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HYDROGEN PEROXIDE TREATMENT OF TCE CONTAMINATED SOIL

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ABSTRACT

Solvent contaminated soils are ubiquitous in the industrial world and represent a significant environmental hazard due to their persistence and potentially negative impacts on human health and the environment. Environmental regulations favor treatment of soils with options which reduce the volume and toxicity of contaminants in place. One such treatment option is the in-situ application of hydrogen peroxide to soils contaminated with chlorinated solvents such as trichloroethylene (TCE). This study investigated hydrogen peroxide mass loading rates on removal of TCE from soils of varying organic matter content. Batch experiments conducted on contaminated loam samples using GC headspace analysis showed up to 80% TCE removal upon peroxide treatment. Column experiments conducted on sandy loam soils with high organic matter content showed only 25% TCE removal, even at hydrogen peroxide additions of 25 g peroxide per kg soil.

INTRODUCTION

Soils contaminated by trichloroethylene (TCE) represent a significant environmental problem at numerous federal and commercial facilities. TCE has been shown to adversely impact human health through ingestion, inhalation, and dermal contact at part-per-million concentrations. In order to support a technology demonstration for potential environmental restoration methods at the Department of Energy's Portsmouth Gaseous Diffusion Plant, research was conducted to assess the ability of hydrogen peroxide to remove TCE from contaminated soil.

Hydrogen peroxide is a powerful oxidant which reacts under certain conditions to form hydroxyl radical intermediates with oxidative potentials second only to fluorine [1]. As a result of its significant oxidizing capability, low cost, and environmentally acceptable by-products (i.e. oxygen and water), hydrogen peroxide has long been used as a disinfectant, a bleach, and to oxidize soil organic material [2].

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Recently, hydrogen peroxide has been used to treat organic contaminants in soils. Gurol and Ravikumar [3] demonstrated that TCE and pentachlorophenol (PCP) were oxidized with iron catalyzed hydrogen peroxide (i.e. Fenton's Reagent) in coarse grained sand with low organic content. Watts et al. [4] concluded that PCP was effectively degraded in sandy soils using Fenton's Reagent, although hydrogen peroxide alone was most effective at PCP removal in soils with appreciable organic content.

The purpose of this study was to determine the mass loading rate of hydrogen peroxide necessary to effectively remove TCE from soils of varying organic matter content. In addition, the formation of halogenated degradation products was evaluated.

MATERIALS AND METHODS

Experiments were conducted in two phases. Vial experiments were conducted using headspace TCE analysis, while column experiments were conducted using scintillation counting to measure radiolabelled TCE and its degradation products.

VIAL EXPERIMENTS

Vial experiments were performed on a loam soil with a dry-basis moisture content of 15% and an organic carbon content of 0.3%. Soil was sieved using a Number 5 Screen then added to glass 40 ml volatile organic analysis (VOA) vials in 2 g quantities. After placement in the vials, the soil was contaminated with TCE to a concentration of 24 mg TCE per kg of wet soil using a disposable syringe. To avoid puncturing the Teflon septa, TCE was added to each vial by placing a needle between the septa and glass vial while holding the septa in place using a modified C-Clamp.

After adding the TCE solution to the soil, vials were equilibrated for 24 hours to allow sufficient sorption of TCE onto the soil. Equilibration was conducted in a darkened hood to minimize TCE photodegradation. After equilibration, 2 ml of hydrogen peroxide, ranging from 0 to 30% (w/w), were added to each vial. Off-gas was collected using 200 ml five layer offgas collection bags (Calibrated Instruments). In each experiment, an equal volume of deionized water was added to a triplicate set of vials as a control. In all cases, peroxide mass loading rates were in excess of the stoichiometric requirement needed to completely oxidize the TCE in each vial. Equation 1 describes the stoichiometric hydrogen peroxide requirement to completely oxidize TCE.

Following a 24 hour peroxide contact time, headspace TCE concentration was measured by collecting 4 μl of headspace gas using a gas tight syringe. Samples were analyzed using a Shimadzu gas chromatograph with an electron capture detector and a 60 meter Restek capillary column designed for volatile halocarbon analysis. Samples of daughter products (e.g. cis, trans dichloroethylene) were also analyzed to verify their absence on each chromatogram. All vial experiments were conducted using triplicate samples.

COLUMN EXPERIMENTS

Column experiments were used to more closely simulate in-situ soil conditions. Radiolabelled (^{14}C) TCE and its oxidation by-products were evaluated throughout the peroxidation process (i.e. TCE remaining in the soil system, TCE volatilized after peroxide addition, and CO_2 produced from TCE peroxidation). Sixty ml disposable polyethylene syringes (2.54 cm i.d.) with teflon covered plungers were used as soil columns. These systems allowed uniform packing of soil, minimal headspace volumes, and inherent pressure relief from gas buildup.

