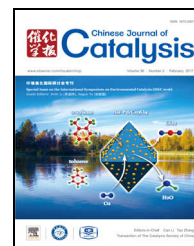


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# Heterogeneous catalytic activation of peroxymonosulfate for efficient degradation of organic pollutants by magnetic $\text{Cu}^0/\text{Fe}_3\text{O}_4$ submicron composites



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## ABSTRACT

Magnetic  $\text{Cu}^0/\text{Fe}_3\text{O}_4$  submicron composites were prepared using a hydrothermal method and used as heterogeneous catalysts for the activation of peroxymonosulfate (PMS) and the degradation of organic pollutants. The as-prepared magnetic  $\text{Cu}^0/\text{Fe}_3\text{O}_4$  submicron composites were composed of  $\text{Cu}^0$  and  $\text{Fe}_3\text{O}_4$  crystals and had an average size of approximately 220 nm. The  $\text{Cu}^0/\text{Fe}_3\text{O}_4$  composites could efficiently catalyze the activation of PMS to generate singlet oxygen, and thus induced the rapid degradation of rhodamine B, methylene blue, orange II, phenol and 4-chlorophenol. The use of 0.1 g/L of the  $\text{Cu}^0/\text{Fe}_3\text{O}_4$  composites induced the complete removal of rhodamine B (20  $\mu\text{mol/L}$ ) in 15 min, methylene blue (20  $\mu\text{mol/L}$ ) in 5 min, orange II (20  $\mu\text{mol/L}$ ) in 10 min, phenol (0.1 mmol/L) in 30 min and 4-chlorophenol (0.1 mmol/L) in 15 min with an initial pH value of 7.0 and a PMS concentration of 0.5 mmol/L. The total organic carbon (TOC) removal higher than 85% for all of these five pollutants was obtained in 30 min when the PMS concentration was 2.5 mmol/L. The rate of degradation was considerably higher than that obtained with  $\text{Cu}^0$  or  $\text{Fe}_3\text{O}_4$  particles alone. The enhanced catalytic activity of the  $\text{Cu}^0/\text{Fe}_3\text{O}_4$  composites in the activation of PMS was attributed to the synergistic effect of the  $\text{Cu}^0$  and  $\text{Fe}_3\text{O}_4$  crystals in the composites. Singlet oxygen was identified as the primary reactive oxygen species responsible for pollutant degradation by electron spin resonance and radical quenching experiments. A possible mechanism for the activation of PMS by  $\text{Cu}^0/\text{Fe}_3\text{O}_4$  composites is proposed as electron transfer from the organic pollutants to PMS induces the activation of PMS to generate  $^1\text{O}_2$ , which induces the degradation of the organic pollutants. As a magnetic catalyst, the  $\text{Cu}^0/\text{Fe}_3\text{O}_4$  composites were easily recovered by magnetic separation, and exhibited excellent stability over five successive degradation cycles. The present study provides a facile and green heterogeneous catalysis method for the oxidative removal of organic pollutants.

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## 1. Introduction

Advanced oxidation technologies (AOTs) are becoming increasingly important for wastewater treatment owing to their

strong oxidizing ability and their ability to convert organic pollutants into  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and other harmless small molecules [1–3]. Peroxymonosulfate (PMS), peroxydisulfate (PDS) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) are common oxidants used for the genera-

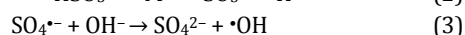
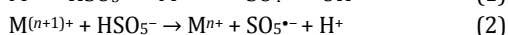
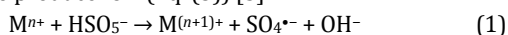
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tion of highly reactive species, such as sulfate radicals ( $\text{SO}_4^{\bullet-}$ , 2.5–3.1 V) and hydroxyl radicals ( $\bullet\text{OH}$ , 1.9–2.7 V), through activation processes [4]. Common methods of activation include addition of transition metal ions and their oxides [5], heating, UV illumination [6] and addition of a base [7,8]. Catalytic mechanisms for the activation of PMS can be divided into radical and non-radical mechanisms. Among these catalytic systems, the coupling of transition metals and PMS is attractive for the production of  $\text{SO}_4^{\bullet-}$  radicals owing to the low energy costs, versatile metal sources and high efficiency [4–6]. The radical mechanism for the activation of PMS by transition metals involves two steps: production of  $\text{SO}_4^{\bullet-}$  radicals through reaction of PMS with the transition metal at low oxidation states (Eq. (1)), and regeneration of the transition metal with the production of  $\text{SO}_5^{\bullet-}$  (Eq. (2)). The  $\text{SO}_4^{\bullet-}$  generated in Eq. (1) reacts with  $\text{H}_2\text{O}$  or  $\text{OH}^-$  to produce  $\bullet\text{OH}$  (Eq. (3)) [5].



