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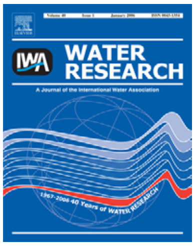

Combination of surfactant solubilization with permanganate oxidation for DNAPL remediation

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ABSTRACT

A combination of surfactant solubilization with permanganate oxidation of trichloroethylene (TCE) was studied in batch, flow-through column, and three-dimensional (3-D) tank tests. Batch results showed that chloride production, an indication of TCE degradation, followed a pseudo-first-order reaction kinetics with respect to $KMnO_4$ in the presence of free-phase TCE. A higher chloride production rate was achieved when anionic surfactants were present. The observed pseudo-first-order reaction rate constant increased as the concentrations of anionic surfactants Ninate 411 and Calfax increased from 0% to 0.1%, 0.3%, and 1.0%. Column experiments on TCE reduction by permanganate in the presence and absence of surfactants were carried out using well-sorted coarse Ottawa sand. The peak effluent TCE concentration reached 1700 mg/L due to enhanced solubilization when both sodium dodecyl sulfate (SDS) and permanganate were used, in contrast to less than 300 mg/L when only permanganate solution was used. In addition, the effluent TCE concentration decreased much faster when SDS was present in the permanganate solution, compared with the case when SDS was absent. With an initial 1 mL of TCE emplaced in the columns, the effluent TCE concentration dropped to <5 mg/L after 29–31 h of flushing with 1% SDS and 0.1% $KMnO_4$ solution in contrast to 37–73 h when only 0.1% $KMnO_4$ was used. Furthermore, $KMnO_4$ breakthrough occurred after 21–25 h of injection when SDS was present compared with 45–70 h later when SDS was absent. A slightly higher chloride concentration was observed in the earlier stage of the column experiment and the chloride concentration decreased quickly once $KMnO_4$ was seen in the effluent. The 3-D tank test showed that the MnO_2 precipitation front formed more quickly when 1% SDS was present, which further confirmed the observation from the column study.

1. Introduction

At some industrial sites, free-phase chlorinated solvents in soils and aquifers impose potential threats to groundwater. Remediation of dense non-aqueous-phase liquids (DNAPLs) presents a great challenge to modern remediation science and technology. A common practice to remove DNAPL contamination from groundwater is by “pump-and-treat”, i.e. clean water is injected into the ground from the up-gradient of the contaminant plume and the contaminated water withdrawn from the down-gradient of the plume. As the clean water moves through the plume area, the

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free-phase contaminants dissolve in water that is then pumped out. The contaminated water is subject to onsite decontamination before the water can be reused. The major problem associated with pump-and-treat is the low aqueous solubility of the DNAPLs, thus, many pump-and-treat cycles are needed before the contaminant concentration decreased to below the standard. To overcome the low solubility of DNAPLs in water, surfactants have been used to increase the solubility of the contaminants and decrease the interfacial tension between water and the organic phase. The addition of surfactants to the pump-and-treat system greatly enhanced the remediation performance by reducing the operation time and cost. In a flow-through column study, Fountain et al. (1991) showed that the tetrachloroethylene (PCE) solution concentration increased by three orders of magnitude from 10 mg/L when water was used to 6000 mg/L when a 5% phosphated nonionic/anionic surfactant solution was used. Field demonstration using a vertical circulation well system in a shallow unconfined aquifer showed an increase of contaminant mass removal by 40-fold and 90-fold for PCE and jet fuel constituents, respectively, when surfactant was used (Knox et al., 1997). In addition to enhanced contaminant solubilization and mobilization, the rate of trichloroethylene (TCE) desorption from soil increased by 30% as a result of Triton X-100 injection at a concentration of 400 mg/L during a field study (Sahoo et al., 1998). Although the contaminant extraction efficiency increased dramatically in the presence of surfactant, the extracted water contains high concentrations of contaminants; thus, onsite treatment of the contaminated water becomes inevitable, which would dramatically increase the treatment cost. Furthermore, the decrease in interfacial tension between water and DNAPLs will greatly increase the mobility of the DNAPLs, which will trigger further DNAPLs' migration and spreading.

