



## Tailoring the current density to enhance photocatalytic activity of CuO/HY for decolorization of malachite green



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### ABSTRACT

CuO supported on HY zeolite (CuO/HY) catalyst was prepared via a simple electrolysis method under different levels of current density, and its properties and photoactive performance were investigated. The physicochemical properties of the catalyst were examined using X-ray Diffraction (XRD), surface area analysis, Ultraviolet–Visible Diffuse Reflectance Spectroscopy (UV–Vis DRS), Fourier Transform Infrared (FTIR) spectroscopy, and pyridine adsorption FTIR. The analyses indicated that CuO/HY catalyst contains both CuO nanoparticles and incorporation of copper into the HY framework. In parallel with the formation of Cu<sup>0</sup> in the electrolysis system, the Cu<sup>2+</sup> ions also underwent isomorphous substitution subsequent to dealumination to form a Si–Cu–O bond, as confirmed by the FTIR result. The formation of the Si–Cu–O bond was found to decrease at elevated current density and this lowered the photocatalytic decolorization of malachite green (MG) by CuO/HY. The CuO/HY prepared at 10 mA cm<sup>-2</sup> was the optimum catalyst and produced complete and 50% decolorization of 10 and 15 mg L<sup>-1</sup> of MG, respectively. The results indicating the decrease in chemical oxygen demand (COD) and total organic carbon (TOC) demonstrated the degradability of MG molecules. The CuO/HY is also stable and showed no leaching effect even after six reaction cycles, with just small decreases in the decolorization percentage (<89%). The catalyst has the potential to be applied in textile wastewater treatment which is always in low concentration level. It is also believed that this study will be useful for synthesis of other catalysts that necessitate a degree of isomorphous substitution of metal ions in a zeolite network.

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### 1. Introduction

Up to 200,000 tons/year of dyes, used extensively in various textile industries, are discharged into the effluent during drying and finishing operations [1]. This is an important source of environmental pollution. Therefore, treatment of the wastewater is necessary before releasing it into the environment because the dyes are carcinogenic and mutagenic and inhibit photosynthesis. Three main treatment techniques have been applied for the removal of dyes from wastewater including physical, chemical, and biological methods. However, biological and physical processes are always reported as ineffective methods [2] and generate secondary waste [3]. Therefore, the use of a heterogeneous photocatalyst for wastewater treatment has become more popular because it can be operated in mild conditions and transforms the toxic organic pollutants into nontoxic products [4,5].

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Recently, copper oxide (CuO) photocatalyst has received much attention from researchers due to its narrow band gap ( $\approx 1.7$  eV), low cost, low toxicity, and high availability [6,7]. It has been also reported to be more photoreactive than Al<sub>2</sub>O<sub>3</sub>, ZnO, and NiO [6]. Accordingly, many techniques have been developed for the synthesis of nanosized CuO, including microwave radiation, impregnation, co-precipitation, and the sol–gel method [8–10]. However, the size control, size distribution, shape, degree of acidity, and so on, remains a challenge [11]. Later, it has been reported that CuO on various supporting matrixes such as zeolites and mesoporous materials could enhance the photoactivity of the catalysts [7,12]. The high surface area and cation exchange capabilities of such materials offer good interactions with the metal oxides and improve the properties of the catalysts [13].

We have reported a new method for the preparation of zinc metal nanoparticles by a simple electrochemical technique and its successful use in the synthesis of various types of drug precursors [14,15]. By applying the corresponding method, Zn and Ni promoted on zeolite catalysts led to efficient isomerization of petrochemical products [16–18]. Recently, we also reported the

preparation of highly photoreactive  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and ZnO supported on HY zeolite catalysts for efficient decolorization of dyes [19–21]. Although the metal/metal supported catalysts were prepared by the same technique, they underwent different synthesis mechanisms, which led to different properties in terms of particle size, acidity, and structure, which gave advantages to their application.

It was also found that variation of the electrolysis conditions such as temperature, current density, type of solvents, and so on affects the efficiency of the subsequent applied organic reactions [22,23]. However, until now there is no detailed report relating the effect of such specific electrolysis conditions on the physicochemical properties of the supported metal oxide catalysts. New findings regarding this matter would be advantageous for the design of new catalysts for various applications because the corresponding electrosynthesis method is very facile as the catalyst can be prepared in a short time without using metal salts solutions. Recently, we found that the properties and photoactive performance of the metal supported on zeolite catalysts were strongly affected by the current density applied during electrolysis. Therefore, in this study we report, for the first time, on the effect of the level of current density on the physicochemical properties of CuO supported on HY zeolite (CuO/HY) catalyst. The characterization of the catalyst was carried out by X-ray Diffraction (XRD), surface area analysis, Ultraviolet–Visible Diffuse Reflectance Spectroscopy (UV–Vis DRS), Fourier Transform Infrared (FTIR) spectroscopy, and pyridine adsorption FTIR. The performance of CuO/HY prepared under different levels of current density for the photodecolorization of malachite green (MG) dye under fluorescent lamp irradiation was examined. Different levels of current density were found to affect the dealumination of the HY framework, ion exchange capacity, particle size, and acidity of the catalysts, which then influenced the band gap and subsequent MG photodecolorization. The activation energy, kinetics, and reusability of the catalysts were also investigated in detail.

