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Use of Sonication for In-Well Softening of Semivolatile Organic Compounds

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Research Objective

This project investigates the in-situ degradation of semivolatile organic compounds (SVOCs) and volatile organic compounds (VOCs) using in-well sonication, in-well vapor stripping, and biodegradation. The project has the primary objectives of developing this integrated system for efficient and economical removal and degradation of SVOCs and VOCs from groundwater. The project has as its goal the partial degradation (softening) of the more recalcitrant organic compounds in order to convert them into compounds that are more amenable to both air sparging and biological treatment. By performing the softening in-well, the treated organics can be reinjected and percolated through the subsurface, thereby enhancing biodegradation by generating organics that are more easily biodegraded.

Research Progress and Implications

This report summarizes work after nearly 2 years of a 3-year project. Argonne National Laboratory is developing a new technology that combines in-well sonication, in-well vapor stripping, and in-situ biodegradation for removal of SVOCs and VOCs from solution. Bench-scale batch experiments have been performed investigating the separate treatment systems involving stripping and sonication of halogenated organics in groundwater, along with the combined sonication/stripping system. Organic contaminants studied include: trichloroethylene (TCE), carbon tetrachloride (CCl_4), tetrachloroethylene (PCE), trichloroethane (TCA), and ethylene dibromide (EDB). Initial organic concentrations range from ~10 to ~100 mg/L. Results of the sonication and vapor stripping experiments are available upon request.

For the in-well vapor stripping experiments, air flow rates of 500, 1000, and 1500 mL/min were used. Over the entire concentration range, the first order rate constant was typically in the range of 0.15 to 0.28 min^{-1} for removal of CCl_4 , TCE, PCE, and TCA from solution at 500 mL/min air flow rate, and 0.45 to 0.62 min^{-1} for these same compounds at 1500 mL/min air flow rate. EDB was much less volatile, with rate constants ranging from 0.025 to 0.028 min^{-1} and 0.056 to 0.066 min^{-1} at 500 and 1500 mL/min air flow rates, respectively.

The first order rate constants obtained for CCl_4 and TCE using only sonication indicated that CCl_4 is easier to degrade than TCE. The higher the power intensity, the higher the rate constant. The rate constants also exhibit a slight concentration effect; the lower the initial chlorinated organic concentration, the higher the rate constant (albeit a slight increase). Greater differences between the degradation rates of CCl_4 and TCE are observed at the higher concentrations and higher power intensities tested. The major degradation mechanism of volatile organic compounds under ultrasonic irradiation is considered to be direct pyrolysis within the cavitation bubbles.

In an effort to describe the acoustic cavitation effects, a mathematical model has been developed that incorporates acoustic pressure produced in solution by sonication; nuclei generation contributed by gas pockets in suspended particles or pre-existing small bubbles; the onset, growth, and collapse of bubbles; and pyrolysis reactions due to the high temperature of the collapsing bubbles. Two different pathways, stable cavitation and transient cavitation, contribute to the sonochemical reactions because both processes produce high temperature and pressures to decompose organic chemicals in solution.

To analyze the halogenated compounds in solution, the methodology for gas chromatography using head space analysis has been successfully employed. Maximum sample holding times for CCl₄, TCE, and PCE, were in the order of CCl₄ > TCE > PCE. In the laboratory setting where rapid analysis of samples is possible, limited holding times were acceptable to increase the precision of the analytical results. Experiments conducted in which TCE and CCl₄ were injected together, the loss of TCE through the septum was unaffected by the presence of CCl₄ whereas the loss of CCl₄ was affected by the presence of TCE, indicating that CCl₄ loss through the septum was facilitated by the presence of TCE.

Stanford University has performed numerical modeling of the combined sonication/vapor stripping laboratory system on the basis of hypothetical parameter values. In this initial modeling effort, the contaminant of concern was assumed to be TCE. The hydraulic conductivity, porosity, and retardation factors selected are typical for a clean sand aquifer. The treatment well was placed at the center of the tank, and water was withdrawn near the bottom of the well. Two different flow rates were used to perform the simulations. For the purposes of the simulations, the sonication rate was assumed to be independent of concentration. The modeling indicates that the contaminant is removed quite rapidly, although higher concentration regions persist in the corners of the tank. Concentrations drop more rapidly at the higher pumping rate. Further modeling will indicate if there are monitoring locations at which the effects of sonication are more pronounced. The effect of sonication is likely to have the greatest effect for relatively nonvolatile compounds such as EDB.

Preliminary efforts at the California Institute of Technology (CIT) have determined that the optimum ultrasonic frequency for the degradation of CCl₄ is around 500 kHz. The CIT work has also identified the degradation products following the sonication of CCl₄, CHCl₃, and CH₂Cl₂. The intermediate degradation products identified include: C₂Cl₄, C₂Cl₆, CCl₄, and CHCl₃. CIT has initiated some preliminary modeling efforts for the various mechanisms of the sonication/degradation of the VOCs and SVOCs.

Planned Activities

Bench-scale research experiments will continue to be performed involving sonication and vapor stripping of the various halogenated organic compounds. Batch sonication and air stripping experiments will be completed by the end of FY 1998, moving towards the continuous flow treatment. Methods to enhance the reaction rate constants will be examined (e.g., application of higher ultrasonic frequencies; addition of oxidants such as ozone, hydrogen peroxide, etc.). Preliminary optimal conditions will be identified for the operation of the continuous flow system. The corrosion potential and salt formation potential will be identified and quantified. Chemical reaction mechanisms will be modeled. A 3-D computer model simulation is being developed to describe the combined sonication/vapor stripping/biodegradation system for simulating field operation. During FY 1999, a large laboratory-scale pilot system will be tested for application prior to field demonstration.

Other Access To Information

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