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Preparation of Cuprous Oxide to Degrade 4,4-Isopropylidenediphenol by Photo Fenton-Like Process

Cheng-Chun He[1], Yi-Cian Chen[1], Chin-Min Cheng[2], Chao-Yin Kuo[1]*

[1] Institute of Safety Health and Environmental Engineering, National Yunlin University of Science and Technology, Yunlin 640, Taiwan

[2] Department of Civil and Environmental Engineering and Geodetic Science, 470 Hitchcock Hall, 2070 Neil Ave., Columbus, OH 43210, USA

ABSTRACT

Degradation of aqueous 4,4-isopropylidenediphenol by a photo Fenton-like process was investigated in this study using granular cuprous oxide (Cu_2O) as the photocatalyst. The granular Cu_2O, coated on glass beads, was prepared by a microwave-assisted thermoethanol method. Results from XRD analysis show the thermoethanol method successfully synthesized cuprous oxide. The UV-vis results demonstrate that the band gap energy of granular Cu_2O photocatalyst was narrower and imply the granular Cu_2O can be easily excited comparing to standard powder cuprous oxide. After considering operation cost, the optimal 4,4-isopropylidenediphenol degradation condition in this study was achieved when the system was exposed to 365 nm irradiation with light intensity of 2.79 mW/cm^2 and the presence of 30 mM hydrogen peroxide. The reaction rate constant reached $1.61x10^{-2}$ min^{-1} and a degradation efficiency of 82% was achieved after 90 minutes of reaction. The results demonstrate that the system can effectively degrade aqueous 4,4-isopropylidenediphenol.

Keywords: cuprous oxide; photocatalyst ; 4,4-isopropylidenediphenol; photo Fenton-like; degradation

1. INTRODUCTION

4,4-isopropylidenediphenol, also called Bisphenol A (BPA), is one of endocrine disrupting chemicals (EDCs). After entering human or animal body, EDCs are capable of altering hormonal homeostasis in the endocrine ecological system (Colborn et al., 1993; Vos et al., 2000) and causing long-term harmful effects on the development, growth, and reproduction, which are also called environment hormones (Sonnenschein and Soto, 1998). One of the major pathways for BPA to enter human or animal body is through oral exposure or ingestion. Surface water has been identified as the major compartment where BPA may be found (Cousins et al., 2002), and therefore, effective treatment processes to degrade BPA in water streams are needed. Among varieties of treatment approaches that have been tested by researchers, the photo-assisted degradation in a Photo-Fenton-like system with TiO_2, which produces oxidative free radicals (Martins et al., 2010), has been a proven technique that can effectively decompose BPA (Wang et al., 2006; Okada et al., 2003). However, this method is practically infeasible due to the small particle size of TiO_2 powder and limited

* *Corresponding to*: kuocy@yuntech.edu.tw

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operation condition. The approach is only effective when using ultra violet light. To promote the application potential, in this study, instead of using TiO_2 powder, cuprous oxide (Cu_2O) is assessed as an alternative photocatalyst to facilitate the photo Fenton-like degradation of BPA. Cu_2O is a p-type semiconductor material with the energy gap is between 1.9 ~ 2.2 eV (Yang et al., 2006; Chen et al., 2008; Mancier et al., 2008), which can be easily excited by visible light and good for photocatalytic degradation of pollutants (Jongh et al., 2009).

Several methods have been reported in Cu_2O preparation, including solvothermal treatment method (Wei et al., 2007), liquid phase chemical method (Huang et al., 2009; Wang et al., 2009), electrolysis method (Tang et al., 2008), radiation method (He et al., 2009), electrochemical method (Zhao et al., 2010), hydrothermal method (Zhang et al., 2008), and add a surface-active agent (Dong et al., 2010). This study used the solvothermal treatment method, which is advantageous because it is able to quickly supply energy to the whole material body, and therefore, effectively increase the material density (Zhang et al., 2010). The prepared Cu_2O was immobilized on glass beads and the removal efficiency of BPA by the photocatalytic process was evaluated under different photodegradation conditions (i.e., H_2O_2 concentration, Cu_2O dosage, and UV irradiation).

2. EXPERIMENTAL

Pretreatment of glass beads was first carried out to increase the surface roughness by mixing with SiO_2 powder in a 1 M NaOH solution. The slurry was then put into a furnace and calcined at 400˚C for 4 hours. The pretreated glass beads were then reacted with a solution containing 0.1 M copper acetate and 0.3 M glucose. The pH of the mixture was adjusted to pH=12 by 0.1 M NaOH. After reaction, the particulate portion of the slurry was separated by centrifugation at 3500 rpm and washed with 95% Ethanol. After separation, the particulate sample was heated in a microwave oven with 200W power output for 20 minutes and sequentially quenched in a freeze dryer (FD-T10, HC Company). The Cu_2O-coated glass beads were then obtained after being washed with deionized water repeatedly and dried in an oven for eight hours.

