



Removal of chloramphenicol from aqueous solution by nanoscale zero-valent iron particles

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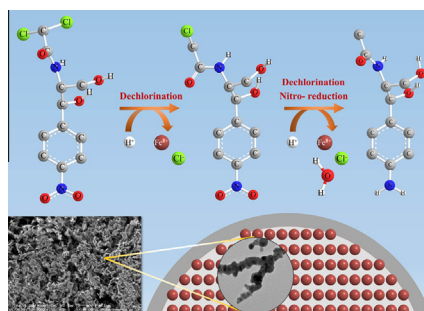
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HIGHLIGHTS

- Chloramphenicol (CAP) removal by nanoscale zero-valent iron (nZVI) was investigated.
- Effects of dosage, initial pH and air on chloramphenicol removal were ascertained.
- Removal kinetics model of CAP by nZVI was constructed.
- Removal mechanisms of CAP by nZVI were disclosed via various analyzing techniques.
- Rational reduction pathway of CAP by nZVI was provided.

GRAPHICAL ABSTRACT



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ABSTRACT

The chloramphenicol (CAP) removal from aqueous solution by nanoscale zero-valent iron (nZVI) particles was systematically investigated using batch experiments. The effects of the key parameters including nZVI dosage, initial pH and air on the CAP removal were ascertained. The removal process of CAP followed a pseudo-first order kinetics model. The removal efficiency was found to be enhanced with increasing nZVI dosage and decreasing initial pH. Due to the Fenton reaction of the nZVI catalyzed by the oxygen in the air, the nZVI process with air showed higher CAP removal efficiency than that with N₂. Under the conditions of nZVI dosage 1.06 g/L, initial pH 6.8 and air presence, CAP (100 mg/L) was completely removed by nZVI within 5 min. The Raman analyses of nZVI particles before and after the process indicated that CAP was adsorbed and reduced on the surface of nZVI particles. The XPS analyses along with the ICP results further confirmed that Fe⁰ was oxidized after the process. From the LC-MS and GC-MS results of the CAP reduction products, dechlorination followed by nitro group reduction was proposed to be the potential reduction routine of CAP by nZVI.

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1. Introduction

Contamination by pharmaceuticals and personal care products (PPCPs) in surface water and ground water are emerging as a

potential threat to the ecosystem and human health [1,2]. PPCPs, especially pharmaceuticals, are reported to act as an inhibitor of multi-xenobiotic resistance, which creates adverse effects on aquatic organisms [3]. Due to antibiotic effects and their high molecular

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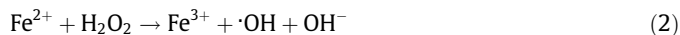
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complexity, these contaminants usually cannot be removed effectively by conventional wastewater treatment methods [3,4]. Accordingly, a great deal of efforts are being made to find out ways of inactivating or eliminating this class of substances in surface water or wastewater [5–7].

Among the medicines, antibiotics receives extensive concern because of a wide usage all over the world [8]. Chloramphenicol (CAP, Fig. 1) is a broad-spectrum antibiotic with excellent antibacterial properties, isolated from *Streptomyces venezuelae* in 1947. Inhibiting protein synthesis in microorganisms, CAP is effective against Gram-positive and Gram-negative cocci and bacilli, which makes it a popular choice to treat human and animal diseases [9]. Various side effects of CAP, however, were revealed, e.g., fatal bone marrow depression and aplastic anemia [10]. It is reported that the detected concentrations of CAP in municipal sewage, the Nanming River and the sediment of Nanming River of Guiyang City, China were up to 47.4 µg/L, 19.0 µg/L and 1138 µg/kg, respectively [11]. In Germany, CAP was also found in sewage treatment plant effluents and river water at concentrations up to 0.56 and 0.06 µg/L, respectively [12]. Up to present, only a few studies on CAP removal from water or wastewater have been reported. Chatzidakis et al. [13] and Zhang et al. [14] reported photo-catalytic oxidation of CAP by TiO₂, while radiation induced CAP removal was also reported by Kapoor and Varshney [15] and Csay et al. [16]. However, the products of CAP during photocatalytic degradation and irradiation might be more toxic for human health [17]. Moreover, great investments in infrastructure limit their applications for large scale operations [18]. Fan et al. [19] reported using bamboo charcoal as an adsorbent to remove CAP from wastewater. During this process, CAP is simply accumulated and then separated from water without any degradation, which was unsatisfactory in the field of pollution abatement [18]. Development of new techniques like nanotechnology may help solving this problem.

