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High efficient removal of tetracycline from solution by degradation and flocculation with nanoscale zerovalent iron

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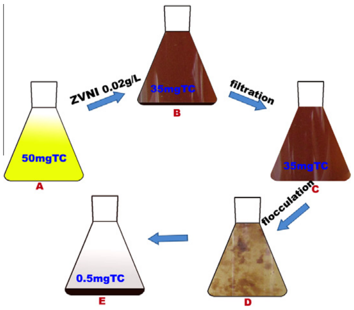
HIGHLIGHTS

- The long-term process of TC reacted with ZVNI was investigated.
- The 99% removal was obtained when 500 mg/L TC was processed with 0.2 g/L ZVNI.
- The flocculation (69%) is more important than the degradation and adsorption (30%) in removal of TC with ZVNI.
- The degradation process and flocculation was analyzed.

GRAPHICAL ABSTRACT



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ABSTRACT

The removal of tetracycline (TC) with nanoscale zerovalent iron modified by starch (starch-NZVI) was investigated using batch experiments as a function of reactant concentration, pH, time, competitive anions and ionic strength. The removal efficiency of 99% was obtained, 30% which was contributed from the adsorption and degradation and 69% which was attributed to flocculation when 500 mg/L TC was processed with 0.20 g/L starch-NZVI. The TC removal capacity of starch-NZVI increases with increasing the TC concentration. Furthermore, the flocculation kinetics was strongly dependent on pH and ionic strength. Neutral environment and high ionic strength can improve efficiently the sedimentation rate. The XPS analysis of flocculation showed that the Fe consisted of mainly Fe(III) and some Fe(II). LC–MS analysis revealed that the organic components included TC and the degradation products which resulted from the oxidization effect for TC. Our results firstly demonstrated that the combination degradation with flocculation is an efficient method on TC removal from solution with NZVI.

1. Introduction

Antibiotics discharged from wastewater treatment plants (WWTPs) to the environment have received increasing attentions due to propagation of antibiotic resistance in microorganisms [1,2]. Tetracycline (TC) is one of the most widely used antibiotics worldwide, and is difficult to be metabolized in animals. Consequently, large fraction of TC has been end up in the wastewater system. Due to its inability to be treated in WWTPs, TC has been widely detected in soils, surface waters, ground water, coastal environment, and even drinking water due to discharge into the environment [3].

The removal efficiencies of TC are very low in WWTPs with active sludge treatment processes [4,5] because TC is non-

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biodegradable and also lethal to most microorganisms. Therefore, adsorption [6–8], electron pulse radiolysis [9] and photocatalysis [10] have been adopted to treat TC before WWTPs. Recently the nanoscale zerovalent iron (NZVI) has received wide attention for the treatment of toxic compounds since it is a high efficient, inexpensive and nontoxic [11]. There have been several attempts to eliminate a variety of pollutants, including chlorinated organic compounds [12,13], nitroaromatic compounds [14], pesticides [15], dyes [16] and heavy metals [17,18]. However, a little attention has been given to the interaction of antibiotics with NZVI [19–21]. The NZVI degradation and adsorption effect for TC has been reported by Chen et al. [22] and Ozge Hanay et al. [23]. The degradation products mainly included the 4-epi-tetracycline and loss of amine and water as TC-like matter. The iron (hydroxyl) oxides were transformed from NZVI in solution, and then adsorb the TC and its degradation products in 15–240 min. The TC is an efficient chelating agent for metal ion with high valent. The TC would be chelating with the iron ion as Fe–TC complex in solution. This complex cannot decrease the antibiotic effect of TC [24], so it should be removed from the wastewater before WWTPs.

The metal–TC complex has found widely in environment. Some recent reports indicate that the presence of Cu(II) could greatly enhance the adsorption of TC onto resin [25], montmorillonite [26] and soils [27] through the formation of ternary surface complexes. Conversely, the presence of TC also increased the adsorption of copper, which may significantly influence their bioavailability [28]. However, the TC can dissolve the metal ion from FeOOH adsorbent, indicating that the Fe–TC complex in solution is more stable than the FeOOH-TC [29]. This result is adverse for the removal TC with the NZVI, because the complex decreases the amount of FeOOH adsorbent. However, this effect has not been investigated in detail on the process of TC removal with NZVI, though increasing evidences suggest that Fe–TC complex has important effect on the TC removal.

Furthermore, the long-term result of TC processed with NZVI has not been investigated up to now. The TC degradation and adsorption by NZVI is a quick process, which usually receive much attention. However, the fate of the Fe–TC complex is unclear in the removal TC with NZVI, in that this process need chase for long time. The Fe–TC complex is macromolecular colloid in solution. And the flocculation phenomenon of Fe-chelating with TC and degradation products was found in our experiment. Factually, this flocculation was more efficient than the degradation and adsorption on TC removal.

