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Reductive dechlorination of tetrachloroethene by two compost samples with different maturity

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ABSTRACT

This study sets up microcosms using two types of compost samples, bagasse/manure compost, and yard-trimming compost with different maturity, to evaluate their capacity for reductive dechlorination of tetrachloroethene (PCE). The experimental results show that less matured compost samples could reduce 300 μM of PCE to ethene within 180 days of incubation. Decreasing initial PCE concentration and removing dissolved oxygen from the solution could enhance reducing efficiency. The solution remains near neutral pH throughout the experiment, and ethene emerged when the redox potential dropped to below −150 mV. Different microbial inhibition agents, such as 2-bromoethanesulfonic acid and sodium molybdate 2-hydrate, exhibit different effects on the dechlorination efficiency. The potential advantages of using compost to remove PCE are discussed. Overall, due to their high carbon content, diverse microbial activity, high buffer capacity, and complex physical structure, compost samples could serve as suitable media for dechlorinating PCE.

1. Introduction

Chlorinated aliphatic hydrocarbons are among the most common organic contaminants in groundwater. Because chlorine atoms block oxygenase attacking sites, current evidence suggests that a highly chlorinated solvent, such as tetrachloroethene (perchloroethylene or PCE), is recalcitrant to aerobic biotransformation (Rittmann and McCarty, 2001; Robinson et al., 2009).Under anaerobic conditions, PCE microbiologically transforms to less-chlorinated compounds, such as trichloroethene (TCE), dichloroethenes (DCEs), vinyl chloride (VC), and ethene (ETH), through reductive dechlorination processes (Magnuson et al., 2000; Kao et al., 2003). At each process, a hydrogen atom replaces a chlorinate atom, and the reaction rates for each step decrease as chlorine is removed. Therefore, researchers have considered transformation from VC to ethene (ETH) to be a rate-limiting step in complete reductive dehalogenation of PCE under an anaerobic environment (He et al., 2003; Broholm et al., 2005). Studies have observed accumulating VC during reductive PCE dehalogenation, even in studies with mixed bacterial cultures (Rosner et al., 1997; Broholm et al., 2005). Because VC is a known human carcinogen and more toxic than PCE, investigating the final reduction of VC to ETH has become especially important during groundwater bioremediation.

Sequential reductive dechlorinating processes require additional electron donors and nutrients to inject to the contaminated zone to stimulate microbial activity. Several liquid electron donors, such as acetate, benzoate, butyrate, glucose, lactate, methanol, and pyruvate have all shown to support reductive dechlorination (Aulenta et al., 2005, 2007; Yang and McCarty, 2000, 2002), but injecting these liquid electron donors into the subsurface could cause excess microbial growth and result in well-clogging (Brennan et al., 2006). An alternative solution uses solid polymeric organic materials as electron donors to stimulate reductive processes (Vera et al., 2001). Brennan et al. (2006) examined the feasibility of using chitin and corncobs as electron donors for reductive dechlorination of PCE, and the results showed that chitin fermentation supported PCE reduction but not corncobs. The difference in PCE dechlorinating efficiency by chitin and corncobs were mainly resulting from their buffering capacities, because chitin obtained from crab shells contained residual calcium carbonate and thus could maintain neutral pH for dehalogenating bacteria. In addition, degrading chitin releases nitrogen, a nutrient for biologic growth. Our previous study shows that a yard-trimming compost sample serves as an electron donor for denitrification, and maintains a neutral pH in the system due to its high buffering capacity (Tsui et al., 2007). Therefore, it would be interesting to see whether compost could serve as an electron donor to support the reductive dechlorination of PCE to ETH.

Previous studies have reported reductive dechlorination under a denitrifying and iron-reducing condition, but the most rapid biodegradation rates occur under a methanogenic and sulfate-reducing environment through cometabolic mechanisms (Kao et al., 2003). However, methanogens and sulfate-reducing bacteria compete with dehalogenating microorganisms for electron donors,

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and reduce the dehalogenation rate (Cabirol et al., 1998; Ndon et al., 2000; Yang and McCarty, 2000). The current study selects two types of compost samples, one yard-trimming compost and one bagasse/manure compost, to evaluate their capacity for reductive dechlorination of PCE. This work examines the effects of compost maturity on dechlorination efficiency, and evaluates the effect of dissolved oxygen on the dechlorination process. This research uses 2-bromoethanesulfonic acid (BES) to inhibit methanogens, and sodium molybdate 2-hydrate (molybdate) to inhibit sulfate reducers, in order to assess the roles of these two microbial populations on the dechlorination process (Cabirol et al., 1998).

2. Methods

2.1. Materials

Tetrachloroethene (PCE), trichloroethene (TCE), dichloroethene (DCE) isomers (1, 1-DCE, *trans*-DCE, and *cis*-DCE), vinyl chloride (VC), and ethene (ETH) were obtained from the Aldrich Chemical Co. (Milwaukee, WI, USA). H_2 was purchased from Scotland Gases (Taipei, Taiwan). Sodium azide (NaN_3), BES, and molybdate were obtained from Sigma Chemical Co. (St. Louis, MO, USA).

