



Enhanced reductive dechlorination of tetrachloroethene by nano-sized mackinawite with cyanocobalamin in a highly alkaline condition



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ABSTRACT

In this study, we characterize the reductive dechlorination of tetrachloroethene (PCE) by nano-sized mackinawite (nFeS) with cobalamin (Cbl(III)) at a high pH and investigate the effects of environmental factors, including the concentrations of the target contaminant, reductant, and catalyst and suspension ions on the dechlorination kinetics of PCE. Ninety five percent of the PCE was degraded by nFeS with Cbl(III) in 15 h. Cyclic voltammetry conducted with regard to the reductive dechlorination showed a higher redox potential of mackinawite under a high-pH condition (−1.01 V), suggesting that the oxidation state of the central cobalt ion in the cobalamin could be reduced to Cbl(I). The change of cobalamin species on the nFeS surface was verified under different pH conditions by UV–vis spectroscopy. The rate constant of PCE dechlorination increased from 0.1582 to 0.4284 h^{−1} due to the increase in the nFeS content (2.085–20.85 g/L). As the concentration of Cbl(III) increased from 0 to 0.5 mM, the dechlorination kinetics of PCE was accelerated (0–1.4091 h^{−1}) but reached a state of equilibrium from 0.5 to 1 mM. The increase in the initial PCE concentration (0.035–1.0 mM) slowed down the dechlorination kinetics (0.2036–0.0962 h^{−1}). The dechlorination kinetics was enhanced by 1.5–11 times when 10 mM of ions (Na⁺, K⁺, Mg²⁺, Ca²⁺, CO₃^{2−}, SO₄^{2−}, and NO₃[−]) were added, while an addition of HCO₃[−] decelerated it by 10 times. This study can provide background knowledge pertaining to the PCE dechlorination by a natural reductant under a high-pH condition and the effect of environmental factors on the dechlorination kinetics for the development of novel remediation technologies.

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1. Introduction

Carcinogenic and toxic chlorinated organic compounds (COCs) are widely spread in a number of groundwater systems due to the extensive industrial usage of these compounds (Doherty, 2000a; Lee and Batchelor, 2002). Tetrachloroethene (PCE), one of the most commonly found COCs, has been widely used as a solvent in the dry cleaning, textile, and degreasing industries. PCE is known to be stable and recalcitrant in natural environments (Doherty, 2000b). However, due to its extensive usage, the development of treatment technology for wastewater and groundwater contaminated with PCE has continuously attracted attention in the area of environmental technology.

Over the last few decades, much effort has been made to develop novel remediation processes of diverse COCs (Demeestere

et al., 2005; Doong and Lai, 2005; Huang et al., 2002; Hwang and Batchelor, 2000; Lee and Batchelor, 2004; Pignatello et al., 2006). Among them, in situ redox manipulation by an injection of mackinawite (FeS) has been developed as an effective remediation technology able reductively to dechlorinate COCs due to the high mobility and reactive chemical species on the mackinawite surface (Butler and Hayes, 1999; Elsner et al., 2003). In anoxic environments, sulfate-reducing bacteria reduce sulfate to sulfide and subsequently form FeS by means of precipitation with ferrous iron (Berner, 1964; Rickard, 1969). The reductive dechlorination of COCs by FeS is known to be significantly influenced by the reactive functional groups on the FeS surface under diverse environmental conditions (Jeong and Hayes, 2003, 2007). The reductive dechlorination of COCs by FeS was also significantly affected by microbial activities due to the extracellular secretion of a microbial enzyme. Butler and Hayes investigated the effects of the pH and solution composition on the reductive dechlorination of hexachloroethane (HCA) and trichloroethylene (TCE) (1998; 1999). Gander et al. observed 1,1,1-trichloroethane (1,1,1-TCA) removal was enhanced as

