Iron-mediated trichloroethene reduction within nonaqueous phase liquid

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ABSTRACT

Aqueous slurries or suspensions containing reactive iron nanoparticles are increasingly suggested as a potential means for remediating chlorinated solvent nonaqueous phase liquid (NAPL) source zones. Aqueous-based treatment approaches, however, may be limited by contaminant dissolution from the NAPL and the subsequent contaminant transport to the reactive nanoparticles. Reactions occurring within (or at the interface) of the NAPL may alleviate these potential limitations, but this approach has received scant attention due to concerns associated with the reactivity of iron within nonaqueous phases. Results presented herein suggest that iron nanoparticles are reactive with TCE–NAPL and exhibit dechlorination rates proportional to the concentration of (soluble) water present within the NAPL. Reactivity was assessed over a 12-day period for five water contents ranging from 0.31 M to 4.3 M, with n-butanol used to enhance water solubility in the NAPL. Rates of dechlorination were generally slower than those reported for aqueous-phase dechlorination, but were not observed to slow over the course of the 12-day period. The lack of observed deactivation may indicate the potential that highly efficient (with respect to utilization of available electrons) dechlorination reactions can be engineered to occur within nonaqueous liquids. These results suggest a need for subsequent investigations which focus on understanding the mechanisms of the reactions occurring within NAPL, as well as those assessing the utility of controlling both the iron and water content within a NAPL source zone.

1. Introduction

Treatment of subsurface regions contaminated with dense nonaqueous phase liquid (DNAPL) is a significant challenge to environmental restoration. Introduction of nanoscale zero valent iron (Fe^0) particles within the subsurface for the purpose of degrading chlorinated solvents is an attractive approach that is often considered for application in DNAPL source zones (e.g., Lien and Zhang, 2001; Liu et al., 2005a, 2007; Elliott and Zhang, 2001; Henn and Waddill, 2006; Quinn et al., 2005). It is within the context of chlorinated solvent remediation that many have explored the reactivity of iron particles within the aqueous phase (e.g., Arnold and Roberts, 2000; Liu et al., 2005a, 2007).

Fe^0 nanoparticles are highly reactive with chlorinated solvents in the presence of excess water suggesting that they may prove effective in reducing DNAPL mass located within a source zone (e.g., Liu et al., 2005a, 2007; Elliott and Zhang, 2001). The success of Fe^0 mediated reduction techniques, however, depends on both reactivity and particle delivery (i.e., co-location of NAPL and iron particles). Given that some Fe^0 nanoparticles have been reported to deactivate (i.e., decrease in reactivity due to build up of an oxide shell), leaving as much as 35 wt.% Fe^0 unreacted (Liu et al. 2007), effective particle distribution within DNAPL source zones may prove critical for source treatment. Transport of aqueous-based suspensions of reactive iron particles within sandy porous media often requires high velocity (10–100 m/d) slurry injections (e.g., Saleh et al., 2007; Schrick et al., 2004). Application of these high velocities opens new questions related to potential for DNAPL mobilization, and the effects of relative permeability on particle

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distribution. These challenges have prompted many important innovations which aid particle delivery within DNAPL source zones (Berge and Ramsburg, 2009; Phenrat et al., 2009; Saleh et al., 2007; Zhan et al., 2009).

Alternative approaches for using nanoparticles within source zones aim to deliver particles to the NAPL–water interface or potentially add particles within the NAPL (Quinn et al., 2005; Saleh et al., 2005a, 2007; Zhan et al., 2008; Berge and Ramsburg, 2009; Zhan et al., 2009). Iron-mediated reduction of contaminants within a NAPL, however, raises several important questions regarding particle reactivity. The majority of studies examining iron-mediated transformation of chlorinated solvents have focused on contaminant removal at relatively low, aqueous-phase concentrations (Arnold and Roberts, 2000; Li and Farrell, 2001; Liu and Lowry, 2006; Liu et al., 2005a, 2007; Nurmi et al., 2005; Sarathy et al., 2008). An important exception is the work of Liu et al. (2007). These authors found that acetylene formation and efficiency of iron utilization increased as TCE concentrations approached the aqueous solubility limit. Under iron-limited conditions (which would be likely in a NAPL), the primary gaseous products measured in aqueous-phase reactivity studies using RNIP (reactive nanoscale iron product, Toda America) are acetylene, ethene and ethane. These results suggest RNIP particles reduce TCE via a beta elimination pathway (Liu et al. 2005a).

