available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article (Special Issue on the International Symposium on Environmental Catalysis (ISEC 2016))

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

Gang Nie, Jia Huang, Yezhou Hu, Yaobin Ding*, Xiaoyan Han, Heqing Tang#

Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission and Ministry of Education, College of Resources and Environmental Science, South-Central University for Nationalities, Wuhan 430074, Hubei China

ARTICLE INFO

Article history:

Received 14 September 2016

Accepted 28 October 2016

Published 5 February 2017

Keywords:

Heterogeneous catalysis

Magnetic $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composite

Peroxymonosulfate

Singlet oxygen

Oxidative degradation

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 Cu^0 and Fe_3O_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 Cu^0 or Fe_3O_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 Cu^0 and Fe_3O_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.

© 2016, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

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 CO_2 , H_2O and other harmless small molecules [1–3]. Peroxymonosulfate (PMS), peroxydisulfate (PDS) and hydrogen peroxide (H_2O_2) are common oxidants used for the genera-

* Corresponding author. Tel/Fax: +86-27-87543632; E-mail: yaobinding@mail.scuec.edu.cn

Corresponding author. Tel/Fax: +86-27-87543632; E-mail: tangheqing@mail.scuec.edu.cn

This work was supported by the National Natural Science Foundation of China (21377169, 21507168), the Fundamental Research Funds for the Central Universities (CZW15078), and the Natural Science Foundation of Hubei Province of China (2014CFC1119, 2015CFB505).

DOI: 10.1016/S1872-2067(16)62566-4 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 2, February 2017

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 H_2O or 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 Fe_3O_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 Fe_3O_4 . We prepared CuFe_2O_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 CuFe_2O_4 nanoparticles and 1.5 mmol/L PMS. The good catalytic performance of these CuFe_2O_4 nanoparticles was attributed to the united effect of the Cu(II) and Fe(III) species on the CuFe_2O_4 surface [21]. The same synergistic effect was also observed

with several other bimetallic heterogeneous catalysts, including Fe-Co/SBA-15 [22], 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 (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 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 Cu^0 and Fe_3O_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

reducing agent, the suspension (66 mL) was transferred to a 100 mL autoclave, sealed and allowed to react at 180 °C for 24 h. After the reaction, the autoclave was cooled naturally to room temperature. The solid products were collected by magnetic separation, washed several times with distilled water, and then dried in air under ambient conditions. To investigate the effect of the Cu:Fe molar ratio on the catalytic activity of the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ catalysts, Cu:(Cu+Fe) molar ratios of 0.1–0.75 in the precursor solutions were used. The resultant composites were denoted $\text{Cu}^0/\text{Fe}_3\text{O}_4$ - x catalysts, where x represents the Cu:(Cu+Fe) molar ratio. Because the optimal value of x was 0.25, the magnetic $\text{Cu}^0/\text{Fe}_3\text{O}_4$ catalysts described in the present work refer to $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -0.25 unless otherwise specified. As a control, Cu^0 and Fe_3O_4 nanoparticles were separately prepared under the same conditions by using $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ or $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as the precursor.

To obtain the exact chemical composition of the as-prepared $\text{Cu}^0/\text{Fe}_3\text{O}_4$ particles, quantitative colorimetric analysis of their Cu and Fe contents was performed on a UV-vis spectrophotometer (Varian, Cary 50, Varian, USA). The experiment was conducted as follows: 15 mg of the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ sample was added to 15 mL of 6 mol/L HCl. After ultrasound irradiation for 10 min, the total Cu and Fe ion concentrations in the solution were analyzed. The Cu and Fe contents in 1 g $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -0.25 were 208 and 573 mg, respectively. The calculated Cu:Fe molar ratio was 0.32, close to that in the precursors (0.33).

2.3. Characterization

Surface morphology was characterized on a Quanta 200 scanning electron microscopy (SEM, FEI, The Netherlands). X-ray powder diffraction (XRD) patterns were obtained on a diffractometer with $\text{Cu K}\alpha$ radiation (PANalytical B.V. X'Pert PRO, PANalytical BV, The Netherlands), operated at 40 mA and 40 kV. X-ray photoelectron microscopy (XPS) were recorded on a VG Multilab 2000 spectrometer (Thermo Fisher Scientific, USA) with $\text{Al K}\alpha$ radiation as the excitation source (300 W). Binding energies were calibrated versus the carbon signal at 284.64 eV. The magnetic properties (M - H curve) were measured at 27 °C on an ADE 4HF vibrating sample magnetometer (ADE, USA). The Brunauer-Emmett-Teller (BET) specific surface area was measured at -196 °C using an Autosorb-iQ analyzer (Quantachrome Instruments, USA). The zeta potential measurements were performed on a Zeta PALS analyzer (Zetasizer Nano ZS90, Malvern, UK).

2.4. Catalytic degradation

In a typical run, the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ catalyst (0.1 g/L) was well dispersed into 50 mL of an aqueous solution of RhB (20 $\mu\text{mol/L}$), and the suspension was mechanically stirred in the dark for 20 min. After the adsorption-desorption equilibrium between the RhB solution and the catalyst was reached, a 1.0 mL sample of the solution was taken, and the RhB concentration was measured by UV-vis spectroscopy. The measured concentration was regarded as the initial concentration (c_0) for the subsequent study of the degradation of RhB. Next, a speci-

fied amount of PMS (Oxone) was added to the solution to initiate the reaction. The initial pH of the reaction solution was adjusted by addition of 0.1 mmol/L HNO_3 or NaOH, and was not controlled during the degradation process. After the degradation was initiated, 1.0 mL solution samples were taken at given time intervals during the reaction, quenched by addition of 0.5 mL methanol and immediately filtered through a 0.2 μm membrane filter. The residual RhB concentration in the filtrate was determined by UV-vis spectroscopy. All measurements were repeated three times and the results were reproducible within experimental error ($\pm 5\%$).

