



Removal of bismethiazol from water using zerovalent iron: Batch studies and mechanism interpretation



Chongyang Shen^{a,*}, Weilan Lu^a, Yuanfang Huang^a, Junxue Wu^b, Hongyan Zhang^{b,*}

^a Department of Soil and Water Sciences, China Agricultural University, Beijing 100193, China

^b Department of Applied Chemistry, China Agricultural University, Beijing 100193, China

HIGHLIGHTS

- We examine the removal of bismethiazol from water using zerovalent iron.
- The removal of bismethiazol by zerovalent iron follows second-order kinetic interaction.
- The removal is due to surface complex interaction of bismethiazol with iron.
- Na⁺ and Ca²⁺ have little influence on the removal at concentrations ≤ 0.01 M.
- NO₃ significantly influences the removal even at low concentrations (e.g., 0.01 M).

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ABSTRACT

Bismethiazol [N,N'-methylene-bis(2-amino-5-mercapto-1,3,4-thiadiazole)] is one of the most widely used thiadiazole fungicides. While the bismethiazol has great mobility in the subsurface environments (e.g., soil), the bismethiazol and its derivative (i.e., thiadiazole) were shown to be toxic to organisms. The methods used for treatment of bismethiazol, however, have not been presented to date. This study thus investigated the effectiveness of using microscale zerovalent iron to remove bismethiazol from water. Batch experiments were performed to investigate the kinetics of removal of bismethiazol by zerovalent iron at different bismethiazol concentrations, iron dosages and solution pHs. Results show that the zerovalent iron is very effective to remove bismethiazol from water. The removal can be described by pseudo-second-order kinetic model. X-ray diffraction and mass spectrometry examinations show that bismethiazol was removed from water through complex with iron surfaces by forming Fe-S bond. The presence of NaCl in the solutions has minor influence on the remove of bismethiazol whereas CaCl₂ can decrease the removal efficiency at high concentrations (e.g., 0.1 M). The presence of NaNO₃ has significant influence on the removal of bismethiazol even at low concentrations (e.g., 0.01 M). Whereas pesticides are commonly removed by zerovalent iron thorough degradation, our results indicate that removal of bismethiazol by zerovalent iron is due to surface complex. Our study shows that the zerovalent iron might be potentially useful for utilities to control fungicides in water and wastewater treatment.

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1. Introduction

Bismethiazol [N,N'-methylene-bis(2-amino-5-mercapto-1,3,4-thiadiazole), Fig. 1] has been one of the most commonly used fungicides since the 1970s [1]. This bactericide has been shown to be very effective to treat bacterial blight of rice, bacterial leaf streak of rice (caused by *Xanthomonas oryzae* pv. *oryzicola*), and citrus canker (caused by *Xanthomonas campestris* pv. *citri*) [2–5]. About

2 million kg of bismethiazol are produced annually in China, a large portion of which is export to other regions in the world [6]. Despite its effectiveness to treat plant disease, a number of studies [7–10] showed that the bismethiazol is toxic to humans and organisms. For example, Bu et al. [7] examined the genotoxicity of bismethiazol on *Vicia faba* root tip cells and showed that this pesticide induced chromosomal aberration. Ren et al. [8] reported that humans can suffer from contact dermatitis by exposure to bismethiazol. Chen et al. [9] presented that bismethiazol could be converted to 2-amino-5-mercapto-1,3,4-thiadiazole (denoted as thiadiazole) through photolysis and hydrolysis and the derivative has greater toxicities. The wide use of bismethiazol inevitably causes it to enter the subsurface environments (e.g., soil). Du [11] conducted

* Corresponding authors. Tel.: +86 1062733596 (C. Shen), tel.: +86 1062733219 (H. Zhang).

E-mail addresses: chongyang.shen@gmail.com (C. Shen), hongyan@cau.edu.cn (H. Zhang).

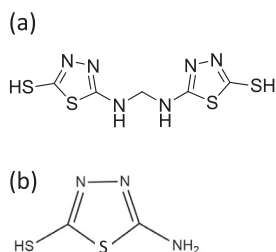


Fig. 1. Chemical structures of (a) bismertiazol [N,N'-methylene-bis-(2-amino-5-mercapto-1,3,4-thiadiazole)] and (b) 2-amino-5-mercapto-1,3,4-thiadiazole.

laboratory column experiments to examine the fate and transport of bismertiazol in sandy soil porous media. It was found that sandy soil has low affinity for the bismertiazol to adsorb at different ionic strengths. The presence of clay in the pore water enhances the transport of bismertiazol in the sand. The results in Du [11] indicate that the bismertiazol has great mobility in the subsurface environments, which is likely to enter into groundwater. Indeed, the bismertiazol has been frequently detected from groundwater samples, in which the bismertiazol concentration was as high as 2 mg/L [8,11]. However, the methods used for treatment of bismertiazol in groundwater have not been reported to date.

Zeravalent iron (ZVI), as a readily available and low-cost elemental material, has been widely adopted in water and wastewater treatment [12]. For example, ZVI has been adopted in subsurface permeable reactive barriers to remove contaminants in groundwater for nearly two decades [13]. ZVI can serve as a sorbent, (co-)precipitant or contaminant immobilizing agent to remove contaminants such as chlorinated solvents [14]. ZVI can also act as an electron donor to break down or convert contaminants (e.g., phosphate, arsenic) into less toxic or mobile forms. Whereas ZVI has been shown to be effective in removing various types of non-biological contaminants (e.g., chlorinated solvents, heavy metals, radionuclides, and nutrients) and biocolloids (e.g., bacteria, viruses) [15–17], whether ZVI is effective for treatment of fungicides is unclear to date. To find physical and chemical methods for treatment of fungicides is of importance because biological methods may be ineffective due to toxicities of fungicides to bacteria.

