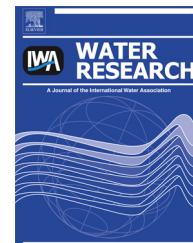




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Efficient degradation of atrazine by magnetic porous copper ferrite catalyzed peroxymonosulfate oxidation via the formation of hydroxyl and sulfate radicals

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ABSTRACT

Magnetic porous copper ferrite (CuFe_2O_4) showed a notable catalytic activity to peroxymonosulfate (PMS). More than 98% of atrazine was degraded within 15 min at 1 mM PMS and 0.1 g/L CuFe_2O_4 . In contrast, CuFe_2O_4 exhibited no obvious catalytic activity to peroxodisulfate or H_2O_2 . Several factors affecting the catalytic performance of PMS/ CuFe_2O_4 were investigated. Results showed that the catalytic degradation efficiency of atrazine increased with PMS and CuFe_2O_4 doses, but decreased with the increase of natural organic matters concentration. The catalytic oxidation also showed a dependence on initial pH. The presence of bicarbonate stimulated atrazine degradation by PMS/ CuFe_2O_4 at low concentrations but inhibited the degradation at high concentrations. Furthermore, the reactive species for atrazine degradation in PMS/ CuFe_2O_4 system were identified as hydroxyl radical (HO^\bullet) and sulfate radical ($\text{SO}_4^{\bullet-}$) through competition reactions of atrazine and nitrobenzene, instead of commonly used alcohol scavenging, which was not a reliable method in metal oxide catalyzed oxidation. Surface hydroxyl groups of CuFe_2O_4 were a critical part in radical generation and the copper on CuFe_2O_4 surface was an active site to catalyze PMS. The catalytic degradation of atrazine by PMS/ CuFe_2O_4 was also effective under the background of actual waters.

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1. Introduction

Atrazine is a kind of triazine herbicides widely used for crops and weed control. Photolysis of atrazine by sunlight is slow due to the weak absorption at the wavelength above 220 nm. Atrazine is also resistant to microorganism degradation and therefore persistent in water and soil. Various studies were conducted to generate HO• for the destruction of atrazine, such as photolysis of hydrogen peroxide (De Laat et al., 1999), Fenton and photo/electrochemical-Fenton (De Laat et al., 1999; Ventura et al., 2002), ozone and catalytic ozonation (Acero et al., 2000; Ma and Graham, 2000).

Sulfate radical ($\text{SO}_4^{\cdot-}$) is a strong oxidant with the redox potential of 2.5–3.1 V (Neta et al., 1988), similar to HO•. It is usually generated from peroxymonosulfate (PMS) and peroxydisulfate (PDS) by UV, heat, base, transition metals, or quinones activation (Anipsitakis and Dionysiou, 2004; Fang et al., 2013b; Furman et al., 2010; Guan et al., 2011; Waldemer et al., 2007). Comparing with PDS, PMS is easy to be activated by transition metals due to the asymmetric molecular structure. Homogeneous catalytic oxidation by PMS coupled with transition metals showed efficient decontamination of organic pollutants, among which Co(II) was found to be a best activator (Anipsitakis and Dionysiou, 2004). However, cobalt has been recognized as a possible human carcinogen by International Agency for Research on Cancer (IARC). In order to reduce the concentration of free cobalt ions, attentions have been focused on heterogeneous catalysis of PMS by supported cobalt, cobalt oxides, and metal-cobalt mixed oxides (Chan and Chu, 2009; Qi et al., 2013; Yang et al., 2009).

