



Research article

Removal of sulfamethazine antibiotics using Ce–Fe-graphene nanocomposite as catalyst by Fenton-like process

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ABSTRACT

The presence of sulfonamide (SMT) antibiotics in aquatic environments has received increasing attention in recent years, and they are ubiquitous pollutants which cannot be effectively removed by conventional wastewater treatment processes. In this paper, the nanocomposites Ce⁰/Fe⁰-reduced graphene oxide (Ce⁰/Fe⁰-RGO) were synthesized through chemical reduction method, and characterized by Raman and FTIR before and after use. The addition of RGO can prevent the agglomeration of Ce⁰ and Fe⁰. The elimination of SMT can be divided into adsorption and degradation process. The adsorption of SMT onto the catalyst can enhance its degradation. The effect of pH value, concentration of H₂O₂, catalyst dosage, temperature and initial SMT concentration on the removal efficiency of SMT was determined. When pH = 7, T = 25 °C, H₂O₂ = 8 mM, Ce⁰/Fe⁰-RGO = 0.5 g/L, SMT = 20 mg/L, the removal efficiency of SMT and TOC was 99% and 73%, respectively. The stability of the catalysts was evaluated with repeated batch experiments using ethanol, water and acid as solvents to wash the used catalysts, respectively. The surface change of the catalysts after each use was characterized by Raman and FTIR analysis. The intermediates were detected by GC-MS and IC, the possible degradation pathway of SMT was tentatively proposed.

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1. Introduction

Sulfamethazine (SMT) is a kind of antibiotics belonging to pharmaceutically active compounds (PhACs), due to its wide application as bacteriostatic agent, it has become an ubiquitous pollutant, which cannot be effectively removed by conventional wastewater treatment processes. Many technologies have been used to remove SMT, including membrane filtration (Koyuncu et al., 2008; Taheran et al., 2016), adsorption (Braschi et al., 2010; Qiang et al., 2013) and advanced oxidation processes (Wang and Xu, 2012; Liu and Wang, 2013; Zhou et al., 2013; Kitsiou et al., 2014; Wang and Chu, 2016).

Heterogeneous catalysts have displayed good performance in the Fenton-like process compared with homogeneous catalysts. These kinds of catalysts can be used in neutral pH condition, can be easily separated in solution, and less iron sludge produced in the

process. It has been reported that many kinds of iron oxide catalysts have been used in Fenton-like process, for example, lepidocrocite (γ-FeO(OH)) (Chou et al., 2001), hematite (α-Fe₂O₃) (Guo et al., 2010), magnetite (Fe₃O₄) (Costa et al., 2008), Fe₃O₄/CeO₂ composite (Xu and Wang, 2012) and goethite (α-FeO(OH)) (Neppolian et al., 2004).

Agglomeration and metal leaching are the main problems should be overcome for the preparation of catalysts (Zubir et al., 2014; Ziolk, 2004). Different supporters have been used for the attachment of magnetic nanoparticles, such as, silica-based support (Shylesh et al., 2010; Gill et al., 2007), carbon-based support (Yang et al., 2015a,b) and so on. The hybrids can effectively reduce the metal leaching, keep the catalysts dispersity, improve the catalytic performance and can be easily separated through the external magnetic field, such as Fe/activated carbon (Quintanilla et al., 2006), carbon-Fe (Ramirez et al., 2007), a zeolite Y-Fe catalyst (Rache et al., 2014), transition metals on carbon aerogels (Duarte et al., 2009) and so on.

Carbon-based materials are widely used for adsorption (Xing et al., 2016) and catalytic process (Lee et al., 2013) due to their large surface area and stability. Graphene is a single layer

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framework with six carbon rings in two dimensions. The π - π bonds connecting each carbon atom and its large specific surface area are contributed to the strong adsorption ability. Graphene can be prepared through oxidation reaction. However, graphene oxide (GO) has many oxygen-containing groups, such as carbonyl, carboxyl, epoxy and hydroxyl group, which make GO has poor electrical conductivity (McAllister et al., 2007). Reduced graphene oxide (RGO) has less oxygen-containing groups leading to its recalcitrant in chemical reaction which can be prepared through chemical reduction of GO. RGO has partial graphene-conjugated structure which can lead to outstanding electronic (Zhang et al., 2005), mechanical and thermal properties (Fang et al., 2009; Tang et al., 2013). Iron-RGO and iron oxide-RGO have been widely used for removal of dye pollutants, such as Fe-RGO (Guo et al., 2012), Fe₃O₄-RGO (Sun et al., 2011), Ce–Fe bimetallic oxides on graphene (Ling et al., 2014).

In our previous studies, we have studied the degradation of sulfamethazine using Ce doped Fe composites as catalyst in Fenton-like process, which displayed excellent catalytic performance. However, the Ce⁰/Fe⁰ nanoparticles are prone to aggregate to form large particles because of the anisotropic dipolar interactions, which decreased the activity of catalyst (Zubir et al., 2014; Yang et al., 2015a,b). The leaching of iron was detected in the solution, which also decreased the stability of the catalyst. Therefore, the Ce⁰/Fe⁰ composites were anchored on reduced graphene oxide to preserve their properties.

In this study, the Ce⁰/Fe⁰-RGO composites were prepared through reduction method (Cheng et al., 2007; Xu and Wang, 2013). The influencing factors such as the initial SMT concentration, H₂O₂ concentration, pH, catalyst dosage and temperature were studied to optimize the degradation condition. The stability of the catalysts was evaluated based on the results of the repeated batch experiments. The intermediates were detected and the possible degradation pathway of SMT was tentatively proposed.

