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New approaches to degradation of waste chlorinated solvents using nanoscale zerovalent iron

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Chlorinated solvents are used in large quantities as cleaning agents in various industrial operations, despite their high toxicity to humans and environmental receptors. The treatment of waste chlorinated solvents and chlorinated solvent-contaminated water is a challenge. Recently, nanoscale zerovalent iron (NZVI) has been shown to effective for degradation of chlorinated organic pollutants. However its aggregation and passivation of the NZVI surface due to reaction to water are major challenges to its implementation in scaled-up operations. Two recent advances, from our recent research, that significantly enhance the reactivity of nanoscale zerovalent iron (NZVI) to chlorinated solvents such as trichloroethene (TCE) will be presented. The first study shows that rhamnolipid (biosurfactant)-coated, palladium-doped-NZVI (RL-Pd-NZVI) when reacted with TCE in a water-immiscible butanol organic phase results in 50% more TCE mass degraded per unit mass of Pd-NZVI than in the aqueous phase and with a 7-times higher reaction rate. RL-Pd-NZVI is very hydrophilic, and we demonstrate that their rapid phase transfer to an organic phase can be achieved by creating water-in-oil emulsions in the butanol/TCE organic phase by addition of salts. The significant enhancement in reactivity is caused by a higher electron release (3e- per mole of Fe(0)) from Pd-NZVI in the butanol phase compared to the same reaction with TCE in the aqueous phase (2e- per mole of Fe(0)) as shown by XPS. In the second study we show that sulfidation of NZVI enhances the rate of dechlorination of TCE, and the enhancement depends on the extent of sulfidation. Experiments where TCE was reacted with NZVI sulfidated to different extents (Fe/S molar ratios 0.62 to 66) showed that the surface-area normalized first-order TCE degradation rate constant increased up to 40 folds compared to non-sulfidated NZVI. Fe/S ratios in the range of 12 to 25 provided the highest TCE dechlorination rates, and rates decreased at both higher and lower Fe/S. In contrast, sulfidated NZVI showed significantly lower hydrogen evolution rate compared to that by unamended NZVI, suggesting that sulfidation suppressed corrosion reactions of NZVI with water.