All photocatalytic experiments were carried out in a column system shown in Fig.1. Each tube was filled with 40 granule Cu_2O photocatalyst beads. In selected experiments, reaction was carried out without the presence of photocatalyst. Along with H_2O_2 solution with various concentrations, 10 mg/L BPA solution was induced into a series of reaction tubes by a peristaltic pump at a flow rate of 2.8cm^3/min. The decomposition of BPA was evaluated by placing the system in the dark and exposing to 365nm UV light. Each experiment was carried out for 90 minutes. Aliquots of the solution were taken out from the system periodically using sampling syringes. Each aliquot was filtered using a 0.22 um filter and analyzed for BPA by high performance liquid chromatography (Aglient HPLC 1200, column XDB-C18, detector VMD) with an UV detector at the maximum peak of adsorption at197 nm. The eluent was prepared from 60% (v/v) acetonitrile and 40% water.

The XRD analysis of Cu_2O powder was performed by a Brukeraxs D8-Advanced X-ray diffractometer with a scanning range from 20^o-80^o. The ultravioletevisible diffuse reflection spectra were recorded by an UV-vis spectrometer (MODEL V-670, Jasco, UK) equipped with an integrating sphere accessory in the diffuse reflectance mode. $BaSO_4$ was used as the reference material.

3. RESULT AND DISCUSSION

Fig. 2 shows the diffractogram of the prepared Cu_2O. The UV-Vis spectra of standard and powder Cu_2O are shown in Fig. 3. The band gap of the Cu_2O samples was obtained according to the absorption onset. The results show that the optical band gaps of Cu_2O particles shift towards lower energy suggesting the granule cuprous oxide photocatalyst can also be easily excited as commercially available cuprous oxide.

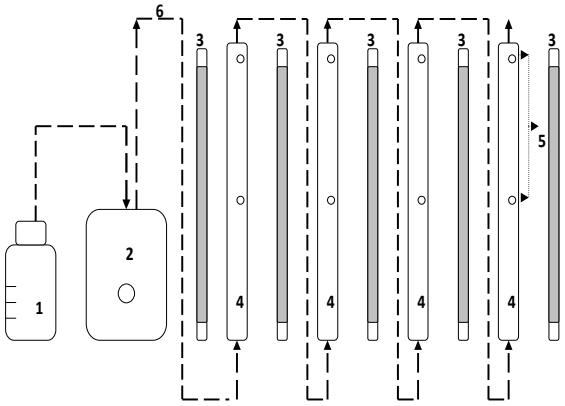

Figure 1 Photocatalytic system (1.tank for BPA soultion 2.pump 3.UV light 4.reactional column system 5.sampling part 6. pipeline)

