Preparation of immobilized Cu$_2$O using microwave irradiation and its catalytic activity for bisphenol A: comparisons of Cu$_2$O/H$_2$O$_2$ and visible-light/Cu$_2$O/H$_2$O$_2$ systems

C. Y. Kuo, C. H. Wu, J. T. Wu and Y. C. Chen

ABSTRACT

This study produced immobilized Cu$_2$O via microwave irradiation. The surface properties of Cu$_2$O were assessed by X-ray diffraction, scanning electron microscopy, and UV–vis spectroscopy. The catalytic activity of the generated Cu$_2$O was examined for bisphenol (BPA) degradation in Cu$_2$O/H$_2$O$_2$ and visible-light/Cu$_2$O/H$_2$O$_2$ systems under various H$_2$O$_2$ concentrations. Cu$_2$O can decompose H$_2$O$_2$ to generate radicals, similar to the Fenton-like process. The BPA degradation rate followed pseudo-first-order kinetics. The optimal H$_2$O$_2$ concentration was 30 mM and the BPA degradation rate under 30 mM H$_2$O$_2$ in the Cu$_2$O/H$_2$O$_2$ and visible-light/Cu$_2$O/H$_2$O$_2$ systems was 1.43 and 2.69 h$^{-1}$, respectively. The original Cu$_2$O partly oxidized into CuO in the visible-light/Cu$_2$O/H$_2$O$_2$ system and the BPA degradation percentage declined to 51% from 100% after the fifth cycle.

Key words | bisphenol A, Cu$_2$O, H$_2$O$_2$, visible-light, Fenton-like, photo-Fenton-like

INTRODUCTION

A large amount of bisphenol A (BPA) is manufactured and used as a monomer for the production of polycarbonate and epoxy resins. As an environmental disrupter, extensive use of BPA has attracted considerable attention from scientists and environmentalists. The removal of BPA from wastewater is regarded as essential for environmental protection. Thus, a rapid and simple treatment for BPA is required urgently.

Advanced oxidation processes (AOPs) are effective in degrading and reducing recalcitrant wastewater loads from industrial processes. Several studies have developed different AOPs to treat BPA, such as visible-light/TiO$_2$ (Kuo et al. 2010; Wu et al. 2013); visible-light/N-TiO$_2$ (Wu et al. 2013); ultraviolet (UV)/Cu$_2$O/TiO$_2$/zeolite (Kuo et al. 2014); Fe$^{2+}$/H$_2$O$_2$ (Loan et al. 2007); UV/Fe$^{2+}$/H$_2$O$_2$ (Katsumata et al. 2004); UV/Fe$^{3+}$/H$_2$O$_2$ (Molkenthin et al. 2015); Cu$_2$O/H$_2$O$_2$ (Zhang et al. 2014); Fe$_3$O$_4$/H$_2$O$_2$ (Zhang et al. 2014) and CuFeO$_2$/H$_2$O$_2$ (Zhang et al. 2014). Among these AOPs, the Fenton and Fenton-like processes yielded very good treatment results. Moreover, UV irradiation can decompose H$_2$O$_2$, generating radicals and promoting the degradation of BPA in Fenton and Fenton-like reactions.

Cuprous oxide, an important metal oxide p-type semiconductor, has a direct small band gap of 1.9–2.0 eV. The major attraction of Cu$_2$O is its low toxicity, low cost and good environmental acceptability (Huang et al. 2009). Although Cu$_2$O can utilize visible light, the photocatalytic activity of pure Cu$_2$O is very low because of the rapid recombination of photogenerated electrons and holes or because it is easily oxidized. In addition, most iron-oxide Fenton-like catalysts are used as nanoparticles, which are difficult to separate for recycling. This study attempts to solve the problems of Cu$_2$O and suspended Fenton-like systems. No study has degraded BPA using immobilized Cu$_2$O/H$_2$O$_2$ and visible-light/immobilized Cu$_2$O/H$_2$O$_2$ systems. This study synthesized Cu$_2$O using the microwave/glucose method and immobilized Cu$_2$O on glass balls to form fixed beds. The study objectives were to: (i) compare the BPA degradation efficiency of Cu$_2$O/H$_2$O$_2$ and visible-light/Cu$_2$O/H$_2$O$_2$ systems; (ii) determine the effects of the H$_2$O$_2$ dose in Cu$_2$O/H$_2$O$_2$ and visible-light/Cu$_2$O/H$_2$O$_2$ systems; and (iii) evaluate the stability and reusability of the visible-light/Cu$_2$O/H$_2$O$_2$ system.

