Dechlorination of Chlorinated Ethylenes by a Layered Fe(II)-Fe(III) Hydroxide (Green Rust) Composite

Jing Ai (jingai@plen.ku.dk) (University of Copenhagen, Faculty of Science, Denmark)
Weizhao Yin (wey@plen.ku.dk) (Jinan University, Guangzhou, China)
Hans Christian Bruun Hansen (University of Copenhagen, Faculty of Science, Denmark)

Background. Green rusts (GRs) are Fe(II)-Fe(III) hydroxide salts with brucite-type layer structures, which are strong reductants for diverse reducible contaminants in soils and water including chlorinated ethylenes (CEs). Although the reduction of CEs by GRs is thermodynamically favorable, experimental results have not provided consensus on the reactivity towards trichloroethylene (TCE) degradation varying from 8.55×10^{-5} L/m^2/day to zero (no detectable degradation within 148 d), and thus the dechlorination reaction appears to be kinetically constrained by the reaction conditions. Modification of GRs with transition metals (e.g., Pt, Ag), or by organic compounds with electron conductive properties represent two operational ways to enhance GRs reactivity towards dechlorination of CEs. However, the introduction of either metals or artificial organic compounds may not be eco-friendly or economically sound. Carbonaceous materials have been used to stimulate TCE dechlorination by zero-valent iron (ZVI), in which the carbonaceous material serves as both adsorbent and an electron mediator for the reaction. We have now investigated how different types of carbonaceous materials enhance GR reduction of CEs.

Approach. GR$_{Cl}$ suspension was freshly synthesized by the glycine-buffered method, transferred to an anoxic chamber, and mixed with stock suspensions of carbonaceous material (CM) by magnetic stirring at 400 rpm for 10 min to get composite suspension composed of 22 mM [Fe^{II}] GR$_{Cl}$ and 1.0 g/L CM (GR+CM) at pH 8.0. Batch experiments were used for all kinetic studies, in which 5 mL composite suspension was added to 10 mL headspace glass vials; 25 µL of 4 mM stock solution (prepared in methanol) was added to obtain an initial concentration 20 µM. The vials were sealed by crimping the PTFE/Si-septa-equipped caps and transferred from the anaerobic chamber to outside, followed by shaking on an orbital shaker at 300 rpm at ambient temperature. Triplicate vials were measured by Triplus300 combined with TRACE1300 equipped with PoraBOND U column (25 m × 0.35 mm × 7 µm) coupled to dual ECD and FID detectors.

Results. All CEs could be removed efficiently by the GR+CM composite. PCE, TCE, cis-DCE and trans-DCE followed first order reduction kinetics with observed rate constants of 0.21, 0.17, 0.16 and 0.39 h^{-1}, respectively, in which β-elimination is proposed as the major reductive pathway as acetylene was observed to contribute over 80% of total carbon mass of the products. The very slow dechlorination of 1,1-DCE and VC might mainly follow hydrogenolysis as VC and ethene constituted the main dechlorination products. The presence of CM was able to stabilize the GR structure as the solubility of GR was much lower in presence of CM than in its absence. The composite aged for over 1 month still kept 57.4% of original reactivity towards PCE dechlorination. The rate of dechlorination by the GR composite showed insignificant decrease with increasing the TCE concentration from 10 µM to 80 µM, while increase of the CM dosage from 0.1 g/L to 5.0 g/L enhanced the reaction rate proportionally. Further investigations are performed to understand the reaction mechanism. In general, the highly reactive GR+CM composite is a promising and inexpensive material for remediation of CE contaminated groundwater.