ESR spectroscopy was used to confirm the generation of singlet oxygen. In this study, 5 mg of the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ catalyst was suspended in 50 mL ultrapure H_2O containing 2 mmol/L TEMP. Then, 0.5 mmol/L PMS (Oxone) was added to the solution to initiate the reaction. The initial pH of the reaction solution was adjusted to 7.0 by the addition of 0.1 mmol/L HNO_3 or NaOH. After 5 min reaction time, 100 μL samples were collected from the reaction solution and used for ESR measurements.

2.5. Chemical analysis

RhB, MB and orange II concentrations were determined from the UV-vis absorption. The concentrations of phenol and 4-chlorophenol were analyzed by high performance liquid chromatography (HPLC, Agilent 1200 infinity series) with a G1315D 12600 DAD detector. An amethyst C18-P column (5 μm , 4.6 $\times$ 250 mm) was used as the separation column.

Fe and Cu leaching was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Baird Plasma Spectrovac PS-6(N+1)). The Fe and Cu contents of the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ catalysts were determined colorimetrically by UV-vis spectroscopy at 510 and 457 nm after addition of the chromogenic agents 1,10-phenanthroline and 2,9-dimethyl-1,10-phenanthroline, respectively [32,33]. TOC was assayed with a micro N/C model TOC analyzer (Elementar, Germany).

3. Results and discussion

3.1. Characterization of $\text{Cu}^0/\text{Fe}_3\text{O}_4$ catalysts

As evidenced by the well-defined diffraction peaks in Fig. 1, the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composite had good crystallinity. The distinct peaks at $2\theta = 43.4^\circ$, 50.5° and 74.2° were assigned to the (111), (200) and (220) crystal planes of metallic Cu (JCPDS No. 85-1326), which demonstrates the presence of Cu^0 in the composite [34]. Additionally, the typical (220), (311), (400), (511) and (440) crystal planes of Fe_3O_4 (JCPDS No. 19-0629) at $2\theta = 30.18^\circ$, 35.48° , 43.13° , 57.05° and 74.2° were observed for the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composites [32], confirming the formation of spinel Fe_3O_4 . These results indicate that $\text{Cu}^0/\text{Fe}_3\text{O}_4$ catalysts were successfully prepared by a hydrothermal method.

The crystalline size can be evaluated on the basis of the XRD patterns using the Debye-Scherrer formula $D = K\lambda/(\beta\cos\theta)$, where K is the Scherrer constant (0.89), λ is the X-ray wavelength (0.15418 nm), β is the peak width at half maximum

Fig. 1. XRD patterns of $\text{Cu}^0/\text{Fe}_3\text{O}_4$ and the control samples. (1) Fe_3O_4 ; (2) $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -0.1; (3) $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -0.25; (4) $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -0.5; (5) $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -0.75; (6) Cu^0 .

height and θ is the Bragg diffraction angle. From the most intense peaks—(311) for the spinel Fe_3O_4 crystals and (111) for the Cu^0 crystals—the average crystalline size of the spinel Fe_3O_4 and Cu^0 crystals in the composites was calculated. The crystalline size of the spinel Fe_3O_4 and Cu^0 crystals were 106.2 and 33.8 nm, respectively. In comparison, the crystalline sizes of the spinel Fe_3O_4 species in the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ samples were 36.9, 31.9, 35.2 and 37.6 nm, and those of the Cu^0 species were 17.8, 20.8, 26.5 and 29.5 nm, for $x = 0.1, 0.25, 0.5$ and 0.75 , respectively. These results indicate that the combination of spinel Fe_3O_4 and Cu^0 crystals enhanced the dispersion and reduced the crystalline size of each crystal type in the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composites.

As shown in Fig. 2(b), the as-prepared $\text{Cu}^0/\text{Fe}_3\text{O}_4$ catalysts were composed of submicron polyhedra with an average size of approximately 220 nm. SEM images of the as-synthesized Cu^0 and Fe_3O_4 samples were also obtained. Compared with the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ sample, the majority of the particles in the as-prepared Cu^0 sample were hexahedral in shape, with an average size of about 250 nm (Fig. 2(c)). The as-prepared Fe_3O_4

samples (Fig. 2(a)) mainly comprised aggregate particles about 100 nm in size. The observed particle size was larger than that calculated for the crystalline Cu^0 , Fe_3O_4 and $\text{Cu}^0/\text{Fe}_3\text{O}_4$ catalysts, which suggests that the as-prepared catalysts formed self-assembled structures or aggregates of their smaller crystals. The BET specific surface area (S_{BET}) of the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ samples was $4.6 \text{ m}^2/\text{g}$, comparable to that of Cu^0 ($4.2 \text{ m}^2/\text{g}$) but smaller than that of the Fe_3O_4 particles ($15.6 \text{ m}^2/\text{g}$).

XPS was conducted to further confirm the surface composition and chemical state of the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ catalyst (Fig. 3). It was found that only C, O, Fe and Cu were present on the surface of the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ samples (Fig. 3(a)). The atomic percentages of C, O, Fe and Cu were 29.6%, 44.3%, 17.2% and 8.9%, respectively. The high carbon content is attributed to adventitious carbon contaminants from ambient air, which are commonly observed on the surfaces of other catalysts [35,36]. As shown in Fig. 3(b), the XPS O 1s envelope was deconvoluted into three parts, namely the lattice oxygen at 530.0 eV, the hydroxylate oxygen at 531.5 eV and the oxygen in adsorbed H_2O at 533.0 eV [37]. Based on this deconvolution, the proportion of surface lattice oxygen was determined to be 72%, and those of the hydroxylate oxygen and the oxygen in adsorbed H_2O were 21% and 7%, respectively. Two intense peaks located at 952.7 and 932.8 eV were observed in the XPS spectrum of Cu 2p (Fig. 3(c)), and were attributed to the Cu $2p_{1/2}$ and Cu $2p_{3/2}$ spin-orbitals of Cu^0 , respectively [31,34]. As shown in Fig. 3(d), the Fe 2p peaks at binding energies of 711.2 and 725.0 eV, with a satellite signal at 719.0 eV, were identified as Fe(III), whereas the peaks at 709.9 and 723.4 eV, with a satellite signal at 715.5 eV, were characteristic of Fe(II). The two peaks at 709.9 and 711.2 eV for the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composite were thus indicative of the presence of both Fe(II) and Fe(III), and the satellite signal at 715.5 eV suggested the presence of ferrous iron oxide [32]. It was found that the Fe(II):Fe(III) molar ratio on the catalyst surface was 0.52, close to the theoretical value (0.5) for Fe_3O_4 crystals. These XRD, SEM and XPS results thus indicate that submicron polyhedral $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composites were successfully prepared using a hydrothermal method.