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MATERIALS AND METHODS

Materials

BPA, the parent compound, was obtained from Sigma-Aldrich (St. Louis, Missouri, USA). Copper acetate was the precursor of Cu2O. Glucose was the reducing agent when preparing the Cu2O. Solution pH was adjusted using 0.1 M HNO3 and 0.1 M NaOH. Except for BPA, all chemicals were purchased from Katayama (Osaka, Japan). All solutions were prepared using deionized water (Milli-Q, Darmstadt, Germany) and reagent-grade chemicals.

Experimental methods

Glass balls (Horng-Li Chemical Co., Yunlin, Taiwan) (5 mm in diameter) were etched for 5 h at 400 °C to generate a rugged surface on 1 M NaOH. After the pH of copper acetate (0.1 M, 500 mL) was increased to 12 using 1 M NaOH, Cu(OH)2 formed. Glucose (0.3 M, 60 mL) was completely mixed with the generated precipitates and etched glass balls. The mixture was then irradiated in a 200 W microwave oven (Chang-Chia Co., Taipei, Taiwan) for 20 min. The resulting products were then frozen in a vacuum dryer (Chang-Chia Co., Taipei, Taiwan) for 8 h to produce immobilized Cu2O balls.

The initial characterization of Cu2O was performed when it was not immobilized on glass beads. The crystallinity of Cu2O was analyzed by X-ray diffraction (XRD) using CuKα radiation (Rigaku-TTRAX III, Tokyo, Japan). Accelerating voltage and applied current were 40 kV and 30 mA, respectively. The XRD patterns were recorded as 2θ values at 20 – 80°. The UV–vis spectroscopy (Jasco V-670, Jasco, Tokyo, Japan) technique was applied to profile the absorbance spectrum of Cu2O at wavelengths of 200–800 nm. The UV–vis diffuse reflectance spectra were applied to derive Cu2O band gap energy. The size and morphology of generated Cu2O were characterized using scanning electron microscopy (SEM) (JEOL 6330 TF, JEOL, Tokyo, Japan). The BPA concentration was measured using high-performance liquid chromatography (HPLC) and a UV detector (1200 Series, Agilent Technologies, Santa Clara, California, USA). The UV detector was set to a wavelength of 197 nm. Separations were performed using a Supelcosil C18 column (Supelco, Sigma-Aldrich, St. Louis, Missouri, USA). The mobile phase was Milli-Q water and CH3CN (40:60 v/v) at a flow rate of 0.5 mL/min. Injection volume was 20 µL. An inductively coupled plasma-optical emission spectrometer (ICP-OES, Optima 2100DV, Perkin-Elmer Inc., Waltham, Massachusetts, USA) measured the concentration of released copper ions in effluent.

The column photo-reactor was same as that used by Kuo et al. (2010) and Wu et al. (2013). The initial BPA concentration was 10 mg/L and the total Cu2O dose in the column photo-reactor was 0.112 g. The effects of H2O2 dosage were investigated using doses of 20, 30, and 50 mM. The initial solution pH was 6 in all experiments. The BPA solution flow rate was 2.8 mL/min. The column photo-reactor was irradiated with 410 nm (8 W, 13.44 mW/cm2) visible light (Sunblaster, T5/FH, USA) at room temperature. Samples were separated by filtration through a 0.22 µm filter (Millipore) and the concentration of each sample was measured by HPLC. All BPA degradation experiments were performed in triplicate and average values were presented.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of Cu2O. The Cu2O peaks were at 29.6°, 36.5°, 42.4°, 61.5°, 73.7°, and 77.6° (JCPDS no. 65–3288). The CuO crystal phases corresponded to peaks at 32.5°, 35.5°, 35.6°, 38.7°, 48.8°, 61.6°, 66.2°, and 68.1° (JCPDS no. 05–0661). The powder produced by microwave irradiation and frozen vacuum drying was Cu2O, and no CuO or noise peak was obtained in this study.

