Project Summary

Title: Combination of Surfactant Solubilization with Permanganate Oxidation for Groundwater Remediation

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Background/Need: At some heavy industrial sites and DOE nuclear weapon manufacture and test sites, free phase chlorinated solvents in soils and aquifers impose potential threat to groundwater. Pump-and-treat, a common practice to remove subsurface contaminants proved inefficient to remove these solvents, due to their lower water solubility and higher density. Although the contaminant extraction efficiency increased dramatically in the presence of surfactant, the extracted water will need further onsite decontamination. Oxidation of chlorinated solvent by permanganate is an emerging technology. However, the reaction occurs only in dissolved phase. Thus, a test for combination of surfactant solubilization with permanganate oxidation was proposed.

Objectives: The central goal of this research is to test the feasibility of using surfactant to significantly increase the solubility of chlorinated solvents while using permanganate to degrade solubilized chlorinated solvents. The objectives are to investigate the effects of types of surfactants, concentration of surfactants and of permanganate on oxidation of different types of chlorinated solvents.

Methods: The tests were conducted in batch, column as well as 3-dimensional tank scales. Batch tests were focused on effects of types of surfactants, concentrations of surfactants and permanganate on reduction kinetics of chlorinated solvents. The best surfactant with an optimal concentration was tested in one-dimensional column studies to investigate the efficiency of present surfactant on TCE reduction by permanganate at different volumes of free phase TCE. Finally, a 3-dimensional tank test was performed to verify the column test results. Aqueous concentrations of chlorinated contaminants, permanganate, and product chloride were monitored with time to determine the reaction rate and rate constants as well as the TCE removal efficiency.

Results and Discussion: 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 seen when anionic surfactant, particularly sodium dodecyl sulfate (SDS), was present. When the surfactant concentration was less then its critical micelle concentration (CMC), the TCE reduction rate constant k_{obs} increased by a factor of three while the TCE half-life $t_{1/2}$ decreased by three folds. With the surfactant concentration greater than the CMC, further increase in k_{obs} and decrease in $t_{1/2}$ was seen. The reaction rates also increased when ninate 411 and Calfax, both anionic surfactants, were present in the system at concentrations of 0.1, 0.3 and 1.0%.

Contrast to the much greater enhancement for TCE oxidation, no significant increase in PCE oxidation by $KMnO_4$ in the presence of SDS was found.

Column experiments on fine beach sand lasted for only 6 hours. A higher effluent chloride (about 20%) and TCE (about 100%) concentration was found from the columns eluted with 1% SDS, indicating enhanced solubilization and oxidation of TCE. However, hydraulic conductivity of the sand decreased significantly caused by precipitates of MnO_2, making it essentially impermeable after 6 hours. Column experiments on well sorted coarse Ottawa sand showed increase in effluent TCE concentration during earlier stage of flushing. TCE concentration decreased much faster in the presence of SDS. For example, after 1 mL of TCE was placed in the columns, the effluent TCE concentration for the columns fed with SDS and permanganate was below 5 mg/L after 1740 to 1870 minutes. While for columns fed with permanganate only, it took 2200 and 4400 minutes before the effluent concentration reached 5 mg/L or below. For the columns fed with SDS and permanganate, The highest effluent TCE concentration was about 1700 mg/L when SDS was present contrast to less than 300 mg/L when SDS was absent, indicating enhanced solubilization. In addition, MnO_4 breakthrough occurred after 21-25 hour injection when SDS was present. Without SDS, MnO_4 breakthrough occurred 45-70 hours later. The earlier MnO_4 breakthrough indicates exhaustion of dissolved TCE during the flushing stage. Chloride analysis revealed a slightly high chloride concentration in the earlier stage of the column experiment and chloride concentration decreased quickly once permanganate is seen in the effluent. Mass balance of TCE eluted plus chloride generated showed that only 25-50 % of the input TCE was either eluted or degraded, the rest may be entrapped within the sand, possibly due to the formation of MnO_2 zone, or being transformed into other intermediates which were not monitored.

The 3-dimensional tank test further confirmed the results from column study, i.e. with the presence of surfactant SDS a higher amount of TCE was removed within given time. Furthermore, visualization showed that a MnO_2 precipitation front was formed much quickly when 1% SDS was present.

Conclusions/ Implications/ Recommendations: The research shows that anionic surfactants, such as SDS, are able to increase the chloride production in batch test. In column tests, the removal of TCE in the presence of SDS is faster, particularly when the volume of free phase TCE was large. Although no clogging was found when course Ottawa sand was used in the column study, the decrease in hydraulic conductivity when fine beach sand was used imposes a limitation to the method.

Related Publications: Li, Z. (2004). Surfactant-Enhanced Oxidation of Trichloroethylene by Permanganate – Proof of Concept, *Chemosphere* **54**, 419-423.

Key Words: Permanganate, Perchloroethylene, Trichloroethylene, Surfactant.

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