The magnetization hysteresis loop of the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ submicron composite was recorded at 27 °C (Fig. 4). The S-like magnetization hysteresis loop of the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ submicron composite suggested that the composite was superparamagnetic. The specific saturation magnetization was 20 emu/g. Therefore, the superparamagnetic $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composite could easily be sepa-

Fig. 2. Scanning electron microscopy images of Fe_3O_4 (a), $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -0.25 particles (b) and Cu^0 particles (c).

Fig. 3. XPS of as-prepared $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composites: wide survey spectrum (a), and high-resolution spectra of O 1s (b), Cu 2p (c) and Fe 2p (d). In (b), O_I , O_II and O_III stand for oxygen in the form of oxide, surface hydroxylate and adsorbed H_2O , respectively.

rated from the reaction solution after the degradation reaction by applying an appropriate magnetic field for 1 min (inset of

Fig. 4. M - H hysteresis loop of $\text{Cu}^0/\text{Fe}_3\text{O}_4$ particles at 27 °C. The inset shows photographs of the dispersion before and after recycling by magnetic separation for 1 min.

Fig. 4).

3.2. Catalytic activity of $\text{Cu}^0/\text{Fe}_3\text{O}_4$ toward organic pollutant degradation

RhB degradation was used to investigate the catalytic activity of the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ submicron composites in the activation of PMS. As shown in Fig. 5(a), in the control test with only $\text{Cu}^0/\text{Fe}_3\text{O}_4$ submicron composites (0.1 g/L), about 5% RhB removal was obtained after 15 min stirring owing to the adsorption on the composite surface. The use of PMS alone (0.5 mmol/L) induced about 13% RhB removal as a result of direct oxidation by PMS [38]. When the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composites and PMS were used together, the degradation of RhB was enhanced and complete degradation was achieved in 15 min. In contrast, use of individual Cu^0 and Fe_3O_4 particles as catalysts yielded 28% and 20% degradation, respectively, under the same conditions. Moreover, a physical mixture of Cu^0 and Fe_3O_4 with a Cu:Fe atomic ratio of 1:3 induced 50% RhB degradation, which was better than that obtained for Cu^0 and Fe_3O_4 particles individually, but considerably poorer than the degradation observed with the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ submicron composites. Absorption spectra of RhB measured over time in the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -PMS sys-

Fig. 5. (a) Degradation profile of RhB in the different systems. (1) $\text{Cu}^0/\text{Fe}_3\text{O}_4$; (2) PMS; (3) Fe_3O_4 -PMS; (4) Cu^0 -PMS; (5) physical mixture of Cu^0 and Fe_3O_4 with PMS; (6) $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -PMS. (b) Absorption spectra of RhB in the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -PMS system over time. Reaction conditions: initial RhB concentration 20 $\mu\text{mol/L}$, initial PMS concentration 0.5 mmol/L, catalyst loading 0.1 g/L, initial pH value 7.0.

tem are shown in Fig. 5(b). It is clear that the absorbance of the RhB solution rapidly decreased with time. These results indicate that there is a considerable synergistic effect between the Cu^0 and Fe_3O_4 species in the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composites for PMS activation and RhB degradation. The S_{BET} of the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ sample (4.6 m^2/g) was comparable to that of Cu^0 (4.2 m^2/g) and smaller than that of the Fe_3O_4 particles (15.6 m^2/g). The synergistic effect between the Cu^0 and Fe_3O_4 species was therefore attributed to enhanced dispersion and the decreased crystalline size of the spinel Fe_3O_4 and Cu^0 crystals in the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composites.

To further explore the synergistic effect, the effect of the Cu:Fe ratio in the precursors (x value in the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ - x parti-

cles) on the oxidative degradation of RhB catalyzed by the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ particles was investigated. As shown in Fig. 6(a), as x was increased from 0 to 0.1 and 0.25, the RhB degradation in 15 min improved from 20% to 28% and 100%, respectively. When x was higher than 0.25, the catalytic activity of the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ - x particles clearly decreased. For example, for $x = 0.5$ and 0.75, the RhB degradation decreased to 68% and 63%, respectively. Therefore, the optimum Cu:Fe molar ratio was determined to be 1:3 and the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -0.25 composite was used for further experiments.

As shown in Fig. 6(b), the RhB degradation, except for that catalyzed by the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -0.25 composites, followed two-stage second-order kinetics, which consisted of a rapid

Fig. 6. (a) Effect of Cu:(Cu+Fe) molar ratio on the degradation of RhB in the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -PMS system. (b) Corresponding second-order kinetic fitting. Reaction conditions: initial RhB concentration 20 $\mu\text{mol/L}$, initial PMS concentration 0.5 mmol/L, catalyst loading 0.1 g/L, initial pH 7.0.

degradation stage (first stage), followed by a period of slower degradation (second stage). The corresponding second-order kinetic rate constants can be calculated according to Eq. (4).

$$\frac{1}{c} - \frac{1}{c_0} = kt \quad (4)$$

where t is the reaction time (min), k is the pseudo second-order kinetic rate constant (L/mol min), and c_0 and c are pollutant concentrations (mol/L) at $t = 0$ and $t = t$, respectively. As shown in Fig. 6(b) and Table 1, the second-order kinetic rate constant in the first stage was usually higher than that in the second stage when $\text{Cu}^0/\text{Fe}_3\text{O}_4$ - x composites ($x = 0, 0.1, 0.5, 0.75$) were used as catalysts, whereas there was no obvious decrease during the overall degradation process when the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -0.25 composites were used. This result further demonstrates the high catalytic activity of the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -0.25 composites.

