



## Research paper

# Degradation mechanism of amoxicillin using clay supported nanoscale zero-valent iron



Xiulan Weng<sup>a</sup>, Wanling Cai<sup>a</sup>, Shen Lin<sup>b</sup>, Zuliang Chen<sup>a,c,\*</sup>

<sup>a</sup> Fujian Key Laboratory of Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Fujian Normal University, Fuzhou 350007, Fujian Province, China

<sup>b</sup> School of Chemistry and Chemical Engineering, Fujian Normal University, Fuzhou 350007, Fujian Province, China

<sup>c</sup> Global Centre for Environmental Remediation, University of Newcastle, Callaghan, NSW 2308, Australia

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## ABSTRACT

Antibiotics such as amoxicillin (AMX) have been considered emerging pollutants due to their persistence in the aquatic ecosystem even at low concentrations. Thus, it is an emerging issue to develop materials effective for removal of antibiotics pharmaceuticals from wastewaters. Bentonite supported nanoscale zero-valent iron (B-nZVI) as one of the alternatives was used to remove amoxicillin. Batch experiments revealed that the degradation of amoxicillin depended on pH value of the solution, initial concentration of B-nZVI, initial concentration of amoxicillin and reaction temperature. The removal of AMX was based on an integration of adsorption and reductive degradation, which was confirmed by either adsorption or reductive kinetics. The potential AMX degradation pathway was proposed by analysis of the degraded products using high performance liquid chromatography-mass spectrometry (HPLC-MS). The removal mechanism of amoxicillin using B-nZVI includes: (1) the adsorption of amoxicillin onto iron corrosion products; and (2) reduction of AMX by nZVI on B-nZVI. Finally, the reusability of B-nZVI for degradation of amoxicillin was tested.

## 1. Introduction

In the last years, the presence and fate of antibiotics in environmental matrices have received attention since antibiotics are persistent and resistant to biodegradation, accumulating in the environment, and consequently they pose a risk for aquatic and terrestrial organisms (Homem and Santos, 2011; Lissemore et al., 2006; Pan et al., 2008). Antibiotics such as amoxicillin have been extensively used over the past 80 years in medicine, agriculture, veterinary practices, and fish farming, where they are inevitably excreted into the environment (Homem and Santos, 2011; Pan et al., 2008). Unfortunately, conventional wastewater treatment technologies are unable to quantitatively remove these largely non-biodegradable species (Homem and Santos, 2011; Pan et al., 2008). Therefore, new technologies are being used for the purpose of removing antibiotics from wastewater. These include adsorption (Adriano et al., 2005; Putra et al., 2009), ozonation (Andreozzi et al., 2005) and membrane (RO-UF) filtration (Li et al., 2004). However, these methods need to dispose of the adsorbed contaminants or they will prove ineffective in treating wastewaters containing amoxicillin. Adsorption is considered to be the most effective method for removing contaminants residing in wastewater, because it is

simple and cost-effective, where the removal of amoxicillin from wastewater using adsorbents such as chitosan beads (Adriano et al., 2005), activated carbon and bentonite have been reported (Putra et al., 2009). Magnetite nanoparticles ( $\text{Fe}_3\text{O}_4$ ) have recently been reported in the adsorption of chlorotetracycline from aqueous solution, and  $\text{Fe}_3\text{O}_4$  certainly exhibits a high adsorption capacity (Zhang et al., 2011a,b). While adsorbents are often used to remove various contaminants, the adsorbed contaminants need further disposal (Zhang et al., 2011a,b).