A requirement of Fe^0-mediated TCE reduction within a NAPL is the presence of water (or a suitable alternative hydrogen donor). Unlike aqueous-phase reactions, where water is abundant, TCE–NAPL located in the subsurface contains little water (water solubility in TCE is ~5.4 mM, Ramsburg and Pennell, 2002a). Few studies have examined the influence of water content on iron reactivity, mainly because most iron reactivity studies are conducted in the aqueous phase. Results from gas phase studies, however, suggest that the relative humidity must be 72 and 92% for TCE dechlorination by acid-washed iron particles and partially oxidized iron particles, respectively (Uludag–Demirer and Bowers, 2000). In addition, Uludag–Demirer and Bowers (2000) also observed competitive adsorption between the water and TCE to the surface active sites of the iron. Surface coverage of adsorbed TCE and hydrogen has been reported to influence reaction rates (Li and Farrell, 2001). These studies suggest that control of the NAPL water content may prove critical to facilitating the iron-mediated reaction within the NAPL. The overall objective of this research is to assess the reactivity of iron particles within a TCE–NAPL. Specific objectives of this study include: (i) assessment of reactivity within TCE–NAPL using commercially available iron nanoparticles; (ii) identification of the extent to which reductive dechlorination within the NAPL depends upon water content, and (iii) development of empirical models that can describe the macroscopic rate (or pseudo-order rate expression) of the reactions occurring within TCE–NAPL.

2. Experimental methods

2.1. Iron particles

Nanoscale iron particles manufactured via plasma vapor deposition (PVD) under vacuum were acquired from MTI Corporation, Inc (MTI Corporation, Inc., 2009). The particles are shipped as a powder and are reported by the manufacturer to have an average particle size of 50 nm and a specific surface area of approximately 40 m²/g. PVD iron particles were found to contain 90+ % Fe^0 (measured via H_2 production during HCl digestion). This high degree of purity is consistent with an X-ray diffraction (XRD) pattern that suggests PVD iron particles are nearly pure Fe^0 (Supplementary Data Fig. S1a).

Borohydride reduced iron (referred to as BH) was synthesized by reducing an aqueous solution of ferrous iron with sodium borohydride to produce 30–40 nm size particles (following the procedures described by Liu et al., 2005a). Synthesized BH particles were dried for 24 h at 105 °C under argon, and subsequently ground under argon (using a mortar and pestle in a Coy vinyl glove box where the partial pressure of O_2 was continuously monitored with a trace oxygen analyzer (Alpha Omega Instruments)) to a fine powder prior to use in the reactors. The specific surface area of the dried and ground BH particles was determined to be 8 m²/g via N_2-BET analysis (Particle Technology Labs, Ltd.). Dried BH particles contained 80% Fe^0, which is supported by the XRD pattern that is indicative of Fe^0 and perhaps amorphous iron (Supplementary Data Fig. S1b).

RNIP (Toda America, Inc.) is manufactured via a reduction of goethite and hematite by hydrogen at 200–600 °C (Uegami et al., 2003; Sarathy et al., 2008) and is thus referred to as HR herein. RNIP is a commercially available product of iron particles that are between 40 and 60 nm at the time of manufacturing (Liu et al., 2005a). These HR iron particles represent a Fe^0 core surrounded by an iron oxide (Fe_3O_4) shell, and are shipped as an aqueous slurry (pH between 10 and 12) having a solids content of approximately 26 wt.%. HR particles were dried for 24 h at 105 °C under argon, and subsequently ground under argon (as described for the BH iron particles) to a fine powder prior to use in the reactors. The specific surface area of the dried and ground HR particles was determined to be 11 m²/g via N_2-BET analysis (Particle Technology Labs, Ltd.). Dried HR particles contained 26% Fe^0, with the XRD pattern confirming the presence of Fe^0 and magnetite (Supplementary Data Fig. S1c).

2.2. Nonaqueous-phase liquid mixtures

Solutions of organic liquids were designed to contain between 0.31 M and 4.3 M dissolved water. High purity water (resistivity ≥ 18.2 MΩ-cm and TOC ≤ 25 ppb) was obtained from a Millipore Milli-Q Gradient A10 water purification system. Water content in the NAPL was enhanced using a low molecular weight alcohol, n-butanol, as a cosolvent (Ramsburg and Pennell, 2002a). HPLC grade n-butanol was obtained from Fisher Scientific and used as received. Results from control experiments (in which n-butanol was employed as the NAPL following the batch reactor procedures described below) suggest that n-butanol does not react with the iron particles employed herein. Prior to making each NAPL solution, each component (TCE, butanol, and water) was sparged with argon (in an argon atmosphere) to remove any dissolved oxygen. HPLC grade TCE was obtained from Sigma-Aldrich and used as received. The deoxygenated components were then combined and mixed, with a magnetic stir bar, under an argon atmosphere until a single phase was present. A TCE concentration of 230 g/L was employed in all experiments to eliminate