Further, synergistic extent ($\Lambda_{\text{synergism}}$, %) was defined to evaluate the synergistic effect between the Cu^0 and Fe_3O_4 species in the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composites for the degradation of RhB as described in Eq. (5) [39].

$$\Lambda_{\text{synergism}} (\%) = \frac{k_{\text{Cu}^0/\text{Fe}_3\text{O}_4} - (k_{\text{Cu}^0} + k_{\text{Fe}_3\text{O}_4})}{k_{\text{Cu}^0/\text{Fe}_3\text{O}_4}} \times 100 \quad (5)$$

where $k_{\text{Cu}^0/\text{Fe}_3\text{O}_4}$ is the pseudo-second-order rate constant for the degradation of RhB in the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -PMS system, k_{Cu^0} is the pseudo-second-order rate constant for degradation of RhB in the Cu^0 -PMS system, and $k_{\text{Fe}_3\text{O}_4}$ is the pseudo-second-order constant for degradation of RhB in the Fe_3O_4 -PMS system. As shown in Table 1, when x in the range of 0.25 to 0.75, the calculated synergistic extent was greater than zero and the highest value was observed for the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -0.25 composites. These results further indicate that there is a considerable synergistic effect between the Cu^0 and Fe_3O_4 species in the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composites.

3.3. Effects of reaction parameters on the catalytic degradation of RhB

The effects of the reaction parameters, including catalyst loading, PMS concentration and solution pH, on the catalytic degradation of RhB were investigated for the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -PMS system.

As displayed in Fig. 7(a), enhanced RhB degradation was observed when the loading of the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ catalyst was increased. When the catalyst loading was 0.05 g/L, the degrada-

tion of RhB observed in 15 min was 56%; this increased to 87% and 100% when the catalyst loading was increased to 0.075 and 0.1 g/L, respectively. When 0.2 g/L of the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composites was used as the catalyst, complete degradation of RhB was obtained in 5 min. This increase was due to the increased number of active sites for the formation of reactive oxygen species [40].

PMS is a reactive oxygen species precursor; therefore, the concentration of added PMS has a marked effect on the degradation of RhB in the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -PMS system. As shown in Fig. 7(b), when the catalyst loading was fixed at 0.1 g/L, an increased initial PMS concentration accelerated the removal of RhB. For example, when the PMS concentration was increased from 0.3 to 0.5 and further to 0.8 mmol/L, RhB removal in 15 min was increased from 31% to 100%, and further to 100% in 10 min. A similar effect has also been observed on increasing the concentration of added PMS in other PMS/heterogeneous catalytic systems [40–42].

The effect of the initial solution pH on the degradation of RhB in the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -PMS system is shown in Fig. 7(c). It was observed that the catalytic activity of the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composites was markedly enhanced as the pH of the initial solution was decreased from 9.0 to 6.0. For example, about 30% and 76% removal of RhB was achieved in 15 min at pH = 9.0 and 8.0, but complete removal of RhB was achieved in 15 and 5 min when the pH was decreased to 7.0 and 6.0, respectively. As shown in Fig. 7(d), the pH_{PZC} (pH at the point of zero charge) of the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composites was about 5.3. The surfaces of the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ catalyst are therefore negatively charged at pH = 6.0–9.0. In addition, PMS mainly exists as HSO_5^- at pH = 6.0–8.5, and as SO_5^{2-} and HSO_5^- at pH = 8.5–9.0 [41]. Therefore, at pH = 6.0 and 9.0, the adsorption of PMS on the surface of the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ catalyst becomes increasingly more difficult owing to increased electrostatic repulsion. Consequently, decreased production of reactive oxygen species and lower RhB degradation was observed. The pH effect observed in this study is consistent with that in the manganese oxide-PMS system [43,44], but different to that observed for NiFe_2O_4 -PMS [45], $\text{CuFe}_2\text{O}_4/\text{Fe}_2\text{O}_3$ -PMS [46], CoFe_2O_4 /titanate nanotubes-PMS [47] and Co_3O_4 @metal organic frameworks-PMS [48] systems.

3.4. Metal leaching and stability of $\text{Cu}^0/\text{Fe}_3\text{O}_4$ catalysts

The concentrations of leached Cu and Fe in the reaction solution were measured during the degradation of RhB at pH 7.0 in the presence of 0.1 g/L $\text{Cu}^0/\text{Fe}_3\text{O}_4$ and 0.5 mmol/L PMS. The concentrations of total Cu and Fe ions in the solution were 0.22 and 0.1 mg/L at a reaction time of 60 min, equivalent to about 1.1% and 0.2% of the Cu and Fe in the used catalyst, respectively. The low leaching of Cu and Fe into the reaction solution indicates that the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composites had good chemical stability. We also determined the catalytic stability of $\text{Cu}^0/\text{Fe}_3\text{O}_4$ in the degradation of RhB (Fig. 8(b)). After complete degradation of the RhB, the used catalyst was collected by magnetic separation (inset of Fig. 4), washed several times with water to neutral pH, and re-dispersed in a fresh RhB solution. Then, 0.5 mmol/L PMS was added, and the second cycle of

Table 1

Two-stage second-order kinetic rates of RhB degradation and synergistic extent.

x	First-stage		Second-stage	
	$k \times 10^6$ (L/mol min)	$\Lambda_{\text{synergism}}$ (%)	$k \times 10^6$ (L/mol min)	$\Lambda_{\text{synergism}}$ (%)
0	0.0077		0.00011	
0.1	0.086	−48.5	0.0091	87.8
0.25	2.5	94.9	2.54	99.9
0.5	0.65	80.5	0.072	98.4
0.75	0.87	85.3	0.095	98.8
1	0.12		0.001

Fig. 7. Effects of catalyst loading (a), PMS concentration (b) and solution pH (c) on the catalytic degradation of RhB in the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -PMS system. (d) Zeta potential of $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composites versus pH values.

degradation was conducted. These steps were repeated several times. After the fifth run, RhB removal remained at about 98% for the recycled $\text{Cu}^0/\text{Fe}_3\text{O}_4$ catalysts, confirming their excellent catalytic stability. The concentrations of leached Cu and Fe ions were measured after each degradation cycle. As shown in Fig. 8(b), the concentrations of Cu and Fe ions leached in 15 min were 0.095–0.11 and 0.035–0.042 mg/L, respectively. The total amounts of leached Cu and Fe ions over six degradation cycles were 0.623 and 0.237 mg/L, respectively, which accounts for only 3.1% of the total Cu and 0.47% of the total Fe in the catalyst. The low leaching of Cu and Fe ions over successive degradation cycles confirms the long term stability of the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composites during the RhB degradation process.

