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Preparation of wheat straw-supported Nanoscale Zero-Valent Iron and its removal performance on ciprofloxacin

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ABSTRACT

Wheat straw-supported Nanoscale Zero-Valent Iron particles (WS-NZVI) were successfully synthesized, which were used for Ciprofloxacin hydrochloride (CIP) removal in simulation wastewater. The structure, chemical composition and micro-morphology of WS-NZVI and Nanoscale Zero-Valent Iron (NZVI) were characterized by scanning electron microscopy analysis (SEM), X-ray diffraction (XRD), as well as the Fourier Transformed IR spectra (FT-IR). XRD results proved the existence of Fe°, and SEM images indicated that the agglomeration of NZVI was effectively inhibited when loaded on wheat straw. Besides, the effects of initial solution pH, CIP concentration, adsorbents dosage and contacting time on the removal efficiency of CIP by WS-NZVI and NZVI were investigated. The experimental results showed that, compared with NZVI and wheat straw, WS-NZVI possessed higher removal efficiency for CIP, and the maximum removal capacity of CIP by WS-NZVI was 363.63 mg g^{-1} (25 °C). Furthermore, WS-NZVI was suitable for wider pH range (pH = 4–10) in comparison with NZVI. For the WS-NZVI, the kinetic was better fitted with pseudo-second-order equation, rather than pseudo-first-order equation. The Mass spectrometry (MS) analysis deduced that the degradation reaction mainly occurred on quinolone groups piperazinyl ring. Therefore, it is feasible that using wheat straw as a support material to enhance the performance of NZVI, and the synthesized WS-NZVI has a potential in the organic compounds elimination because of its redox reaction activity.

1. Introduction

In recent decades, nanomaterials have attracted a wide attention because of its strong adsorption capacity, redox ability and anti-bacterial function (Liang et al., 2012). Nanoscale Zero-Valent Iron (NZVI) enjoys small size, large specific surface area, as well as high activity, and NZVI can avoid the production of toxic by-products (Martin et al., 2008; Rao et al., 2009). However, there are still some problems for the application of NZVI. The reaction activity of NZVI decreased because of the aggregation of NZVI resulting from the force between each particle, and oxidization of Fe° exposed to the air (Cao and Zhang, 2006; Shi et al., 2011; Xiao et al., 2015). Therefore, the application of NZVI has been seriously restricted.

Recently, some studies have shown that using materials with special structures or functional groups as mechanical supports can not only hinder the agglomeration of NZVI particles, but also enhance its stability and improve the reactivity (Lv et al., 2011; Yan et al., 2015; Qian et al., 2017). Up to date, NZVI supported by activated carbon (Chang et al., 2011; Xiao et al., 2015), bentonite (Shi et al., 2011; Diao et al., 2016), and mesoporous silica (Petala et al., 2013) have been reported to increase the reactivity and durability of NZVI. Some studies also have reported support materials based on agricultural wastes. For example, wheat straw (Li et al., 2017) and rice straw (Oh et al., 2017; Qian et al., 2017) were successfully used to produce biochar by pyrolyzing and then supported NZVI for removal of contaminants. However, no studies have focused on the feasibility of using raw straw as a support material. Straw is a kind of agricultural wastes which is the rest of wheat, rice, corn, cotton, and other crops after harvest seed (Augusta et al., 2016). A large amount of straw is produced in China, with only a few of straw utilized as industrial raw materials, animal feed or biomass energy. A large quantity of straw is incinerated and in general, the resource utilization degree of straw is low (Panthapulakkal et al., 2006). Cellulose is the most abundant natural polymer resource on earth (Zhang et al., 2017), which is an important proportion of straw. There're lots of hydroxyl in cellulose molecule, which is beneficial to combine straw with NZVI. In addition, because of its biodegradable property, straw can be further degraded in the natural environment with no secondary pollution produced. In this paper, wheat straw was used as a supporter for

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synthesized NZVI.

Nowadays, extensive and excessive use of pharmaceuticals ingredients, such as antibiotics, analgesic, painkillers, antidiabetics, antidepressants, and growth regulators, has resulted in the contamination of groundwater and surface water (Robinson et al., 2007; Ternes et al., 2007). Recently, antibiotics were detected in municipal wastewater, in hospital sewage water, in effluents of wastewater treatment plants, and in effluents from drug manufacturers (Renew and Huang, 2004; Larsson et al., 2007; Verlicchi et al., 2010; Ling et al., 2013). Ciprofloxacin (CIP) is one of the important fluoroquinolone antibiotics which is widely used in poultry livestock breeding, aquiculture, and human use (Zhang and Huang, 2005; Paul et al., 2007; Babić et al., 2013). A large quantity of CIP is excreted with feces and urine in the form of metabolite from human or animal bodies, which is the same as most antibiotics (Aristilde and Sposito, 2008). Besides, CIP has low biodegradability, with only a small part of CIP eliminated in WTPs and plenty of remanent CIP are discharged into the environment (Jiang et al., 2013). The presence of CIP, even in low concentrations, may lead to antibiotic-resistant bacterial strains (Paras Trivedi and Vasudevan, 2007). Therefore, CIP must be substantially removed from the sewage before being emitted into environmental water systems. At present, there are many methods for CIP removal, such as oxidation (Dodd et al., 2005), photolytic and photocatalytic (Doorslaer et al., 2011), ozonation (De et al., 2010), and sorption (Carabineiro et al., 2012).

