

Kinetic investigation of photocatalytic degradation of dimethyldisulfide by zeolite A containing nano CdS

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ABSTRACT

In this research, zeolite A was synthesized from waste porcelain and CdS nano-particles were doped in zeolite framework by a precipitation after an ion exchanging process. All raw and modified samples were characterized by FT-IR, XRD and SEM methods. Primary experiments showed that the good efficiency of loaded nano CdS onto the zeolite A for photodecomposition of dimethyldisulfide (DMDS) under UV irradiation. Hence the effect of some experimental parameters on the kinetics of the photodegradation experiments was studied and the optimal conditions were found as: pH 3, 3 g L⁻¹ of the catalyst and 8 ppm of DMDS concentration. UV-Vis spectrophotometric measurements were performed to determine the degradation extent. The degradation process obeyed first-order kinetics.

Keywords: Zeolite A, Dimethyldisulfide, CdS nanoparticles, Heterogeneous catalysis.

1. Introduction

Dimethyl-disulfide (DMDS) is an organo-sulfur compound with high toxicity, strong corrosive material and also the volatile organic compound which it can be oxidized in the atmosphere to sulfuric acid (as main component of acid rain) [1]. It is released either by natural processes such as anaerobic biological activities or by anthropogenic [2] and also it will generate during poultry meat production [3] and is commonly found in various industrial processes, waste streams and disposal facilities. Photocatalytic oxidation has reported as a good method to degrade different pollutants such as DMDS [4,5]. In this method, electrons and holes will form by illuminating a semiconductor with a UV or Vis radiation with a suitable energy. These electron-holes pairs can further produce free-radicals to decompose a large number of organic pollutants [6].

The goal of this research is investigation of the kinetics of the photodegradation of DMDS by incorporated CdS nanoparticles onto the zeolite A. Hence, cadmium sulfide nano-particles were produced inside the framework of zeolite A by precipitation after an ion exchanging process and the obtained compound was referred as nCdS/A.

2. Experimental

2.1. Materials and synthesis procedures

All agents (except waste porcelain which was prepared from Esfahan glass factory in Iran) were of analytical grade (Merck and Aldrich). Distilled water was used throughout the experiments. Waste porcelain (with major component as: SiO₂: 64.4; Al₂O₃: 22.6; LOI: 8.8) was grounded by a mill and particles smaller than 1 mm were sorted. The pH of solutions was appropriately was adjusted by sodium hydroxide or hydrochloric acid solution.

The synthesis procedure method for synthesis of zeolite A is completely described in the literature [7] and our previous work [8]. To this goal, waste porcelain was digested in 4 M NaOH and the diluted filtrate (2 times) was mixed with aluminate solution to adjust the Si/Al molar ratio of 0.5. The mixed solution was heated at 80 °C for 24 h to synthesis zeolite A.

The nCdS/zeolite A sample was prepared by a precipitation process using zeolite A as reported in the literature [8,9]. After ion-exchanging the zeolite in a cadmium solution, it was stirred with 100 mL of 1 M Na₂S solution for 12 h to obtain nCdS/zeolite A. Finally, the sulfurized compound was digested with a 48% HF solution to prepare the nano CdS sample.

2.2. Characterization

Characterization of the raw and modified samples was performed by XRD, XRF, SEM and FTIR as reported in our previous work [8]. The extracted Si and Al from waste porcelain were measured by ICP (GBC Integra XL). Atomic Absorption Spectrometer Perkin Elmer AAnalyst 300 (Air-

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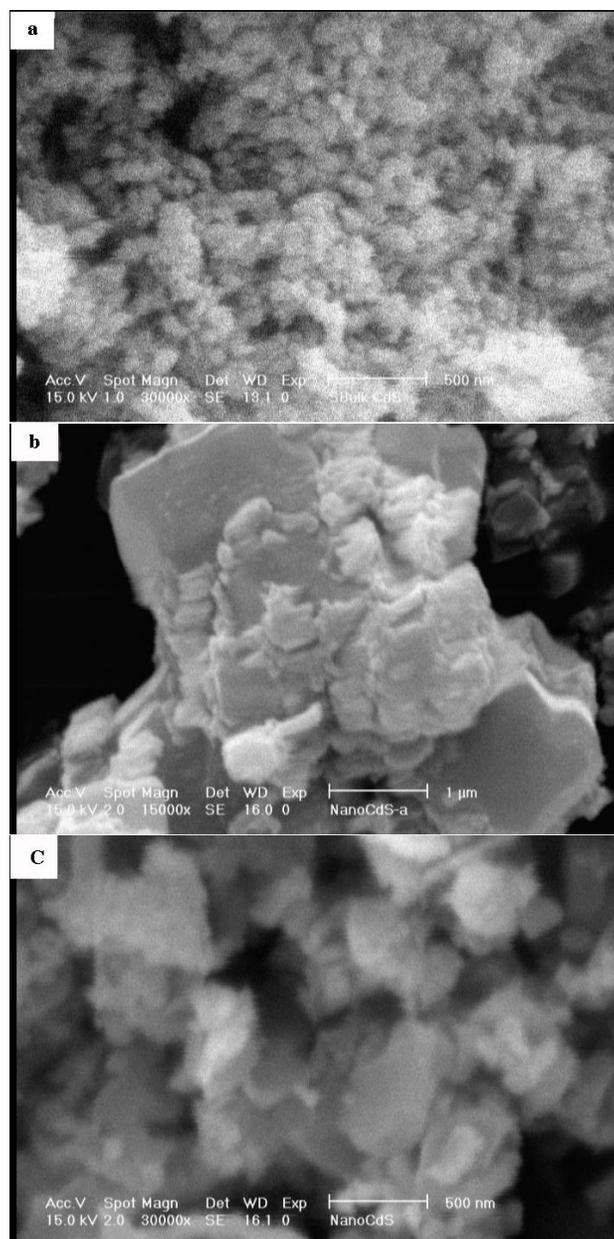


