



Comparison of photocatalytic efficiency of supported CuO onto micro and nano particles of zeolite X in photodecolorization of Methylene blue and Methyl orange aqueous mixture

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ABSTRACT

The present study compares the photocatalytic decolorization ability of CuO as supported onto both micronized zeolite X (CuO/MX) and zeolite X nano-particles (CuO/NX) toward aqueous mixture of Methyl Orange (MO) and Methylene Blue (MB). Both photocatalysts were characterized by XRD, SEM, BET, FT-IR and DRS. The progress of the photodecolorization of the proposed mixture was monitored using UV–vis spectrophotometer. The decolorization of dyes was systematically studied by varying the experimental parameters in order to achieve maximum decolorization efficiency. Application of the Langmuir–Hinshelwood kinetics allowed calculating the photodecolorization rate constants. CuO/NX was more efficient than CuO/MX and also, MO was more degraded than MB. The reusability of the photocatalysts was also tested and the decolorization activities of 90% and 88% were respectively obtained for CuO/NX and CuO/MX after four recycles.

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1. Introduction

Semiconducting materials mediated photocatalytic decolorization is a successful and convenient method for the treatment of polluted water [1]. As a significant p-type semiconductor, CuO with a narrow band gap has various applications in heterogeneous catalysts, gas sensors, optical switch, magnetic, etc. [2]. In our previous works, the photocatalytic activity of CuO as doped onto zeolite X was studied for the degradation of methylene blue and *o*-phenylenediamine [3,4]. The decolorization of pollutants takes place via formation of partially oxidized intermediates, which afterwards undergo complete mineralization. Since the reactions predominantly occur on the surface, supported semiconductors on suitable adsorbents draw much attention due to three potential advantages, viz., concentration of pollutant near the semiconductor particles, adsorption of formed intermediates and recyclability of adsorbents [5]. Among the various supports, zeolites are considered to be important due to their special features such as: high surface area, high ion exchange capacity, hydrophilic and easily tunable chemical properties, high thermal stability and eco-friendly nature [6]. Our works confirmed that the supported

semiconductors onto zeolite surfaces significantly increased their photocatalytic efficiency [3,4,7,8]. The ability of zeolites to favor the photo induced electron transfer reactions and retarding undesired back electron transfer has been studied [9] and the results showed that H-zeolite increased the adsorption of pollutants and generated large amount of hydroxyl and peroxide radicals, which are critical species in the photocatalytic decolorization processes. Nano-sized zeolite crystals with the small particles size distribution have received much attention because of their great potential applications in the catalysis and adsorption fields. The decrease in the crystal sizes results in higher external surface areas, reduced diffusion path lengths, and more exposed active sites, which have an impact on the performance of the zeolitic nanoparticles [10].

In this work, an aqueous mixture of MO and MB was decolorized using supported CuO onto both micronized zeolite X and zeolite X nano-particles. MO is a stable azo dye and it resist to biodegradation [11]. MB is a heterocyclic aromatic chemical compound, a member of thiazine dyes [12]. It can have some harmful effects such as: heartbeat increase, vomiting, shock, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans [13]. Both dyes are extensively used in important industries such as textile and printing [14,15]. Hence, development of new catalysts and methods to degrade these dyes from water is important. The mixture of dyes was selected to have more similarity to a wastewater sample.

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2. Experimental

2.1. Materials

Methylene Blue, Methyl Orange, Tetraethylorthosilicate (TEOS), Sodium hydroxide, Sodium aluminate, Aluminum trihydrate, Sodium silicate solution, Copper(II) sulfate pentahydrate and other chemicals used were obtained from Aldrich or Merck Companies and used without further purification. All experiments were prepared using deionized water. The pH of solutions was appropriately adjusted with HCl or NaOH solution.

2.2. Synthesis of catalysts

Nano-particles of zeolite Na-X (NX) was synthesized by hydrothermal crystallization in a temperature-controlled condition [16] from homogeneous mixture with molar composition of: 5.5 Na₂O:1.0 Al₂O₃:4.0 SiO₂:190 H₂O. An aluminosilicate gel containing 5.34 g NaOH, 2.42 g NaAlO₂, 3.43 g SiO₂, and 50.0 g H₂O was prepared. To start, a plastic bottle containing freshly prepared sodium aluminate solution and a stirring bar was immersed into an ice-water bath. The mixture was cooled for 1 h with stirring. Then, TEOS was added and stirring was continued at 0 °C for 6 h and then at room temperature for another 24 h. Hydrothermal crystallization was conducted at 60 °C for 4 days on a shaker (250 rpm). The suspension was centrifuged and the powdered product was washed with copious water until pH < 8 and dried at room temperature for 24 h. The synthesis of micronized zeolite X (MX) was described in our previous work [4]. To prepare the copper(II) exchanged zeolites, 4 g of NX and MX were separately added to 100 mL of 0.2 M Cu²⁺ solution (as nitrate salt) and suspensions were shaken for 24 h. The obtained solid Cu(II)-exchanged forms (Cu/NX and Cu/MX) were centrifuged, washed with water and dried at 100 ± 5 °C for 30 min and finally calcined at 450 °C for 12 h for preparation of CuO/NX and CuO/MX samples [3,4].

