Chemical Engineering Journal 334 (2018) 508–518

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Insight into the kinetics and mechanism of removal of aqueous chlorinated nitroaromatic antibiotic chloramphenicol by nanoscale zero-valent iron

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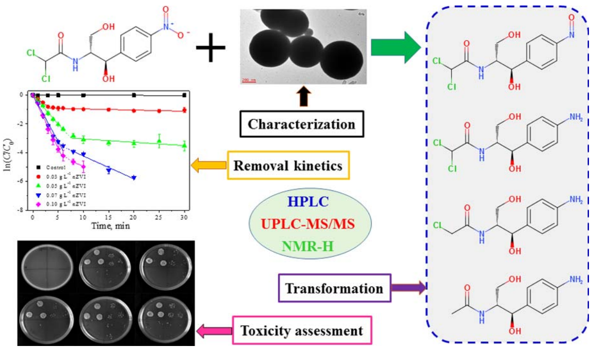
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Nanoscale zero-valent iron
Chloramphenicol
Removal
Kinetics
Mechanism
Antibacterial activity

ABSTRACT

Nanoscale zero-valent iron (nZVI) is very efficient in removing chlorinated nitroaromatic antibiotic chloramphenicol (CAP) from different waters including DI water, surface water, groundwater, and seawater. The corrosion of nZVI and product distribution after reaction in these water matrices were also investigated. Based on the identification of four main reduction products via HPLC, UPLC-MS/MS, and NMR-H spectrums, a more detailed pathway of CAP degradation by nZVI was proposed than ever reported. The two O atoms on the NO_2 group were successively reduced first, and then two Cl atoms were removed via dechlorination. The process of CAP removal could be divided into two stages according to the pseudo-first-order kinetic model. A total of 97.0% of 0.30 mM CAP was rapidly removed by 1.8 mM nZVI in the first stage (6 min) with a surface-area-normalized reaction rate of $1.13\ \mathrm{L\ min^{-1}\ m^{-2}}$. Notably, after reaction with nZVI, the antibacterial activity of the CAP solution was greatly reduced. This study demonstrates that nZVI is a promising alternative to remediate CAP-contaminated water to reduce the antibiotic selection pressure of the environment.

1. Introduction

Widespread attention has been paid to water pollution from emerging organic contaminants (EOCs), which are broadly regarded as newly generated or detected naturally occurring compounds and synthetic chemicals that are not controlled by legislation [1]. As a special

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http://dx.doi.org/10.1016/j.cej.2017.10.060
Received 16 June 2017; Received in revised form 9 October 2017; Accepted 13 October 2017

category of EOCs, antibiotics in water and food have become an emerging issue due to their threats to ecosystems and human health via the generation of antibiotic-resistant bacteria and genes [2,3]. Chloramphenicol (CAP), a chlorinated nitroaromatic antibiotic, is an effective bacteriostatic pharmaceutical that has been applied in a large scale since its first application in clinical practice in 1949. Although its use has been banned in many countries, it is still used in many developing nations due to its wide availability and low production costs. China is the largest producer and consumer of antibiotics, such as CAP. The existence and frequent detection of CAP in sewage influent and effluent, as well as surface and underground water in China, have been reported in previous studies by ourselves and others [4–7]. The concentration of CAP in municipal sewage, river water, and river sediment in Guiyang City in China was reported to be up to 47.4 $\mu g\,L^{-1}$, 19.0 $\mu g\,L^{-1}$, and 1138 $\mu g\,kg^{-1}$, respectively [8].

Various technologies have been developed to remove antibiotics from water, including adsorption, photo-degradation, catalytic oxidation, biodegradation, and microwave radiation [9–14]. Nanoscale zero valent iron (nZVI) is a useful nanomaterial that can remove a wide range of pollutants, including nitrate, heavy metals, and organics because of its large surface area and strong activity [15–21]. The use of nZVI has been proposed as a new strategy to remove non-biodegradable organic pollutants via adsorption and reduction, thereby eliminating the functional groups on the pollutant, decreasing the toxicity, and increasing the biodegradability, especially for halogenated organics pollution [22–25]. The antibiotic properties of CAP are greatly influenced by the NO_2 functional group on the CAP molecule, and the antibiotic characteristic can be effectively decreased via the reduction of nitroaromatics to aromatic amines, which are less toxic and more readily biodegradable [26,27]. Similar effects are also expected after dechlorination of CAP. However, only two degradation products of CAP by nZVI were detected by LC-MS in previous studies [28,29] and the detailed CAP degradation pathway remains unclear. Whether or not and to what extent the reduction of CAP by nZVI reduces solution toxicity remains unknown. In addition, current limited studies on CAP removal by nZVI were all performed in DI waters and its performance in real water matrices remains to be investigated.