Recently, nanoscale zero-valent iron (nZVI) has been extensively investigated in numerous studies for the remediation of groundwater and other environmental applications owing to their small size and large surface area. However, the aggregation of nZVI particles into chain-like structure constitutes one of their major characteristics, which is responsible for reducing the surface area to volume ratio (O'arroll et al., 2013). The stability of iron nanoparticles against aggregation can be improved by imparting electrostatic repulsion, applying organic surfactants, or through the use of capping agents (O'arroll et al., 2013). Another approach that would serve this goal is to synthesize iron nanoparticles in the presence of supporting inorganic material (Shi et al., 2011; Su et al., 2011; Zhang et al., 2011a,b). A few studies have focused on removing antibiotics using nZVI or supported nZVI. Recently, the

\* Corresponding author at: Global Centre for Environmental Remediation, University of Newcastle, Callaghan, NSW 2308, Australia.  
E-mail address: [zuliang.chen@newcastle.edu.au](mailto:zuliang.chen@newcastle.edu.au) (Z. Chen).

removal of amoxicillin and ampicillin from aqueous solution using nZVI has been reported, where amoxicillin and ampicillin completely disappeared through a lactam ring opening mechanism followed by hydrolysis after 3 h of contact with nZVI (Ghauch et al., 2009). This is due to nZVI having an intrinsic aggregation that may limit its reaction rate (Shi et al., 2011). In addition, the mechanism, reaction intermediates and effect of solution parameters on the degradation also provide new requires to be provided new insight of the degradation process. Our recent report on bimetallic bentonite/Fe/Ni nanoparticles used for catalytic degradation of amoxicillin has shown that > 94% of AMX was removed (Weng et al., 2014). However, Ni is leaching as  $\text{Ni}^{2+}$  which could be toxic (Jiang et al., 2013), while nZVI shown that it was less or no-toxicity (Liu et al., 2014).

For these reasons, we focused on bentonite supported nZVI (B-nZVI) for the degradation of amoxicillin. Batch removal kinetics experiments at various conditions, and reusing B-nZVI in the removal of AMX were conducted. Moreover, analysis of the degraded products by HPLC-MS was performed to understand the degradation mechanism of amoxicillin using B-nZVI. Hence, the aspects include (1) conduct batch removal kinetics experiments in various conditions and its kinetics and (2) test intermediates by HPLC-MS to confirm the mechanism.

## 2. Experimental

### 2.1. Materials and chemicals

Bentonite was supplied by Longyan Kaolin Co. Ltd., Fujian, China. The cation exchange capacity (CEC) was 32.4 meq/100 g. The chemical composition (mass %) of bentonite was 62.5%  $\text{SiO}_2$ , 18.5%  $\text{Al}_2\text{O}_3$ , 1.75%  $\text{Fe}_2\text{O}_3$ , 4.25%  $\text{MgO}$ , 0.95%  $\text{CaO}$ , and 2.75%  $\text{Na}_2\text{O}$  as previously reported (Chen et al., 2011). Raw bentonite was ground and sieved with a 200 mesh screen prior to use.  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was obtained from Tianjin Chemical Reagent Co. (Tianjin, China).  $\text{NaBH}_4$  was purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). AMX was supplied from Shanghai Shize Biotechnology Co. (Shanghai, China), and the structural formula of amoxicillin was shown in Fig. 1. All the chemicals used in this study were analytical reagent grade and utilised without further purification. A solution containing amoxicillin was prepared by dissolving various amounts of amoxicillin with deionized water to the desired initial concentrations.

### 2.2. Synthesis of bentonite supported zero-valent iron

B-nZVI particles were synthesized using the liquid-phase reduction method with bentonite as a support material as previously reported (Chen et al., 2011; Shi et al., 2011). A preparation of B-nZVI with bentonite via  $\text{Fe}^0$  mass ratio of 1:1;  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was dissolved in 50 mL of miscible liquids, along with 1 g of bentonite. The mixture was stirred with an electric rod for 15 min in a nitrogen atmosphere, and then 100 mL  $\text{NaBH}_4$  solution (0.047 mol) was added dropwise with vigorous stirring continuously for 30 min, the whole reaction process was carried under nitrogen atmosphere. The ferric ion ( $\text{Fe}^{3+}$ ) is reduced to zero-valent iron ( $\text{Fe}^0$ ) by excessive  $\text{NaBH}_4$  according to the following reaction:

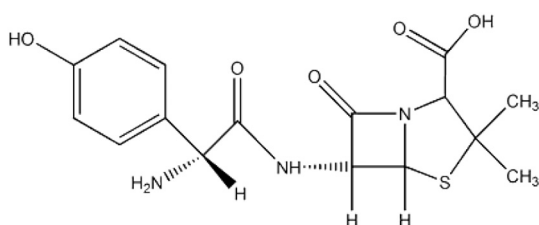
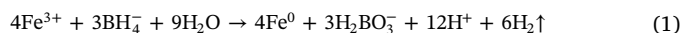


Fig. 1. The structural formula of amoxicillin.