3.5. Application of $\text{Cu}^0/\text{Fe}_3\text{O}_4$ for removal and mineralization of other dyes and phenols

As shown in Fig. 9, the use of PMS alone (0.5 mmol/L) induced about 13% removal of RhB and 9.5% removal of MB by

direct oxidation by PMS. When the PMS concentration was increased to 2.5 mmol/L, removal of RhB and MB was improved to 37% and 24%, respectively. No obvious degradation of orange II, phenol and 4-chlorophenol was observed in the presence of 0.5 or 2.5 mmol/L PMS during the overall reaction process. Removal of MB, orange II, phenol and 4-chlorophenol simply by adsorption onto the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ surface was 4% in 15 min, 10% in 20 min, 12% in 30 min and 14% in 20 min. In comparison all tested dyes and phenolic pollutants were completely degraded in 30 min in the presence of 0.5 mmol/L PMS and 0.1 g/L of the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ catalyst (Fig. 9(a)–(e)). Under the same conditions, the TOC removal for five pollutants was 15.9%–25.2% in 30 min owing to the insufficient quantity of PMS. When the PMS concentration was increased to 2.5 mmol/L, the TOC removal for all of these five pollutants was higher than 85% in 30 min, considerably higher than that obtained through direct oxidation by PMS (2.5 mmol/L) and that through adsorption onto the catalyst surface. These results all further confirm the high catalytic activity of the $\text{Cu}^0/\text{Fe}_3\text{O}_4$

Fig. 8. (a) Leaching of Cu and Fe ions during the RhB degradation process in the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -PMS system. (b) Degradation of RhB and leaching of Cu and Fe ions during successive degradation cycles with recycled $\text{Cu}^0/\text{Fe}_3\text{O}_4$ catalysts in the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -PMS system. Reaction conditions: initial RhB concentration $20 \mu\text{mol/L}$, initial PMS concentration 0.5 mmol/L , catalyst loading 0.1 g/L , initial pH value 7.0.

Fig. 9. Degradation profile of $20 \mu\text{mol/L}$ RhB (a), $20 \mu\text{mol/L}$ MB (b), $20 \mu\text{mol/L}$ orange II (c), 0.1 mmol/L phenol (d) and 0.1 mmol/L 4-CP (e) in the different reaction systems. (f) Total organic content removal of five organic pollutants in 30 min in the $\text{Cu}^0/\text{Fe}_3\text{O}_4$, PMS and $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -PMS systems. Reaction conditions: catalyst loading 0.1 g/L , initial pH value 7.0.

composites.

3.6. Possible catalytic mechanism for the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -PMS system

In previously reported heterogeneous reactions for the activation of PMS, the $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ radicals are usually consid-

ered to be the main reactive oxygen species [4,5,23,24,41]. Tert-butyl alcohol reacts with $\cdot\text{OH}$ ($3.8\text{--}7.6 \times 10^8 \text{ L}/(\text{mol}\cdot\text{s})$) much faster than it reacts with $\text{SO}_4^{\cdot-}$ ($4.0\text{--}9.1 \times 10^5 \text{ L}/(\text{mol}\cdot\text{s})$) [5], and is therefore often used as an $\cdot\text{OH}$ radical scavenger. As shown in Fig. 10(a), the addition of tert-butyl alcohol (100 mmol/L) resulted in almost no reduction in the degradation of

Fig. 10. Effect of addition of ethanol and NaN_3 on the degradation profile of 20 $\mu\text{mol/L}$ RhB (a), 20 $\mu\text{mol/L}$ MB (b), 20 $\mu\text{mol/L}$ orange II (c), 0.1 mmol/L phenol (d) and 0.1 mmol/L 4-CP (e) in the $\text{Cu}^0/\text{Fe}_3\text{O}_4\text{-PMS}$ system. Reaction conditions: initial PMS concentration 0.5 mmol/L, catalyst loading 0.1 g/L, initial pH value 7.0. (f) Tetramethylpiperidine spin-trapping electron spin resonance spectra of singlet oxygen ($^1\text{O}_2$) radicals in the $\text{Cu}^0/\text{Fe}_3\text{O}_4\text{-PMS}$ and PMS systems.

RhB, indicating that the $\cdot\text{OH}$ radical was not the reactive oxygen species in the $\text{Cu}^0/\text{Fe}_3\text{O}_4\text{-PMS}$ system. Ethanol can be applied as a radical scavenger to quickly react with both $\cdot\text{OH}$ ($1.2\text{--}2.8 \times 10^9 \text{ L}/(\text{mol}\cdot\text{s})$) and $\text{SO}_4^{\cdot-}$ ($1.6\text{--}7.8 \times 10^7 \text{ L}/(\text{mol}\cdot\text{s})$) [28]. As shown in Fig. 10(a), the addition of 100 mmol/L ethanol had no obvious effect on RhB degradation. Addition of 100 mmol/L ethanol had the same effect on the degradation of MB, orange II, phenol and 4-chlorophenol (Fig. 10(b)–(e)). These results thus indicate neither the $\cdot\text{OH}$ nor the $\text{SO}_4^{\cdot-}$ radical is the reactive oxygen species involved in the $\text{Cu}^0/\text{Fe}_3\text{O}_4\text{-PMS}$ system, and that instead a non-radical mechanism is involved.

