



# Enhanced superoxide radical production for ofloxacin removal via persulfate activation with Cu-Fe oxide

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## HIGHLIGHTS

- The activities of CuFe oxides were dependent on their redox ability.
- CuFe oxide (Cu:Fe = 1:1) exhibited the highest activity for ofloxacin degradation.
- $\cdot\text{O}_2^-$  rather than  $\cdot\text{SO}_4^-$  and  $\cdot\text{OH}$  was the reactive species for ofloxacin degradation.
- Possible mechanism for  $\cdot\text{O}_2^-$  production from persulfate activation was discussed.

## ARTICLE INFO

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## ABSTRACT

Cu-Fe composite oxides with different Cu:Fe ratios were synthesized by a hydrothermal method and investigated as a heterogeneous catalyst for persulfate activation. The obtained samples exhibited much higher activity than  $\text{CuFe}_2\text{O}_4$  for the degradation and mineralization of ofloxacin with persulfate, and the optimized Cu:Fe ratio was 1:1 (CuFe1). The results of catalyst characterization and electron paramagnetic resonance analysis indicate that the activities of the catalysts for ofloxacin degradation and superoxide radical ( $\cdot\text{O}_2^-$ ) production are highly positively correlated with their redox ability. The removal efficiencies of ofloxacin in the presence of different scavengers further demonstrate that  $\cdot\text{O}_2^-$  is the dominant reactive species in this process, which is quite different from previous studies. It is suggested that CuFe1 with higher oxidation ability could weaken the S–O bond of adsorbed persulfate, thus promoting the decomposition persulfate into  $\cdot\text{O}_2^-$ . Finally, the possible degradation pathway of ofloxacin was proposed according to the liquid chromatography–mass spectrometry result.

## 1. Introduction

Water pollution with antibiotics has become a serious problem because it has detrimental effects on environment and may lead to the development of antibiotic resistant bacteria [1,2]. Most of them cannot be biodegraded and are frequently detected in wastewater effluent, surface and ground waters. Advanced oxidation processes (AOPs), which can generate highly reactive species that can oxidize refractory organic pollutants, have exhibited potential applications in the removal of antibiotics [3–7]. In particular, sulfate radicals ( $\cdot\text{SO}_4^-$ ) based AOPs have attracted considerable attention due to their wide working pH range. Various methods, including UV irradiation, alkali, thermal treatment, electrochemistry and low valent transition metals, have been applied to accelerate the production of  $\cdot\text{SO}_4^-$  from persulfate (PS) activation [8–13]. Among them, the heterogeneous catalytic process without the aid of external energy is considered to be more promising

for large scale water treatment due to its low cost and easy operation.

Up to now, the possible mechanism for PS activation over solid catalysts has been extensively studied for the sake of rational design of effective catalyst. It is generally considered that low valent transition metals such as Fe(II), Co(II) and Cu(I) can promote the decomposition of PS into  $\cdot\text{SO}_4^-$  and  $\text{SO}_4^{2-}$  through the cleavage of O–O bond [7,14]. Recently, some new mechanisms were also proposed. Zhou et al. reported that the activation of PS over magnetite was attributed to superoxide radical ( $\cdot\text{O}_2^-$ ) produced from the reaction between Fe(II) and dissolved oxygen [15].  $\cdot\text{O}_2^-$  can react with PS to produce more  $\cdot\text{SO}_4^-$ . Tian et al. found that singlet oxygen rather than  $\cdot\text{OH}$  or  $\cdot\text{SO}_4^-$  was the dominant reactive species for ofloxacin and phenol degradation, which was generated due to the low activation energy of peroxomonosulfate over  $\text{LaMnO}_3$  [16].