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caused by the interaction between FeS and a methanogenic consortium (2002). Amir and Lee found that cyanocobalamin (Cbl(III)) secreted by microbes significantly enhances the reductive dechlorination of PCE (2012). Anaerobic bacteria such as sulfate-reducing bacteria, methanogens, and acetogens excrete transition-metal coenzymes such as Cbl(III), cofactor F₄₃₀ and hematin. They have redox-active metal at the center, playing a significant role as an electron-transfer mediator (ETM) (Gantzer and Wackett, 1991; Krone et al., 1989; Schanke and Wackett, 1992). Among them, cobalamin (Cbl(III)) has been widely used to effectively mediate electron transfer for COCs dechlorination (Argüello et al., 2005; Amir and Lee, 2012; Kim and Carraway, 2002). Cbl(III) was found to be remarkably efficient for the reductive dechlorination of PCE (Amir and Lee, 2011) with zero-valent iron (ZVI). Additionally, Cbl(III) with titanium(III) citrate showed faster dechlorination kinetics of TCE and PCE than other coenzymes, such as hematin, and cofactor F₄₃₀ (Gantzer and Wackett, 1991).

Most of the previous studies on the reductive dechlorination of COCs by FeS were conducted under neutral or weak acid/base conditions. However, textile industries using high contents of COCs can generate high pH wastewater (Alinsafi et al., 2007; Khlifi et al., 2010; Pala and Tokat, 2002), and chloralkali industries can also release high amount of COCs in strong alkali effluents (Kannan et al., 1998; Basu et al., 2013). In addition, COCs degradation system under a high-pH condition could be applied to degradative solidification/stabilization system (dS/S) which generates a high-pH condition due to its hydration (Hwang and Batchelor, 2000). Therefore, investigation of reductive dechlorination of COCs under high-pH conditions should be clearly understood. In this research, FeS and Cbl(III) were selected respectively as a reductant and ETM, and PCE was used as a target chlorinated chemical to study the degradation of COCs. The objectives of this research are investigation of reductive dechlorination of PCE using natural reductant and ETM in strong alkaline condition, evaluation of the effects of various environmental factors on the reductive dechlorination of PCE, and identification of PCE removal reaction mechanism by nFeS-Cbl(III) system. The experimental results provide basic knowledge about the PCE dechlorination and the effects of a natural reductant and cobalamin on the dechlorination kinetics of PCE under a high-pH condition.

2. Experimental

2.1. Chemicals

Cobalamin (III) (vitamin B₁₂, 99%, Sigma), PCE (99+%, Sigma), trichloroethene (TCE) (99.5+%, Sigma), cis-dichloroethene (cis-DCE) (99+%, TCI), trans-dichloroethene (trans-DCE) (98+%, TCI), 1,1-dichloroethene (1,1-DCE) (99+%, Sigma), and vinyl chloride (VC) (99+%, Supelco) were used for the stock solution. A mixture of gases (methane (1%), ethane (1%), ethene (1%), acetylene (1.03%), carbon monoxide (1%), and carbon dioxide (1%) in nitrogen gas (Supelco)) was used as a standard sample for a gas chromatographic analysis with a flame ionization detector. Hexane (99.9%, Merck) and methanol (99.9%, Merck) were used as an extractant and for the preparation of the stock solution, respectively. Sodium sulfide nonahydrate (Na₂S·9H₂O) (98+%, Sigma) and ferrous chloride (FeCl₂·4H₂O) (99+%, Sigma) were used for the synthesis of nano-mackinawite (nFeS). Sodium hydroxide (NaOH) (98+%, Sigma) and hydrochloric acid (HCl) (36.5+%, Sigma) were used to control the pH. Deaerated deionized water (DDW) used in this study was prepared using ultra-pure water (18 MΩ cm) purged by N₂ for 12 days and kept in an anaerobic chamber. All of the reagents and solutions used in the experiments were prepared with DDW.