A recent study reported that PMS could selectively decolorize cationic dyes without activation via a non-radical mechanism [38]. The proposed mechanism involves a strong electronic interaction between the cationic dye and PMS (HSO_5^-), and subsequent direct electron transfer from the cationic dye to HSO_5^- that induces the bleaching of the cationic dyes. In the present study, the contribution of the non-activated process to the degradation of RhB was about 13% in 15 min, considerably lower than the complete degradation of RhB obtained in the $\text{Cu}^0/\text{Fe}_3\text{O}_4\text{-PMS}$ system under similar conditions (Fig. 5). Moreover, the non-activated process is only effective for the decolorization of cationic dyes [38]. However, in the present

study with the $\text{Cu}^0/\text{Fe}_3\text{O}_4\text{-PMS}$ system, the anionic dye orange II and phenolic pollutants also underwent rapid degradation. Therefore, it is rational to infer that a novel non-radical mechanism is involved in the $\text{Cu}^0/\text{Fe}_3\text{O}_4\text{-PMS}$ system.

A non-radical mechanism has also been reported for PMS activation by reduced graphene oxide [27], N-doped carbon nanotubes [28] and benzoquinone [29]. In these PMS activation processes, the strong interaction between PMS and defective sites in the carbocatalysts could activate the PMS molecules to directly oxidize target components by electron extraction from organics without the generation of free radicals. The used carbon nanotubes, N-doped carbon nanotubes and benzoquinone can thus be regained by electron transfer. Further, Zhou and co-workers [29] reported that $^1\text{O}_2$ acted as an oxidizing species for the degradation of sulfamethoxazole in the PMS/benzoquinone process. In the present study, the addition of NaN_3 (100 mmol/L), a scavenger of singlet oxygen with a rate constant of approximately $3 \times 10^8 \text{ L}/(\text{mol}\cdot\text{s})$ [49], almost completely quenched the degradation of all the tested organic pollutants (Fig. 10). This result indicates that $^1\text{O}_2$ was generated as the oxidizing species in the $\text{Cu}^0/\text{Fe}_3\text{O}_4\text{-PMS}$ system. Further evidence for this conclusion comes from the three characteristic peaks of TEMP- O_2 adducts observed in the

Scheme 1. Possible mechanism for the activation of PMS and degradation of organic pollutants by $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composites.

$\text{Cu}^0/\text{Fe}_3\text{O}_4$ -PMS system. These results indicate that the reaction mechanism in the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ -PMS system may be similar to that observed in the PMS/benzoquinone process [29], namely that the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composites activate the PMS molecules to directly oxidize target pollutants through electron transfer from the organic pollutants to PMS without the generation of free radicals.

Based on the radical scavenging and ESR trapping results obtained in this study, a possible mechanism for the activation of PMS by $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composites is proposed in Scheme 1. PMS is first adsorbed onto the surface of the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composites. In the presence of organic pollutants, electron transfer from the organic pollutants to PMS induces the activation of PMS to generate $^1\text{O}_2$, which in turn induces the degradation of the organic pollutants.

4. Conclusions

$\text{Cu}^0/\text{Fe}_3\text{O}_4$ submicron composites were prepared and used as heterogeneous catalysts for the activation of PMS. Markedly higher activity was observed towards the degradation of or-

ganic pollutants in the presence of $\text{Cu}^0/\text{Fe}_3\text{O}_4$ in comparison with the use of Cu^0 and Fe_3O_4 particles as catalysts. The combination of 0.1 g/L $\text{Cu}^0/\text{Fe}_3\text{O}_4$ microparticles and 0.5 mmol/L PMS resulted in efficient degradation and mineralization of RhB, MB, orange II, phenol and 4-chlorophenol. The high catalytic activity of the $\text{Cu}^0/\text{Fe}_3\text{O}_4$ composites is attributed to the synergistic effect of the Cu^0 and Fe_3O_4 crystals. $^1\text{O}_2$ was identified as the major reactive oxygen species responsible for pollutant degradation. This study thus provides a highly efficient, facile and green chemical method for the oxidative removal of various organic pollutants.

References

- [1] S. Esplugas, D. M. Bila, L. G. T. Krause, M. Dezotti, *J. Hazard. Mater.*, **2007**, 149, 631–642.
- [2] H. Hori, A. Yamamoto, E. Hayakawa, S. Taniyasu, N. Yamashita, S. Kutsuna, H. Kiatagawa, R. Arakawa, *Environ. Sci. Technol.*, **2005**, 39, 2383–2388.
- [3] W. Luo, L. H. Zhu, N. Wang, H. Q. Tang, M. J. Cao, Y. B. She, *Environ. Sci. Technol.*, **2010**, 44, 1786–1791.
- [4] G. P. Anipsitakis, D. D. Dionysiou, *Environ. Sci. Technol.*, **2003**, 37, 4790–4797.
- [5] G. P. Anipsitakis, D. D. Dionysiou, *Environ. Sci. Technol.*, **2004**, 38, 3705–3712.
- [6] S. Y. Yang, P. Wang, X. Yang, L. Shan, W. Y. Zhang, X. T. Shao, R. Niu, *J. Hazard. Mater.*, **2010**, 179, 552–558.
- [7] O. S. Furman, A. L. Teel, R. J. Watts, *Environ. Sci. Technol.*, **2010**, 44, 6423–6428.
- [8] C. D. Qi, X. T. Liu, J. Ma, C. Y. Lin, X. W. Li, H. J. Zhang, *Chemosphere*, **2016**, 151, 280–288.
- [9] D. Lison, *CRC Crit. Rev. Toxicol.*, **1996**, 26, 585–616.
- [10] P. Nfodzo, H. Choi, *Chem. Eng. J.*, **2011**, 174, 629–634.
- [11] J. Madhavan, P. Maruthamuthu, S. Murugesan, S. Anandan, *Appl. Catal. B*, **2008**, 83, 8–14.
- [12] A. Rastogi, S. R. Al-Abed, D. D. Dionysiou, *Appl. Catal. B*, **2009**, 85,

Graphical Abstract

Chin. J. Catal., 2017, 38: 227–239 doi: 10.1016/S1872-2067(16)62566-4

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

Gang Nie, Jia Huang, Yezhou Hu, Yaobin Ding*, Xiaoyan Han, Heqing Tang*
South-Central University for Nationalities

Magnetic $\text{Cu}^0/\text{Fe}_3\text{O}_4$ submicron composites showed superior catalytic activity for the activation of peroxymonosulfate and degradation of organic pollutants through the generation of singlet oxygen.

