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Zn-Fe-CNTs catalytic in situ generation of H_2O_2 for Fenton-like degradation of sulfamethoxazole

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HIGHLIGHTS

- Zn-Fe-CNTs was capable of converting O_2 to H_2O_2 and further to $^\bullet$ OH.
- The Fenton-like degradation of sulfamethoxazole (SMX) using Zn-Fe-CNTs as catalyst was studied.
- The removal efficiency of SMX and TOC was 100% and 51.3%, respectively.
- The possible reaction mechanism of Zn-Fe-CNTs/O_2 process was tentatively proposed.

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ABSTRACT

A novel Fenton-like catalyst (Zn-Fe-CNTs) capable of converting O_2 to H_2O_2 and further to $^\bullet$OH was prepared through infiltration fusion method followed by chemical replacement in argon atmosphere. The catalyst was characterized by SEM, EDS, TEM, XRD and XPS. The reaction between Zn-Fe-CNTs and O_2 in aqueous solution could generate H_2O_2 in situ, which was further transferred to $^\bullet$OH. The Fenton-like degradation of sulfamethoxazole (SMX) using Zn-Fe-CNTs as catalyst was evaluated. The results indicated that Zn-Fe-CNTs had a coral porous structure with a BET area of 51.67 m^2/g, exhibiting excellent adsorption capacity for SMX, which enhanced its degradation. The particles of Zn^0 and Fe^0/Fe_2O_3 were observed on the surface of Zn-Fe-CNTs. The mixture of Zn^0 and CNTs could reduce O_2 into H_2O_2 by micro-electrolysis and Fe^0/Fe_2O_3 could catalyze in-situ generation of H_2O_2 to produce $^\bullet$OH through Fenton-like process. When initial pH = 1.5, T = 25 °C, O_2 flow rate = 400 mL/min, Zn-Fe-CNTs = 0.6 g/L, SMX = 25 mg/L and reaction time = 10 min, the removal efficiency of SMX and TOC was 100% and 51.3%, respectively. The intermediates were detected and the possible pathway of SMX degradation and the mechanism of Zn-Fe-CNTs/O_2 process were tentatively proposed.

1. Introduction

Advanced oxidation processes (AOPs) have been widely used for the degradation of toxic organic contaminants in water and wastewater in the past decades [1]. The classic Fenton- and related reactions are convenient, economical, and green ways to generate $^\bullet$OH for the removal of non-biodegradable and/or toxic compounds [2]. Fenton-like process, using solid iron compounds/complexes as heterogeneous catalysts [3,4], has received increasing attention in recent years. It is also attractive to develop Fenton process which can spontaneously generate H_2O_2 in situ, such as electro-Fenton system and photo-Fenton process [5,6]. However, the low and hardly regulated concentration of H_2O_2 generated in-situ decreased the degradation efficiency of organic contaminants [7–9]. Therefore, it is necessary to increase the concentration of H_2O_2 in solid iron compounds/O_2 system.

The generation of H_2O_2 in-situ by the reaction between Zn^0 and O_2 was investigated, but the productivity was low [10–12]. According to the theory of electrochemical corrosion, the rate of oxidation-reduction reaction on the surface of metal can be accelerated in the galvanic-type corrosion cell without external power supply. Therefore, the in-situ generation of H_2O_2 can be improved by the electrode reaction in the corrosion cell using Zn^0 as anode. Cathodic H_2O_2 could be produced on the surface of carbon materi-

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als through the electrochemical process [13,14]. Carbon nanotubes (CNTs) may offer significant advantages for the two-electron reduction of O_2 due to their good electrical conductivity, high surface activity and mechanical strength [15]. Thus, high concentration of H_2O_2 can be possibly produced by the reduction of O_2 in the micro-electrolysis system of Zn^0-CNTs, which formed numerous corrosion cells between the particles of Zn^0 and CNTs in aqueous solution. Moreover, the redox potential of Fe^{2+}/Fe^0 (−0.44 V) is higher than that of Zn^{2+}/Zn^0 (−0.76 V), the Fe^0 can be deposited on Zn^0/CNTs via chemical replacement. Therefore, when the composite of Zn^0, CNTs and Fe^0 reacts with O_2, H_2O_2 can be continuously supplied through the micro-electrolysis reaction between O_2 and Zn^0-Fe^0/CNTs, which can catalyze the generated H_2O_2 to produce $^{\bullet}OH$. In this system, Fe^0 or Fe^{2+} can be regenerated either by a direct reduction with Zn^0 or the reaction with H_2O_2.

The release of antibiotics into the aquatic environment caused by extensive use of antibiotics is receiving increasing attention in recent years [16–18]. Sulfamethoxazole (SMX), an antibiotic used worldwide for treatment of urinary infection, has been identified in many wastewater treatment plants (WWTPs) effluents [19]. It is required to develop effective approaches for SMX removal.

In this study, Zn-Fe-CNTs composite was synthesized, characterized and used as catalyst for Fenton-like degradation of SMX. The effect of initial pH, Zn-Fe-CNTs dosage, and initial SMX concentration on the removal efficiency of SMX was determined. The intermediates were detected by LC–MS and IC, and the possible degradation pathway of SMX was tentatively proposed.