In situ chemical oxidation with permanganate is a promising alternative for the remediation of aquifers contaminated with DNAPLs, such as PCE and TCE (Schnarr et al., 1998; Hood et al., 2000). It is accomplished by injecting an aqueous solution of $KMnO_4$ through the source area. The basic stoichiometry for the oxidation of PCE is (Yan and Schwartz, 2000)

$$C_2Cl_4 + MnO_4^- \rightarrow \gamma CA + 4Cl^- + MnO_2(s), \quad (1)$$

$$\gamma CA \rightarrow \eta CO_2, \quad (2)$$

where γ and η are stoichiometric coefficients and CAs are various carboxylic acids. Oxidation of chlorinated compounds to CAs occurs at pH values above 3. Carbon dioxide is formed instead at lower pH values (Huang et al., 2000). Degradation of PCE and TCE by permanganate occurred in the dissolved phase and followed a first-order reaction with respect to their initial concentration (Yan and Schwartz, 2000), although reactions between permanganate and DNAPLs have also been noticed (Crimi and Siegrist, 2005). The kinetics of DNAPL mass removal is thought to be controlled by the interaction of two competing processes, dissolution and oxidation (Schnarr et al., 1998). But, the addition of permanganate reduced the natural source dissolution rate of TCE by as much as 95% (Rivett and Feenstra, 2005). Using phase-transfer catalysts to enhanced TCE degradation by permanganate was tested by Seol and Schwartz (2000). Their results showed a 66% increase in TCE degradation when pentatriphenylphosphonium bromide (PTPP) was present. In a separate study, Seol et al. (2001) found that PTPP increased the permanganate consumption rate constants from 0.1 to 0.12 min^{-1} when TCE was the sole DNAPL; in contrast, the rate constants increased by a factor of three to four when a second DNAPL such as tetrachloroethane or trichloroethane was present. When TCE was solubilized by surfactants, the quantum yields during photodegradation of TCE in the presence of a photosensitizer increased by 25 times (Choy and Chu, 2001). In the presence of sodium dodecyl sulfate (SDS), an anionic surfactant, the pseudo-first-order reaction rate constant between permanganate and TCE increased by three times, while the surfactant and permanganate reaction was minimal as revealed by the persistence of purple color monitored under UV–vis at the wavelength of 525 nm when both were present (Li, 2004). These results show that use of surfactants in conjunction with permanganate may achieve a synergistic effect on DNAPL degradation.

The central goal of this research is to test the feasibility of combining the solubilization and mobilization power of surfactants with a fast contaminant degradation rate of permanganate in batch, column, and three-dimensional (3-D) tank tests to achieve synchronized contaminant solubilization and degradation in a single step during pump-and-treat operations, i.e. to achieve simultaneous "pump-while-treat" for DNAPL remediation, instead of commonly "pump-then-treat" as most pump-and-treat systems do.

2. Materials and methods

2.1. *Chemicals*

The TCE and potassium permanganate used were from Fisher Scientific (Pittsburgh, PA). The surfactants used were anionic SDS from Sigma (St. Louis, MO), C_{10} linear sodium diphenyl oxide disulfonate (Calfax 10L-45) from Pilot Chemical Company (Santa Fe Spring, CA), isopropyl amine branched dodecylbenzene sulfonate (Ninate 411) from Stapan (Northfield, IL), and nonionic octylphenol ethylene oxide condensate (Triton X-100) from LabChem Inc. (Pittsburgh, PA), and nonyl phenol ethoxylate (Witconol NP-120) from Akzo Nobel (Chicago, IL). SDS has a formula weight of 288.4 and critical micelle concentration (CMC) of 8.2 mM (Rosen, 1989). Others were industrial grades having varying amounts of surfactants of different chain lengths. All surfactants were used as received without further purification.

2.2. *Batch TCE degradation kinetics*

All experiments were performed in three to five replicates in a continuous stir batch reactor (CSBR), composed of a 200 mL beaker, a magnetic stir, a chloride electrode, and a pH electrode inserted into the reaction solution. To each CSBR, 98, 99, or 99.5 mL of water or surfactant solution was mixed with 2 mL of ionic strength adjustor (ISA) made of 5 M of $NaNO_3$ (from Thermo Orion, MA), resulting in an ionic strength of 0.1 M. Addition of ISA is a standard procedure