



Rapid degradation of endosulfan by zero-valent zinc in water and soil



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ABSTRACT

Endosulfan has been included in the list of persistent organic pollutants (POPs) in 2011. The degradation of endosulfan by zero-valent zinc in water and soil was first investigated. The results showed that >90% endosulfan could be degraded in 180 min. The degradation was accelerated under acidic conditions with the absence of dissolved oxygen, while the nature of the soil only exhibited a negligible effect. The half-life was decreased from 130.75 min to 41.75 min with the increment of Zn(0) from 0.1 g to 1 g in soil. The use of Zn(0) was more effective than Fe(0) for the degradation of endosulfan with a half-life of 110 min and 330 min. The cationic surfactant was more effective at enhancing the degradation of endosulfan than anionic and nonionic surfactant. The degradation pathway was speculated, and four chlorine of endosulfan were proposed to be reduced. The method exhibited obvious advantages over traditional endosulfan treatments, and the research results will lay a foundation for practical application of the method.

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1. Introduction

Zero-valent metal (ZVM) has been known as an efficient reductant for dealing with the contaminants since the late 1980s (Pourrezaei et al., 2014). Extensive studies on the reduction of pesticides have been focused on the remediation of groundwater and surface water, for example, studies on the remediation of water contaminated by DDT (Sayles et al., 1997), atrazine and parathion (Ghauch et al., 1999), s-triazines (Ghauch and Suptil, 2000), carbaryl (Ghauch et al., 2001), benomyl, picloram, and dicamba (Ghauch, 2001), nitroaromatic pesticides (Keum and Li, 2004), flutriafol (Ghauch, 2008), chlorothalonil (Ghauch and Tuqan, 2008), and thiobencarb (Amin et al., 2008). Most of these pesticides contained one or more chlorine atoms, nitrous and/or carboxylic groups. Non-toxic and inexpensive ZVM continues to be a powerful material that is used by a large number of environmental scientists (Ghauch, 2008). In addition to the extensive research studies on iron (Cao et al., 1999; Dombek et al., 2001; Su and Puls, 2001; Bigg and Judd, 2001; Volpe et al., 2004; Chen et al., 2008; Kim et al., 2008; Cong et al., 2010; Shu et al., 2010), other metals have also

been studied, especially for the Zn(0) which is a stronger reductant than iron (Arnold et al., 1999; Gao et al., 2011).

Endosulfan (1,4,5,6,7,7-hexachloro-8,9,10-trinorborn-5-en-2,3-ylenebismethylenes sulfite, CAS No.115-29-7) is an efficient broad-spectrum organochlorine pesticide that has been applied in various crops for more than 30 years (Fig. 1). Industrial endosulfan is composed of α and β isomers (7:3). With high toxicity, persistence, biological accumulation and migration, endosulfan has been detected in soil, water, air and food products. The degradation-resistant endosulfan is a serious threat to human health because it can cause cancer, deformity and mutation (Verma et al., 2006). Therefore, endosulfan has been included in the list of persistent organic pollutants by the Persistent Organic Pollute Review Committee in 2011.

Methods of degradation of endosulfan have been developed with the use of white-rot fungus (Kamei et al., 2011), ozonation (Begum and Gautam, 2012), *Pseudomonas aeruginosa* (Jayashree and Vasudevan, 2009), hydrophobic zeolites (Yonli et al., 2012), Mg⁰/Pd⁺⁴ bimetallic system (Aginhotri et al., 2011), and so on. According to Laine and Cheng (2007), an effective technology for the destruction of persistent organic pollutants should have the following characteristics: **a.** high destruction efficiency, **b.** formation of non-toxic and environmentally benign intermediates and products and **c.** the reaction should proceed at ambient environmental conditions. In the process of bio-degradation, it sometimes

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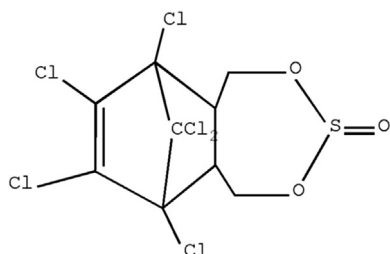


Fig. 1. Chemical structure of endosulfan.

must control the reactive conditions strictly (temperature, oxygen, pH, etc.) because the microorganism can be damaged under an inappropriate environment (Zhou and Crawford, 1995). On the other hand, physical methods may suffer from high cost and reversible adsorption.

In this paper, the rapid degradation of endosulfan by micro-scale zinc powder in water and soil were first investigated. Moreover, as yet there were few studies on the degradation of pesticides in soil applying this method. Based on the study of previous researches, the influence of pH, surfactant, different amount of zero-valent metal and the dissolved oxygen were considerable. Thus, the effects of pH levels (4, 7, and 9), the amount of Zn(0), and the use of different surfactants were discussed in this study. The influence of dissolved oxygen and soils of different natures and a comparison of the performances of iron and zinc were also considered. The degradation products in water were identified by gas chromatography-mass spectrometry (GC/MS), and the relevant reaction route was proposed. The surfaces of zinc powder before and after the reaction were characterized by microscopic morphological analysis.