2. Materials and methods

2.1. Materials and chemicals

Sulfamethoxazole (SMX) ($C_{10}H_{11}N_3O_3S$) was a sigma Aldrich product (≥99.0% purity). Multi-walled CNTs ($d < 8$ nm, $l = 10$–30 μm) were produced by Beijing Deke Daojing Nano-Company, China. Zinc powders (size: 120 meshes, specific surface area: 0.72 m^2/g, purity: >99.8%) were obtained from Shandong Xiya Corporation Ltd., China. Commercial iron powders (≥98.0% purity) with specific surface area of 1.26 m^2/g were purchased from Tianjin Jinke Fine Chemical Industry Research Institute., China. H_2SO_4, NaOH, $FeSO_4{\cdot}7H_2O$ and H_2O_2 were all of analytical grade. De-ionized water was used in all experiments.

2.2. Preparation and characterization of Zn-Fe-CNTs

The Zn-Fe-CNTs preparation was as follows. Firstly, 1.5 g Zinc powder was mixed with 0.5 g multi-walled CNTs. 2 mL 40% w polyethyleneglycol 4000 was dropped into the mixture, stirred for 30 min, then dried at room temperature, sintered in the tube furnace at 550 °C for 120 min with a N_2 flow speed of 60 mL/min and cooled into room temperature to obtain Zn-CNTs. Secondly, $FeSO_4{\cdot}7H_2O$ (0.5 g) were dissolved in 200 mL of aqueous sulfuric acid solution (pH = 3), and Zn-CNTs (1 g) were added in argon atmosphere. After 1 h, Zn-Fe-CNTs composites were obtained. The formation of Zn-Fe-CNTs was based on the following principles: polyethyleneglycol 4000 was used as binder and to bind zinc powder and multi-walled CNTs. When the mixture of zinc powder, multi-walled CNTs and polyethyleneglycol 4000 was heated into 550 °C, zinc powder with melting points of 419.5 °C was melted into liquid and polyethyleneglycol 4000 was decomposed into volatile gases. When the heated mixture was cooled into room temperature, liquid zinc was solidified on the surface of multi-walled CNTs and form Zn-CNTs. When as-prepared Zn-CNTs were put into the Fe^{2+} solution, the chemical replacement between Fe^{2+} and Zn^0 in Zn-CNTs resulted in the formation of Zn-Fe-CNTs composites.

Scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS) analyses were performed on emission scanning electron microscope (SEM, SU8010, Hitachi). Transmission electron microscopy (TEM) images were recorded on a transmission electron microscope (HRTEM, JEM 2100 and JEOL). BET-surface areas were measured using a NOVA 3200e bath at 77 K and degassing at 373 K. The pore size distribution was determined by the BJH method. Powder X-ray diffraction (XRD) measurement was performed with Cu Kα radiation (MiniFlex 600, Rigaku, 40 kV and 15 mA) at a scanning rate of 0.5°/min. X-ray photoelectron spectroscopy (XPS) was measured by an AXIS-Ultra instrument (Kratos Analytical, UK).

2.3. Fenton-like degradation of SMX

Experiments were conducted at room temperature in a glass bottle (500 mL) containing a 250 mL solution. The real effluent of wastewater was collected at a local municipal wastewater treatment plant. The sample had an initial content of TOC of 9.77 ± 0.36 mg/L and pH of 7.0 ± 0.2.

2.4. Analytical methods

H_2O_2 concentration was measured by a photometric method on an UV–vis spectrometer (PerkinElmer Lambda 25) at 385 nm using potassium titanium oxalate as chromogenic reagent. SMX concentration was determined by HPLC (Agilent 1200) equipped with a diode array detector (DAD) and a C18 reversed-phase column (4.6 mm × 150 mm). The mobile phase used for SMX was a mixture of distilled water and acetonitrile (55:45 (v/v)) at a flow rate of 1.0 mL/min with a column temperature of 30 °C, and the analytical wavelength was 255 nm. SMX had a retention time of 3.0 min under these conditions. HPLC–MS equipped with the above-mentioned column coupled to a Shimadzu 2010EV mass spectrometer with ESI ion source (LC–MS 2010, Columbia, USA) was used to analyze organic intermediates. It equipped with a photo diode array (PDA) detector, and operated in a negative mode. The aforementioned solvent conditions were used for the analysis of the intermediates. The injected volume was 30 μL. Total organic carbon (TOC) content was measured by a Multi TOC/TN Analyzer (2100, Analytik Jena. Germany). The concentration of dissolved zinc and iron generated from the reaction process was determined with a flame atomic adsorption spectroscopy (AAS, HITACHI ZA-3000, Japan).

3. Results and discussion

3.1. Characterization of Zn-Fe-CNTs

The N_2 adsorption-desorption isotherms and pore size distributions of Zn-Fe-CNTs and Zn-CNTs were given in Fig. 1. The Zn-Fe-CNTs sample provided the IV type isotherm, which are typical for the highly ordering mesoporous material with narrow size distribution. The isotherm of Zn-CNTs was identified as type an III/IV mixed type isotherm, which was characteristic of co-existence of microporous and mesoporous. Zn-Fe-CNTs had a larger BET specific surface area (51.67 m^2/g) than that of Zn-CNTs (26.99 m^2/g). The pore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) method (Fig. 4b). The result showed that the average pore sizes of Zn-Fe-CNTs and Zn-CNTs were 16.89 nm and 13.52 nm, respectively.

TEM image and SEM micrograph of Zn-Fe-CNTs were shown in Figs. 2 and 3.

The samples exhibited coral porous structure and large dispersive metal nano-particles were adhered to the surface of CNTs in the Zn-Fe-CNTs. In order to confirm the element distribution and relative element content in Zn-Fe-CNTs, EDS spectra and element