



## Full Length Article

# Sulfate radical degradation of acetaminophen by novel iron–copper bimetallic oxidation catalyzed by persulfate: Mechanism and degradation pathways



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## ABSTRACT

A novel iron coupled copper oxidate ( $\text{Fe}_2\text{O}_3@\text{Cu}_2\text{O}$ ) catalyst was synthesized to activate persulfate (PS) for acetaminophen (APAP) degradation. The catalysts were characterized via field-emission scanning electron microscopy and energy-dispersive X-ray spectrometry. The effects of the catalyst, PS concentration, catalyst dosage, initial pH, dissolved oxygen were analyzed for treatment optimization. Results indicated that  $\text{Fe}_2\text{O}_3@\text{Cu}_2\text{O}$  achieved higher efficiency in APAP degradation than  $\text{Fe}_2\text{O}_3/\text{PS}$  and  $\text{Cu}_2\text{O}/\text{PS}$  systems. The optimal removal efficiency of APAP (90%) was achieved within 40 min with 0.6 g/L PS and 0.3 g/L catalyst. To clarify the mechanism for APAP degradation, intermediates were analyzed with gas chromatography–mass spectrometry. Three possible degradation pathways were identified. During reaction, Cu(I) was found to react with Fe(III) to generate Fe(II), which is the most active phase for PS activation. Through the use of methanol and *tert*-butyl alcohol (TBA) as radical trappers,  $\text{SO}_4^{\bullet-}$  was identified as the main radical species that is generated during oxidation.

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## 1. Introduction

Advanced oxidation processes, such as ozone [1], UV [2], photocatalytic [3], Fenton [4] and Fenton-like [5] oxidation, are important techniques for the removal of organic pollutants. In these techniques, most of the contaminants are destroyed with the generation of free radicals [6]. However, the applications of these techniques are limited by their harsh reaction conditions [7,8] (i.e., pH value is approximately 3) and high cost [9]. Thus, developing a cost-effective method is of significance for industrial and sustainable development.

Persulfate (PS) oxidation has gained popularity as an advanced oxidation process because of its stability [10] and relatively mild reaction conditions [11]. During reaction, PS can be activated by heat [12], UV radiation [13], metal ions [14], metal oxides [15], and bases [16].  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{HO}$ , which have standard redox potentials [ $E_0$ ] of 2.6 and 2.8, respectively, are subsequently generated as efficient radicals [17,18].

Transition metals, such as Co [19],  $\text{Fe}^{2+}$  [14],  $\text{Fe}^0$  [20],  $\text{Fe}_3\text{O}_4$  [21], and Cu [22], have been used as catalysts to activate PS. However, the stability of traditional transition metals is unsatisfactory.

Although Cu is considerably more stable than iron, it has low activity for PS activation. Liang et al. [22] used CuO to activate PS in *p*-chloroaniline degradation but found that the reaction time was excessively long. Their results suggested that the catalytic activity of CuO for PS is lower than that of iron oxidate.

Thus, novel materials should be developed to improve the stability of iron and activity of Cu.  $\text{CuFe}_2\text{O}_4$  [23] was recently used as an activator in a peroxymonosulfate (PMS) system for the removal of tetrabromobisphenol A. Feng et al. [24] synthesized  $\text{CuFeO}_2$  to activate PMS in sulfadiazine removal. In their experiments, simply mixing  $\text{Fe}_2\text{O}_3$  and  $\text{Cu}_2\text{O}$  efficiently removed sulfadiazine. They consequently suggested that Fe(III) is reduced to Fe(II) by Cu(I), and that the Cu(III) produced in the process also plays a role in oxidation. Despite the high efficiency of PMS activation, Guan et al. [25] indicated that only PMS can be activated by  $\text{CuFe}_2\text{O}_4$ . Compared with PMS activation, PS activation achieves relatively high efficiency because of the symmetric structures of the S=O bond and the simultaneous generation of two  $\text{SO}_4^{\bullet-}$  radicals [26].