The primary aim of this study was to verify the feasibility of wheat straw as a support material, and to provide a new way for the treatment of CIP. The specific aims were as follows: (1) to study the kinetic and isotherm of CIP removal by Wheat straw-supported Nanoscale Zero-Valent Iron particles (WS-NZVI); (2) to investigate the influence of different factors on CIP removal; (3) to elucidate the degradation products and the degradation mechanism of CIP by WS-NZVI.

2. Materials and methods

2.1. Chemicals and materials

Ciprofloxacin Hydrochloride (≥ 98%, USP Grade) was purchased from Sangon Biotech (Shanghai). Wheat straw was obtained from Jinan, Shandong Province. The rest of primary chemicals were of analytical reagent grade. Polyethyleneglycol-4000 (PEG), Sodium borohydride ($NaBH_4$, 96%), ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$), and anhydrous ethanol, were purchased from Shanghai Chemical Plant Co.,Ltd (China).

2.2. Preparation of NZVI and WS-NZVI

The WS-NZVI particles were synthesized by liquid-phase reduction method (Petala et al., 2013; Xiao et al., 2015). Ultrapure water was purged with high purity nitrogen for 15 min before use to remove the oxygen. The supporter straw was washed three times and then dried at 60 °C. Finally, the straw sample was smashed to 100–200 mesh for the following use. For the synthesis of WS-NZVI, ferrous sulfate heptahydrate (4.96 g) was added in 100 mL of ethanol and deionized water with a 3:7 volume ratio, 0.5 g PEG was added as dispersant. And 0.5 g of straw was then mixed with the solution and the suspension was stirred for 30 min under a nitrogen atmosphere. Then, the $NaBH_4$ solution (1 M, 50 mL) was added drop-wise. Subsequently, the suspension was stirred for another 30 min. The particles were washed by deoxygenated ultrapure water and anhydrous ethanol subsequently (Fu et al., 2013; Kim et al., 2013) and then vacuum-dried at 60 °C for 8 h. The NZVI was synthesized in the same way but without straw.

The whole process of preparation occurred in N_2 atmosphere. The dried materials were sealed in brown glass bottle with full nitrogen. The synthesis of NZVI can be described in the following reaction (Xiao et al., 2015):

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

2.3. Characterizations of NZVI and WS-NZVI

Both NZVI and wheat straw-supported NZVI (WS-NZVI) particles were analyzed using different equipment to reveal their physical and chemical properties. Scanning electron microscopy analysis (SEM, FEI, NOVA NANOSEM450, USA) was used to analyze the differences of the surface morphology. X-ray diffractometer (XRD) detected the composition of investigated particles using Cu Ka radiation in the range of 10–80°. Fourier Transform Infrared (FTIR) of NZVI and S-NZVI particles were recorded in KBr pellet at ordinary temperature in the spectral range of 400–4000 cm^{-1}.

2.4. Experimental procedures

A certain amount of synthesized adsorbents were added into CIP aqueous solution at the working pH and then the concentration of remanent CIP was measured at predetermined time intervals. Each sample was taken out after being shaken in a constant temperature air vibrator at 150 rpm and then filtered using 0.22 μm filter before further analysis. The effects of contact time (5–240 min) with initial CIP concentrations (20–100 mg L^{-1}), adsorbent dosages (0.25–1 g L^{-1}) and initial solution pH (3–11) were also investigated at room temperature (25 °C). HCl and/or NaOH (0.1 M) solutions were used for solution pH value adjustment. The equilibrium removal quantity q_e (mg g^{-1}) was calculated as the equation listed below,

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where W (g) is the mass of absorbent, C_0 (mg L^{-1}) is the initial CIP concentration, C_e (mg L^{-1}) is the equilibrium CIP concentration in aqueous phase. V (L) is the solution volume.

The kinetics of CIP removal was investigated to elucidate the adsorption mechanism of CIP removal from water by WS-NZVI. First, 0.0375 g (0.75 g L^{-1}) of samples were introduced into 50 mL of 50 mg L^{-1} CIP solution in a constant temperature air vibrator at 150 rpm. Then the CIP concentration was detected at the following durations: 5, 10, 15, 30, 60, 120, 180, 240 min.

To study the isotherm of CIP removal on WS-NZVI, 0.0375 g (0.75 g L^{-1}) sample was introduced into 50 mL CIP solution at a series of different initial concentrations in a constant temperature air vibrator at 150 rpm for 24 h, at 25 °C, 35 °C, 45 °C, respectively. All the investigations were repeated three times to guaranteed the veracity of the experimental results.

2.5. Sample analysis

The concentrations before and after removal of CIP were quantified with High Performance Liquid Chromatography (HPLC). A WondaSil C18 column (150 mm × 4.6 mm × 5 μm) was equipped for all separations, while the wavelength was set at 277 nm. The mobile phase consists of phosphoric acid and acetonitrile (85:15 by volume), adjust to pH 3.0 ± 0.1 with triethylamine. The injection volume was 10 μL and flow rate was 1.0 mL/min at isocratic mode. The CIP elution profile was shown in Fig. S1.

CIP and its degradation products were further determined with LC/MS/MS (Thermo, LCQ FLEET) operating in a positive mode. The scan range was from 100 m/z (mass to charge ratio) to 500 m/z.

2.6. Statistical analysis

Analysis of Variance (ANOVA) was performed using Graphpad Prism 7.0 software. ANOVA was used to analyze the CIP removal kinetics, with Time (0, 5, 10, 15, 30, 60, 120, 180 and 240 min) as one