This study investigated the effectiveness of using ZVI to remove the fungicide bismertiazol from water. Batch experiments were conducted to examine the influence of initial bismertiazol concentration, ZVI dosage and solution pH on the removal of bismertiazol using ZVI. We showed that ZVI is very effective to remove both bismertiazol and its derivative (i.e., thiadiazole) from water. The removal of bismertiazol follows pseudo-second-order interaction. X-ray diffraction (XRD) and mass spectrometry examinations showed that the removal is due to complex of bismertiazol and thiadiazole with ZVI by forming Fe–S bond. However, the presence of Ca^{2+} can significantly decrease the removal efficiency at high concentrations (e.g., ≥ 0.1 M). NO_3^- has significant influence on the removal efficiency even at low concentrations (e.g., 0.01 M). Whereas pesticides are commonly removed by ZVI through degradation, our results show that bismertiazol is removed by sorption. Our study indicates that the zerovalent iron might be potentially useful for utilities to control thiadiazole fungicides (e.g., ethaboxam, etridiazole, octhilineone, and benthiazole) in water and wastewater treatment.

2. Materials and methods

2.1. Materials

Standard bismertiazol (82.0%, w/w) was supplied by the Zhejiang Yifan Chemical Ltd Co. (Zhejiang, China). The

bismertiazol is a member of thiadiazole bactericides. The chemical structure of bismertiazol was shown in Fig. 1. Bismertiazol is non-polar, hydrophobic, and fat-soluble. The bismertiazol stock solutions were prepared by dissolving 0.04 g of bismertiazol power and cosolvent dimethyl sulfoxide (<0.1%, V/V, Sinopharm Chemical Reagent Beijing Co., Ltd., China) into 1 L deionized (DI) water (Millipore Milli-Q equipment, Shanghai Hetai Instrument Co., Ltd., China) and stored at 4 °C in the dark.

The granular zerovalent iron (0.12–0.15 mm) adopted was obtained from Wode-Tai Co., Ltd., China. The iron was used as received without pretreatment. The specific surface area of the ZVI is $0.234 \text{ m}^2 \text{ g}^{-1}$. The manufacturer reported that the content of elemental iron for the ZVI is more than 99%. In addition to elemental iron, the ZVI grains contain a minor amount of C and Mn (<100 and $0.1 \mu\text{g g}^{-1}$, respectively).

2.2. Batch experiments

Batch experiments were conducted using 50 mL glass vials at room temperature (25 ± 1 °C). The first set of experiments investigated the effects of ZVI dosage on bismertiazol removal. Specifically, different amounts of ZVI grains were added to 40 mL bismertiazol solution (10 mg/L) at pH 6 (adjusted by addition of NaOH and HCl) in the glass vials. Four dosages of ZVI grains were considered: 0.5, 2.5, 5, and 12.5 g L^{-1} . Then the vials were immediately sealed with Parafilm and shaken at 160 rpm. At times of 10 min, 30 min, 2 h, 4 h, 8 h, 12 h, and 24 h, samples were taken to determine the amount of bismertiazol removed by ZVI. The concentrations of total dissolved Fe(II, III) in the suspensions were measured using the Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The second and third sets of experiments examined the effects of initial bismertiazol concentration and solution pH on the removal, respectively. The two sets of experiments followed the same procedure as that for the first set of experiments. However, for the second set of experiments, the initial bismertiazol concentration were 0.1, 1, 10, and 40 mg L^{-1} . ZVI dosage was fixed at 12.5 g L^{-1} and solution pH was 6. For the third set of experiments, three values of solution pH (i.e., 4, 6, and 10) were considered. The ZVI dosage was 12.5 g L^{-1} and the initial bismertiazol concentration was 10 mg L^{-1} . The fourth set of experiments investigated effects of ions on the removal of bismertiazol by ZVI. Electrolyte (NaCl, CaCl_2 or NaNO_3) was added to 40 mL bismertiazol solutions (10 mg L^{-1}) with 12.5 g L^{-1} ZVI grains in the glass vials, resulting in ionic strengths of 0.01 M or 0.1 M. After reaction of 24 h, samples were taken to determine the concentration of remained bismertiazol. For selected experiments, the ZVI grains after 24 h reaction were recycled and added to 40 mL new bismertiazol solution to examine the reusability for removal of bismertiazol. Because bismertiazol could be decomposed slowly to thiadiazole by photolysis and hydrolysis, the concentrations of thiadiazole were measured for all samples. All aforementioned experiments were done in triplicate.

2.3. Determination of bismertiazol and thiadiazole concentrations

The vial samples collected from batch experiments were centrifuged for five minutes at 3800 rpm. The supernatants were filtered through $0.22 \mu\text{m}$ water nylon membrane filter. The concentrations of bismertiazol and thiadiazole were determined by High Performance Liquid Chromatograph (HPLC). Details about determination of the concentration of bismertiazol and thiadiazole using HPLC can be found in Wu et al. [18]. Briefly, the HPLC was performed with an Agilent 1100 HPLC series (Agilent technologies, USA) consisting of a G1379A degasser, a G1311A quaternary pump, a G1313A Autosampler, a 1316A Thermostatted Column Compartment, a G1315B Diode Array Detector, and a $5 \mu\text{m}$ reversed phase

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