Vacuum filtration was employed to separate the B-nZVI particles and the residual solution. Residual concentration of ferric ion in the filtrate was not detected with the atomic absorption spectrometer (AAS, VARIAN AA240, U.S.A.) because the ferric ion ( $\text{Fe}^{3+}$ ) is completely reduced to zero-valent iron ( $\text{Fe}^0$ ) by excessive  $\text{NaBH}_4$ . The B-nZVI particles were quickly rinsed three times with distilled water and absolute ethylalcohol. Doing so prevented the nZVI from being oxidized and then it was dried at 333 K under vacuum overnight, and kept in a nitrogen atmosphere prior to use.

### 2.3. Batch experiments

To investigate the removal efficiency of B-nZVI, an experiment was carried out using B-nZVI (0.10 g), which was added to 25 mL solution of an initial concentration of 20 mg/L of AMX. The obtained dispersion were left at their initial pH level stirred at 250 r/min at 298 K to the desired time intervals. Various parameters affecting the reaction rate of amoxicillin in aqueous solution by B-nZVI particles were investigated, such as pH, dosage of B-nZVI, initial concentration of amoxicillin, and temperature of the amoxicillin solution. All these experiments were carried out in triplicate.

The concentration of amoxicillin solution was measured using a UV-Spectrophotometer (722N, Shanghai, China) at  $\lambda = 228.3$  nm (Zhang et al., 2011a,b).

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \quad (2)$$

where  $R$  (%) represented the AMX removal,  $C_0$  (mg/L) was the initial concentration of AMX in the solution and  $C_t$  (mg/L) stood for the concentration of AMX at  $t$  min.

### 2.4. Characterization and method

X-ray diffraction analysis of bentonite and prepared B-nZVI was conducted by a Philips-X'Pert Pro MPD (Netherlands) diffractometer at 40 kV and 40 mA. Copper  $\text{K}\alpha$  radiation was used to produce X-rays with a wavelength of 0.154 nm. All samples were scanned from  $5^\circ$  to  $70^\circ$   $2\theta$  at a scanning rate of  $3^\circ$   $2\theta$  per minute in glass holder.

### 2.5. HPLC-MS analysis

HPLC-MS analysis of degraded products was performed by HPLC/Q-TOF-MS (Bruker, Germany) with a  $\text{C}_{18}$  analytical column ( $2.1 \times 100$  mm,  $1.7 \mu\text{m}$  particle size). The mobile phase consisting of A (methanol)-B (distilled water) at a flow rate 0.3 mL/min, i.e.: 0–1 min 10% A; 1–11 min 75% A; 11–14 min 10% A. The sample was used to perform 20  $\mu\text{L}$  of the samples were injected at 303 K. The mass spectrometers were operated under the following conditions: an ESI interface in positive mode; 6.0 L/min of drying gas; 453 K of gas dry temperature; 0.6B bar of Nebulizer; 70–500  $m/z$  of mass range; 5.0 eV of quadrupole ion energy.

## 3. Results and discussion

### 3.1. Characterization

X-ray diffraction (XRD) pattern of bentonite, the synthesized B-nZVI is shown in Fig. 2. Fig. 2(a) demonstrated that bentonite was composed primarily of montmorillonite, with the characteristic diffraction peaks at  $2\theta = 6.0^\circ, 19.8^\circ, 34.9^\circ, 36.5^\circ$  and  $61.8^\circ$  (Chen et al., 2017). Other important minerals such as quartz, kaolinite, and feldspar were present in the bentonites (Chen et al., 2017; Sun et al., 2015). The XRD pattern of synthesized B-nZVI (Fig. 2(b)) showed that the largest peak at the  $2\theta$  of  $44.8^\circ$  indicated the presence of  $\text{Fe}^0$  and confirmed its existence in

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