- 171–179.
- [13] Y. R. Wang, W. Chu, *Appl. Catal. B*, **2012**, 123–124, 151–161.
- [14] F. Ji, C. L. Li, L. Deng, *Chem. Eng. J.*, **2011**, 178, 239–243.
- [15] J. Liu, J. H. Zhou, Z. X. Ding, Z. W. Zhao, X. Xu, Z. D. Fang, *Ultrason. Sonochem.*, **2017**, 34, 953–959.
- [16] C. Q. Tan, N. Y. Gao, Y. Deng, J. Deng, S. Q. Zhou, J. Li, X. Y. Xin, *J. Hazard. Mater.*, **2014**, 276, 452–460.
- [17] Y. F. Rao, D. Xue, H. M. Pan, J. T. Feng, Y. J. Li, *Chem. Eng. J.*, **2016**, 283, 65–75.
- [18] H. Lin, J. Wu, H. Zhang, *Chem. Eng. J.*, **2014**, 244, 514–521.
- [19] J. Zou, J. Ma, L. W. Chen, X. C. Li, Y. H. Guan, P. C. Xie, C. Pan, *Environ. Sci. Technol.*, **2013**, 47, 11685–11691.
- [20] L. J. Xu, J. L. Wang, *Environ. Sci. Technol.*, **2012**, 46, 10145–10153.
- [21] Y. B. Ding, L. H. Zhu, N. Wang, H. Q. Tang, *Appl. Catal. B*, **2013**, 129, 153–162.
- [22] C. Cai, H. Zhang, X. Zhong, L. W. Hou, *J. Hazard. Mater.*, **2015**, 283, 70–79.
- [23] Y. B. Ding, H. B. Tang, S. H. Zhang, S. B. Wang, H. Q. Tang, *J. Hazard. Mater.*, **2016**, 317, 686–694.
- [24] Y. Feng, D. L. Wu, Y. Deng, T. Zhang, K. Shih, *Environ. Sci. Technol.*, **2016**, 50, 3119–3127.
- [25] J. Liu, Z. W. Zhao, P. H. Shao, F. Y. Cui, *Chem. Eng. J.*, **2015**, 262, 854–861.
- [26] Y. J. Yao, Y. M. Cai, G. D. Wu, F. Y. Wei, X. Y. Li, H. Chen, S. B. Wang, *J. Hazard. Mater.*, **2015**, 296, 128–137.
- [27] X. G. Duan, Z. M. Ao, L. Zhou, H. Q. Sun, G. X. Wang, S. B. Wang, *Appl. Catal. B*, **2016**, 188, 98–105.
- [28] X. G. Duan, H. Q. Sun, Y. X. Wang, J. Kang, S. B. Wang, *ACS Catal.*, **2015**, 5, 553–559.
- [29] Y. Zhou, J. Jiang, Y. Gao, J. Ma, S. Y. Pang, J. Li, X. T. Lu, L. P. Yuan, *Environ. Sci. Technol.*, **2015**, 49, 12941–12950.
- [30] K. J. Koski, J. J. Cha, B. W. Reed, C. D. Wessells, D. S. Kong, Y. Cui, *J. Am. Chem. Soc.*, **2012**, 134, 7584–7587.
- [31] Z. Z. Wang, S. R. Zhai, J. L. Lv, H. X. Qi, W. Zheng, B. Zhai, Q. D. An, *RSC Adv.*, **2015**, 5, 74575–74584.
- [32] N. Wang, L. H. Zhu, D. L. Wang, M. Q. Wang, Z. F. Lin, H. Q. Tang, *Ultrason. Sonochem.*, **2010**, 17, 526–533.
- [33] X. Yuan, A. N. Pham, G. W. Xing, A. L. Rose, T. D. Waite, *Environ. Sci. Technol.*, **2012**, 46, 1527–1535.
- [34] G. H. Dong, Z. H. Ai, L. Z. Zhang, *Water Res.*, **2014**, 66, 22–30.
- [35] Y. S. Li, F. L. Jiang, Q. Xiao, R. Li, K. Li, M. F. Zhang, A. Q. Zhang, S. F. Sun, Y. Liu, *Appl. Catal. B*, **2010**, 101, 118–129.
- [36] R. Wang, Y. H. Li, R. H. Shi, M. M. Yang, *J. Mol. Catal. A.*, **2011**, 344, 122–127.
- [37] X. Y. Zhang, Y. B. Ding, H. Q. Tang, X. Y. Han, L. H. Zhu, N. Wang, *Chem. Eng. J.*, **2014**, 236, 251–262.
- [38] Y. Lei, C. S. Chen, J. Ai, H. Lin, Y. H. Huang, H. Zhang, *RSC Adv.*, **2016**, 6, 866–871.
- [39] R. R. Solís, F. J. Rivas, O. Gimeno, J. L. Pérez-Bote, *J. Chem. Technol. Biotechnol.*, **2016**, 91, 51–58.
- [40] P. Shukla, H. Q. Sun, S. B. Wang, H. M. Ang, M. O. Tadé, *Catal. Today*, **2011**, 175, 380–385.
- [41] Y. H. Guan, J. Ma, Y. M. Ren, Y. L. Liu, J. Y. Xiao, L. Q. Lin, C. Zhang, *Water Res.*, **2013**, 47, 5431–5438.
- [42] Y. J. Yao, H. Chen, C. Lian, F. Y. Wei, D. W. Zhang, G. D. Wu, B. J. Chen, S. B. Wang, *J. Hazard. Mater.*, **2016**, 314, 129–139.
- [43] L. Duan, B. Z. Sun, M. Y. Wei, S. L. Luo, F. Pan, A. H. Xu, X. X. Li, *J. Hazard. Mater.*, **2015**, 285, 356–365.
- [44] S. L. Luo, L. Duan, B. Z. Sun, M. Y. Wei, X. X. Li, A. H. Xu, *Appl. Catal. B*, **2015**, 164, 92–99.
- [45] Z. L. Wang, Y. C. Du, Y. L. Liu, B. H. Zou, J. Y. Xiao, J. Ma, *RSC Adv.*, **2016**, 6, 11040–11048.
- [46] W. D. Oh, Z. L. Dong, Z. T. Hu, T. T. Lim, *J. Mater. Chem. A*, **2015**, 3, 22208–22217.
- [47] Y. C. Du, W. J. Ma, P. X. Liu, B. H. Zou, J. Ma, *J. Hazard. Mater.*, **2016**, 308, 58–66.
- [48] T. Zeng, X. L. Zhang, S. H. Wang, H. Y. Niu, Y. Q. Cai, *Environ. Sci. Technol.*, **2015**, 49, 2350–2357.
- [49] Y. B. Ding, P. Zhou, H. Q. Tang, *Chem. Eng. J.*, **2016**, 291, 149–160.