Fig. 1. (a) SEM pictures of the bulk CdS, (b) NCdS/A zeolite and (c) nano CdS particles.

C_2H_2 , $\lambda=288.8$ nm) was used to measure the amount of cadmium loaded on the zeolite.

2.3. Photodegradation experiments

In a typical photocatalytic experiment, a 50 mL aqueous suspension of DMDS with certain concentration was added to certain amount of the proposed photocatalyst to reach a 3 g L^{-1} dosage in a flat-surfaced glass reactor. The reaction mixture was magnetically stirred during the irradiation process with a 75 W UV lamp. After selected irradiation times, the reaction mixtures were centrifuged and subjected to spectrophotometer analysis. The photodegradation reaction was followed spectrophotometrically by monitoring the disappearance of peak corresponding to DMDS at

wavelength of absorbance maximum (λ_{max}) in 251 nm. The degradation of DMDS was fitted with the first order kinetics [$\ln(C/C_0) = -kt$], where C_0 and C are the initial and final DMDS concentration at time t , respectively, and (k, min^{-1}) is the reaction rate constant. The rate constant, k , was calculated from the slopes of the straight-line portion of the plots.

3. Results and discussion

3.1. Characterization

Characterization of the synthesized zeolite A sample and also its modified sample containing nano CdS particles (NCdS/A) were studied using XRD and FTIR techniques

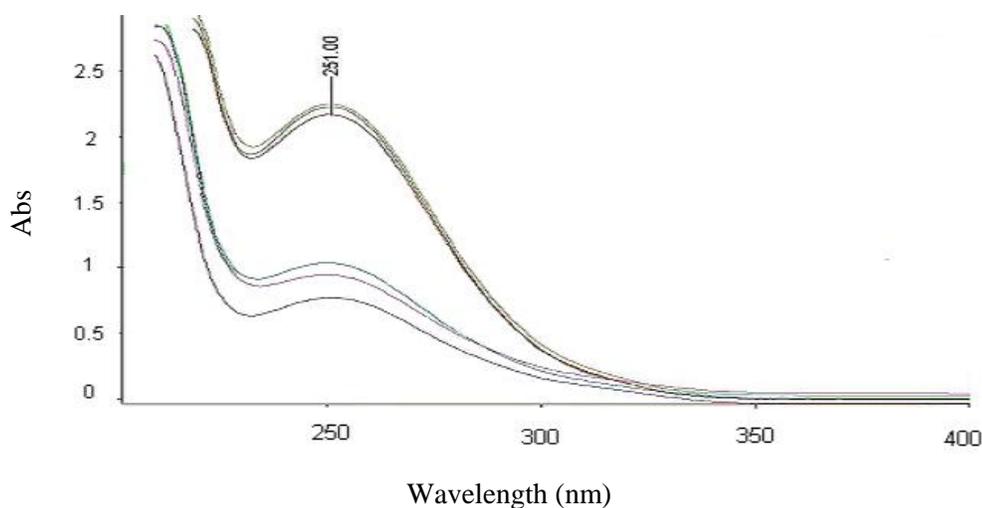


Fig. 2. Variation of the DMDS absorption during the degradation process, conditions: 8ppm of DMDS, 3 gL⁻¹ of nCdS/A, irradiation times of 8, 14, 21, 36, 60 and 90 min (from top to bottom).

and the obtained results were reported in our previous work [8]. Comparing the XRD results with the data of Na-A zeolite in the library of the instrument (JCPDS No 38-0241) and also with the literature [10] confirmed the successful synthesis of zeolite A. In addition, comparing the XRD pattern of the modified zeolite with the beta phase of the CdS particles (pdf No 01-0647) confirmed formation of CdS in the zeolite structure. FT-IR spectrum of the synthesized zeolite was also in accordance with the infrared spectral data for zeolite A [11]. Due to the loading of CdS nano particles into the zeolite framework some changes such as slightly shifts of some peak positions were observed.