## 2. Materials and methods

### 2.1. Materials

HY zeolite (Zeolyst International, USA, Si/Al = 80) was used as a support for CuO. Naphthalene (Fluka Chemie) was used as a mediator in the electrolysis reaction. Platinum and copper plate cells (Nilaco and Tanaka Metal Corporation, Japan) were utilized as electrodes. Hydrochloric acid and sodium hydroxide were added to adjust the pH of the sample solution. *N,N*-dimethylformamide (DMF) was used as solvent, and MG was used as an organic pollutant. All reagents were purchased from Merck (USA).

### 2.2. Preparation of the catalyst

The CuO loading on the HY support was maintained at 5 wt% for all catalysts studied. The procedure for the preparation of 5 wt% CuO/HY catalyst was as follows: a DMF solution was added to a one-compartment cell fitted with a platinum plate cathode (2 cm × 2 cm) and a copper plate anode (2 cm × 2 cm) containing tetraethylammonium perchlorate, naphthalene, and HY zeolite. Naphthalene was added as a mediator to accelerate the reaction by producing anion radicals for the reduction of the copper cations [22]. Then, the electrolysis was conducted at a constant current of 10 mA cm<sup>-2</sup> and 273 K under an N<sub>2</sub> atmosphere. The required copper loading on the HY support was calculated based on Faraday's law of electrolysis. After electrolysis, the mixture was impregnated at 353 K in an oil bath before being dried overnight at 373 K and calcined for 3 h at 823 K to give gray-colored CuO/HY. The 5 wt%

CuO/HY was prepared under three different levels of current density by adjusting the electrolysis time according to the Faraday's law of electrolysis, which were 10, 30 and 120 mA cm<sup>-2</sup> in 99.9, 33.3 and 8.32 min, respectively.

### 2.3. Characterization of the catalysts

The properties of catalysts were determined using differential analytical techniques. XRD patterns of the catalysts were obtained using a Bruker Advance D8 X-ray powder diffractometer with a Cu K $\alpha$  ( $\lambda$  = 1.5418 Å) radiation source. The UV–Vis diffuse reflectance spectroscopic studies were carried out using a Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer with an integrating sphere. The surface area was calculated with the Brunauer–Emmett–Teller (BET) method, and pore distributions were determined by the Barrett–Joyner–Halender (BJH) method whereas the micropore area, micropore volume, and external surface area were estimated by t-plots. FTIR spectra were obtained with a KBr pellet using a Perkin Elmer GX FTIR spectrometer over the range of 4000–370 cm<sup>-1</sup>.

### 2.4. Photocatalytic activity measurement

The photocatalytic testing was carried out by placing a dosage of 0.38 g L<sup>-1</sup> of catalyst in a 200 mL MG solution at a certain concentration and stirring in the dark for 2 h in a batch reactor to allow the mixture to reach the adsorption–desorption equilibrium. A fluorescent lamp with a definite power of 20 W as the light source was mounted above 10 cm of the solution. The entire system was placed inside a chamber covered with aluminum foil to prevent the passage of other light into the reactor. During irradiation, aliquots of approximately 2 ml of the solution were taken at intervals of 30 min over a 3 h period. The concentration of the samples was verified by measuring their absorption band at 616 nm, the  $\lambda_{\text{max}}$  of MG, using a UV–Vis spectrophotometer. The decolorization efficiency was calculated as follows:

$$\text{Decolorization\%} = \left( \frac{A_i - A_t}{A_i} \right) \times 100 \quad (1)$$

where  $A_i$  is initial absorbance of the MG and  $A_t$  is absorbance of the MG at any time interval after irradiation of the MG at 616 nm.

The COD test values were measured using a HACH DR4000 spectrometer and COD reactor. A Shimadzu TOC-VCPH spectrophotometer was used for TOC measurements in each experiment before and after a reaction time of 180 min for evaluation of the mineralization of MG dye.

## 3. Result and discussion

### 3.1. Characterization of the catalyst

#### 3.1.1. XRD

Fig. 1 illustrates the XRD pattern of HY zeolite and 5 wt% CuO/HY catalysts which were prepared under three different current densities: 10, 30, and 120 mA cm<sup>-2</sup>. No other diffraction peaks were observed except HY, indicating the absence of any structural damage to the catalysts [24]. The peak intensity of HY decreased as the current density increased, most probably due to the presence of copper oxide, which affects the morphology of the HY fingerprint. In fact, our previous study confirmed that the diffraction peaks at  $2\theta$  = 35.15° and 38.45°, which are shown in the inset, correspond to the peaks of copper oxide. Similar results showing that the peaks between  $2\theta$  = 35° and 39° correspond to the formation of copper oxide have also been reported in the literature [8,10].

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