

# Improvement of the photocatalytic activity of cupric oxide by deposition onto a natural clinoptilolite substrate



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## ABSTRACT

CuO was loaded onto clinoptilolite particles and used in the photodegradation of benzene-1,2-diamine (BD) under UV irradiation. The photocatalyst was prepared by ion exchanging of parent natural clinoptilolite with copper(II) sulfate aqueous solution ( $0.4 \text{ mol L}^{-1}$ ) for 20 h followed by drying and calcination at  $450 \text{ }^\circ\text{C}$  for 8 h. Raw and modified samples were characterized by XRD, SEM-EDAX, DRS and BET methods. The degradation extents were evaluated by UV-vis absorption spectrophotometric, chemical Oxygen demand (COD) and HPLC methods. The primary objective was to determine the optimal conditions for experimental parameters which were obtained as:  $2.0 \text{ g L}^{-1}$  of the photocatalyst,  $20 \text{ mg L}^{-1}$  of benzene-1,2-diamine, pH 6.0 and  $43 \text{ mmol L}^{-1}$  of  $\text{H}_2\text{O}_2$ . The degradation process obeyed first-order kinetics.

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## 1. Introduction

There are several treatment processes for the destruction or detoxification of hazardous organic wastes in water and wastewater [1–4], among them the advanced oxidation processes (AOPs) are the most promising alternatives. These methods involve the generation of hydroxyl radicals ( $\cdot\text{OH}$ ) that are highly reactive oxidants [5,6]. Heterogeneous photocatalysis is an AOP method which has been widely used to degrade a wide range of pollutants because it can degrade organic molecules at a low energy cost. In this method, irradiation of a semiconductor such as CuO by photons with proper energy causes to excitation of electrons from the valence band of semiconductor to its conduction band which finally produce electrons ( $e^-$ ) in the conduction band and positive holes ( $h^+$ ) in the valence band, as well as the formation of  $\text{OH}$  and  $\text{O}_2^-$  radicals [7–9]. These highly reactive free radicals can oxidize different

organic pollutants and eventually mineralize them to carbon dioxide and water [10].

In general, copper is an important material because of its high electrical and thermal conductivities [11,12]. Copper oxides ( $\text{Cu}_2\text{O}$  and  $\text{CuO}$ ) are also known as p-type semiconductors exhibiting narrow band gaps (2.0 eV for  $\text{Cu}_2\text{O}$  and 1.2–1.5 eV for  $\text{CuO}$ ) and have been widely used as powerful heterogeneous catalysts (especially  $\text{CuO}$ ) especially in the photodegradation of different organic pollutants [13–16].

As we know, a major problem in photodegradation processes is  $e/h$  recombination which significantly decreases the degradation efficiency. Hybridizing of two semiconductors ( $p-n$  junction) [17] and supporting of semiconductor onto a suitable support such as silica, alumina, zeolites etc. [18] are two common strategies to overcome to this problem. In this work, supporting of  $\text{CuO}$  onto clinoptilolite particles was used to increase its photocatalytic activity for degrading benzene-1,2-diamine as subjected pollutant. Zeolites are good ion exchangers and due to their unique properties including size, shape and charge selectivity can exchange their common alkaline and alkaline earth cations with cations present in the contacted solution [19,20]. In the research area of green chemistry,

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using of new supports to be environmentally friendly is very important subject. In this regard, an Iranian natural clinoptilolite was subjected in the present study as a suitable support for CuO semiconductor. Abundance of the zeolite in Iran significantly decreases the cost of our method which is of economic importance. The prepared CuO-clinoptilolite was used in the degradation of benzene-1,2-diamine under UV irradiation. Choosing this amine as pollutant is because of its importance in textile industry and other applications. Hence, discharging of these industrial effluents can significantly pollute water by this amine. Entering this amine to the human body causes various harmful effects such as: increasing heart attack and causing mutational activities. In general, aromatic amines such as Benzene-1,2-diamine are a class of pollutants which are not easily biodegradable and entering them to environment causes so many problems [21]. Hence, constructing new materials or methods for removing/degrading of such amines is of great importance.

## 2. Experimental

### 2.1. Reagents and preparations

Natural clinoptilolite was obtained from the Semnan region in the north-east of Iran. Benzene-1,2-diamine ( $C_6H_8N_2$ ) and other chemicals were obtained from Merck. Distilled water was used throughout the experiments. The pH of solutions was appropriately adjusted by NaOH or HCl solution.