2. Materials and methods

2.1. Reagents and materials

Endosulfan (96.20%) was provided by Jiangsu Red Sun Limited Company (Nanjing, China). Micro-scale zinc and iron powder (analytical grade) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Anhydrous sodium sulfate, ethyl acetate, cetyl pyridinium chloride (CPC), sodium dodecyl sulfate (SDS) and tween-20 (TW-20) of analytical grade were purchased from Solarbio Company (Beijing, China). Acetate buffer (pH 4), phosphate buffer (pH 7), and carbonate buffer (pH 9) were prepared according to standard methods.

2.2. Instrumental analysis

Reactions were monitored via gas chromatography (GC) using an Agilent 6890N instrument (Agilent, USA) equipped with an HP-5 capillary column (30 m × 0.25 mm × 0.25 μm) and an electron capture detector (μECD). Products were detected using an Agilent 6890/5973N gas chromatography mass spectrometer (GC/MS) with an EI ion source (Agilent, USA).

Programmed temperature vaporization was used to perform GC. The column temperature started at 100 °C for 1 min, was increased to 280 °C at a rate of 10 °C/min and was finally held for 5 min. The injection port temperature was 280 °C, and the detector temperature was 300 °C. The carrier gas was N₂ at a flow rate of 1 mL/min. The MS was operated in electron impact mode (70 eV) and scanning mode to obtain the mass spectrometry results. Under these conditions, the typical retention time for α-endosulfan and β-endosulfan were 20.91 min and 23.58 min, respectively.

2.3. Pretreatment of metallic powder

The Zn and Fe powder were treated with 0.4% H₂SO₄ and then repeatedly rinsed with deionized water five times to remove oil film and oxides on the surface of the metallic powder. The cleaned metallic powder were dried in a vacuum oven at 60 °C for 2 h and then stored in a sealed desiccator.

2.4. Characterization of metallic powder

The specific surface area of micro-scale zinc powder was 34.89 m²/g and that of micro-scale iron was 22.55 m²/g, as measured by the Brunauer–Emmet–Teller gas adsorption isotherm with N₂ gas on a V-sorb 2800P surface area analyzer (Gold App Instruments, China). The surface morphological analyses of zinc powder were performed using a Hitachi S-3000N scanning electron microscope (Hitachi, Japan) at a 10 kV beam potential.

2.5. Endosulfan removal experiments in water

A total of 0.2 g of pre-cleaned Zn(0) was added into 200 mL of acetate buffer with endosulfan (40 mg/L, pH 4). The reaction bottles were sealed with rubber plugs and placed in a magnetic stirring apparatus (HJ-4, Guohua Company, China) at room temperature (22 ± 0.1 °C). Control experiments were also performed in the buffer solution with endosulfan without Zn(0). The experiment was performed in triplicate and the reaction time was 180 min. The samples were withdrawn by syringe at the given times, extracted by ethyl acetate using a separatory funnel and analyzed by GC. The extraction method was less interference from impurities and with high recovery (above 87.92%).

The phosphate buffer (pH 7) and carbonate buffer (pH 9) were chosen to evaluate the effect of pH on the degradation according to the above procedure.

To compare the influence of oxic and anoxic conditions on the degradation of endosulfan, the comparison test under anoxic conditions was performed in acetate buffer (pH 4). The vial was first purged with nitrogen to assume the absence of dissolved oxygen, and then a continuous nitrogen sparging flow (3 mL/min) was run during the reaction.

Moreover, the experiment was conducted using Fe(0) instead of Zn(0) in the acetate buffer containing 40 mg/L endosulfan and 0.2 g pre-cleaned metal under oxic condition to compare the degradation ability.

2.6. Endosulfan removal experiments in soil

Endosulfan (40 mg/kg) was prepared in 10 g of sterile sandy loam. After two hours, 20 mL of acetate buffer and pre-cleaned Zn(0) (0.1 g, 0.5 g, 1.0 g) were added and the initial pH value of the reaction system was 4. The initial pH of the solution was adjusted to the designated value with HCl or NaOH. The reaction tubes were then sealed and shocked in a constant-temperature shaker at 25 ± 0.1 °C and 180 rpm. Control experiments were also performed according to the above procedure (without Zn(0)). Each experiment included three repetitions and the reaction time was 180 min. Samples were extracted with ethyl acetate by vortex and centrifuged and then analyzed by GC. The extraction method was with high recovery (above 83.59%) and less interference from impurities.

Phosphate buffer (pH 7) and carbonate buffer (pH 9) were chosen to evaluate the effect of pH on the reaction according to the above procedure.

Shin et al. (2008) stated that surfactant might modify the surface property of the metal and the reduction on the surface of metal

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