



# Dramatically enhanced Fenton oxidation of carbamazepine with easily recyclable microscaled $\text{CuFeO}_2$ by hydroxylamine: Kinetic and mechanism study



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## ABSTRACT

In this study, an inorganic reductant hydroxylamine was used to enhance the Fenton degradation of carbamazepine by easily recyclable microscaled  $\text{CuFeO}_2$  in a wide pH range (pH 4.0–9.0). It was found that the addition of hydroxylamine could dramatically enhance the degradation rate and TOC removal of carbamazepine, better than other reductants such as benzoquinone and ascorbic acid. In the  $\text{CuFeO}_2$ - $\text{H}_2\text{O}_2$  Fenton system, only 31% CBZ ( $50 \mu\text{mol L}^{-1}$ ) was removed at pH of 7.0 in 60 min in the presence of  $1.0 \text{ g L}^{-1}$   $\text{CuFeO}_2$  and  $20 \text{ mmol L}^{-1}$   $\text{H}_2\text{O}_2$ , while CBZ can be nearly completely removed in 60 min after the addition of  $0.1 \text{ mmol L}^{-1}$  hydroxylamine under the similar conditions. Moreover, CBZ degradation followed the pseudo first-order kinetics in the  $\text{CuFeO}_2$ - $\text{H}_2\text{O}_2$  Fenton system, while in the hydroxylamine enhanced  $\text{CuFeO}_2$ - $\text{H}_2\text{O}_2$  Fenton system, CBZ degradation followed the pseudo second-order kinetics. In the  $\text{CuFeO}_2$ - $\text{H}_2\text{O}_2$  Fenton system,  $t_{1/2}$  value for CBZ degradation was calculated as 114.4 min and the value was greatly decreased to 1.8 min after the addition of hydroxylamine. This hydroxylamine induced dramatic carbamazepine degradation enhancement could be attributed to the hydroxylamine enhanced Fe(III)/Fe(II) and Cu(II)/Cu(I) redox cycles. Hydroxyl radicals were the primary radical species responsible for the carbamazepine degradation. As a microscaled catalyst, micro- $\text{CuFeO}_2$  can be easily recovered by gravity settlement and exhibited good catalytic stability during six successive degradation cycles. Therefore, the couple of  $\text{CuFeO}_2$ - $\text{H}_2\text{O}_2$ -hydroxylamine is a promising method for oxidative degradation of organic pollutants in the actual aqueous environmental systems.

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## 1. Introduction

Pharmaceuticals, as emerging pollutants in aquatic environments, have received increasing concerns recently. The production of pharmaceutical drugs has been estimated in several hundred tons per year [1]. Carbamazepine (CBZ), as a typical pharmaceutical compound, is widely used to treat epilepsy, bipolar disorder and trigeminal neuralgia [2]. Due to its wide use, discharging from private households and hospitals and persistent nature in wastewater, CBZ is one of the most frequently detected pharmaceuticals in various types of water [1,3–6]. For example, CBZ has been detected in wastewater treatment plants (WWTPs) effluents at concentrations up to  $0.95 \mu\text{g L}^{-1}$  [1], in surface water with the concentration of  $4.5$ – $61 \mu\text{g L}^{-1}$  [6], and even in drinking water with the concentration of up to  $18 \text{ ng L}^{-1}$  [3]. CBZ has been evaluated as toxic to

aquatic life including bacteria, algae, invertebrates, and fish [7]. Therefore, there is an urgent need for efficient water treatment technologies for the degradation of CBZ contained wastewaters.

Several physical and chemical methods have been developed to remove CBZ from aqueous solutions, including adsorption [8,9], photolysis [10,11] and photocatalysis [12–14]. It was reported that CBZ is persistent and its removal efficiency by the WWTPs are mostly below 10% [15] due to its resistance to biodegradation at low concentrations [16] and hard attachment onto sludge [17]. The efficient adsorption of CBZ can be achieved by activated carbon and carbon nanotube sorption [8,9]. However, the method is non-destructive and needs post-treatment to avoid potential secondary pollution. The Fenton-like process is generally regarded as a rapid, efficient and simple water treatment technologies due to the generation of highly oxidizing hydroxyl radicals ( $\cdot\text{OH}$ ) via the reaction of Fenton-like catalysts and  $\text{H}_2\text{O}_2$  [18–20]. Domínguez et al. investigated the degradation of CBZ ( $2.11 \times 10^{-5} \text{ mol L}^{-1}$ ) during the Fenton-like oxidation process and found that CBZ can be totally removed in 120 min under optimal conditions ( $[\text{H}_2\text{O}_2]$

