Relationship Between Sulfidated Nano Zero Valent Iron and a Reductive Dechlorinating Microbial Culture - Synergistic or Antagonistic?

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Abstract

Sulfidated nano zerovalent iron (S-nZVI) has garnered significant attention from researchers due to its potential for effective *in-situ* remediation applications. Compared to bare nZVI, sulfidation process enhances its reactivity towards chlorinated volatile organic compounds (cVOCs) and improves its longevity (Nunez Garcia et al. 2021). Stabilizing the particles with a polymer, like carboxymethyl cellulose (CMC), can further improve the performance of S-nZVI by imparting higher stability, less toxicity towards microbial cells, and a potential biostimulatory effect, making CMC-S-nZVI a promising *in-situ* remediation technology (Nunez Garcia et al. 2021).

Recently, CMC-S-nZVI has also been applied for field-scale remediation (Nunez Garcia et al. 2020;Brumovský et al. 2021). The contaminated sites usually have multiple pollutants and not all can be degraded by CMC-S-nZVI, thus, leaving some recalcitrant cVOCs untreated (Zhang et al. 2021). Biodegradation of cVOCs by dechlorinating microbial cultures may generate highly toxic intermediates like vinyl chloride (Kocur et al. 2016). However, coupling the two treatments may be able to compensate for each other's drawbacks, resulting in higher efficiency, longer effectiveness, non-accumulation of intermediates, and degradation of a wider range of target contaminants. However, interacting effects of CMC-S-nZVI on dechlorinating microbial cultures have not been studied yet.

This research investigates the potential of combining CMC-S-nZVI and a reductive dechlorinating microbial culture (KB-1) to degrade trichloroethylene (TCE) and 1,2-dichloroethane (1,2-DCA). CMC-S-nZVI was synthesized by a two-step method: (1) CMC-nZVI was first synthesized by reducing ferrous sulfate-CMC solution with dropwise addition of sodium borohydride solution with continuous mixing and (2) then sodium dithionite solution was added as a sulfidation agent to the freshly-synthesized CMC-nZVI (Nunez Garcia et al. 2020). Effects of different sulfur-iron ratios (S/Fe), iron, and CMC

concentrations on TCE degradation were studied to obtain an effective CMC-S-nZVI formulation. Results showed a successful TCE removal by the CMC-S-nZVI but 1,2-DCA was not degraded. TCE degradation by CMC-S-nZVI fitted the first-order kinetic model, with the highest degradation rate constant (0.35 h^{-1}) achieved at S/Fe = 0.1 with iron and CMC concentrations of 1 gL^{-1} and 0.4 wt%, respectively. This CMC-S-nZVI formulation was further tested to examine its interaction with KB-1 in terms of cVOCs dechlorination and microbial population responses. A four-day aged CMC-S-nZVI was also tested to study the effect of aging. Degradation pathways for TCE and 1,2-DCA were proposed, based on the formation of degradation products.

For the coupled treatment, an increase in microbial abundance was observed by quantifying DNA concentrations. This demonstrated a synergistic relationship between CMC-S-nZVI and KB-1. Unlike the CMC-S-nZVI only treatment, microcosms containing both CMC-S-nZVI and KB-1 were found to successfully degrade the 1,2-DCA. The coupled treatment degraded TCE and 1,2-DCA at faster rates and generated lesser amounts of vinyl chloride than the KB-1 only treatment, confirming the biostimulatory effect of CMC-S-nZVI. In the KB-1 only treatment with CMC as the sole carbon and energy source, TCE and 1,2-DCA were successfully dechlorinated. Transmission electron microscopy illustrated that CMC-S-nZVI particles were attached to the microbes but did not penetrate the bacterial cells.

In summary, synergistic abiotic-biotic dechlorination of TCE and 1,2-DCA was achieved by the combined treatment of CMC-S-nZVI and KB-1, suggesting that multi-contaminant sites can benefit from this approach. Additionally, the four-day aged CMC-S-nZVI performed similar to the freshly-synthesized one, demonstrating that the field-scale remediation can have a more feasible time scale for the preparation and application of these amendments.

Keywords

dithionite sulfidation, S-nZVI, 1,2-dichloroethane, carboxymethyl cellulose, microbial analysis, bioremediation

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Conflicts of interest

The authors have declared that no competing interests exist.

References

- Brumovský M, Oborná J, Lacina P, Hegedüs M, Sracek O, Kolařík J, Petr M, Kašlík J, Hofmann T, Filip J (2021) Sulfidated nano-scale zerovalent iron is able to effectively reduce in situ hexavalent chromium in a contaminated aquifer. Journal of Hazardous Materials 405 https://doi.org/10.1016/j.jhazmat.2020.124665
- Kocur CD, Lomheim L, Molenda O, Weber K, Austrins L, Sleep B, Boparai H, Edwards E, O'Carroll D (2016) Long-Term Field Study of Microbial Community and Dechlorinating Activity Following Carboxymethyl Cellulose-Stabilized Nanoscale Zero-Valent Iron Injection. Environmental Science & Technology 50 https://doi.org/10.1021/acs.est.6b01745
- Nunez Garcia A, Boparai H, Chowdhury AA, de Boer C, Kocur CD, Passeport E, Sherwood Lollar B, Austrins L, Herrera J, O'Carroll D (2020) Sulfidated nano zerovalent iron (S-nZVI) for in situ treatment of chlorinated solvents: A field study. Water Research 174 https://doi.org/10.1016/j.watres.2020.115594
- Nunez Garcia A, Zhang Y, Ghoshal S, He F, O'Carroll D (2021) Recent Advances in Sulfidated Zerovalent Iron for Contaminant Transformation. Environmental Science & Technology 55 https://doi.org/10.1021/acs.est.1c01251
- Zhang Y, Ozcer P, Ghoshal S (2021) A comprehensive assessment of the degradation of C1 and C2 chlorinated hydrocarbons by sulfidated nanoscale zerovalent iron. Water Research 201 https://doi.org/10.1016/j.watres.2021.117328