The band gap (Eg) of Cu2O was calculated using the formula

\[ E_g = \frac{1240}{\lambda_g} \]

where \( \lambda_g \) is the wavelength for the intersection point of the vertical and horizontal sections of the spectra (Shao & Ma 2012). The threshold peak of Cu2O was at 653 nm, correlating with a band gap of 1.9 eV (figure not shown). The obtained band gap was similar to that acquired by Huang et al. (2009). Compared to TiO2,
Cu$_2$O can use visible-light instead of UV light to catalyze BPA degradation.

Figure 2 displays the SEM image of Cu$_2$O. The prepared Cu$_2$O consisted mainly of sphere-like microparticles with a strong tendency to agglomerate. The surface of Cu$_2$O looked rough, suggesting that the microparticles were composed of small sheets. The aggregates in Cu$_2$O were approximately 0.5–1.5 µm in size. Huang et al. (2013) indicated that Cu$_2$O microparticles have a higher photocatalytic activity than Cu$_2$O nanoparticles because of the slower photo-corrosion rate of Cu$_2$O microparticles. This study produced Cu$_2$O microparticles that may have good photocatalytic activity. The photocatalytic activity, reusability, and stability of the Cu$_2$O microparticles were then evaluated.

After a 60 min reaction, the BPA removal percentage by Cu$_2$O adsorption and visible-light direct photolysis was 2% and 3%, respectively. The BPA was not removed by Cu$_2$O adsorption and photolysis. Figures 3(a) and 3(b) show the effects of H$_2$O$_2$ concentration on the degradation of BPA in Cu$_2$O/H$_2$O$_2$ and visible-light/Cu$_2$O/H$_2$O$_2$ systems, respectively. After a 60 min reaction, the BPA degradation percentage with the doses of 20, 30 and 50 mM H$_2$O$_2$ in the Cu$_2$O/H$_2$O$_2$ system was 72%, 78% and 49%, respectively, and that in the visible-light/Cu$_2$O/H$_2$O$_2$ system with these H$_2$O$_2$ doses was 88%, 100% and 75%, respectively. BPA degradation approximately followed pseudo-first-order kinetics, as expressed as $\ln(C_t/C_0) = -kt$, where $t$ is reaction time, $k$ is the pseudo-first-order rate constant, and $C_0$ and $C_t$ are BPA concentrations at time of $t = 0$ and $t = t$, respectively. Figures 4(a) and 4(b) plot the regressions of pseudo-first-order kinetics for Cu$_2$O/H$_2$O$_2$ and visible-light/Cu$_2$O/H$_2$O$_2$ systems, respectively. Table 1 summarizes the pseudo-first-order reaction rate constants and correlation coefficients of the Cu$_2$O/H$_2$O$_2$ and visible-light/Cu$_2$O/H$_2$O$_2$ systems. The BPA degradation rate satisfies pseudo-first-order kinetics, and various studies have demonstrated that BPA degradation rates can be approximated using pseudo-first-order kinetics (Kuo et al. 2010, 2014; Wu et al. 2013; Zhang et al. 2014). The $k$ values for BPA degradation first increased after adding 20–30 mM H$_2$O$_2$ and then decreased after adding 30–50 mM H$_2$O$_2$. In the Cu$_2$O/H$_2$O$_2$ and visible-light/Cu$_2$O/H$_2$O$_2$ systems, the 30 mM H$_2$O$_2$ doses generated the highest BPA degradation rate; moreover, the $k$ value in the visible-light/Cu$_2$O/H$_2$O$_2$ system was larger than that in the Cu$_2$O/H$_2$O$_2$ system.

