Synergistic effect of ferrous ion and copper oxide on the oxidative degradation of aqueous acetaminophen at acid conditions: A mechanism investigation

Yunfei Zhang [a,b,c], Jinhong Fan [a,*], Bo Yang [c,*], Luming Ma [a]

[a] National Engineering Research Center for Urban Pollution Control, State Key Laboratory of Pollution Control and Resources Reuse, College of Environmental Science and Engineering, Tongji University, 200092 Shanghai, PR China
[b] School of Environment and Civil Engineering, Dongguan University of Technology, Dongguan, 523000 Guangdong, PR China
[c] Department of Environmental Engineering, College of Chemistry and Environmental Engineering, Shenzhen University, 518060 Shenzhen, PR China

HIGHLIGHTS

- The CuO surface has high sorption affinity for the ferrous ion in solution.
- The sorbed Fe(II) on CuO surface processed higher reactivity than solution Fe(II).
- The formed Cu(I) can act as the electron mediator between the sorbed iron and O_2.
- It was proposed for the scheme of the ROSs generation in the $Fe(II)/CuO/O_2$ system.

GRAPHICAL ABSTRACT
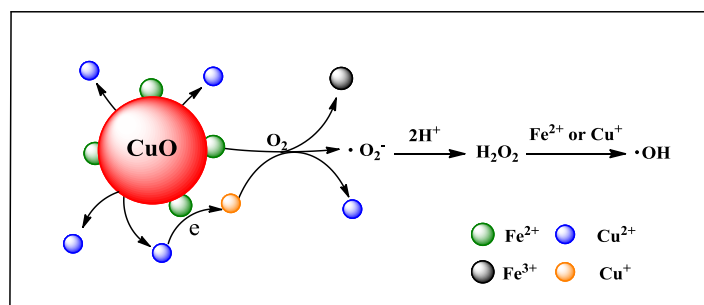
ABSTRACT

A synergistic effect of Fe(II) and copper oxide (CuO) was observed on the degradation of acetaminophen (ACT) in the presence of O_2. The results showed that 89% of ACT (50 mg/L) was degraded within 6 h by 10 mM Fe^{2+} with 5 g/L CuO powder at pH 3.0, among which about 30% of ACT was mineralized. The sorbed Fe(II) on the CuO surface which is more reactive than the dissolved Fe(II) was capable of reducing both Cu(II) and O_2. The resulting Cu(I) significantly accelerated the destruction of ACT by serving as an electron-mediator between the sorbed Fe(II) and O_2. In addition, the hydrogen peroxide (H_2O_2), hydroxyl radical ($\cdot OH$) and superoxide anion radical ($\cdot O_2^-$) were identified as the main reactive oxygen species (ROSs) generated in Fe(II)/CuO suspension by Electron paramagnetic resonance (EPR) technique and quenching studies; however, only $\cdot OH$ was found to have caused the decomposition and mineralization of ACT. First $\cdot O_2^-$ was generated by reduction of O_2 through a one-electron transfer pathway. Then the generated $\cdot O_2^-$ mediated the production of H_2O_2, which further decomposed into $\cdot OH$ by Cu(I)- and Fe(II)-catalyzed Fenton reactions. The effects of Fe(II) concentration, CuO dose, solution pH and the degradation pathway were investigated, respectively.
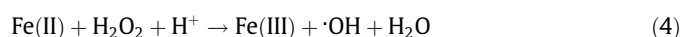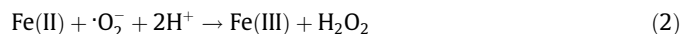
© 2017 Published by Elsevier B.V.

1. Introduction

Recently, copper- and iron-based catalysts (including zero-valent metals, minerals, oxide and bimetals) have been widely used to degrade many environmental pollutants in the aquatic

media [1–5]. For example, the zero-valent iron (ZVI) particles could reductively degrade various organic [4] and inorganic contaminants [6]. Besides, both the copper (Cu^0, Cu(I)) and iron (Fe(II), Fe^0) could also oxidatively remove a number of environmental contaminants by activating molecular oxygen (O_2) to generate more powerful reactive oxygen species (ROSs), such as hydrogen peroxide (H_2O_2), superoxide radical anion ($\cdot O_2^-$), ferryl iron (Fe (IV)), and hydroxyl radical ($\cdot OH$) [7–9]. For example, Ardo et al. [10] recently reported that Nalidixic Acid could be effectively degraded by magnetite/O_2. The generation of ROS can be mainly described in the following reactions.

$$Fe(II) + O_2 \rightarrow Fe(III) + \cdot O_2^- \quad (1)$$

$$Fe(II) + \cdot O_2^- + 2H^+ \rightarrow Fe(III) + H_2O_2 \quad (2)$$

$$2\cdot O_2^- + 2H^+ \rightarrow H_2O_2 + O_2 \quad (3)$$

$$Fe(II) + H_2O_2 + H^+ \rightarrow Fe(III) + \cdot OH + H_2O \quad (4)$$

On the other hand, in the aquatic media, the metal ions usually dissolve from the catalysts at the solid/liquid interface [11,12]. The interfacial reaction of the metal ions and its solid surface would undoubtedly have important effect on the adsorption and transformation of the environmental pollutants [13–15]. Thus, understanding the interactions between the ions and its solid surface is critically important to understand the removal mechanisms of the contaminants. However, to our knowledge, such study is still seldom reported. Although, several investigations have demonstrated the sorption of Fe(II) on metal surface are much more reactive than dissolved Fe(II), especially at the circumstance when certain transition metal ions (Ag(I), Au(III), and Cu(II)) are present [16]. For example, Hofstetter et al. [13] found that the Fe(II) complexed by hydroxyl groups on mineral surface reduced nitroaromatics to aniline more effectively than the Fe(II) bound by ion exchange. Maithreepala and Doong [17] found that the addition of Cu(II) significantly enhanced the dechlorination efficiency of carbon tetrachloride (CT) by Fe(II)/Goethite. However, those studies only focused on the reductive transformation of the environmental contaminants. Little attention has been paid to the role of O_2 as the first electron acceptor and the possible contribution of the oxidative process to the degradation of the pollutants.