Clinoptilolite was mechanically pretreated by crushing in an agate mortar and sieving in analytical sieves for the separation of fractions with mesh: 100, 200 and 300 mesh. In order to remove water soluble and also magnetic impurities, it was refluxed three times at 70 °C for 8 h on a magnetic stirrer. To prepare the CuO-clinoptilolite (CuO-CP), 3.0 g of clinoptilolite powder was added to a 100 mL of 0.4 mol L<sup>-1</sup> copper sulfate aqueous solution (as optimum concentration) and stirred for 20 h. The sample was filtered off, washed and dried at 60 °C. The obtained sample was referred as Cu-clinoptilolite (Cu-CP). Finally, the obtained Cu-CP was calcinated at 450 °C in a furnace for 8 h to form CuO-CP catalyst.

To study the effect of the amount of loaded CuO on the degradation efficiency, some catalysts were prepared by ion exchanging of clinoptilolite (mesh: 300) in 0.1, 0.2, 0.3, 0.4 and 0.5 mol L<sup>-1</sup> of Cu<sup>2+</sup> aqueous solutions.

### 2.2. Characterizations

XRD patterns of samples were recorded using X-ray diffractometer (Bruker, D8ADVANCE, Germany, X-ray tube anode: Cu, wavelength: 1.5406 Å (Cu K $\alpha$ ), filter: Ni). The amount of copper was measured using atomic absorption spectrometer (AAS) (AAnalyst 300, Perkin-Elmer Co. USA). Infrared spectra (FT-IR) on KBr pellets were recorded with a Nicolet single beam FT-IR (Impact 400D) spectrometer. The surface morphology and surface texture properties of samples were obtained using a Philips XL30 scanning electron microscope (SEM) and a BET instrument (model Nova 1200), respectively. The UV-vis DRS spectra of

samples were recorded with a spectrophotometer model V-670, JASCO, Japan.

### 2.3. Catalytic activity

A photocatalytic reactor including the cylindrical quartz cells (10 cm height, 5 cm i.d.) which positioned 20 cm away from Hg lamp (75 W) was used. The experiments were performed by suspending an optimized amount (2.0 g L<sup>-1</sup>) of the CuO-CP catalyst in a 20 mg L<sup>-1</sup> of BD solution (initial pH 6.0) under constant (200 rpm) stirring rate.

At specific time intervals, the suspension was centrifuged and the absorbance of the cleaned sample was measured at 290 nm ( $\lambda_{max}$  of BD pollutant) using a UV-vis spectrophotometer (Cary 100 Scan). The degradation percentage of the BD pollutant was calculated using the following formula:

$$\text{Degradation \%} = [(A_0 - A_t)/A_0] \times 100 = [(C_0 - C_t)/C_0] \times 100 \quad (1)$$

where  $A_0$  and  $A_t$  are the initial and final absorbance of the BD solution.  $A_0$  and  $A_t$  relate to the initial ( $C_0$ ) and final ( $C_t$ ) concentrations according to the Beer-Lambert law, respectively. Hence, for easy calculations  $A_0$  and  $A_t$  were used to calculate the degradation extent of the pollutant. The rate constants ( $k$ , min<sup>-1</sup>) were calculated from the slopes the straight-line portion of the plots of  $\ln(C_0/C)$  vs. time. The blank solution had the same conditions of analyte without any photocatalyst. According to control experiment results in dark condition, the surface adsorbed of BD was maximum 6% and this value was decreased from total degradation values. The COD and HPLC analysis were performed on the selected samples after and before degradation process to confirm degradation of the BD pollutant.

## 3. Results and discussions

### 3.1. Characterization

#### 3.1.1. XRD patterns

XRD patterns of CP and CuO-CP samples are shown in Fig. 1. The observed characteristic lines at  $2\theta$  values of 10°, 11.4°, 17.4°, 23°, 26°, 28.2°, 30.2° and 32° in the XRD patterns of the raw zeolite used and its calcinated CuO-form are in agreement with the crystalline XRD data of clinoptilolite in the library of the instrument [JCPDS # 39-1383] and also in

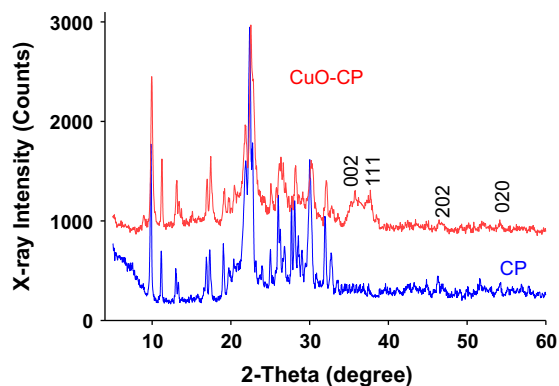


Fig. 1. X-ray patterns of parent natural CP and CuO-CP samples.

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