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Performance of bimetallic nanoscale zero-valent iron particles for removal of oxytetracycline

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ABSTRACT

In this study, bimetallic nanoscale zero-valent iron particles (nZVI), including copper/nanoscale zero-valent iron particles (Cu/nZVI) and nickel/nanoscale zero-valent iron particles (Ni/nZVI), were synthesized by one-step liquid-phase reduction and applied for oxytetracycline (OTC) removal. The effects of contact time and initial pH on the removal efficiency were studied. The as-prepared nanoscale particles were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). Finally, the degradation mechanisms of OTC utilizing the as-prepared nanoparticles were investigated by using X-ray photoelectron spectroscopy (XPS) and mass spectrometry (MS). Cu/nZVI presented remarkable ability for OTC degradation and removed 71.44% of OTC (100 mg/L) in 4 hr, while only 62.34% and 31.05% of OTC was degraded by Ni/nZVI and nZVI respectively. XPS and MS analysis suggested that OTC was broken down to form small molecules by ·OH radicals generated from the corrosion of Fe^0. Cu/nZVI and Ni/nZVI have been proved to have potential as materials for application in OTC removal because of their significant degradation ability toward OTC.

Introduction

Oxytetracycline (OTC), a member of the tetracycline family that is one of the broad-spectrum antibiotics used in veterinary medicine and aquaculture, has received increasing attention due to the spread of antibiotic resistance in microorganisms (Chen et al., 2011; Storteboom et al., 2010). It has been widely used for decades as a feed additive in farmed fish, as a growth-stimulating substance in domestic animals and as preventive therapy for bacterial diseases in plants (Chi et al., 2010). However, its difficulty being metabolized in animals results in contamination of manure or urine in the form of the parent compound or its metabolites (Heuer et al., 2008). Furthermore, as a result of its water-solubility and degradation resistance, OTC has been widely detected in soil environments, coastal environments, and even drinking water (Li et al., 2011; Tang et al., 2015). OTC can cause inhibition of the antibody levels in fish, deoxyribonucleic acid (DNA) damage in carp, and reduction in erythrocyte counts and hemoglobin values, when it is absorbed into organisms (Chi et al., 2010; Li et al., 2011; Lunden et al., 1998; Omoregie and Oyebanji, 2002; Qu et al., 2004).

Recently, nanoscale zero-valent iron (nZVI) has been extensively utilized as an environmental remediation material, especially for treatment of organic contaminants, owing to its unique advantages, including high specific surface area and great capacity for reductive reaction (Fu et al., 2013). However, the tendency of nZVI particles to agglomerate into large particles and the generation of oxide layers on the surface of particles lead to inferior reaction activity and low removal efficiency (Dong et al., 2015; Shi et al., 2016; Xiao et al., 2014). In order to overcome the

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above-mentioned disadvantages, the reactivity and functionality of nZVI have been enhanced through immobilization of nZVI onto support materials (Xiao et al., 2014) and deposition of a discontinuous layer of other metals (Cu, Ni, Pd *etc.*) onto nZVI surfaces (Chang et al., 2011; Shi et al., 2016). In most studies, nanoscale bimetallic particles have showed much higher activity than monometallic particles. Palladium (Pd) has exhibited extremely high removal efficiency as an additive in Pd/Fe bimetallic catalytic reductants, but the application is limited because of its high cost (Chang et al., 2011; Han et al., 2008). As much more economical metals, Cu and Ni were added into nZVI in this study instead of Pd. Thus, the formation of [H] on the surface of nZVI was enhanced by bimetallic Cu/nZVI and Ni/nZVI nanoscale particles (Gao et al., 2016; Zhu et al., 2010).

Bimetallic nanoscale particles are increasingly used to promote the efficiency of organics removal, but research on the improvement of OTC removal using iron-based nanoparticles remains limited. This study was conducted in an effort to improve OTC removal from actual wastewater by Cu/nZVI and Ni/nZVI produced through liquid-phase reduction. The effects of significant factors on OTC removal, including initial pH and contact time, were investigated during the experiments. In addition, scanning electron microscopy (SEM) was utilized to explore the morphologies of as-prepared and exhausted nZVI, Cu/nZVI and Ni/nZVI. The crystal structures of original and modified iron-based nanoparticles were characterized by X-ray diffraction (XRD), meanwhile the chemical properties were analyzed by X-ray photoelectron spectroscopy (XPS). Subsequently, structural data on the degradation products of OTC was obtained by using mass spectrometry (MS), and the mechanisms of the degradation process were also investigated. This study investigated the transformation of Fe^0 during reaction as well as the products of OTC degradation, providing insight into the mechanism of OTC removal by bimetallic nanoscale zero-valent iron particles.