In this study, the synergistic effect of Fe(II) and copper oxide (CuO) in the presence of O_2 was investigated for the degradation of acetaminophen (ACT), one of the mostly used drugs worldwide [18]. CuO was selected for the following two reasons: (i) it could serve as a source of Cu(II), which may enhance the degradation efficiency of the organic pollutants according to the previous investigations; (ii) the CuO co-exists all the time with Fe(II) in the copper-iron based bimetallic catalysts (such as Fe/Cu, CuO_x–FeOOH, $CuFe_2O_4$, $CuFeO_2$) [4,11,19,20], but their interaction with O_2 was scarcely reported. In addition, the ROSs generated during this process were identified and their roles in the degradation of ACT were elucidated. Furthermore, the effects of Fe(II) concentration, CuO dosage and pH were investigated, respectively. Finally, the possible degradation pathways for ACT were proposed.

2. Materials and methods

2.1. Materials

CuO powder (AR, >99%), $FeCl_2\cdot4H_2O$ (AR, >99%), $CuCl_2\cdot2H_2O$ (99.9%), thiourea (AR, 99%), 1,4-benzoquinone (BQ, 99%), CuCl (≥99.95%), NaOH, HCl (36–38%), H_2O_2 (30%), ethylenediamine and ACT (≥99.0%) were of analytical-grade and purchased from Aladdin, Inc., China. Methanol, *tert*-butyl alcohol (TBA) and

ethylacetate were HPLC-grade and acquired from Sinopharm Chemical Reagent Co., Ltd, China. Horseradish peroxidase (POD,≥300 units/mg), 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), Xanthine, and N,N-Diethyl-p-phenylenediamine sulfate (DPD, 98.5%) were purchased from J &K Chemical Technology. Xanthine Oxidase, N,O-Bis(trimethylsilyl)trifluoroacetamide/Trimethyl chlorosilane (BSTFA/TMCS, 99:1, *v/v*) and Bathocuproin sulfonate disodium salt hydrate (97%) were obtained from Sigma-Aldrich. The BET surface areas (S_{BET}) of the CuO was determined to be 13.51 m^2/g by nitrogen adsorption (NOVA 1200E). Deionized water was produced from a Millipore-Q system with a resistance of 18.2 MΩ and used throughout this study.

2.2. Aerobic degradation of ACT

Experiments were performed in the 250 mL glass beakers equipped with magnetic stirrer at room temperature (25 ± 2 °C). A 100 mL ACT solution with a concentration of 50 mg/L was oxygen-saturated through continuous stirring for 30 min before the reaction. Fe(II) solutions were prepared freshly every time in deoxygenated water in sealed bottles and were introduced into the beaks in the desired concentrations. The aqueous pH was adjusted using NaOH or HCl. The degradation reaction was initiated with the addition of solid CuO to the oxygen-saturated ACT solution. The beakers were open to the air to prevent the depletion of dissolved oxygen during the reaction. At the given reaction time intervals, samples were taken out using a 2.5 mL syringe and filtered through a 0.22 μm Suporfone film to remove the solid particles. The concentration of ACT and the content of the total organic carbon (TOC) were measured immediately with a high performance liquid chromatography (HPLC) system (Agilent 1260, USA) and a TOC analyzer (TOC-L CPH, Shimadzu), respectively. Data were plotted as mean of duplicates, and error bars indicated deviation from the mean.

2.3. Analytical method

The concentration of ACT was measured using a HPLC equipped with a Diode Array Derector (243 nm) [18] and a reversed phase ZORBAX Eclipse XDB-C18 column (4.6 mm × 150 mm, 5 μm). The eluent consisted of 30/70 (*v/v*) of methanol/water with a flow rate of 1.0 mL min/L at 40 °C. Hydrogen peroxide was analyzed using the DPD-POD method developed by Bader et al. [21]. Typically, 0.4 mL of phosphate buffer solution (pH 6) and 0.1 mL of 0.01 mol/L bipyridine solution were premixed in a quartz cell, followed by the addition of 2 mL of the sample, 30 μL of 1% DPD reagent in 0.1 mol/L H_2SO_4 and 30 μL of POD reagent successively. The absorbance at 551 nm was measured after the addition of the POD. $\cdot O_2^-$ and hydroxyl radical $\cdot OH$ were detected by EPR spectroscopy (Bruker EMX-8/2.7, Germany). DMPO was used as the spin trap agents [22]. The concentrations of dissolved Fe(II), total Fe(II), Cu(I), and total Cu species were measured by the colorimetric method, which was described in Supporting Information (SI) in detail (Text S1). Dissolved Oxygen (DO) was registered by an online monitoring system (YSI Inc., USA). In addition, the composition of the sample was characterized by X-ray diffraction (XRD) and X-ray photoelectron spectrometry (XPS) before and after the reaction (Text S2 and Fig. S1 in SI). A pseudo-first-order kinetic model was described in the Supporting Information (Text S3).

2.4. Identification of intermediates

To identify the potential degradation intermediates, 10 mL of filtered solution was extracted three times with 10 mL of ethylacetate and then dried with anhydrous Na_2SO_4; and once filtered, the extracted solution was concentrated to complete dryness under a