Yard-trimming compost samples (3-month and 15-month) and bagasse/manure compost samples (3-month and 6-month) were collected from two composting facilities in Taiwan. The yard-trimming samples were made of yard waste without adding an additional nitrogen source, which took 15 months. The bagasse/manure samples were produced by mixing bagasse with pig manure at an approximate ratio of 20:1 weight/weight (w/w) on a dried weight basis, which took 6 months. Both facilities used the windrow process to produce compost, and the piles were turned mechanically every month. After the compost samples were collected, they were stored in plastic bags at room temperature for 2 months. These samples were then screened through a 4-mm sieve, and smaller subsamples were selected for chemical characterization. Measurements of organic carbon contents were obtained using a TOC 1010 Total Organic Carbon Analyzer (O.I. Analytic Corporation, College Station, TX). The pH was determined on a 1:10 compost:deionized water suspension using a combination glass-reference electrode connected to a pH meter (Consort C833). The sieved samples were heated at 105 °C overnight, and the weight loss related to its initial compost weight was used to measure the water content. Table 1 summarizes the characteristics of collected compost samples.

2.2. Microcosms setup and analytical methods

Microcosms were constructed by placing 5 g different compost sample (dried base) and 80-mL deionic water into 125-mL serum bottles. To assess whether dissolved oxygen would inhibit PCE dechlorination, a set of bottles were purged with ultra-high-purity N_2 to remove any residual oxygen from the water before adding the compost sample, and the remaining bottle sets were prepared without an initial purging N_2 process. Neat PCE dissolved in 5 mL of hexadecane was subsequently added to each bottle to produce the initial aqueous PCE concentration of ca. 300 μM, and the bottles were immediately sealed with a Teflon-lined septa and aluminum cap seals.

Table 1
The characteristics of selected four compost samples.

Compost samples	pH	Organic carbon content (%)	Moisture content (%)
3-Month bagasse/manure compost	7.5	24.23	66.23
6-Month bagasse/manure compost	7.3	17.86	11.94
3-Month yard-trimming compost	8.1	27.19	41.77
15-Month yard-trimming compost	7.8	22.39	34.10

To examine the effects of initial PCE concentrations on the dechlorination efficiency, another set of microcosms were set up by placing 5 g of compost (3-month bagasse/manure compost sample; dried base) with an initial PCE concentration of 30 μM. Each treatment was conducted with duplicates, and the average values are reported in this study. All the microcosms were incubated in a stationary condition in the dark at 25 °C upside down to minimize volatile organic loss.

The volatile components (PCE, TCE, DCE isomers, VC, and ETH) were periodically analyzed using a Hewlett–Packard model 5890 Series II gas chromatograph (Hewlett–Packard, Palo Alto, CA) equipped with a capillary column (60 m × 0.32 mm × 0.25 μm film, Supelco SPB-624 capillary column). PCE and TCE were detected using an electron capture detector, while DCE isomers, VC, and ETH were quantified using a flame ionization detector. Headspace samples (100 μL) in microcosms were withdrawn with a 250-μL gas-tight glass syringe (Hamilton Co., Reno, NV) and manually injected into a split injector operated at a split ratio of 1:1. Nitrogen was used as the carrier gas at 3 mL/min. The injector temperature was 220 °C and the detector temperature was set at 300 °C. The column temperature initially held at 50 °C for 2 min, and gradually increased to 150 °C at a rate of 10 °C/min. The microcosms were also samples for H_2 by injecting 3 mL of headspace gas into a Varian 3400 GC equipped with a stainless-steel column (Supelco) and a thermal conductivity detector. Helium was used as the carrier gas at a rate of 40 mL/min. Standards of volatile components and H_2 were prepared by adding a known amount of the compounds to a serum bottle with the same headspace-to-liquid ratio as the analyzed samples (Tandoi et al., 1994).

To assess the effects of pH and redox potential on dechlorination during the incubation period, two microcosms incubated with bagasse/manure compost samples were sacrificed at selected sampling time. After the sealed septa were removed from the serum bottle, the solution redox potential was immediately measured using an Ag/AgCl redox reference electrode. Calibration was performed using ZoBell's solution [3.2 mM potassium ferrocyanide ($K_4Fe(CN)_6 \cdot 3H_2O$) and 2.8 mM potassium ferricyanide ($K_4Fe(CN)_6$) in 0.1 M potassium chloride (KCl)] (Ionode Redox Electrode Manual). The system redox potential was obtained by adding 235 mV to the raw data referenced to Ag/AgCl electrolyte, to represent the potential relative to the hydrogen standard electrode (Olivas et al., 2002). The solution pH was measured using a combination glass-reference electrode connected to a pH meter (Consort C833).

2.3. Microbial inhibition study

To evaluate the roles of different microorganisms on PCE dechlorination, other sets of microcosms were established by adding different microbial inhibition agents. In addition to 5 g compost and 300 μM PCE, sodium azide (NaN_3), BES, or molybdate was added into the serum bottles to eliminate microbial activity of total microbial, methanogens, or sulfur reducers. The concentrations of microbial inhibition agents were set as 500 ppm or 1000 ppm (based on compost weight).

3. Results and discussion

3.1. PCE dehalogenation without previous purging of N_2

When the microcosms were set up with initial PCE concentration of 300 μM, the dechlorination products occurred in all microcosms