According to the reported mechanism, low valent metal and metal oxides, such as zerovalent iron,  $\text{Fe}_3\text{O}_4$ ,  $\text{Co}_3\text{O}_4$ , CuO and industrial iron

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waste, are widely used catalysts in previous studies [13,17–22]. For instance, Ghauch et al. reported that industrial iron waste had some advantages over commercial iron in terms of sustainability and less sludge formation [22]. In order to improve the activity and stability of the catalysts, some multicomponent catalysts were developed. In comparison with  $\text{Fe}^0$ , bimetallic and trimetallic iron-based systems showed higher reaction stoichiometric efficiency with lesser formation of iron sludge [23]. More recently, Fe-Cu bimetallic oxides were found to be more effective for the removal of organic pollutants with PS, which might be ascribed to the synergistic effect between different components [24–27]. Although the Fe-Cu oxides are composed of Fe(III) and Cu(II) oxides,  $\cdot\text{SO}_4^-$  generated from the reaction of Fe(II)/Cu(I) with PS was reported to be the reactive species in this process, while the generation of  $\cdot\text{O}_2^-$  was rarely studied. Because this process is sophisticated and involved many reactive species, its mechanism is controversial and needs further investigation.

Hence, in this work, the catalytic performance and mechanism of Cu-Fe composite oxides with different Cu:Fe ratios for PS activation were investigated using ofloxacin (OFX), a widely used fluorinated quinolone-type antibiotics as the target pollutant. The role of  $\cdot\text{O}_2^-$  in this process and its possible formation pathway were studied. Among the catalysts, CuFe1 with the Cu:Fe ratio of 1:1 exhibited the highest activity, and the effect of reaction parameters on its activity was investigated. The degradation intermediates of OFX were also determined. Accordingly, the possible catalytic mechanism for PS activation and the degradation pathway of OFX were proposed.

## 2. Experimental section

### 2.1. Catalyst preparation

Cu-Fe composite oxides were prepared by a hydrothermal method. Typically, the solution containing a certain amount of  $\text{Fe}(\text{NO}_3)_3$  and  $\text{Cu}(\text{NO}_3)_2$  was adjusted to pH 10. Then the mixture was maintained at 120 °C for 12 h in an autoclave. The obtained solid product was washed with water until the filtrate was neutral. Finally, it was dried at 110 °C overnight. The samples prepared with the Cu:Fe mole ratio of 2:1, 1:1 and 1:2 were designated as CuFe2, Cu-Fe1 and Cu-Fe1/2. For comparison,  $\text{CuFe}_2\text{O}_4$  was prepared according to the literature [27].

### 2.2. Catalyst characterization

X-ray diffraction (XRD) and Brunauer–Emmett–Teller analyses were carried out with a Bruker D8–Advance diffractometer and a NOVA 4000e instrument, respectively. The surface chemical state was measured by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250). Hydrogen temperature-programmed reduction ( $\text{H}_2$ -TPR) experiments were performed on an adsorption apparatus equipped with a TCD detector (PCA-1200). The adsorbed  $\text{CO}_2$  and  $\text{H}_2\text{O}$  were removed by heating the sample in Ar at 200 °C for 1 h. After cooling to 50 °C, the sample was treated with a  $\text{H}_2$ :Ar mixture (10 vol%  $\text{H}_2$ , 30 mL  $\text{min}^{-1}$ ) from 50 °C to 800 °C (10 °C  $\text{min}^{-1}$ ).

### 2.3. Catalytic activity evaluation

Catalytic degradation of OFX solution was carried out in a foil-covered glass reactor to avoid the influence of photoreaction. In a typical experiment, the mixture of the catalyst and OFX solution was magnetically stirred until the adsorption of OFX reached equilibrium. Then the degradation reaction was started by adding a certain amount of  $\text{Na}_2\text{S}_2\text{O}_8$ . The concentration of OFX was determined by high performance liquid chromatography (HPLC, Agilent 1200) at the wavelength of 294 nm. Acetonitrile and formic acid aqueous solution with the ratio of 25:75 were used as the mobile phase. The total organic carbon (TOC) of the solution was analyzed using a TOC analyzer (Phoenix 8000). The degradation intermediates of OFX were identified