亚微米级Cu⁰/Fe₃O₄复合物多相催化过一硫酸盐降解有机污染物

聂 刚, 黄 佳, 胡冶州, 丁耀彬*, 韩小彦, 唐和清[#]

中南民族大学资源与环境学院, 国家民委-教育部共建催化材料重点实验室, 湖北武汉430074

摘要: 过一硫酸盐催化活化技术因其可产生强氧化性活性氧化物种, 可快速氧化降解并矿化有机污染物的优异性能而备受关注。本文成功制备了亚微米级Cu⁰/Fe₃O₄复合物, 发现其能多相催化过一硫酸盐产生单线态氧降解有机污染物。首先, 以CuCl₂·2H₂O, FeCl₃·4H₂O和FeCl₃·6H₂O为铜源和铁源, 水合肼为还原剂, 采用水热法在180 °C反应24 h制备了亚微米级磁性Cu⁰/Fe₃O₄复合物。表征结果显示, 所制材料为Cu⁰和Fe₃O₄的复合物, 颗粒大小约为220 nm; 单一相Cu⁰和Fe₃O₄晶体粒径分别为33.8和106.2 nm, 而Cu⁰/Fe₃O₄复合物中Cu⁰和Fe₃O₄晶体粒径分别减为20.8和31.9 nm。这表明Cu⁰和Fe₃O₄复合降低了Cu⁰和Fe₃O₄晶体粒径, 有利于Cu⁰和Fe₃O₄的分散。BET测试结果表明, Cu⁰/Fe₃O₄复合物比表面积为4.6 m²/g, 与Cu⁰颗粒的(4.2 m²/g)相当, 但远小于Fe₃O₄的(15.6 m²/g)。制备的Cu⁰/Fe₃O₄复合物可有效催化过一硫酸盐产生单线态氧降解罗丹明B、亚甲基蓝、金橙II、苯酚和对氯酚。当Cu⁰/Fe₃O₄复合物的用量为0.1 g/L, 过一硫酸盐浓度为0.5 mmol/L和初始pH为7时, Cu⁰/Fe₃O₄复合物可在30 min内完全降解20 μmol/L的罗丹明B、亚甲基蓝、金橙II以及0.1 mmol/L的苯酚和对氯酚。对比试验显示, 在相同条件下, Cu⁰和Fe₃O₄颗粒分别可以降解28%和20%的罗丹明B。这表明Cu⁰/Fe₃O₄复合物中的Cu⁰和Fe₃O₄晶体在催化过一硫酸盐降解污染物的反应中具有协同作用, 这主要来源于Cu⁰/Fe₃O₄复合物中Cu⁰和Fe₃O₄的晶体粒径变小和更好的分散。采用分光光度法测定了降解反应液中铜和铁离子的溶出量。当Cu⁰/Fe₃O₄复合物的用量为0.1 g/L, 过一硫酸盐浓度为0.5 mmol/L和初始pH为7时, 反应60 min后, 降解液中铜和铁离子的浓度分别为0.22和0.1 mg/L, 仅占复合物中总铜和总铁量的1.1%和0.2%, 表明Cu⁰/Fe₃O₄复合物具有较强的化学稳定性。所制Cu⁰/Fe₃O₄复合物具有超顺磁性, 借助磁场实现快速分离回收, 可循环利用五次, 表明其优越的催化稳定性。通过加入乙醇和叠氮化钠, 考察了Cu⁰/Fe₃O₄复合物催化活化过

一硫酸盐体系中的活性氧化物种。发现100 mmol/L乙醇的加入对污染物的降解无明显影响, 而加入同等量的叠氮化钠可完全抑制污染物的降解, 表明 $\text{Cu}^0/\text{Fe}_3\text{O}_4$ 复合物催化活化过一硫酸盐产生的主要活性氧化物种为单线态氧。采用电子顺磁共振进一步证实了单线态氧的生成。

基于以上研究, $\text{Cu}^0/\text{Fe}_3\text{O}_4$ 复合物催化活化过一硫酸盐的机理为 $\text{Cu}^0/\text{Fe}_3\text{O}_4$ 作为一个电子媒介加速过一硫酸盐和污染物之间的电子转移, 从而导致污染物被快速降解。该反应机理不同于常见的金属催化过一硫酸盐产生硫酸根和羟自由基的反应机理。我们推测, 电导性优良的 Cu^0 在此催化反应中起着关键性作用。本催化方法可作为一种绿色的氧化技术用于环境污染物的氧化降解处理。

关键词: 多相催化; $\text{Cu}^0/\text{Fe}_3\text{O}_4$ 磁性复合物; 过一硫酸盐; 单线态氧; 氧化降解

收稿日期: 2016-09-14. 接受日期: 2016-10-28. 出版日期: 2017-02-05.

*通讯联系人. 电话/传真: (027) 87543632; 电子信箱: yaobinding@mail.scuec.edu.cn

#通讯联系人. 电话/传真: (027) 87543632; 电子信箱: tangheqing@mail.scuec.edu.cn

基金来源: 国家自然科学基金(21377169, 21507168); 湖北省自然科学基金(2014CFC1119, 2015CFB505); 中央高校基本科研基金(CZW15078).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).