Nanotechnology is one of the most rapidly growing sectors of the global economy. For the treatment of persistent pollutants, a growing body of theoretical and empirical evidences have proven that nanoscale zero-valent iron (nZVI) particles are both highly effective and versatile due to their high specific surface area, environmental harmlessness and capabilities for catalytic reduction of contaminants [20]. The removing mechanism of contaminant by nZVI is still unclear and several mechanisms have been proposed: reduction, oxidation, adsorption and co-precipitation. In terms of reduction, the dehalogenation mechanism of nZVI in aqueous solution is a multi-step process depending on the target substances. Fe⁰ acts as an electron donor to reduce organic pollutants [21]. As for the oxidation process, in the Fe⁰–H₂O system, strong oxidants are generated in the presence of oxygen, including hydroxyl radicals, ferryl ions, and superoxide radicals. In the oxidation process with nZVI under aerobic conditions, hydrogen peroxide (H₂O₂) is produced as an intermediate product and the desorbed H₂O₂ is able to react with ferrous iron following the Fenton reactions (Eqs. 1–3) [22–24]. For adsorption and co-precipitation, iron hydroxides or oxides are formed on the surface of nZVI, which are well known for their adsorption capacities [25]. To the best of our knowledge, the CAP removal from aqueous solution by nZVI has not been

reported previously. Therefore, it appears interesting to investigate the efficacy of this novel technique and its mechanisms.



The present study is aimed to investigate the removal mechanisms of CAP from aqueous solution by nZVI. The effects of the key parameters including nZVI dosage, initial pH, and air on the CAP removal were examined to study removal kinetics. Several techniques, including XPS, Raman, ICP, LC–MS and GC–MS, were used to obtain the structural features of CAP reduction products and further analyze the removal mechanisms.

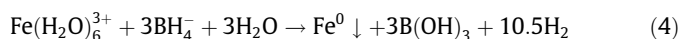
2. Materials and methods

2.1. Materials

Sodium borohydride (NaBH₄, Analytical Reagent), ferric chloride hexahydrate (FeCl₃·6H₂O, Analytical Reagent) and ethanol (C₂H₅OH, Analytical Reagent) were purchased from Sinopharm Chemical Reagent Shanghai Co., Ltd. (China); chloramphenicol (C₁₁H₁₂Cl₂N₂O₅, Analytical Reagent) was obtained from Sangon Biotech Shanghai Co., Ltd. (China); acetonitrile (CH₃CN, HPLC grade), methanol (CH₃OH, HPLC grade), N-Hexane (C₆H₁₄, HPLC grade) and formic acid (HCOOH, HPLC grade) was from Shanghai ANPEL Scientific Instrument Co., Ltd. (China). Chloramphenicol standard used for establishing standard curve was obtained from Dr. Ehrenstorfer GmbH (Germany). Bis(trimethylsilyl)trifluoroacetamide trimethylchlorosilane (BSTFA:TMCS, 99:1) was purchased from Regis Technologies, Inc. (USA).

2.2. nZVI preparation

The nZVI particles were prepared via a liquid phase reduction method described by Wang and Zhang [26]. Deionized water was deoxygenated by purging with N₂ for 30 min before use. nZVI particles were produced by adding 1.6 M NaBH₄ aqueous solution dropwise to a 1.0 M FeCl₃·6H₂O aqueous solution at ambient temperature with vigorous stirring. Ferric iron (Fe³⁺) was reduced according to the following reaction [27]:



The synthesized nZVI particles were washed with deoxygenated deionized water and pure ethanol three times and stored in ethanol for further use.

2.3. Characterization analyses of nZVI

Prior to the measurements, nZVI particles were dried using a vacuum freeze-drying method. The measurement of specific surface area of nZVI was performed using a nitrogen adsorption isotherm with a specific surface area pore size analyzer (JW BK122W, Beijing JWGB Sci & Tech Co., Ltd., China). The surface, morphology and size of nZVI were examined using scanning electron microscopy (SEM, XL-10, Koninklijke Philips N.V., Netherland) and transmission electron microscopy (TEM, JEM-2011, Jeol, Japan). The crystal structures of prepared nanoparticles were examined with X-ray powder diffraction (XRD, D8 Advance X, BRUKER AXS GMBH, Germany). Elemental composition of nZVI was determined with XPS (PHI 5000C ESCA, Physical Electronics, Inc., USA).

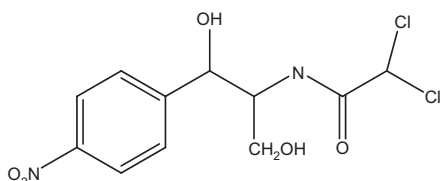


Fig. 1. Chemical structure of CAP.

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