2.2. Synthesis and characterization of nFeS

A modified method adapted by Paknikar et al. (2005) was used to synthesize nFeS. A Na₂S · 9H₂O solution (0.618 M) was slowly dropped into 0.534 M of a FeCl₂·4H₂O solution and purged with N₂ gas. The precipitates were washed three times with DDW and then freeze-dried. The nano-sized powder was used a couple of days after the synthesis; it was stored in an anaerobic chamber before it was used. A Brunauer-Emmett-Teller (BET) analysis was conducted to measure the surface area of the nFeS particles. The specific surface area of nFeS was 18.32 m²/g, which was 8 times higher than those of FeS reported in the literature (Amir and Lee, 2012). An X-ray diffraction analysis was performed for confirming the crystallinity of the synthesized nFeS; it was found that its diffractogram was in good agreement with that of previous reports (Jeong et al., 2008; Lennie et al., 1995). The broad and weak peaks indicate poor crystallization of the nFeS or a small size of the crystallite shown (2θ) at 17.6°, 30°, 39°, 50° (Data not shown).

2.3. Experimental procedures

Experiments were carried out for the investigation of PCE reductive dechlorination under a high-pH condition (pH 12) and for identifying the effect of environmental factors, in this case the pH; ions; and concentrations of cobalamin, nFeS and PCE on the dechlorination kinetics. All of the experiments were performed using 24 mL amber glass vials. A three-layered septum system consisting of a lead foil tape, Teflon-lined silicon septum, and Teflon tape was designed and used to minimize the oxidation and volatilization of the PCE (Lee and Batchelor 2005). Most experimental steps were conducted in an anaerobic chamber, except for the sampling steps. All samples prepared in this study were in duplicate.

The vials were filled with the nFeS slurry, the Cbl(III) stock solution, and pH-adjusted deaerated deionized water (DDW) without headspace, yielding initial nFeS and Cbl(III) concentrations of 4.17 g/L and 0.1 mM, respectively. The pH of the DDW was set to 12 using an aliquot of a deoxygenated 0.2 M NaOH solution. The reductive dechlorination of PCE was initiated by spiking 100 μL of the PCE stock solution, yielding an initial PCE concentration of 0.035 mM. The vials were tightly capped and placed on a tumbler that provided end-over-end rotation at 7 rpm at room temperature (25 ± 0.5 °C). At each sampling time, the vials were taken out from the tumbler and then centrifuged at 3000 rpm for 5 min. 100 μL of the supernatant was moved to a 2 mL vial containing 1.4 mL of hexane as an extractant and 1, 2-dibromopropane (1.5 ppm) as an internal standard. The extracted samples were placed in an orbital shaker at 175 rpm for 30 min, and then analyzed. Control tests were conducted using pH 12 DDW, pH12 DDW with Cbl(III), and pH12 DDW with nFeS.

To investigate the effect of the pH on PCE reductive dechlorination, the pH of the DDW was controlled using an aliquot of deoxygenated 0.2 M HCl or NaOH at pH 5, 7, 9, and 12. The reductive PCE degradation started as described above. To investigate the effects of other geochemical factors (Cbl(III), nFeS, PCE, and the suspension cation and anion) on the PCE reductive dechlorination in nFeS with Cbl(III), the pH was fixed at 12. The conditions of other factors were fixed (0.1 mM of Cbl(III), 0.035 mM of PCE, and 4.17 g/L of nFeS), except for the factor investigated in each test. Four different concentrations of Cbl(III) (0.1 mM, 0.25 mM, 0.5 mM, and 1.0 mM) were used to investigate its effect on PCE reductive dechlorination kinetics in nFeS suspensions. To verify the effects of the nFeS and PCE concentrations on the dechlorination kinetics, four different nFeS concentrations (0.05 g, 0.1 g, 0.25 g, and 0.5 g per vial) and five different PCE concentrations (0.035 mM, 0.1 mM, 0.25 mM, 0.5 mM,

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