1. Materials and methods

1.1. Materials and chemicals

The water used for all experiments was generated from an ultrapure water system (FFX1502-RO, Qingdao FLOM Technology Co., Ltd., China), with the exception of WaHaHa pure water used for liquid chromatography. The standard of OTC hydrochloride was purchased from Aladdin industrial corporation (purity >95%, Shanghai) and its chemical structure is shown in Fig. 1 below. $FeSO_4{\cdot}7H_2O$, $NaBH_4$ and ethanol for synthesis were obtained from Shanghai Chemical Plant Co. (China). $CuSO_4{\cdot}5H_2O$ was purchased from Tianjin Kermel Chemical Reagent Co. $NiCl_2{\cdot}6H_2O$ was purchased from Tianjin Bodi Chemical Co., Ltd.

1.2. Preparation of nZVI, Ni/nZVI and Cu/nZVI

Zero-valent iron nanoscale particles (nZVI) were synthesized by liquid-phase reduction according to reference (Schrick et al., 2002; Wang et al., 2006) by the following reaction:

$$4Fe^{2+} + 2BH_4^- + 6H_2O \rightarrow Fe^0\downarrow + 2B(OH)_3 + 7H_2\uparrow \quad (1)$$

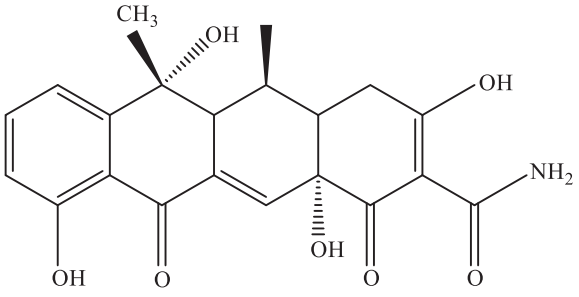

Fig. 1 – Chemical structure of oxytetracycline (OTC).

To obtain nZVI, iron (II) sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$) (4.97 g) was dissolved in a 100-mL miscible solution with a volume ratio of absolute ethyl alcohol and distilled water of 3:7. Then the above mixture was stirred at 120 r/min in a 25°C water bath under nitrogen for 5 min, and 0.054 mol/L $NaBH_4$ solution (50 mL) as a strong reductant was added drop-wise (2 mL/min) into the three-necked flask followed by vigorous stirring under a N_2 atmosphere. The solution was shaken for another 30 min after the addition of $NaBH_4$ was complete. After that, the synthesized nZVI particles were cleaned using distilled water and ethanol three times in turn.

1.2.1. Ni/nZVI (Cu/nZVI) bimetallic nanoparticles

The bimetallic Ni/nZVI (Cu/nZVI) was synthesized by the borohydride reduction of 4.97 g $FeSO_4{\cdot}7H_2O$ and 0.1 g $NiCl_2{\cdot}6H_2O$ (0.9776 g $CuSO_4{\cdot}5H_2O$) in solution containing 30 mL ethanol and 70 mL degassed reverses osmosis (RO) water. The rest of the preparation process was the same as the synthesis of nZVI described above.

After the same washing sequence as above, the freshly washed nanoscale particles were dried at 70°C in vacuum for 4 hr, and stored in a nitrogen atmosphere at room temperature before use.

1.3. Characterization of nZVI, Ni/nZVI and Cu/nZVI

The morphological properties and characteristics of the as-prepared particles were observed utilizing a scanning electron microscope (SEM, JEOL, JSM 6700F, Japan). In addition, an energy dispersive spectroscopy (EDS, INCA, Oxford Instruments, UK) was utilized to analyze the localized compositional information of the iron-based nanoscale particles. The crystal structures of the synthesized nanoparticles were characterized by XRD (Bruker SMART APEX II, BRUKER, Germany) and chemical properties were obtained by XPS analysis using a multifunctional imaging electron spectrometer (Thermo ESCALAB 250XI, Thermo Fisher Scientific, USA).

1.4. Analytical methods

All the aqueous solutions of OTC for analysis were filtered by a 0.22-μm membrane filter and then analyzed by a liquid chromatograph (SPD-20A, Shimadzu, Japan) with a C18 chromatographic column (25 cm × 4.6 mm). The mobile phase was a mixture of 0.01 mol/L aqueous citric acid-acetonitrile ($V_{\text{citric acid}}$:$V_{\text{acetonitrile}}$ = 75:25) at a flow rate of 1 mL/min; the wavelength for absorbance detection was

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