

Treatment of Chlorinated Solvents by Copper-Amended Nanoscale Zero-Valent Iron Stabilized with Carboxymethylcellulose

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Background/Objectives. The objective of this bench-scale study was to evaluate the effectiveness of using copper-amended nanoscale zero valent iron (Cu-nZVI) to degrade select chlorinated hydrocarbons (CHCs). Cu-nZVI performance was compared relative to nZVI performance. The effect of Cu loading and Cu-nZVI concentration on CHC degradation kinetics and reaction byproducts were characterized in this study. Further, nZVI particle stabilization with carboxymethylcellulose (CMC) was investigated. Particle longevity experiments were conducted to determine the effects of particle aging and agglomeration on nZVI reactivity.

Approach/Activities. Freshly prepared Cu-nZVI and nZVI particles were synthesized in an anaerobic chamber for each experiment. Experiments were conducted using 160 mL serum bottles. Degradation and byproduct distribution were measured via gas chromatography. A pseudo first-order degradation rate model was used to evaluate the kinetics of CHC degradation. Degradation of chloroform, 1,1,1- and 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, 1,2,3-trichloropropane, and various chlorinated ethenes (perchloroethylene, trichloroethylene, cis-1,2-dichloroethylene) with Cu-nZVI and nZVI was evaluated.

Results/Lessons Learned. The pseudo first-order degradation kinetics (k_{obs}) were faster and the byproduct distributions were more favorable for Cu-nZVI than nZVI for most CHCs examined in this study. Increasing Cu% loading in nZVI and increasing Cu-nZVI concentrations yielded faster degradation rates with regard to chloroform treatment. Furthermore, greater Cu% loading in Cu-nZVI particles resulted in systematically increased methane byproduct production. Cu-nZVI outperformed most other bimetallic nZVI reductants reported in the literature for chloroform and chlorinated ethanes treatment. The degradation byproducts of chloroform and 1,1,1-trichloroethane, when treated with Cu-nZVI, suggest the formation of reactive carbene intermediates through α -elimination that degraded further into methane, ethene, and ethane. In comparison to nZVI, Cu-nZVI also showed a more effective treatment potential for 1,2,3-trichloropropane. However, Cu-nZVI did not show much improvement over nZVI in degrading chlorinated ethenes.

Longevity experiments have shown that the reactivity of unstabilized and CMC-stabilized Cu-nZVI towards 1,1,1-trichloroethane decreased with nanoparticles aging. Unstabilized Cu-nZVI particles showed a linear decline in reactivity (k_{obs}) with time, whereas CMC-stabilized Cu-nZVI particles showed a faster, power-function decline in reactivity with time. The k_{obs} for 1,1,1-trichloroethane with unstabilized Cu-nZVI particles were 12-fold greater in comparison to the CMC-stabilized Cu-nZVI particles 24 hr after synthesis. Unstabilized Cu-nZVI particle agglomeration was visibly evident during longevity experiments. Even with decline in reactivity, 1,1,1-trichloroethane was rapidly degraded (over a few hours) seven days after nanoparticle synthesis by both unstabilized and CMC-stabilized Cu-nZVI.