



Enhanced Fenton-like degradation of pharmaceuticals over framework copper species in copper-doped mesoporous silica microspheres



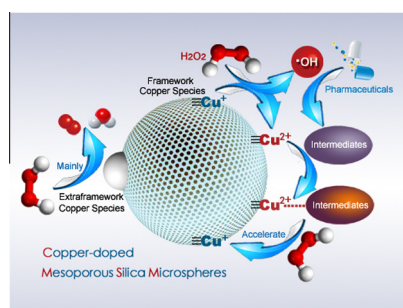
Lai Lyu, Lili Zhang, Chun Hu*

Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

HIGHLIGHTS

- 0.91 wt% Cu could exist in the framework of Cu-MSMs by the binding of Si—O—Cu.
- PHT, IBU and DP disappeared within 75, 120 and 90 min, respectively, in the M_2/H_2O_2 system at neutral pH.
- The leaching of Cu was much lower than the EU directives in the M_2/H_2O_2 system.
- The phenolic products complexed with the framework Cu(II), forming $\equiv\text{Cu}$ -ligands.
- $\equiv\text{Cu}$ -ligands interacted with H_2O_2 , accelerating the Cu(II)/Cu(I) cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

Copper-doped mesoporous silica microspheres (Cu-MSMs) with the coexistence of Cu(I) and Cu(II) were prepared using a hydrothermal process and characterized by several methods. The characterization studies suggested that 0.91 wt% of the copper species could exist in the framework of the mesoporous silica microspheres by chemical binding of Si—O—Cu; excess copper species were located in the extraframework sites, leading to more oxygen vacancies on the surface of the catalysts. The framework Cu of Cu-MSMs was found to be highly effective and stable for the degradation of pharmaceutical pollutants, as demonstrated with phenytoin, ibuprofen and diphenhydramine in the presence of H_2O_2 at neutral pH values. The conversion of the three pharmaceuticals could reach 100% within 75, 120 and 90 min, respectively; the leaching of Cu was much lower than the EU directives and USA regulations. By the studies of electron spin resonance, gas chromatography–mass spectrometry, Fourier-transform infrared spectra, *in situ* Raman spectra and X-ray photoelectron spectroscopy, an interaction process among the framework Cu of Cu-MSMs, pharmaceuticals and H_2O_2 was proposed: During the Fenton-like reaction, the framework $\equiv\text{Cu(I)}$ in Cu-MSMs primarily converted H_2O_2 into $\cdot\text{OH}$, and $\equiv\text{Cu(I)}$ was oxidized to $\equiv\text{Cu(II)}$ by H_2O_2 . The pharmaceuticals were attacked by $\cdot\text{OH}$ to form phenolic intermediates, adsorbing on the surface of Cu-MSMs, complexing with the framework $\equiv\text{Cu(II)}$, forming $\equiv\text{Cu}$ -ligands. $\equiv\text{Cu}$ -ligands interacted with H_2O_2 and enhanced the reduction rate of $\equiv\text{Cu(II)}$, resulting in the more $\equiv\text{Cu(I)}$ production; consequently, accelerated the Cu(II)/Cu(I) cycles on the catalyst surface, leading to more $\cdot\text{OH}$ generation for the pharmaceuticals oxidation.

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1. Introduction

Pollution from pharmaceutical compounds (PhACs) in surface and ground waters is an environmental concern in many countries [1,2]. Although the detected concentration levels of PhACs in

* Corresponding author. Tel.: +86 10 62849628; fax: +86 10 62923541.
E-mail address: huchun@rcees.ac.cn (C. Hu).

aqueous environment are low and often range from ng/L to $\mu\text{g/L}$ levels, the potential dangers to human and ecological health exist due to long-term exposure [3]. PhACs show a wide range of persistence in aquatic environments, and most of them are highly persistent, which could not be completely eliminated by the conventional water treatment [4].

Among the advanced oxidation processes (AOPs), the Fenton process is a powerful method to produce the high oxidation potential of the hydroxyl radical ($\cdot\text{OH}$) for the degradation of the recalcitrant organic pollutants [5,6]. However, the application of the classic Fenton process (dissolved Fe^{2+} and H_2O_2) is limited by the narrow working pH range of 2–3 as well as the separation and recovery of the iron species [7]. In order to address these problems, heterogeneous Fenton catalysts such as montmorillonites [8], zeolites [9], and metal oxides [10] were developed for use instead of the homogeneous Fenton process. These developed heterogeneous catalysts avoid the need for large amounts of reducing metal ions, which has been an active research area in this field. However, most of them showed good catalytic activity from pH 3 to 5, and a few of them showed significant catalytic efficiency at neutral pH values in water. It has been accepted that H_2O_2 is decomposed into $\cdot\text{OH}$ by the cycle of reduction state (M^{n+}) and oxidation state ($\text{M}^{(n+m)+}$) of the metal with the reduction of $\text{M}^{(n+m)+}$ to M^{n+} by oxidizing H_2O_2 being the rate-limiting step in the overall reaction [11,12]. For example, Fe(III)/Fe(II) cycling is heavily retarded by the slow step of H_2O_2 reducing Fe(III) due to the low rate constants ($0.001\text{--}0.02\text{ M}^{-1}\text{ s}^{-1}$) in neutral condition [12], which often need the aid of ultrasound and UV/visible light irradiation, increasing the energy requirements and the cost for water treatment.

