

Effect of Nanoscale Zero-Valent Iron Particles on a Mixed Culture Dechlorinating Trichloroethylene

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Background/Objectives. Chlorinated solvents such as trichloroethylene (TCE) have become common contaminants of soil and groundwater and can remain in the subsurface as dense non-aqueous phase liquids. A promising technology for DNAPL source zone remediation is biological degradation by dechlorinating bacteria. Among all the dechlorinating bacteria, of particular interest are members of the genus *Dehalococcoides*, which are the only organisms known to reductively dechlorinate PCE and TCE to vinyl chloride (VC) and ethene. In the meantime, nanoscale zero-valent iron particles (NZVI) are increasingly being used to treat sites contaminated with chlorinated solvents. However, the potential influence of NZVI on the community of indigenous microorganisms that participate in the remediation process is unknown. The objective of this study was to investigate the effects of NZVI on the microbial reduction of TCE in batch microcosms. Specifically, we (1) evaluate the effect of NZVI on a TCE-dechlorinating mixed culture (containing *Dehalococcoides* spp.) to determine whether NZVI has a biostimulatory or inhibitory effect on dechlorinating bacteria and (2) demonstrate the potential for NZVI to serve as a source of electrons for biological dechlorination via cathodic H₂ evolution. Competition for H₂ between dehalorespirers and methanogens in the consortium will also be addressed.

Approach/Activities. The effect of nano zero valent iron on the dechlorinating bacteria was studied in a series of laboratory scale experiments. A *Dehalococcoides*-containing culture was developed from an anaerobic methanogenic consortium that had already shown dechlorination activity in the laboratory. TCE degradation was studied in 250-mL serum bottles containing 4 mL inoculation culture (25-fold dilution), 100 mg NZVI (1 g/L) and mineral salts medium needed to achieve 100 mL final volume. HEPES buffer (final concentration 60 mmol/L) was used to control a corrosion-induced increase in pH. Several batch treatments were examined with NZVI, dechlorinating culture and their combination in the absence/presence of methanol (electron donor) to treat 20 mg/L TCE (15.2 µmol). The pH was adjusted to 7.2 by adding 1 M NaOH as needed. All treatments were amended with TCE (neat or dissolved in methanol) to provide an initial concentration of 20 mg/L (15.2 µmol).

Results/Lessons Learned. NZVI can have a biostimulatory effect associated with water-derived cathodic H₂ production during its anaerobic corrosion (730 ± 30 µmol H₂ was produced in 166 h in abiotic controls with 1 g/L NZVI) or an inhibitory effect upon contact with cell surfaces (assessed by TEM). Methanogens, which are known to compete for H₂ with dechlorinators, were significantly biostimulated by NZVI and methane produc-

tion increased relative to NZVI-free controls from 58 ± 5 to 275 ± 2 μmol . In contrast, bacteria dechlorinating TCE were inhibited by NZVI, and the first-order degradation rate coefficient decreased from 0.115 ± 0.005 h^{-1} ($R^2=0.99$) for controls to 0.053 ± 0.003 h^{-1} ($R^2=0.98$) for treatments with 1 g/L NZVI. Ethene production from TCE was initially inhibited by NZVI, but after 331 hours increased to levels observed for an NZVI-free system (7.6 ± 0.3 μmol ethene produced in 502 h compared to 11.6 ± 0.5 μmol in the NZVI-free system and 3.8 ± 0.3 μmol ethene for NZVI alone). Apparently, cathodic H_2 was utilized as electron donor by dechlorinating bacteria, which recovered following the partial oxidation and presumably passivation of the NZVI. Overall, these results suggest that reductive treatment of chlorinated solvent sites with NZVI might be enhanced by the concurrent or subsequent participation of bacteria that exploit cathodic depolarization and reductive dechlorination as metabolic niches.