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$= 1.39 \times 10^{-4} \text{ mol L}^{-1}$ ,  $[\text{Fe}^{2+}] = 1.25 \times 10^{-5} \text{ mol L}^{-1}$ ,  $[\text{Fe}^{3+}] = 1.68 \times 10^{-5} \text{ mol L}^{-1}$  and  $\text{pH} = 3.52$ ) [21]. To prevent the precipitation of iron ions and enlarge the pH application range, a modified Fenton-like reaction using ferric-nitrilotriacetate ( $\text{Fe}^{\text{III}}$ -NTA) complexes was developed for CBZ degradation over an initial pH range of 5.0–9.0 [22]. Compared with homogeneous Fenton-like reaction, the heterogeneous Fenton-like process attracted more attention for treatment of hazardous pollutants due to the potential of reusability of heterogeneous Fenton-like catalysts after recycling [23–26]. Several heterogeneous Fenton-like catalysts such as nano-zero valent iron [27] and iron oxides [25,28] were developed to activate  $\text{H}_2\text{O}_2$  for the degradation of CBZ. However, most of the reported Fenton-like catalysts show low catalytic activity or low catalytic stability. Ghauch et al. investigated degradation of aqueous carbamazepine in ultrasonic/ $\text{Fe}^0/\text{H}_2\text{O}_2$  systems and found CBZ can be removed at pH values of 3 and 5 due to the homogeneous Fenton reaction of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$  species leached from  $\text{Fe}^0$  oxidation [27].

Recently, we prepared microscaled  $\text{CuFeO}_2$  rhombohedral crystalline particles with sizes in the range of 2–3  $\mu\text{m}$  and found that  $\text{CuFeO}_2$  microparticles showed the catalytic activation of  $\text{H}_2\text{O}_2$  to produce hydroxyl radicals, causing rapid degradation and mineralization of bisphenol A (BPA) [23]. However, it was observed that  $\text{CuFeO}_2$  microparticles were not that valid for the CBZ degradation in our preliminary experiments. It is necessary to increase further the Fenton catalytic ability of  $\text{CuFeO}_2$  microparticles for the degradation of CBZ. In the heterogeneous Fenton-like process, the regeneration of active sites  $\text{Fe}(\text{II})$  and  $\text{Cu}(\text{I})$  was the reaction kinetic-limited step for the activation of  $\text{H}_2\text{O}_2$  and the generation of  $\cdot\text{OH}$  radicals. Very recently, hydroxylamine (HA) was reported to accelerate the  $\text{Fe}(\text{III})/\text{Fe}(\text{II})$  redox cycles and thus, enhance organic pollutants degradation in the  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}/\text{peroxy-monosulfate}$  system [29,30]. Moreover, HA significantly enhanced the inactivation of *Escherichia coli* and MS2 coliphage by  $\text{Cu}(\text{II})$  due to the accelerated reduction of  $\text{Cu}(\text{II})$  into  $\text{Cu}(\text{I})$  and the production of reactive oxidants from the reaction of  $\text{Cu}(\text{I})$  with dissolved oxygen [31]. Therefore, it is anticipated that the addition of HA would enhance the Fenton activity of  $\text{CuFeO}_2$  microparticles for the degradation of organic pollutants by rapidly reducing  $\text{Fe}(\text{III})$  and  $\text{Cu}(\text{II})$  to  $\text{Fe}(\text{II})$  and  $\text{Cu}(\text{I})$ .

The main objective of this work is systematically investigating the effects of HA on the Fenton degradation of CBZ by easily recyclable microscaled  $\text{CuFeO}_2$  in a wide pH range (pH 4.0–9.0). For this purpose, the degradation of CBZ in the  $\text{CuFeO}_2\text{-H}_2\text{O}_2\text{-HA}$  system was studied as a function of different HA concentration,  $\text{H}_2\text{O}_2$  and pH values. It was found that HA induced dramatic carbamazepine degradation enhancement could be attributed to the HA enhanced  $\text{Fe}(\text{III})/\text{Fe}(\text{II})$  and  $\text{Cu}(\text{II})/\text{Cu}(\text{I})$  redox cycles and hydroxyl radicals were the primary radical species responsible for the carbamazepine degradation. The high TOC removal rates of CBZ, easy recovery and good stability of  $\text{CuFeO}_2$  indicate that the hydroxylamine enhanced  $\text{H}_2\text{O}_2\text{-CuFeO}_2$  system is a promising oxidation process for recalcitrant pollutant degradation.

