Comparison of aqueous phase and organic phase redox reactions of Pd-doped nanoscale zerovalent iron with trichloroethene

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Distinct shifts in the redox chemistry, reaction rates and surface properties of zerovalent iron nanoparticles were observed when exposed to trichloroethene (TCE) in an organic phase compared to an aqueous phase. We show that rhamnolipid (biosurfactant)-coated, palladium-doped nanoscale zerovalent iron (RL-Pd-NZVI) when reacted with TCE in a 1-butanol organic phase with limited amounts of water results in 50% more TCE mass degradation per unit mass of Pd-NZVI, compared to the same reactions entirely in the aqueous phase. Furthermore, there was a 4-fold faster TCE degradation rate (k_{obs} of 0.413 d^{-1} in butanol versus 0.099 d^{-1} in aqueous phase). The significantly greater reactivity is caused by a higher electron release ($3e^-$ per mole of Fe^0) from Pd-NZVI in the butanol organic phase compared to the same reaction with TCE in the aqueous phase ($2e^-$ per mole of Fe^0). X-ray photoelectron spectroscopy characterization of Pd-NZVI showed Fe^0 was oxidized to Fe(III) oxides for Pd-NZVI reacted with TCE in the butanol organic phase compared to Fe(II) oxides in the aqueous phase. Although the reaction byproducts formed were generally similar in aqueous phase and organic phase reactions, higher concentrations of ethane and dichloroethenes (1,1-DCE and cis-1,2-DCE) were formed in the organic phase reactions, suggesting a shift in the dechlorination pathway of certain reaction intermediates within the organic phase. In order to utilize the enhanced performance of RL-Pd-NZVI in organic phases for environmental remediation applications, we have designed biphasic organic liquid-water batch systems wherein the hydrophilic coated nanoparticles are rapidly transferred from the aqeuous phase to the organic phase by creating water-in-oil emulsions using NaCl.