Recently, Cu-based catalysts have attracted considerable attention because the redox properties of copper are similar to iron, and the Cu-based Fenton-like system could work over a broader pH range than the Fe-based redox system [13,14]. Importantly, the reduction of Cu(II) by H_2O_2 ($4.6 \times 10^2\text{ M}^{-1}\text{ s}^{-1}$) occurs more easily than that of Fe(III), and the Cu(I)– H_2O_2 system, which possesses a higher reaction rate ($1 \times 10^4\text{ M}^{-1}\text{ s}^{-1}$) than the Fe(II)– H_2O_2 system ($76\text{ M}^{-1}\text{ s}^{-1}$), can efficiently produce $\cdot\text{OH}$ [13,15,16]. Due to the mobilization of Cu(II)/Cu(I) in water, copper has been suggested to be supported on a porous solid substrate. Cu/13X [17], Cu/SBA-15 [18], and Cu-containing MFI [19] zeolites have been reported as catalysts for wet peroxide oxidation of different organic pollutants. But up to now, the correlation between the copper state in the structure of the catalysts and their catalytic activity was still unclear. Moreover, Cu(II) is easily complexed with organic substances [20], which may be used to enhance the catalytic activity [21]. However, the complexing of organic ligands with metal could accelerate the release of metal ions in aqueous solution from the solid catalyst, destructing the structure of the catalyst [22]. It was found that $0.5\text{--}10\text{ mg L}^{-1}$ of Cu were released into the solutions in various reported Cu-based heterogeneous Fenton-like systems [23,24], which was much higher than the standard 1.3 mg L^{-1} of drinking water (National Primary Drinking Water Regulations, the United States). The Cu release might be inhibited by the chemical bonding of Cu in the structure of the catalyst.

In the present study, copper-doped mesoporous silica microspheres (Cu-MSMs) were synthesized by a hydrothermal method. The localized copper species in the structure of Cu-MSMs were characterized, and their catalytic performance was investigated by Fenton-like process. Phenytoin (PHT) is a representative antiepileptic drug. Chronic exposure to it can result in immune suppression and dermatosis even the concentration is low [25]. Ibuprofen (IBU), an anti-inflammatory drug, may alter the postembryonic development of anuran species in freshwater environs [26]. Diphenhydramine (DP) is the active ingredient of Benadryl, a first generation antihistamine drug that combines sedative, antiemetic, antitussive and hypnotic properties, and has shown

high toxicity with mutagenic and carcinogenic effects [27]. The three PhACs occurred extensively in the aquatic environment due to their high usage and their presence in wastewater [28]. Therefore, PHT, IBU and DP were selected to evaluate the activity and properties of the catalyst. The results indicated that the framework copper species in Cu-MSMs exhibited high efficiency and stability for the degradation of the PhACs in the presence of H_2O_2 at neutral pH values. A preliminary effort to identify the interaction process among the framework copper species of Cu-MSMs, PhACs and H_2O_2 has been undertaken.

2. Materials and methods

2.1. Materials and reagents

Two of the PhACs-DP and PHT were purchased from Acros (Geel, Belgium), and IBU was obtained from TCI Japan (Tokyo, Japan). Their purities were higher than 99%. Their molecular structures are shown in Fig. S1. Tetraethyl orthosilicate (TEOS), cetyltrimethyl ammonium bromide (CTAB), copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), hydrogen peroxide (H_2O_2 , 30%, w/w), absolute ethanol and ammonia solution were purchased from Sinopharm Chemical Reagent Co. 5-Tert-butoxycarbonyl-5-methyl-1-pyrrolidine-N-oxide (BMPO) was provided by Dojindo Molecular Technologies. N,N-diethyl-p-phenylenediamine sulphate (DPD) and horseradish peroxidase (POD) were provided by Sigma Ltd. N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) was obtained from TCI Japan (Tokyo, Japan). All of the chemicals were at least of analytical grade. Deionized water was used throughout this study.

2.2. Catalyst preparation

Cu-MSMs were prepared using a hydrothermal method. Typically, 0.029 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in 160 mL of deionized water to form solution A. Then, 1.8 g of CTAB was dissolved in 120 mL of absolute ethanol, and the mixed solution was stirred for 30 min to form solution B. Next, solution A was added to solution B, and the mixed solution was stirred for 30 min followed by addition of 4 mL of TEOS. After stirring for 1 h, 8 mL of ammonia (25 wt%) was added dropwise to the mixed system to form a sol. The synthesis medium was maintained under vigorous stirring for 6 h. Then, the sol was transferred to a Teflon-lined steel autoclave and heated to $100\text{ }^\circ\text{C}$ for 48 h. After natural cooling, the obtained product was filtered, washed with deionized water and dried at $100\text{ }^\circ\text{C}$ for 6 h. Finally, the crystallisation and template removal were carried out in a muffle furnace at a heating rate of $2\text{ }^\circ\text{C}/\text{min}$ to $550\text{ }^\circ\text{C}$, which was maintained for 6 h. In addition, the content of copper in the sample was determined by ICP-OES (Optima 2000) after the sample was completely dissolved using nitric acid. By the same procedure, five samples with different copper content (0 wt%, 0.75 wt%, 0.93 wt%, 1.14 wt% and 1.55 wt%) were prepared, which were designated as M_0 , M_1 , M_2 , M_3 and M_4 , respectively. As a reference, iron-doped mesoporous silica microspheres (designated as M_{Fe}) was also synthesized as described above without the addition of the cupric nitrate but with the addition of ferric nitrate.

2.3. Characterization

The transmission electron microscopy (TEM) images of the samples were obtained using a JEOL-2010 TEM with an acceleration voltage of 200 kV. The scanning electron microscopy (SEM) images of the samples were obtained using a SU8020 FESEM (Hitachi). Nitrogen adsorption/desorption experiments of the samples were

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