The SEM photographs of the samples are presented in Fig. 1. The crystallites of the zeolite have a very well defined cubic shape, being the square crystalline planes. A regular growth-pattern of fine particles of nanosized CdS is clearly observed inside and on the surface of zeolite A as shown in Fig. 1 b. The bulk sample with a large outgrowth of CdS particles in a regular manner is illustrated in Fig. 1-a. Fig. 1c shows nano CdS particles and the zeolite matrix being removed by HF solution. The nanoparticles on the surface of zeolite A are in accordance with particle size distribution in the range of 48-68 nm.

3.2. Investigation of photocatalytic activity

3.2.1. Effect of loaded CdS extent

In preliminary experiments, the photocatalytic activity of NCdS/A for the degradation of DMDS was studied. UV-Vis spectra of the degradation of an 8 ppm DMDS solution after UV irradiation in time interval of 45 min and in the presence of NCdS/A (3g L⁻¹) is presented in Fig. 2. As Fig. 2 shows, a decrease of the sample's absorbance was observed at λ_{max} (251 nm) during the degradation process which it used for studding the degradation extent. The control experiment results showed a 14% maximum surface adsorption for DMDS, which was reduced from total degradation values.

Different catalysts were prepared by ion exchanging the zeolite A in various concentrations of Cd²⁺ aqueous solutions (0.01, 0.1 and 0.2 M of Cd²⁺ solutions, correspond to CdS loading of 0.7, 4.1 and 4.7%, respectively, determined by atomic absorption spectroscopy of cadmium determination) to investigate the effect of nano CdS loading on the degradation of DMDS. Due to small solubility constant of CdS (pK_{sp}=27) and also enough cleaning the sulfurized sample, it can be suppose that all determined cadmium cations in the sample are present as CdS. Hence the total amount of determined cadmium was converted to CdS.

Because of obeying the kinetic of a photocatalytic reaction from the first-order reaction [12], $\ln(C/C_0)$ was plotted versus irradiation time as a function of investigated parameters. First, the rate constants, k (min⁻¹), were determined from the straight-line portion of these first-order plots, as a function of the catalyst loading. The attained results are about 1.6×10^{-3} , 1.0×10^{-2} and 1.1×10^{-2} min⁻¹ for CdS loadings of 0.7, 4.1 and 4.7%, respectively. As shown, no notable difference is detected between the degradation efficiency of the catalyst containing 4.1 and 4.7% CdS. Hence, the catalyst containing 4.1% CdS was used in the next experiments. These observations show DMDS reacts with OH radicals to produce an intermediate (CH₃(OH)SCH₃) which is rapidly broken to form HCHO and SO₂ molecules by cleavage S-S bond [13].

3.2.2. Effect of dosage of the photocatalyst

Fig. 3 shows the obtained results for studying the effect of the catalyst dosage on the degradation rate of DMDS. By increasing in the dosage of catalyst up to 3 g L⁻¹ the rate of degradation process was increased and thereafter decreased. By increasing in the catalyst loading from 1 to 3 g L⁻¹ enhancement in the degradation rate is due to increasing in the catalyst surface area, which elevates absorption of photons and also increase in the surface adsorption extent of

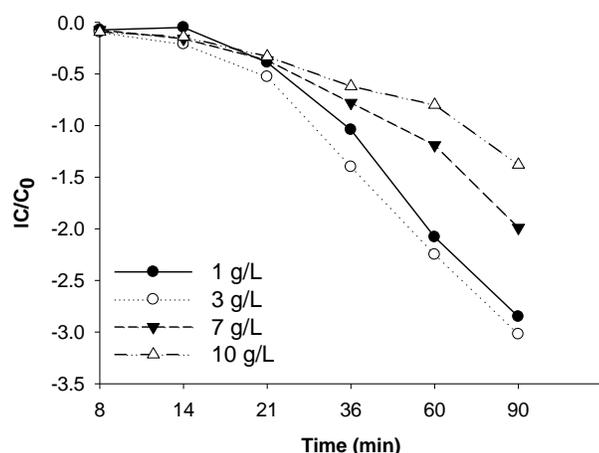


Fig.3. Effect of dosage of nCdS/A on degradation rate of DMDS, (initial concentration of DMDS=1.6 ppm and in its natural pH).

