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Impact of magnetite nanoparticles on the syntrophic dechlorination of 1,2-dichloroethane

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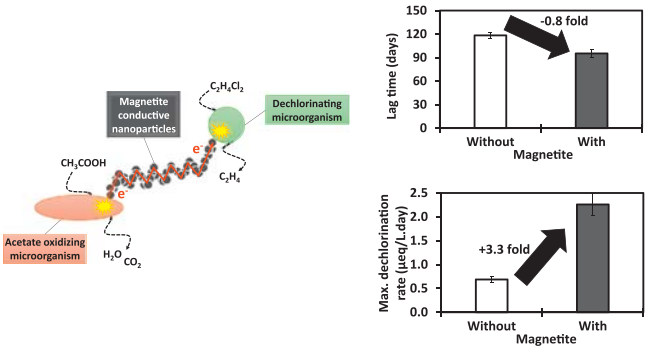
HIGHLIGHTS

- Magnetite nanoparticles enhance the kinetics of 1,2-DCA reductive dechlorination.
- Magnetite nanoparticles shorten the lag-phase of 1,2-DCA reductive dechlorination.
- 1,2-DCA dechlorination was correlated with the abundance of *Dehalococcoides mccartyi*.
- Results provide new insights into interspecies electron transfer mechanisms in dechlorinating communities.

GRAPHICAL ABSTRACT



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ABSTRACT

In anaerobic environments microorganisms exchange electrons with community members and with soil and groundwater compounds. Interspecies electron transfer (IET) occurs by several mechanisms: diffusion of redox compounds or direct contact between cells. This latter mechanism may be facilitated by the presence of conductive nanoparticles (NP), possibly serving as electron conduits among microorganisms. Our study examined the effect of magnetite (Fe_3O_4) NP on the dechlorination of 1,2-dichloroethane (1,2-DCA) by a mixed-culture. The addition of NP (170 mg L^{-1} total Fe) enhanced the acetate-driven reductive dechlorination of 1,2-DCA to harmless ethene (via reductive dihaloelimination) up to 3.3-times (2.3 μeq L^{-1} d^{-1} vs. 0.7 μeq L^{-1} d^{-1}), while decreasing the lag time by 0.8 times (23 days) when compared to unamended (magnetite-free) microcosms. Dechlorination activity was correlated with the abundance of *Dehalococcoides mccartyi*, which accounted up to 50% of total bacteria as quantified by CARD-FISH analysis, pointing to a key role of this microorganism in the process. Given the widespread abundance of conductive minerals in the environment, the results of this study may provide new insights into the fate of 1,2-DCA and suggest new tools for its remediation by linking biogeochemical mechanisms.

1. Introduction

The chlorinated aliphatic hydrocarbon (CAH) 1,2-Dichloroethane (1,2-DCA) is commonly used as a degreasing agent and as a precursor for the production of polyvinylchloride (PVC). As such, it is frequently

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detected in contaminated soil and groundwater due to improper handling, storage and disposal practices (Dinglasan-Panlilio et al., 2006).

CAHs, including 1,2-DCA, may be reduced chemically or biologically under anaerobic conditions. Microorganisms may serve as catalysts to carry out this transformation via reductive hydrogenolysis or dihaloelimination into lesser or even non-chlorinated end products. Dehalorespiration is the growth-linked process whereby microorganisms use an electron donor, such as hydrogen or acetate, and the CAHs as an electron acceptor (De Wildeman and Verstraete, 2003). Several microorganisms have been shown to carry out these reactions and include those from the genus *Dehalococcoides* (Duhamel and Edwards, 2007; He et al., 2003; Maymó-Gatell et al., 1999; Maymó-Gatell et al., 1997), *Dehalobacter* (Grostern and Edwards, 2009) and *Desulfitobacterium* (De Wildeman et al., 2003; Maes et al., 2006; Marzorati et al., 2007).

A variety of techniques have been developed for the remediation of CAHs. In-situ biostimulation of these dechlorinating populations is one technology which is commonly used due to its low cost and high environmental sustainability, when compared to other technologies (Zhang et al., 2016). This is usually done via the injection of a fermentable electron donor in the subsurface contaminated environment, such as lactate.

Recent evidence has shown that magnetite and other conductive minerals, may serve as electrical conduits to facilitate electron transfer between microbial species (Cheng and Call, 2016; Lovley, 2017). A specific example is the combination of *Geobacter sulfurreducens* and *Thiobacillus denitrificans*, which coupled acetate oxidation and nitrate reduction in the presence of magnetite nanoparticles (Kato et al., 2012). In another study, electron transfer during ethanol oxidation by *G. sulfurreducens* was facilitated by activated carbon during the reduction of fumarate by *Geobacter metallireducens* or carbon dioxide by *Methanosarcina barkeri* (Liu et al., 2012; Morita et al., 2011). Similarly, the presence of magnetite nanoparticles was found to accelerate the methanogenic conversion of organic substrates, such as propionate, by facilitating direct interspecies electron transfer (DIET) processes between acetogenic bacteria and methanogenic archaea (Baek et al., 2017; Cruz Viggi et al., 2014; Jing et al., 2017; Yang et al., 2016). Recent studies (Gacitúa et al., 2014; Zhao et al., 2016) have also shown that addition of conductive particles to the anode or cathode of bioelectrochemical systems results in enhanced electron transfer and, in turn, in a stabilized process performance. Despite its promise, the possibility to exploit magnetite-driven DIET for bioremediation applications has received, so far, only little attention. More in general, limited information is available on the interactions between minerals present (or produced) in groundwater and dechlorinating communities. Some studies have suggested that iron and manganese minerals may inhibit CAH dechlorination by serving as more suitable electron acceptors (Lu et al., 2001; Zaa et al., 2010). Others demonstrated that magnetite stimulated trichloroethene reduction using acetate as an electron donor (Aulenta et al., 2013). Interestingly, in microcosms that contained magnetite both *Desulfitobacterium* spp. and *Desulforomonas* spp. were enriched but *Dehalococcoides mccartyi* was outcompeted (Aulenta et al., 2014).

