Reductive dechlorination of chlorinated ethenes by iron nitride nanoparticles

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In situ chemical reduction with nanoscale zero-valent iron (nZVI) particles represents a promising treatment for many groundwater contaminants, such as chlorinated ethenes (CEs). Nevertheless, the low electron selectivity of nZVI, leading to its fast corrosion in the subsurface, hinders the full potential of this technology. Herein, we investigated a new strategy to improve the nZVI selectivity for CEs by incorporating crystalline iron nitride (Fe_xN) phases into particle structure [1].

Two different types of nanoparticles, containing mostly the face-centered cubic (γ'-Fe_4N) and hexagonal close-packed (ε-$Fe_{2\text{-}3}N$) Fe_xN phases were prepared by solid-gas synthesis. Nitriding increased hydrophobicity and availability of iron in reduced states on the surface of both particle types. Batch experiments with CEs typically occurring at contaminated sites, i.e., tetrachloroethene (PCE), trichloroethene (TCE), cis-1,2-dichloroethene (cis-DCE), and their mixture, were performed to assess the particle reactivity with target contaminants. Control experiments were performed with pristine and sulfidated nZVI (S-nZVI), using the same nZVI as used for nitriding. The mechanism of surface-mediated dechlorination reactions was further investigated using DFT calculations.

The two types of Fe_xN nanoparticles degraded all individual CEs and their mixture considerably faster than pristine nZVI and also faster than S-nZVI, except for TCE, which was degraded by S-nZVI at about the same rate as by Fe_xN. The DFT calculations revealed that the cleavage of the first C-Cl bond was the rate-limiting step for the degradation of all compounds on the Fe_4N surface. The CE reaction barriers for the Fe_4N-surface mediated reactions ranged from 27.0-40.8 kJ/mol. This work shows that iron nitride nanoparticles are highly effective in the degradation of CEs.

References

[1] Brumovský, Micić, Oborná, Filip, Hofmann & Tunega (2023), *J. Hazard. Mater. 442*, 129988.