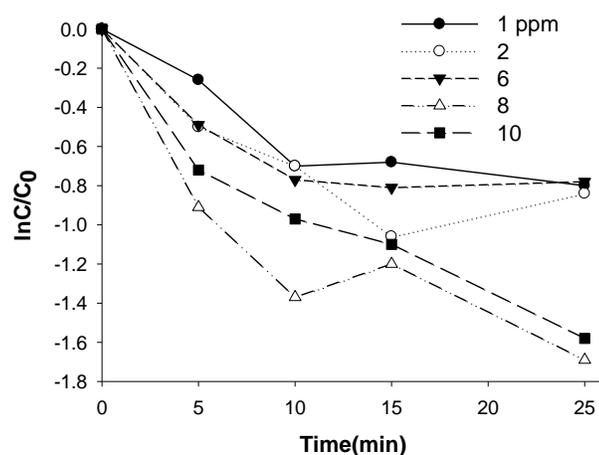


Fig. 4. Effect of initial concentration of the DMDS on rate of the photodegradation using 3g L^{-1} of nCdS/A in its natural pH.

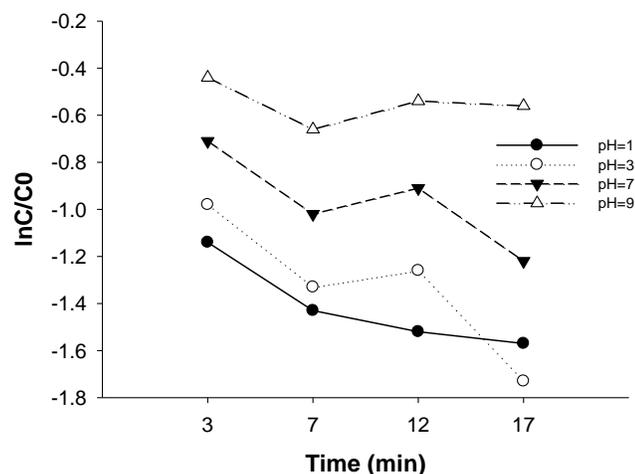


Fig. 5. Effect of solution pH on decolorization efficiency of DMDS, (initial concentration of the pollutant=8 ppm and 3g L^{-1} nCdS/A).

pollutant. But, decrease in the reaction rate in the loadings more than 3g L^{-1} is because of the decreasing in the light penetration and deactivation of activated molecules due to collision with the ground state molecules [14].

The k values of 4.0×10^{-3} , 1.9×10^{-2} , 1.4×10^{-2} and 8.0×10^{-3} were obtained for catalyst dosages of 1, 3, 7, and 10g/L of the catalyst, respectively.

3.2.3. Effect of concentration of the pollutant

The results of the study of DMDS concentration on the kinetics of the degradation process are summarized in Fig. 4. According to the results, reaction rate was increased with increasing in the DMDS concentration up to 8 ppm, and thereafter the degradation efficiency was decreased. With increasing in the DMDS concentration the number of the reached photons at the catalyst surface reduces. Also there is a competition between intermediate products of the DMDS degradation and DMDS molecules for the limited adsorption sites. This competition blocks CdS active sites at the catalyst surface [15] and hence the rate of the reaction reduces. The k values of 1.8×10^{-2} , 1.0×10^{-2} , 8.0×10^{-3} , 5.4×10^{-2} and 3.4×10^{-2} were obtained for concentration of 1, 2, 6, 8 and 10ppm DMDS, respectively.

3.2.4. Influence of initial solution pH

In order to study of the influence of initial solution pH, decomposition of DMDS in solutions with different pH from 1 to 9 were studied and the obtained results are shown in Fig. 5. According to the slope of the straight segment of these curves, the k values of 1.3×10^{-1} , 2.2×10^{-1} , 1.4×10^{-1} and 2.4×10^{-2} were obtained for solution pHs of 1, 3, 7 and 9, respectively. These observations can be interpreted as follow. In $\text{pH}=1$, the charge of catalyst surface will be positive because of the protonation of the surface and can rippled the positively charged protonated DMDS cations in this pH. In addition, in $\text{pH}=1$ it maybe dissolve some CdS particles from the catalyst surface. These in turn reduce the degradation rate. In our idea, in $\text{pH}=3$ protonation of DMDS and also dissolution of CdS maybe reduced. Hence, attractive forces between the positively charged surface of the catalyst and free electron pairs of sulfur atoms in DMDS increases the degradation rate. This trend is true until $\text{pH}=7$. By increasing in the solution pH towards alkaline pHs, the catalyst surface will be negative in charge and it causes a repulsion force between the catalyst surface and free electron pairs of sulfur atoms in DMDS and hence reduces the degradation rate.

4. Conclusions

The results of this study confirmed that waste porcelain can be used as an efficient rout for synthesis of zeolite A. Nano CdS particles loaded onto the zeolite A can be act as a suitable photocatalyst for the decolorization of DMDS under UV irradiation. The photocatalyst exhibited a very good performance in destroying DMDS with consuming low expense and time.

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