Spinel ferrites, expressed as MeFe_2O_4 (Me = Mn, Co, Ni, Cu, Mg, etc.), are kinds of magnetic materials widely used in electronic applications, which could be separated easily from water under magnetic field. The ferrites were used to remove heavy metals from water bodies due to the abundant surface hydroxyl groups and magnetic property (Tang et al., 2013). Studies were also conducted on the photocatalytic and catalytic activities of spinel ferrites. ZnFe_2O_4 exhibited notable photocatalytic activity for H_2O_2 under visible light irradiation (Su et al., 2012). Catalytic ozonation by NiFe_2O_4 was also reported to destruct di-n-butyl phthalate (Ren et al., 2012). Ferrites (Co, Cu, Mn) catalyzed H_2O_2 oxidation could decolorize synthetic dyes via the generation of HO• (Baldrian et al., 2006). PDS catalyzed by magnetite nanoparticles were investigated to degrade 2,4,4'-trichlorobiphenyl and sulfamonomethoxine (Fang et al., 2013a; Yan et al., 2011). CoFe_2O_4 was used to catalyze PMS to reduce the concentration of free cobalt ion (Yang et al., 2009). Our preliminary study found that CuFe_2O_4 was also effective to activate PMS among the ferrites (Mn, Co, Ni, Cu, Zn), although not as effective as CoFe_2O_4 . Furthermore, copper is not recognized as potential carcinogen by IARC. Considering the catalytic activity and the risk of metal leaching of solid catalysts, CuFe_2O_4 might be applicable to activate PMS in water treatment.

The purpose of this research was 1) to investigate the catalytic activities of porous CuFe_2O_4 on peroxides (PMS, PDS and H_2O_2), which was convenient to be separated from water due to its large size compared with nanoparticles, 2) to identify the reactive species for atrazine degradation and possible

mechanism on radical formation in the PMS/ CuFe_2O_4 system, 3) to investigate the influences of water quality parameters on the catalytic performance of PMS/ CuFe_2O_4 including pH value, PMS and CuFe_2O_4 doses, natural organic matters (NOM), and inorganic salts, as well as the influences of actual water backgrounds.

2. Experimental

2.1. Materials

Potassium peroxymonosulfate (available as Oxone®, PMS), potassium peroxydisulfate (PDS), atrazine, sodium phosphate monobasic monohydrate, sodium phosphate dibasic were of ACS reagent grade and purchased from Sigma–Aldrich. Hydrogen peroxide (35% w/w) was obtained from Alfa Aesar. Methanol (Thermo Fisher Scientific) and acetic acid (Dima-Tech) were of HPLC grade. Suwannee River natural organic matter (SRNOM) was purchased from the International Humic Substances Society. *Tert*-butyl-alcohol (TBA) was of guaranteed reagent grade and purchased from Tianjin Chemical Reagent Co., Ltd., China. Copper nitrate, ferric nitrate, sodium hydroxide, perchloric acid, sodium bicarbonate were all of analytical-reagent grade and purchased from Sinopharm Chemical Reagent Co., Ltd., China. All solutions were prepared in Milli-Q water produced on a Milli-Q® Biocel water system.

2.2. Preparation and characterization of CuFe_2O_4

Magnetic porous CuFe_2O_4 was prepared by a sol–gel process with egg white at the copper and ferric molar ratio of 1:2, referring to the preparation of NiFe_2O_4 reported previously (Ren et al., 2012). Detailed information sees Text S1.

The surface morphologies were obtained on a Hitachi S-3000N scanning electron microscopy (SEM). The X-ray powder diffraction (XRD) was performed on a TTR-III diffractometer (Rigaku, Japan) with Cu K α radiation. The magnetic property was measured by a vibrating sample magnetometer (JDM-14D, China). Fourier transform infrared (FTIR) spectra were performed on an IS10 FTIR spectrometer (Nicolet, America) in the range of 500–4000 cm^{-1} . Raman spectra were taken on a LabRAM HR800 confocal microscopic Raman spectrometer (HORIBA Jobin Yvon, France) with 488 nm laser irradiation. X-ray photoelectron spectroscopy (XPS) analysis was performed with PHI 5700 ESCA System (Physic Electronics, America) using an Al K α excitation source (1486.6 eV). All lines recorded were calibrated to the C 1 s line at 284.6 eV. The pH_{PZC} of CuFe_2O_4 was determined by mass titration.

The CuFe_2O_4 was characterized as a magnetic porous material of tetragonal-type structure, with the average particle diameter and pore size being 50–100 μm and 1–5 μm (SI Text S2 and Fig. S1).

2.3. Experimental procedure

Experiments were performed in 250 mL conical flask at 25 ± 2 °C, mixed at 150 rpm. Desired amount of PMS and atrazine stock solutions were added to solution to a final

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