The primary objective of this study is to investigate the removal of CAP by nZVI with a focus on the degradation pathway and toxicity change. The specific objectives are: (1) to study the kinetics of CAP removal by nZVI in DI water and natural waters; (2) to investigate the effects of solution chemistry on CAP removal; (3) to elucidate the degradation pathway of CAP by nZVI and discuss the reaction mechanism through nZVI characterization before and after reaction; and (4) to assess the toxicity change of the organics before and after reaction.

2. Experimental section

2.1. Chemicals

Analytical grade chemicals, including $NaBH_4$, $FeSO_4{\cdot}7H_2O$, NaCl, NaOH, and HCl, were purchased from the Sinopharm Group Chemical Reagent Co., Ltd., China. CAP was obtained from Aladdin Reagent (Shanghai) Co., Ltd. DI water (pH = 7.0) was purged by nitrogen for 1 h prior to use in nZVI preparation and batch experiments. All chemicals were used without further purification.

2.2. Preparation of nZVI

The entire preparation procedure was performed in a 1000 mL three-necked flask that was located in a thermostatic water bath. Briefly, 0.25 g $FeSO_4\ 7H_2O$ was dissolved in a flask with 200 mL DI water purged of nitrogen, and a stoichiometric amount of 200 mL $NaBH_4$ (0.07 g) solution was added dropwise and mechanically stirred at 500 rpm to generate nZVI (0.05 g) according to the following equation [30]:

$$Fe^{2+} + 2BH_4^- + 6H_2\,O \rightarrow Fe + 2B(OH)_3 + 7H_2 \tag{1}$$

2.3. Batch experiments

Batch experiments were all performed under nitrogen flow in 1000 mL three-necked flasks containing 500 mL freshly prepared nZVI and CAP DI water solution. Unless otherwise specified, the reaction between 1.8 mM nZVI and 0.30 mM CAP was carried out under mechanical stirring at 500 rpm, pH = 7.0, and 303 K. Samples were collected at specified times, and the reaction was quenched after filtration through a 0.45 μm polyether sulfone (PES) membrane. CAP removal due to filter sorption was negligible (Fig. S1). The cytotoxicity of the reaction solution was assessed using *E. coli*, which is presented with details in Supporting Information.

Experiments were also carried out with nitrogen purging using four different natural waters, including groundwater (collected from a well in Shandong Province), river water (collected from Suzhou River in Shanghai), seawater (collected from the Yellow Sea in Shandong Province), and wastewater (collected from the secondary effluent of a wastewater treatment plant in Shanghai). A total of 1.8 mM nZVI and 0.30 mM CAP were added for testing.

2.4. Analytical methods

CAP in the filtered aqueous samples were analyzed by HPLC (Agilent 1260 Infinity), and the analysis of the reaction products was carried out using a UPLC-MS/MS system, including a Waters Acquity UPLC system coupled with electrospray ionization and a Waters Quattro Premier quadrupole tandem mass spectrometer. Detailed detection methods are presented in the Supporting Information.

Field emission scanning electron microscopy (SEM, FEI-Quanta 200F), energy dispersive X-ray spectroscopy (EDX, FEI-Quanta 200F), transmission electron microscopy (TEM, FEI-Tecnai G^2 F20), X-ray diffraction (XRD, Rigaku-Ultima IV), X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha), Brunauer-Emmett-Teller (BET, Quantachrome 02108-KR-1), and a Zeta potential meter (Malvern Nano-ZS90) were used to characterize the nZVI.

3. Results and discussion

3.1. Characterization of nZVI

The morphologies of the nZVI particles before and after reaction with CAP were compared using SEM and TEM with the same magnification. The fresh nZVI (6.52 $m^2\,g^{-1}$) showed a chain-like aggregation of smooth and spherical particles (Fig. 1a and c). However, the nZVI particles became rougher and smaller with the appearance of flocculent substances after the reaction (Fig. 1b and d). This change was also indicated by the particle's increased specific surface area (17.78 $m^2\,g^{-1}$). In TEM images with higher magnification (Fig. 1e and f), a core-shell structure was clearly observed. The fresh nZVI particles were enclosed within a thin shell of several nanometers [31]. The shell became much thicker after reaction, indicating that a portion of the nZVI was consumed and iron (hydr)oxides were produced during the reaction.

Fig. 2a shows the XRD patterns of nZVI. The peak appeared at $2\theta = 44.9^\circ$ was the typical Fe^0 peak [32], and peaks corresponding to iron oxides were not observed before the reaction. Since the oxidation of nZVI is inevitable as shown in the EDX spectra (Fig. S2), the absence of iron oxide peaks suggest that their percentage is below detection limits. After reaction, new peaks appeared at $2\theta = 31^\circ/36^\circ/57^\circ/62.5^\circ$, which are corresponding to Fe_2O_3 and Fe_3O_4, indicating the generation or increase of these oxides. The much weakened peak at 44.9° suggests that Fe^0 was significantly consumed but still present in the residual particles.

XPS analysis was performed to study the changes of Fe chemical