Given that PS activation by Cu remains to be clarified, a novel catalyst was synthesized and used to activate PS in the degradation of acetaminophen (APAP), an extensively used analgesic. The catalyst was expected to be efficient in the catalytic activation of PS at room temperature. Moreover, the effects of PS concentration, catalyst dosage, initial pH and dissolved oxygen on APAP degradation and the mechanism for the PS activation were investigated;

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the main radical species was identified; and possible pathways for APAP degradation were proposed.

## 2. Materials and methods

### 2.1. Materials

APAP (CAS NO. 614-80-2, 99% purity) was purchased from Aladdin Reagent (Shanghai, China). Analytical-grade PS, cupric nitrate, ferrous sulfate, methanol, ethanol, ethylene glycol, and *tert*-butyl alcohol (TBA) were procured from Xilong Chemical Co., Ltd. Urea, potassium iodide, sodium bicarbonate, sulfuric acid, and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co., Ltd. The methanol used as the mobile phase in high-performance liquid chromatography (HPLC) was HPLC grade and obtained from Merck (Darmstadt, Germany).

### 2.2. Preparation of flower-like Fe<sub>2</sub>O<sub>3</sub>

The precursor FeOOH was prepared by forced hydrolysis under oil-bath reflux conditions [27]. Fe solution was first prepared by mixing 5.56 g of FeSO<sub>4</sub>·7H<sub>2</sub>O with 40 mL of ethanol and 160 mL of water under continuous stirring. Then, 1.5 g of urea was added into the mixed solution to provide amino groups. The resultant homogeneous solution was transferred to a three-necked bottle and refluxed at 90 °C for 6 h in an oil bath under continuous stirring. The products were obtained via centrifugation and then dried at 70 °C for 12 h. Finally, the products were heated in air at 400 °C for 3 h to obtain flower-like Fe<sub>2</sub>O<sub>3</sub>.

### 2.3. Preparation of Fe<sub>2</sub>O<sub>3</sub>@Cu<sub>2</sub>O and Cu<sub>2</sub>O

Fe<sub>2</sub>O<sub>3</sub>@Cu<sub>2</sub>O and Cu<sub>2</sub>O were prepared via polyol method. First, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.2416 g) was mixed with 8.5 mL of ethanol and 17 mL of ethylene glycol after 20 min of stirring. Then, pre-prepared Fe<sub>2</sub>O<sub>3</sub> (25 mg) was introduced into the mixture. The mixture was subjected to ultrasound for 30 min to ensure the complete dispersion of Fe<sub>2</sub>O<sub>3</sub>. The mixed solution was transferred into a 150-mL Teflon-lined autoclave and heated at 160 °C for 5 h. The final Fe<sub>2</sub>O<sub>3</sub>@Cu<sub>2</sub>O was obtained by centrifugation and then dried in vacuum at 60 °C for 24 h. Cu<sub>2</sub>O was prepared by the same method without the addition of Fe<sub>2</sub>O<sub>3</sub>.

### 2.4. Analysis

The surface morphology and chemical composition of Fe<sub>2</sub>O<sub>3</sub>@Cu<sub>2</sub>O were analyzed using a Hitachi field-emission scanning electron microscopy (FESEM) operated at an acceleration voltage of 3 kV and equipped with an Oxford Energy 7021 energy-dispersive X-ray spectrometer (EDS). Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Nicolet iS50 spectrometer (Thermo Scientific).

pH values were measured using a Sartorius pH meter. The APAP concentration of the aqueous phase was quantified using a Waters ACQUITY HPLC system (Waters) equipped with 2998 PDA detector set to 242 nm. Waters XBridge (46 mm × 15 mm, 5 μm) was used as the HPLC column. The mobile phase was a mixture of water and methanol at a volumetric ratio of 85:15.

PS anion was analyzed by iodide spectrophotometric determination at 352 nm [28] with a UV-vis spectrophotometer (TU-1900, Persee). Metal ions (Cu and Fe) were analyzed by Atomic absorption spectrometry (AA-7002A, EWA). Intermediate analysis and identification were conducted using a gas chromatography-mass spectrometry system (GC-MS, Agilent Technologies, 6890 GC system/5975b inert MSD) with a flame ionization detector in accordance with the procedure followed by Zhang et al. [29].

