO_4^- + h\nu \rightarrow IO_3^{\bullet} + O^{\bullet -} \quad (17)$$

$$O^{\bullet -} + H^+ \leftrightarrow {}^{\bullet}OH \quad (18)$$

$${}^{\bullet}OH + IO_4^- \rightarrow {}^-OH + IO_4^{\bullet} \quad (19)$$

$$H_4IO_6^- + h\nu \rightarrow H_3IO_5^{\bullet -} + {}^{\bullet}OH \quad (20)$$

$$H_3IO_5^{\bullet -} \rightarrow IO_3^- + H_2O + {}^{\bullet}OH \quad (21)$$

3.4. Comparison of UV/ZnS/IO_4^- and UV/ZnS/ $S_2O_8^{2-}$

Comparison of UV/ZnS/IO_4^- and UV/ZnS/$S_2O_8^{2-}$ processes on the photocatalytic decolorization of AB9 are shown in Fig. 5. It can be seen that the efficiency of dye decolorization using UV/ZnS/IO_4^- is higher than UV/ZnS/$S_2O_8^{2-}$, because IO_4^- is one group of oxidants, which has more than two atoms of oxygen and one atom of halogen (I) as a central atom. Polarizability difference in oxidant atoms makes its central atom extremely electropositive. Therefore, IO_4^- can capture the electrons ejected from photocatalyst more than other oxidants [16].

4. Conclusion

In summary

- EDTA was a good complexing agent for the synthesis of ZnS nanocrystals.
- Degree of decolorization of AB9 by UV/ZnS process was affected by illumination intensity and addition of oxidants like $S_2O_8^{2-}$ and IO_4^-.
- The rate of dye decolorization using UV/ZnS/oxidant was higher than that for UV/ZnS and increased with increasing oxidant concentration.
- The rate of dye decolorization using UV/ZnS/IO_4^- was higher than UV/ZnS/$S_2O_8^{2-}$.

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