In this paper, the main aim was to examine long-term process of TC removal by NZVI in different condition such as TC concentration, pH, competitive anions and ionic strength, study the effect of flocculation on the TC removal efficiency and identify the components of flocculation.

2. Materials and methods

2.1. Materials and chemicals

Hydrochloride salt of tetracycline (TC, $\geqslant 95\%$ purity, MW: 480.90), and the structure of TC was showed in Fig. 1. Starch, Na_2SO_4, NaH_2AsO_4, NaOH, HCl, KBH_4, NaCl, $CaCl_2$, and other reagents were of analytical grade. All chemicals were used as received without further purification. All solutions were prepared with deionized water (18 M Milli-Q) and stored at 4 °C.

2.2. Characterization of material

Surface elemental compositions of the materials were measured by an X-ray Photoelectron Spectroscopy (XPS) (Thermo Fisher Scientific, K-Alpha 1063, UK). Scanning electron microscopy (SEM) with Energy Dispersive Spectrometer (EDS) was used to document surface morphologies and element component with H-7500 (JEM-1230 HC, JPN). TEM images were obtained using a JEOL (Japan) JEM-100CX-II transmission electron microscope (TEM) operated at accelerating voltage 100 kV. The crystal forms of the materials were measured with X-ray diffraction (Shimadzu X-ray JPN). The IR-spectrum of the products were carried with PerkinElmer Spectrum 65 (USA).

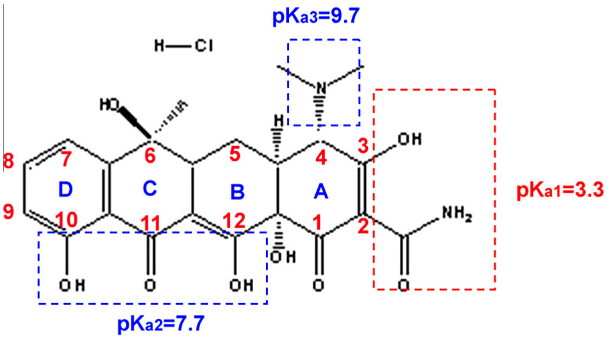

Fig. 1. Structure of tetracycline (TC).

2.3. Synthesis procedures

The starch-NZVI particles were synthesized by using the well-known liquid-phase reduction method. First, 0.04 mol $FeSO_4{\cdot}7H_2O$ was dissolved into 300 mL ethanol solution (70% volume) in a 500-mL flask, then starch powder (the weight ratio of starch to NZVI was 0.2–0.5) was added with vigorous agitation. After sparging with N_2 for 10 min, 100 mL 0.02 M borohydride solution was slowly added into the above mixture and stirred for 20 min at 25 °C. Fe^{2+} was reduced by BH_4^- to form black NZVI particles immediately. NZVI particles were collected by vacuum filtration and washed several times with deionized (DI) water and ethanol. The resulting black solids were vacuum-dried for 15 h at 40 °C, broken up by a spatula and stored in a N_2-purged desiccator.

2.4. Batch experiments

In the batch experiments, TC solutions (TC 500 mg/L; ionic strength 0.01 M NaCl) were prepared fresh daily for each batch test. To start the experiments, 50 mL of the prepared TC solution was purged with nitrogen for 10 min in a 100 mL plastic bottle. Then the solution was mixed with 0.010 g freshly prepared starch-NZVI. The plastic bottle sealed with cover was continuously shaked (150 rpm) for 2 h at 25 °C, and placed in 7 days after filtered. At selected time intervals, pairs of centrifuge tubes were centrifuged (8700*g* for 5 min) and then collected by glass syringes and filtered through a 0.45 μm membrane filter for analysis. The concentrated HCl were added into the filtrate to adjust solution pH to 1–2 in order to dissociate the complex of TC and Fe in solution.

The Fe concentration in the filtrate was determined by the atomic absorption spectrophotometer (AAS Hitachi Corp., Japan) after dissolved with 1.0 M NaOH. Each experiment, including blanks, was run in duplicate. The pH of the samples was measured by a pH electrode. Other experimental conditions and measurements except the pH reaction were set at the condition of dosage of starch-NZVI, 0.010 g; temperature, 25 °C; pH, 6.0 ionic strength 0.01 M NaCl. Ionic strength experiment used solutions of 500 mg/L TC add NaCl, NaH_2AsO_4 and $CaCl_2$ to desired concentration, pH 6.0.