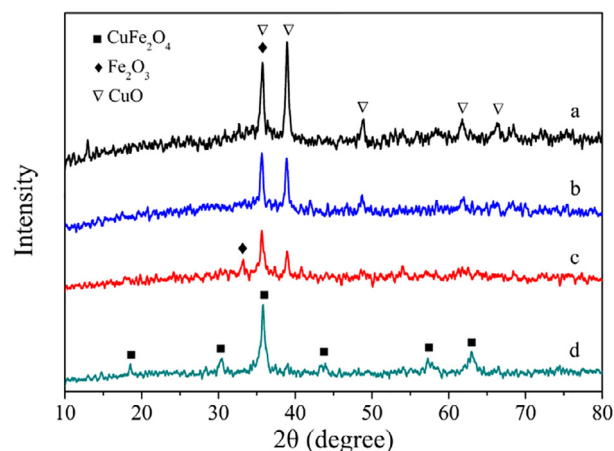


Fig. 1. XRD patterns of (a) CuFe2, (b) CuFe1, (c) CuFe1/2 and (d)  $\text{CuFe}_2\text{O}_4$ .

by LC-mass spectrometry (LC–MS, 3200 Q-TRAP, AB SCIEX). The retention time was 20 min and the ratio of acetonitrile ranged from 90% to 70%. The concentration of PS was determined by a spectrophotometric method [28]. DMPO (5,5-dimethyl-1-pyrroline-N-oxide) was used as a probe to identify active species. DMPO (100 mM) and PS (15 mM) were dissolved in deionized water, and then the catalyst (0.5 g  $\text{L}^{-1}$ ) was added. After reaction for 10 min, samples were taken and analyzed by an electron paramagnetic resonance (EPR) spectrometer (Magnetech, MS-5000).

## 3. Results and discussion

### 3.1. Catalyst characterization

The XRD patterns of the prepared samples are shown in Fig. 1. The diffraction peaks of  $\text{CuFe}_2\text{O}_4$  can be indexed to the cubic spinel phase of  $\text{CuFe}_2\text{O}_4$  (JCPDS 34-0425). The peaks assigned to  $\text{Fe}_2\text{O}_3$  and CuO were both observed in the XRD patterns of the CuFe samples, and the peak intensity of CuO decreased with decreasing the content of Cu. The result indicates the coexistence of  $\text{Fe}_2\text{O}_3$  and CuO in the CuFe samples. Subsequently, the surface chemical state of the samples was investigated by XPS. The Fe 2p spectra in Fig. 2 shows Fe 2p<sub>3/2</sub>, Fe 2p<sub>1/2</sub> and satellite peaks at 711–711.9, 718.3–719.1 and 724.4–725.2 eV, respectively, indicating that the valence state of Fe is +3 [29,30]. The Cu 2p<sub>3/2</sub> peaks at 933.6–934.2 eV can be attributed to Cu(II). The characteristic shake-up satellite peaks at 943.3 and 941.0 eV further demonstrate the presence of Cu(II) [31,32]. No peaks assigned to  $\text{Fe}^{2+}$  and  $\text{Cu}^+$  can be deconvoluted, suggesting that all the samples are composed of Fe(III) and Cu(II) oxides, which agrees well with the XRD result. The Fe 2p and Cu 2p binding energies of CuFe1/2 and  $\text{CuFe}_2\text{O}_4$  are higher than that of CuFe2 and CuFe1, which might be due to the stronger interaction between Fe and Cu.

Fig. S1a presents the  $\text{N}_2$  adsorption–desorption isotherms of the samples. All the isotherms are type IV, which is the characteristics of mesoporous structure. The hysteresis loops of CuFe2, CuFe1 and CuFe1/2 are type H4, indicating the presence of uniform mesopores. Fig. S1b demonstrates that the CuFe samples have a very narrow pore size distribution centered at 3.1–3.8 nm. The surface areas of CuFe2, CuFe1, CuFe1/2 and  $\text{CuFe}_2\text{O}_4$  were calculated to be about 187.8, 225.4, 142.6 and 62.6  $\text{m}^2 \text{g}^{-1}$ , respectively (Table 1).

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.cej.2018.08.055>.

Our previous work found that the performance of a Fenton-like catalyst was associated with its redox ability [33,34]. Hence, the prepared samples were further characterized by  $\text{H}_2$ -TPR. As shown in Fig. 3, two reduction peaks in the range of 150–300 °C can be attributed to the reduction of CuO to  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{O}$  to Cu [35]. The first peak

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