The H$_2$O$_2$/Fe$^{2+}$ system is comprised of several cyclical reactions with catalyst regeneration (Kusic et al. 2009; Gricic et al. 2010). Copper, similar to iron, acts as a catalyst in H$_2$O$_2$ decomposition (Equations (1) and (2)) (Sigel et al. 1979; Brillas et al. 2004; Zhang et al. 2014). This study proposed that the cyclical reactions in the Cu$_2$O/H$_2$O$_2$ system were similar to those in the H$_2$O$_2$/Fe$^{2+}$ system, as shown in Equations (1)–(7). The hydroxyl radicals can oxidize Cu$^{+}$ to
form Cu\textsuperscript{2+} \textsuperscript{1} Equation (3) or, in the presence of excess H\textsubscript{2}O\textsubscript{2}, be consumed by another H\textsubscript{2}O\textsubscript{2} molecule to produce hydro-dioxyl radicals Equation (6). The oxidation potentials of hydrodioxyl radicals are much lower than those of hydroxyl radicals Patel & Willson \textsuperscript{1} ; hence, the BPA degradation rate decreased at H\textsubscript{2}O\textsubscript{2} concentrations above 30 mM. Several studies have demonstrated that the degradation rate of organic compounds increases as the H\textsubscript{2}O\textsubscript{2} concentration increases to a threshold, beyond which degradation efficiency declines as H\textsubscript{2}O\textsubscript{2} increasingly scavenges hydroxyl radicals Yu \textit{et al.} \textsuperscript{1} ; Wu & Wu \textsuperscript{1} ; Kuo \textit{et al.} \textsuperscript{1}.

\begin{align*}
\text{Cu}^+ + \text{H}_2\text{O} &\rightarrow \text{Cu}^{2+} + \text{OH}^- + \text{HO}^* \quad (1) \\
\text{Cu}^{2+} + \text{H}_2\text{O} &\rightarrow \text{Cu}^+ + \text{H}^+ + \text{HO}_2^* \quad (2) \\
\text{Cu}^+ + \text{HO}^* &\rightarrow \text{Cu}^{2+} + \text{OH}^- \quad (3) \\
\text{Cu}^+ + \text{HO}_2^* &\rightarrow \text{Cu}^{2+} + \text{HO}_2^- \quad (4) \\
\text{Cu}^{2+} + \text{HO}_2^* &\rightarrow \text{Cu}^+ + \text{H}^+ + \text{O}_2 \\n\text{HO}^* + \text{H}_2\text{O} &\rightarrow \text{HO}_2^- + \text{H}_2\text{O} \\
\text{Cu}_2\text{O} + \text{visible-light} &\rightarrow \text{Cu}_2\text{O} (\text{e}_{\text{CB}}^- + \text{h}_{\text{VB}}^+) \quad (8) \\
\text{Cu}_2\text{O}(\text{hv}_{\text{VB}}^-) + \text{H}_2\text{O} &\rightarrow \text{Cu}_2\text{O} + \text{H}^+ + \text{HO}^* \quad (9) \\
\text{Cu}_2\text{O}(\text{hv}_{\text{VB}}^-) + \text{OH}^- &\rightarrow \text{Cu}_2\text{O} + \text{HO}^* \\
\text{Cu}_2\text{O}(\text{e}_{\text{CB}}^-) + \text{O}_2 &\rightarrow \text{Cu}_2\text{O} + \text{O}_2^* \\
\text{O}_2^* + \text{H}^+ &\rightarrow \text{HO}_2^* \\
2\text{HO}^* &\rightarrow \text{H}_2\text{O}_2 \quad (7)
\end{align*}

This study assumed the reaction mechanisms in the visible-light/Cu\textsubscript{2}O system are the same as those identified by Konstantinou & Albanis \textsuperscript{1} , who summarized the degradation of organics in the UV/TiO\textsubscript{2} system as follows (Equations (8)–(12)):
BPA degradation rate in the visible-light/Cu2O/H2O2 system was improved. Experimental results suggest that hydroxyl radicals, superoxide radical anions, hydrodioxyl radicals, and photogenerated holes are the oxidizing species in the visible-light/Cu2O/H2O2 system. Moreover, hydroxyl and hydrodioxyl radicals are the oxidizing species in the Cu2O/H2O2 system. Zhang et al. (2014) indicated that hydroxyl radicals were the main active species in the Cu2O/H2O2 system responsible for BPA degradation:

\[
\text{H}_2\text{O}_2 + \text{hv} (< 310 \text{ nm}) \rightarrow 2\text{HO}^* \tag{13}
\]

\[
\text{H}_2\text{O}_2 + \text{Cu}_{2}\text{O} (\text{e}_{\text{CB}}) \rightarrow \text{OH}^- + \text{HO}^* \tag{14}
\]