Among the tested transition metals, which include Ag(I), Ce(III), Co(II), Fe(II), Fe(III), Mn(II), Ni(II), Ru(III) and V(III), Co(II) is the best catalyst for the activation of PMS to produce  $\text{SO}_4^{\bullet-}$  radicals [5]. However, Co-containing catalysts have a potential problem with toxicity because of the possibility of leaching of the Co ion [9]. Fe and Cu species are attractive alternatives to Co-containing catalysts owing to their high abundance in the earth and low toxicity compared with Co species [10]. As a result, Fe(II) and Cu(II) have been used to activate PMS for the degradation of various organic pollutants in aqueous solutions [10–13]. To improve the reusability of the catalysts, heterogeneous catalysts containing Cu and/or Fe were then further used to activate PMS for the generation of  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{OH}$  radicals [14–16]. Tan et al. [16] reported that  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles effectively catalyzed the PMS-activated degradation of acetaminophen through the  $\text{Fe}^{2+}/\text{Fe}^{3+}$ -mediated generation of  $\text{SO}_4^{\bullet-}$  radicals. In both the Fe(III)/PMS and Cu(II)/PMS systems, however, the reduction of Fe(III) and Cu(II) by PMS is the rate-limiting step for the production of reactive oxidants. Methods commonly used to accelerate the reductive recycling of Fe(III) back to Fe(II) in the Fe(III)/PMS system include UV light irradiation (photo-Fenton) [17], application of electricity (electro-Fenton) [18] and coupling with a reductant such as hydroxylamine (HA) [19].

Recently, bimetallic heterogeneous catalytic systems (bimetals or bimetallic oxides) have shown advantages over single zero-valent metals and single metal oxides in the degradation of pollutants as a result of the synergistic effect in the bimetals and/or bimetallic oxides. For example, Xu et al. [20] observed that the Fenton catalytic activity of a  $\text{Fe}_3\text{O}_4/\text{CeO}_2$  composite was higher than that of pure  $\text{Fe}_3\text{O}_4$ . We prepared  $\text{CuFe}_2\text{O}_4$  nanoparticles as a catalyst for PMS activation and observed 56% total organic carbon (TOC) removal in the degradation of tetrabromobisphenol A (10 mg/L) in 180 min by using 0.1 g/L  $\text{CuFe}_2\text{O}_4$  nanoparticles and 1.5 mmol/L PMS. The good catalytic performance of these  $\text{CuFe}_2\text{O}_4$  nanoparticles was attributed to the united effect of the Cu(II) and Fe(III) species on the  $\text{CuFe}_2\text{O}_4$  surface [21]. The same synergistic effect was also observed

with several other bimetallic heterogeneous catalysts, including Fe-Co/SBA-15 [22],  $\text{CuFeO}_2$  [23,24], magnetic  $\text{Fe}_3\text{O}_4\text{--MnO}_2$  [25] and cobalt manganese oxides ( $\text{Co}_x\text{Mn}_{3-x}\text{O}_4$ ) [26]. Moreover, according to Eqs. (1) and (2), transition metals in low oxidation states can efficiently activate PMS and produce reactive oxygen species. Therefore, it was anticipated that zero-valent copper ( $\text{Cu}^0$ ) would show high catalytic activity in the activation of PMS for the production of reactive oxygen radicals.

Very recently, a non-radical mechanism was reported for PMS activation by reduced graphene oxide [27], N-doped carbon nanotubes [28] and benzoquinone [29]. In these PMS activation processes, the used reduced graphene oxide, N-doped carbon nanotubes and benzoquinone can be recovered as electron transfer mediators to activate the PMS molecules to directly oxidize target components by extracting electrons from organics without generating free radicals. Considering the excellent electronic conductivity [30] and catalytic reduction ability of Cu metal [31], we anticipated that  $\text{Cu}^0$  would also show high catalytic activity in the activation of PMS and the degradation of organic pollutants through a non-radical mechanism. In the present work, therefore,  $\text{Cu}^0/\text{Fe}_3\text{O}_4$  composites were prepared, characterized and used as heterogeneous catalysts in the activation of PMS, the production of reactive oxygen species and the degradation of organic pollutants. The  $\text{Cu}^0/\text{Fe}_3\text{O}_4$  composites showed much higher catalytic ability toward the activation of PMS and the degradation of organic pollutants than did  $\text{Cu}^0$  and  $\text{Fe}_3\text{O}_4$  particles. The mechanism for the  $\text{Cu}^0/\text{Fe}_3\text{O}_4$  composite-catalyzed activation of PMS was investigated in detail using electron spin resonance (ESR) spectroscopy and quenching experiments.

## 2. Experimental

### 2.1. Chemicals

Cupric chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ), ferrous chloride ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), sodium hydroxide, hydrazine hydrate, rhodamine B (RhB), methylene blue (MB), orange II, phenol and 4-chlorophenol were provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Oxone ( $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ , 4.7% active oxygen) was purchased from Shanghai D&R Finechem Co., Ltd. (Shanghai, China). Tetramethylpiperidine (TEMP) solution (99.9% atomic purity) was provided by J&K Chemicals (Shanghai, China). All the chemicals were of analytical grade and used as received without further purification.

### 2.2. Preparation of $\text{Cu}^0/\text{Fe}_3\text{O}_4$ catalysts

$\text{Cu}^0/\text{Fe}_3\text{O}_4$  catalysts were prepared using a hydrothermal method. In a typical synthesis, 2.5 mmol  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , 3.75 mmol  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and 3.75 mmol  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  were dissolved in 50 mL distilled water, and then stirred for 10 min to form a clear solution. Then, 15 mL of 0.15 mol NaOH was added dropwise to the solution with stirring, sonicated for 10 min and further stirred for 20 min to give a colloidal suspension. After 1 mL hydrazine hydrate (85 wt% in water) was added to the suspension as a

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