## 2. Materials and methods

### 2.1. Chemicals

Cupric nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ), ferric nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), sodium hydroxide, propionaldehyde, trisodium citrate, sodium acetate, acetic acid, 2,9-dimethyl-1,10-phenanthroline (DMP), 1,10-phenanthroline, 30% (w/w)  $\text{H}_2\text{O}_2$  and hydroxylamine (HA) were provided by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). N,N-di-ethyl-p-phenylenediamine sulfate (DPD), superoxide dismutase (SOD) and carbamazepine (CBZ) were purchased

from Aldrich. CBZ stock solution ( $0.1 \text{ mmol L}^{-1}$ ) was prepared by dissolving 0.236 g CBZ in 1 L ultrapure water. All the chemicals were analytical grade reagents and were used as received without further purification. Ultrapure water was used in the present work.

### 2.2. Preparation and characterization of micro- $\text{CuFeO}_2$

$\text{CuFeO}_2$  microparticles were prepared by a microwave-assisted hydrothermal method [32]. Detailed information sees Text S1. Hydrothermal reaction time was important factor for the synthesis of a highly crystal  $\text{CuFeO}_2$  with all the copper in the valence state of +1. Based on the results of XRD and XPS analysis, the reaction time of 60 min was selected for hydrothermal preparation of pure  $\text{CuFeO}_2$  samples (Fig. 1a and b).

The surface morphology was characterized on a Quanta 200 scanning electron microscopic (SEM) instrument (FEI, the Netherlands) with energy dispersive X-ray (EDX) analysis. XRD pattern was obtained on a diffractometer with  $\text{Cu K}\alpha$  radiation (PANalytical B.V. X'Pert PRO), operated at 40 mA and 40 kV. The element composition and chemical oxidation state were investigated by XPS on a VG Multilab 2000 spectrometer (Thermo Electron Corporation) with  $\text{Al K}\alpha$  radiation as the exciting source (300 W). Binding energies were calibrated versus the carbon signal at 284.64 eV.

### 2.3. Catalytic degradation experiment

In the typical runs,  $\text{CuFeO}_2$  microparticles ( $1.0 \text{ g L}^{-1}$ ) were well dispersed into 50 mL aqueous solution of CBZ ( $50 \mu\text{mol L}^{-1}$ ), and the suspension was mechanically stirred in dark for 20 min. After the adsorption-desorption equilibrium between the CBZ solution and the catalyst, a specified amount of hydroxylamine (HA) was added into the solution, and the initial pH of reaction solution was adjusted by the addition of  $0.1 \text{ mmol L}^{-1}$   $\text{HClO}_4$  or  $\text{NaOH}$  as necessary.  $\text{HClO}_4$  or  $\text{NaOH}$  was used to adjust the reaction pH because their addition at concentration of  $0.01\text{--}0.1 \text{ mol L}^{-1}$  had no obvious effect on the CBZ degradation as shown in Fig. S1. The pH was not controlled during the degradation process. After that, a specified amount of  $\text{H}_2\text{O}_2$  was added into the solution to initiate the reaction, and solution samples (1.0 mL) were taken at given time intervals during the reaction, quenched by adding 50  $\mu\text{L}$  *tert*-butyl alcohol (TBA) ( $1 \text{ mol L}^{-1}$ ) and immediately filtered with 0.2  $\mu\text{m}$  membrane filter into a high performance liquid chromatography (HPLC) vial. The concentration of residual CBZ was analyzed by using HPLC. All measurements were repeated three times and the results were reproducible within the experiments errors ( $\pm 5\%$ ).

Quenching experiments were performed to determine the radical species formed in the  $\text{CuFeO}_2\text{-H}_2\text{O}_2\text{-HA-CBZ}$  system by using TBA and SOD as the quenching agents of  $\cdot\text{OH}$  and  $\cdot\text{O}_2^-$  radicals, respectively [19,33]. Prior to the addition of HA and  $\text{H}_2\text{O}_2$ , a required amount of the radicals quencher was added into the reaction solution.

To evaluate the stability and recyclability of catalysts, after one degradation cycle of CBZ was finished, the catalysts were collected by gravity settling for 20 min, washed with water to neutral pH, and dried at  $60^\circ\text{C}$  for 8 h. The recycled catalysts were re-dispersed into a fresh solution of  $50 \mu\text{mol L}^{-1}$  CBZ, and the CBZ degradation was re-initiated by adding the same amount of HA and  $\text{H}_2\text{O}_2$ . This catalyst recycling and the degradation experiment were repeated several times. Finally, the used  $\text{CuFeO}_2$  catalyst was characterized by X-ray powder diffraction (XRD).

### 2.4. Chemical analysis

The concentration of residual CBZ in degradation solution was analyzed on a HPLC (Agilent 1200 infinity series) with a G1315D

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