2. Materials and methods

2.1. Materials and chemicals

All the materials were used without further purification. The graphene oxides were purchased from Nanjing Xianfeng Nano Co., China. Iron (II) sulfate heptahydrate (FeSO₄·7H₂O), cerium (III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O) and potassium borohydride (KBH₄) were purchased from Sinopharm Chemical Reagent Co., Ltd. A.R. grade hydrogen peroxide (30%, w/w) A.R. grade hydrogen peroxide (30%, w/w) was purchased from Tianjin Yongda Chemical Reagent Company Limited; HPLC grade methanol from Tianjin Hedong District Hongyan Reagent Plant; A.R. grade hydrochloric acid (0.1 M) and sodium hydroxide (0.1 M) were used for pH adjustment. MilliQ water prepared by Milli-Q Advantage A10 System was used in this study. Purified sulfamethazine (>99%) was purchased from Alfa Aesar. Nylon 66 organic membrane filter of 0.22 μ m purchased from Pall Corporation.

2.2. Preparation and characterization of Ce⁰/Fe⁰-RGO composites

The nanoscale Ce⁰/Fe⁰-RGO composites were synthesized via reduction method by KBH₄ in the present of graphene oxide. Graphene oxide (0.056 g) were dispersed in 100 ml of deionized water and ultrasonicated for 2 h with 300 W power to get homogeneous graphene oxide solution. FeSO₄·7H₂O (1.112 g) and Ce(NO₃)₃·6H₂O (0.0868 g) were added in a four-necked flask container and the mixture were stirred (400 rpm) using a magnetic stirrer for 2 h. The argon atmosphere was piped into the flask to keep the system oxygen free and the gas was entered into deionized water to make

oxygen-free deionized water. Then 100 ml 0.2 mol/L of KBH₄ aqueous solution was added into the container through the pump to keep a constant speed (1.7 ml/min). After 1 h of reaction, Ce⁰/Fe⁰-RGO composites were synthesized. The composites were washed with oxygen-free deionized water for three times after deposited, and dried in a vacuum freezing dryer before use.

Emission scanning electron microscope (SEM, SU8010, Hitachi) and Transmission electron microscopies (TEM, JEM 2100 and JEOL) were used to observe the microscopic morphology of catalyst loaded in silicon slice and copper grid, respectively.

The crystalline structure of the composites were characterized by X-ray diffraction (XRD) with Cu K α radiation (D8-Advance, Bruker, 40 kV and 40 Ma) at room temperature with 0.5°/min over scan range (2 θ) of 10°–90°. The specific surface area and pore size distribution were measured by nitrogen adsorption–desorption isotherm measurements at 77 K on a NOVA 3200e sorptometer and degassing at 428 K.

Raman spectrometer (LabRAM HR Evolution of HOEIBA Jobin Yvon Company, French) was used for recording the Raman spectra with a regular model laser operated at wavelength of 633 nm and the laser power was 0.8 mW (Vinodgopal et al., 2012). The spectra was recorded using a 50 \times object lens and 600 gr/mm grating.

The infrared spectra were recorded with Nicolet 6700 Fourier transform infrared spectrometer made by Thermo Fisher Scientific. The samples were prepared using powder pressing method in KBr pellet at room temperature.

2.3. Heterogeneous Fenton-like degradation of SMT

The experiments were performed in serum bottles (100 ml) which were sealed in a shaking incubator with 160 rpm at a certain temperature in the dark. The reaction suspension containing calculated amount of catalysts and sulfamethazine were prepared. HCl (0.1 M) and NaOH (0.1 M) was used to adjust pH. The experiments were carried out twice, and the results were the average value. The samples were analyzed after filtered with 0.22 μ m nylon membrane filter.

2.4. Analytical methods

High performance liquid chromatography (HPLC Agilent 1200) was used to analyze sulfamethazine concentration. It equipped with a diode array detector (DAD) and an XDB-C18 (4.6 \times 150 mm) reversed-phase column. The injection volume was 10 μ L. The column temperature was 30 °C. The mixture of distilled water and methanol (55:45 (v/v)) was used as the mobile phase with a flow rate of 1 ml/min. The detection wavelength for sulfamethazine was 255 nm with retention time of 2.01 min.

Gas chromatography-mass spectrometry (GC–MS) (Agilent, USA; 5975C MS and 7890 A GC) was used to detect the intermediate products. Gas chromatography (GC) system equipped with a DB-5MS column (length 30 m, thickness 0.25 μ m, and diameter 0.25 mm). The carrier gas was high purity (99.99%) helium with a constant flow rate of 1.0 ml/min. The analysis methods are as follows. The initial temperature was 50 °C (2 min hold) at 6.0 °C/min to 80 °C (3 min hold), then at 6.0 °C/min to 300 °C (2 min hold) for a total run of 48.7 min. The injector and detector temperatures were 250 and 280 °C, respectively.

Ion chromatography (Dionex model ICS 2100) coupled with a dual-piston pump, a Dionex IonPac AS19/AS11 analytical column (4 mm \times 250 mm), an IonPac AG19/AG11 guard column (4 mm \times 250 mm), and a DS6 conductivity detector are used to analyze the nitrite ion, nitrate ion, sulfate (SO₄²⁻) and acetic acid. The eluent solution was mixture of 3.5 mM Na₂CO₃ and 1.0 mM NaHCO₃ with a constant rate of 1 ml/min.

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