Aliquots (2 μL) of samples were injected into the GC-MS system for chemical structural elucidation. An HP-5 column (30 m × 0.25 mm × 0.25 μm, Agilent) was used for separation. The inlet temperature was 250 °C, and the detector temperature was 325 °C. The column temperature was fixed at 80 °C for 1 min and then programmed to 150 °C at 7 °C/min and held for 5 min and to 200 °C at the same rate. The final temperature was maintained for 5 min. The flow rate of the carrier gas (helium) was 1.0 mL/min. The temperatures of the transfer line, ion source, and MS detector were 170 °C, 230 °C, and 150 °C, respectively. The MS detector was operated in EI mode at 70 eV. The mass spectra were acquired in the full-scan mode with *m/z* from 40 to 600.

### 2.5. Experiment

Fe<sub>2</sub>O<sub>3</sub>@Cu<sub>2</sub>O-catalyzed PS oxidation was performed in 250-mL batch reactors at 25.0 ± 1 °C. The initial/unadjusted pH of the solution was approximately 6.5 with 100 mg/L APAP. During the reaction, a certain amount of Fe<sub>2</sub>O<sub>3</sub>@Cu<sub>2</sub>O was loaded into 100 mL of APAP solution to trigger oxidation. At designated sampling intervals, 1 mL of aqueous sample was taken and quenched with 1 mL of methanol. All the samples were filtered through 0.22-μm filter before HPLC analysis.

In addition, two series of quenching tests were conducted using either methanol or TBA as the radical scavenger to determine the role of radical species formed in the catalytic system. All experiments were conducted in triplicate and the results were averaged.

## 3. Results and discussion

### 3.1. Characterization of catalysts

The surface morphologies and chemical components of the catalysts were analyzed by FESEM, FTIR, and EDS. The SEM images presented in Fig. 1(a) and (b) clearly shows the uniform flower-like acicular morphology of Fe<sub>2</sub>O<sub>3</sub>. The size of Fe<sub>2</sub>O<sub>3</sub> ranged from 2.0 to 2.5 μm. The space between the acicular crystals provided a large surface area for the adhesion of Cu<sub>2</sub>O. Fig. 1(c) and (d) shows the FESEM images of the Fe<sub>2</sub>O<sub>3</sub>@Cu<sub>2</sub>O composites. Moreover, Cu<sub>2</sub>O covered not only the surfaces of Fe<sub>2</sub>O<sub>3</sub> but also the interior of the acicular crystals. As a result, the composites presented a spherical morphology. In addition, EDS analysis (Fig. 2 and Table 1) suggested that the atomic fraction of Fe was 36.8% and that of O was 63.21%. After Cu was loaded on Fe<sub>2</sub>O<sub>3</sub>, the atomic fraction of Cu was 28.6%, and those of Fe and O decreased to 11.37% and 60.3%, respectively. These results showed that Cu was successfully loaded on Fe and covered the surface of Fe<sub>2</sub>O<sub>3</sub>, thus decreasing the atomic fraction of Fe. The mapping image indicated that Cu and Fe were evenly distributed. Fig. 3 shows the FTIR spectra of Fe<sub>2</sub>O<sub>3</sub> (red line) and Fe<sub>2</sub>O<sub>3</sub>@Cu<sub>2</sub>O (black line). The absorption bands at 470 cm<sup>-1</sup> and 540 cm<sup>-1</sup> were attributed to the metal-oxygen (Fe-O) vibration [30]. The peak at approximately 1638 cm<sup>-1</sup> corresponded to the symmetric and asymmetric stretching of the carboxyl group [31]. After Cu loading, the absorption peaks of the Fe-O bonds decreased and slightly shorten because Cu was coated on the surface, as confirmed by the SEM results.

### 3.2. APAP degradation using different systems

Various catalysts were used under the same operating conditions to achieve the best APAP removal efficiency. As shown in Fig. 4, Fe<sub>2</sub>O<sub>3</sub>@Cu<sub>2</sub>O presented no obvious adsorption onto APAP. Only 35% APAP removal efficiency was achieved via PS oxidation without catalyst because oxidation was initiated only by direct PS anion oxidation (*E*<sub>0</sub> = 2.01) [32]. After the addition of Fe<sub>2</sub>O<sub>3</sub>/PS and

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