The BPA degradation percentage of the visible-light/Cu2O/H2O2 system in runs 1, 2, 3, 4, and 5 was 100%, 63%, 53%, 51%, and 51%, respectively, and the released copper concentration in effluent was 19, 1.8, 0.9, 0.3, and 0.2 mg/L, respectively. The BPA degradation efficiency increased as the released copper concentration increased in the visible-light/Cu2O/H2O2 system. The BPA degradation percentage of the visible-light/TiO2 system in runs 1, 2, 3, 4, and 5 was 60%, 58%, 50%, 42% and 39%, respectively (Wu et al. 2013). The reusability for BPA degradation of the visible-light/Cu2O/H2O2 system exceeded that of the visible-light/TiO2 system. Furthermore, the k value in the visible-light/Cu2O/H2O2 system (1.93 h⁻¹) was greater than that in the visible-light/TiO2 system (0.90 h⁻¹). Zhang et al. (2014) also investigated how the BPA degradation by Cu2O particles was obviously decreased with increasing the run number. To study Cu2O change in the visible-light/Cu2O/H2O2 system, Cu2O immobilized balls were collected for XRD analysis after the reaction. Comparing the Cu2O in the visible-light/Cu2O/H2O2 system with the original Cu2O indicates that the XRD patterns of the reacted Cu2O in the visible-light/Cu2O/H2O2 system had two new peaks at 35.5° and 38.7°, corresponding to CuO (Figure 1). Moreover, the surface color of the immobilized Cu2O balls changed from red to black after reaction (picture not shown). Clearly, some Cu2O was oxidized to CuO. Yang et al. (2006) and Huang et al. (2009) also indicated that Cu2O is oxidized to CuO after photocatalysis. With 20 mM H2O2 in the suspended Cu2O/H2O2 system, the BPA degradation rate was 0.50 h⁻¹ (Zhang et al. 2014), lower than that of the immobilized Cu2O/H2O2 system (0.62 h⁻¹). Experimental data suggest that the immobilized Cu2O system could decrease the Cu2O oxidation rate; hence, the BPA degradation rate in the immobilized Cu2O/H2O2 system exceeded that in the suspended Cu2O/H2O2 system. Notably, CuO is a semiconductor with a narrow band gap of about 1.4 eV, and although it can absorb visible-light, its photocatalytic efficiency is poor due to the excessive recombination of photoexcited electrons and holes when compared with Cu2O (Huang et al. 2009). The number of active sites on the surface of Cu2O decreased due to the oxidation of Cu2O to CuO. Accordingly, the BPA degradation efficiency decreased as the number of repeats increased in the visible-light/Cu2O/H2O2 system. However, the reusability and stability of the immobilized Cu2O/H2O2 system was better than that of the suspended Cu2O/H2O2 system.

**CONCLUSIONS**

This investigation successfully synthesized immobilized Cu2O onto glass balls by microwave irradiation. The immobilized Cu2O acted as a catalyst for the decomposition of H2O2 to degrade BPA. Experimental data suggest that hydroxyl radicals, superoxide radical anions, hydrodioxyl radicals, and photogenerated holes formed in the visible-light/Cu2O/H2O2 system; moreover, hydroxyl and hydrodioxyl radicals were generated in the Cu2O/H2O2 system. The BPA degradation rate of the visible-light/Cu2O/H2O2 system exceeded that of the Cu2O/H2O2 system. In addition, BPA degradation efficiency and reusability of the visible-light/Cu2O/H2O2 system was better than that reported for the visible-light/TiO2 system.

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**REFERENCES**


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