Despite these promising, yet preliminary findings, it is still unknown whether similar results may be obtained with other CAHs. Along this line, the goal of this work was to explore the impact of magnetite nanoparticles on 1,2-DCA dechlorination, which is together with TCE, the most common and dangerous chlorinated solvent occurring in subsurface environments. The need for conducting specific experiments on 1,2-DCA is also justified by the fact that this contaminant is typically degraded via a dechlorination pathway (i.e., dihaloelimination) that is different from that of TCE (i.e., hydrogenolysis).

Overall, in order to accomplish these objective, in the present study microcosm experiments were carried out to examine the impact of magnetite on 1,2-DCA dechlorination rates and lag time, as well as the interactions between different microbial community groups that are involved in the process.

2. Materials and methods

2.1. Magnetite nanoparticles synthesis

Magnetite nanoparticles were synthetized as previously described (Kang et al., 1996). In brief, the procedure consisted of successively adding the following reagents and solutions with constant stirring: 0.85 mL of 12.1 M HCl, 25 mL of ultrapure deoxygenated water, 5.2 g of $FeCl_3$ and 2.0 g of $FeCl_2$. This solution was then added dropwise under vigorous stirring to a 250 mL 1.5 M NaOH solution. The magnetic nanoparticles were isolated, by applying an external magnet, and the supernatant was decanted.

Afterwards, ultrapure deoxygenated water was added to the precipitate which was followed by centrifugation (4000 rpm) and decantation. This procedure was performed in triplicate. To neutralize the anionic charges, present on the surface of the nanoparticles, 500 mL of 0.01 M HCl was added to the precipitate under stirring. Afterwards, the solution was centrifuged (4000 rpm) and peptized with water. The magnetite nanoparticles were stored at 4 °C until use.

2.2. Mixed dechlorinating culture

The dechlorinating culture used for these experiments was an electroactive culture enriched in a microbial electrochemical system (MES) with 1,2-DCA as electron acceptor, a graphite rod as the electron donor, and antraquinone-2,6-disulfonate as redox mediator (Leitão et al., 2016). The original inoculum used for these MES experiments was activated sludge taken from a treatment plant at Roma Nord, Italy. When MES experiments ended, the content of the cathode chamber (95 mL) was anaerobically transferred to 120 mL serum bottles which were then sealed with Teflon faced butyl rubber stoppers and aluminum crimp caps. This reactor was operated in a semi-continuous mode as follows: each week, the serum bottles were sparged with N_2 to remove any remaining volatile compounds. Then, a liquid aliquot was anaerobically replaced with fresh anaerobic media, 1,2-DCA (0.05 mmol) and H_2 (0.8 mmol). The hydraulic retention time was maintained at 30 days. The reactor was operated in this manner for 4.5 hydraulic retention times (135 days) before the beginning of the experiments.

2.3. Microcosm experimental set up and monitoring

Experiments were performed in 120 mL serum bottles with a total liquid volume of 90 mL. Five different experimental conditions (Treatments A–E) were setup, each in duplicate to ensure reproducibility. Components of each treatment are listed in Table 1. The mineral medium added to each microcosm contained the following components: NH_4Cl (0.5 g L^{-1}), $MgCl_2 \cdot 6H_2O$ (0.1 g L^{-1}), K_2HPO_4 (0.4 g L^{-1}), $CaCl_2 \cdot 2H_2O$ (0.05 g L^{-1}), trace metal solution (10 mL L^{-1}) (Zeikus, 1977), vitamin solution (10 mL L^{-1}) (Balch et al., 1979), and $NaHCO_3$ (15 mL L^{-1}, 10% w v^{-1}). The pH of the medium was 7.5.

After the addition of the mineral medium, the bottles were sealed with Teflon-faced butyl rubber stoppers and aluminum crimp caps.

Table 1
Experimental setup of the microcosms. Each treatment was performed in duplicate.

Microcosms component	Treatment A	Treatment B	Treatment C	Treatment D	Treatment E
Mineral media	86 mL	88 mL	84 mL	84 mL	84 mL
Culture	–	2 mL	2 mL	2 mL	2 mL
Magnetite	4 mL	–	4 mL	4 mL	4 mL
1,2-DCA	4 μL	4 μL	–	4 μL	4 μL
Acetate	10 mM	10 mM	10 mM	–	10 mM