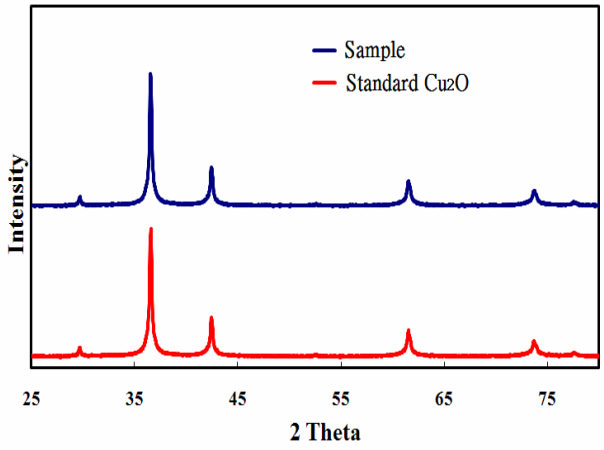

Figure 2 XRD patterns of standard Cu_2O and sample

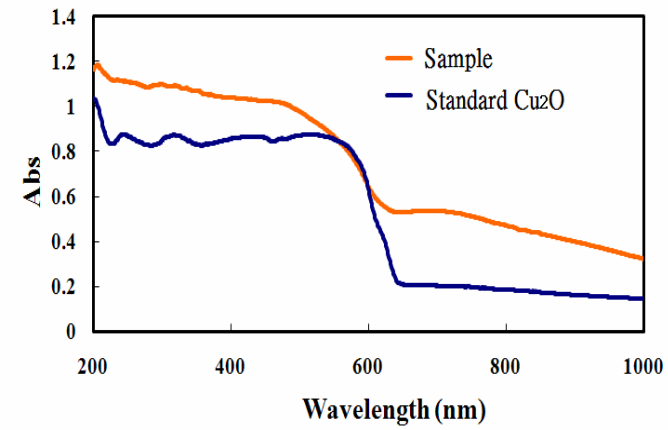

Figure 3 UV-vis spectrum of standard Cu_2O and sample

Fig. 4 demonstrates the photocatalytic activity of fixed Cu_2O particles while reacting with BPA solution. In the absence of H_2O_2, the decomposition efficiency of BPA is only 6% in the dark and 9% under UV light irradiation. The decomposition of BPA was enhanced when H_2O_2 was induced into the system. In the absence of Cu_2O particles, 45% of BPA was degraded after reacting with 50 mL H_2O_2 in the dark for 90 minutes (Fig. 5), which was increased to 74% when exposing the system to UV irradiation (Fig. 6). The results shown in Figs.4 and 5 imply the degradation of BPA requires strong oxidative free radicals produced from H_2O_2. When the system was operated with 50 mM H_2O_2 and Cu_2O photocatalyst, the degradation efficiency of BPA was 81% without UV irradiation after 90 minutes (Fig. 7). It was indicated to compare only H_2O_2, the combination of Cu_2O and H_2O_2 produced more free radicals available for BPA decomposition, and therefore, achieved a higher BPA degradation rate. However, as shown in the figure, the Fenton-like process did not decompose BPA completely. By carrying out the BPA degradation under a photo Fenton-like process using different dose of H_2O_2 with UV-light and Cu_2O photocatalyst, the degradation efficiency reach a plateau of 82% in the combination of UV-light, Cu_2O and 50 nm of H_2O_2 for BPA decomposition was higher than the combination of Cu_2O and 50 nm of H_2O_2 (Fig. 8). Because H_2O_2 needed to react in the system, it decreased form initial concentration of 50 mM to final concentration of 29 mM in experiment.

The assessment of Fenton–like and photo Fenton-like decomposition of BPA was assisted by the Langmuir-Hinshleood model (Tang and An, 1995). As shown in Table 1, the regression results indicate that the degradation of BPA using a Fenton–like or photo Fenton-like process in the presence more than 30 mM hydrogen peroxide fit the Langmuir-Hinshleood model. After considering the operation cost, the optimal 4,4- isopropylidenediphenol degradation condition in this study was achieved when the reaction rate constant of a photo Fenton-like process reached $1.61x10^{-2}$ min^{-1} and a degradation efficiency of 82% was achieved in 90 minutes of reaction.

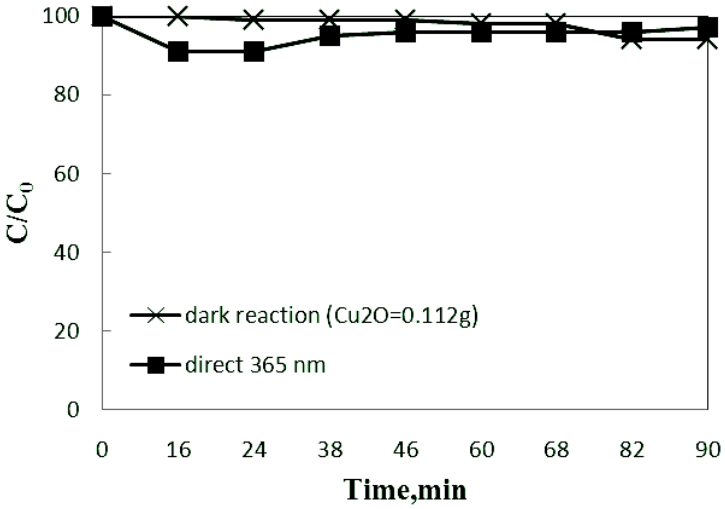

Figure 4 Experimental results of dark and direct light (C_0=10 mg/L、T=25±2 flowrate=2.8cm^3/min)

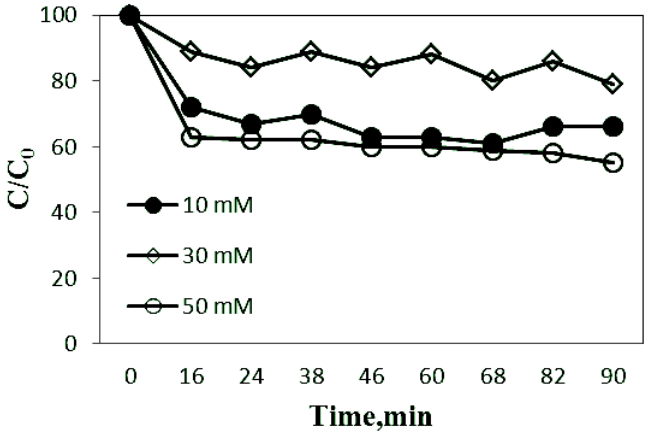

Figure 5 Residue of BPA reacting with various H_2O_2 (C_0=10 mg/L、T=25±2˚C, flowrate=2.8 cm^3/min)