2.3. Characterization techniques

The crystalline structure of the samples was studied using a X-ray diffraction instrument (XRD, Bruker, D8ADVANCE) with a CuK α source in a 2 θ range of 10–60°. The mean size of NX and MX particles was estimated by the Scherrer's equation:

$$S = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where S is the mean crystallite dimension, K the crystallite shape constant (0.89), θ the Bragg angle, λ the X-ray wavelength, and β is the full width at half maximum (FWHM) of the peak in radians [17]. The surface morphology was studied by scanning electron microscope (SEM, Hitachi Model S-3500N). The samples for SEM imaging were coated with a thin layer of gold film to avoid charging. The surface texture properties of samples were determined by Quantachrome Corporation (model Nova 1200). Before the study, all samples were heated at 250 °C for 3 h. Fourier transform infrared spectra of the samples were recorded using FT-IR spectrometer (Nicolet 400D Impact) using KBr pellets in the wavenumber range of 2000–400 cm⁻¹. Diffuse reflectance spectra were recorded using an instrument equipped with an integrating sphere (DRS, JASCO Co., Japan) in the wavelength range of 200–900 nm.

An Agilent 7890 A gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) with a HP-5MS 5% phenylmethylsiloxane capillary column (30.00 m × 0.25 mm, 0.25 μ m film thickness), coupled to an Agilent 5975C (Agilent Technologies, Palo Alto, CA, USA) mass selective detector, was used to detect the degradation products. The initial oven temperature (60 °C for 4 min initially) was raised at the

rate of 4 °C/min to 260 °C. While, injector and detector temperatures were respectively set at 290 °C and 300 °C, helium was used as carrier gas at a flow rate of 2 mL/min (injection volume = 0.1 μ L). The ionization voltage of 70 eV with ion source temperature of 200 °C was applied as operating parameters for MS detector. To prepare sample for GC–MS injection, the decolorized of each MO or MB dyes solution by CuO/MX catalyst was centrifuged and the then organic compounds were extracted using 5 mL of dichloromethane in five replicates. The resulting extractate was then analyzed by GC–MS.

Some characterization results of MX, Cu/MX and CuO/MX have been reported in our previous works [3,4].

2.4. Photocatalytic experiments

For this purpose, 20 mL mixture of MO and MB aqueous solutions (10 mg/L with respect to each dye) containing 0.1 g/L of photocatalysts (CuO/NX or CuO/MX) were subjected to irradiation using a medium pressure Hg lamp (75 W, Philips) which was positioned above the reactor (the distance between the sample cell and radiation source was 30 cm). During irradiation, the suspensions were sampled off at regular intervals and centrifuged to remove the suspended catalyst particles. Finally, absorbency of the solution was measured by UV–vis spectrophotometer at the maximum absorption wavelength of MB (664 nm) and MO (460 nm). The photodecolorization extent of pollutants was estimated by the following equation:

$$\text{decolorization \%} = \left(\frac{A_0 - A_t}{A_0} \right) \times 100 \quad (2)$$

where A_0 and A_t are the initial and final absorbance of each dye in the mixture, which respectively relate to the initial (C_0) and final (C) concentrations according to the Beer-Lambert law [18].

The photodegradation of pollutants follows the pseudo first-order kinetics according to the Langmuir–Hinshelwood model, so the photodecolorization rate of each dye was studied by the following equation:

$$\ln \left(\frac{C}{C_0} \right) = -kt \quad (3)$$

The rate constants (k) were calculated from the slopes of the straight-line segment of the plots of $\ln(C/C_0)$ versus t .

3. Results and discussion

3.1. Characterization results

3.1.1. XRD

Powder X-ray diffraction (XRD) is frequently used to estimate the crystallinity and verify the identity of zeolites. XRD patterns of the raw and modified forms of NX and MX were recorded and the corresponding patterns are shown Fig. 1. The patterns of NX and MX are similar to reflection lines of zeolite X in the library of instrument (JCPDS No. 39-0218) and literature [19] which indicate high degree of crystallinity in both samples. Comparing the XRD patterns of NX and MX shows that the peak intensities was decreased and the line widths was increased for NX due to its smaller crystallite size [20]. The crystal sizes of samples were obtained using Scherrer's equation which of results are collected in Table 1. Although, the original structure of parent zeolite did not changed during ion exchange and calcination processes, but the intensities of some diffraction peaks were decreased or disappeared in Cu/NX and Cu/MX patterns due to the covering of zeolites surfaces by amorphous or crystallized Cu²⁺. As shown, the decrease in the peak intensity was intense for Cu/NX and CuO/NX samples. These results agree with literature which showed that lower Si/Al ratio of zeolite X

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