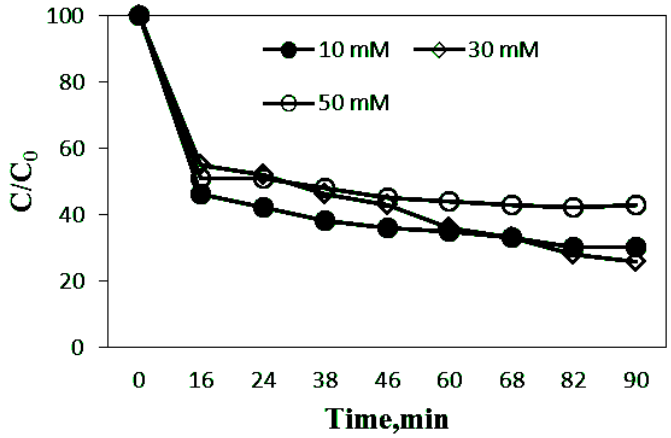

Figure 6 Residue of BPA under UV365 nm irradiation and various H_2O_2 (C_0=10 mg/L、T=25±2˚C, flowrate=2.8 cm^3/min, light=2.79 mW/cm^2)

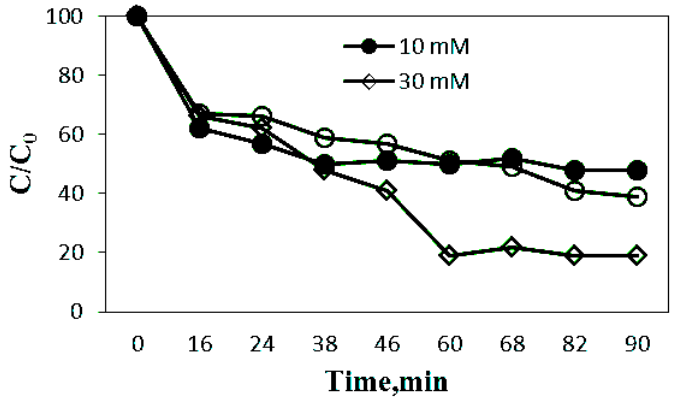

Figure 7 Residue of BPA using a Fenton-like process at various H_2O_2(C_0=10 mg/L, T=25±2˚C, flowrate=2.8 cm^3/min、Cu_2O=0.112 g)

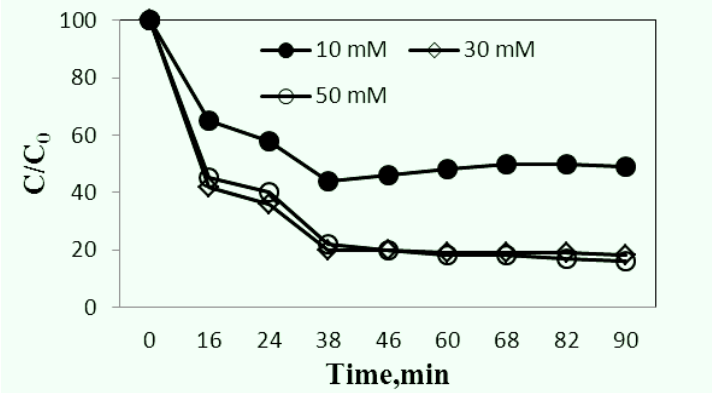

Figure 8 Residue of BPA using a photo Fenton-like process at various H_2O_2 (C_0=10 mg/L、T=25±2˚C, flowrate=2.8 cm^3/min, light=2.79 mW/cm^2, Cu_2O=0.112 g)

Table 1 Fenton-like and 365 nm reaction rate constant

	Fenton-like		**Photo Fenton-like**	
	k x 10^{-2}	R^2	k x 10^{-2}	R^2
10 mM	0.6	0.616	0.6	0.506
30 mM	2.01	0.93	1.61	0.715
50 mM	0.9	0.934	1.82	0.815

CONCLUSIONS

XRD results showed the glass bead-fixed catalyst prepared in this study was cuprous oxide. The band gap energy of this granule cuprous oxide photocatalyst is easier to be excited as standard cuprous oxide. Results obtained from this study suggest the optimal condition for 4,4-isopropylidenediphenol degradation was when the system was irradiated under 365 nm light with an intensity of 2.79 mW/cm^2 and 30 mM hydrogen peroxide82% of degradation efficiency was achieved in 90 minutes with a reaction rate constant of 1.61x10^{-2} min^{-1}.

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