Forty grams of sandy loam, with a dry-basis moisture content of 10% and an organic matter content of 1.23%, was poured into each syringe. Approximately 1 ml of moistened glass wool was placed in the needle end of the syringe to prevent soil carryover into the off-gas collection train. Soil in each syringe was compacted to a volume of 30 ml, thus providing a uniform bulk density of 1.33 g/cc.

Once packed, 6 ml of radiolabelled TCE solution (100,000 dpm) was added to each column using a disposable syringe and a 21-gauge, 5 cm needle. Triplicate samples of this solution were also added to scintillation vials for subsequent counting to determine the activity added to each column. The TCE solution was added to the radial center of the column beginning at the bottom (plunger end) by gradually withdrawing the needle until all TCE solution was applied. This treatment resulted in a final TCE concentration in each column of 10 mg/kg.

Following TCE addition, columns were equilibrated for 24 hours in a darkened hood to allow sorption of TCE onto the soil. Hydrogen peroxide was then added at concentrations ranging from 0 to 30% in 3 ml volumes. Peroxide loading rates ranged from 0 to 25 g H_2O_2 /kg soil. These values were several thousand times the stoichiometric requirement necessary to oxidize the TCE.

Immediately after peroxide addition, an off-gas collection train consisting of an activated carbon trap and an organic base solution (Harvey scintillation liquid) was attached to the column (Figure 1). The activated carbon trapped volatile TCE while the organic base trapped carbon dioxide.

Peroxide contact times of 24 hours were used in all experiments. After this time, traps were removed and 25 mls of a hexane-isopropanol solution (4:1 ratio) were added to the remaining soil in each column. Columns were vortex mixed for one hour to ensure thorough soil-solvent mixing. Radioactivity (^{14}C) in the solvent was then measured by scintillation counting.

Activated carbon was removed from each trap and combusted in a Harvey Biological Oxidizer. In this process, temperatures in the combustion chamber were elevated sufficiently to completely oxidize TCE to CO_2 , H_2O , and ash. Off-gas was bubbled

Figure 1. Soil column apparatus with off-gas collection.

through Harvey scintillation cocktail to capture labelled carbon dioxide for subsequent scintillation counting. $^{14}\text{CO}_2$ collected in the organic base trap was directly measured by scintillation counting.

To minimize chemiluminescent errors, all scintillation vials were stored in the dark for 18 to 24 hours before counting. A Beckman LS 5000 TD scintillation counter, with counting efficiencies and quenching effects calibrated in the autocount cycle, was used for all radiolabelled analyses.

RESULTS AND DISCUSSION

TCE REMOVAL

Data from vial experiments demonstrates that hydrogen peroxide can reduce TCE levels in the headspace above the saturated loam soil. Apparent removal efficiencies, as measured by headspace analysis, varied from 80 to 90 percent (Figure 2). However, an experimental artifact may have affected these results. Off-gasing and oxidation reactions can result in increased system pressures especially at high hydrogen peroxide concentrations. Gas samples at pressures above atmospheric drawn into a syringe would be prone to leakage due to the pressure gradient. The amount of leakage would presumably depend on system pressure inside the vials, which would correlate with the peroxide loading rate. Therefore, pressure effects could account for part of the observed decrease in TCE headspace concentration.

Figure 2. Apparent headspace TCE removal with increased hydrogen peroxide loading using VOA vials.

Data from column experiments conducted on sandy loam soils of high organic matter content (1.23%) yielded only 25% TCE removal at peroxide loading rates equal to 25 g H₂O₂/kg soil (Figure 3). Column experiments conducted on neutral, aqueous TCE solutions without soil showed TCE removal of nearly 70% for peroxide loadings of 10 g H₂O₂/kg contaminated solution (Figure 4). Both systems contained sufficient available iron to catalyze the formation of hydroxyl radicals. The limited TCE removal in the soil columns may be attributed to the high soil organic matter content which can react with hydrogen peroxide in competing oxidation reactions.

OFF-GAS TRAPS

As expected, both carbon and organic base traps showed increased activity with increased peroxide loading in a manner consistent with TCE removal from each column. Increased carbon trap activity was attributed to TCE volatilization, while increased base activity was attributed to carbon dioxide production from TCE oxidation. Essentially no activity was detected in either the carbon or base traps attached to the control column. For soil columns, TCE activity on carbon traps was significantly greater than carbon dioxide activity captured in base traps. This implied volatilization of TCE was the primary removal mechanism for this system (Figure 3).

For columns containing water but no soil, carbon dioxide trap activity was significantly higher than TCE activity collected by activated carbon (Figure 4). Soil minerals, organic

Figure 3. Effect of hydrogen peroxide loading on soil column activity.

Figure 4. Effect of hydrogen peroxide loading on aqueous TCE.

matter, and increased surface area in soil containing columns appeared to create an environment less conducive to TCE oxidation than in strictly aqueous systems. Because these factors tend to contribute to rapid hydrogen peroxide decomposition and off-gasing, more TCE tends to be volatilized from the soil than in the aqueous systems.

OFF-GAS PRODUCTION

Analysis of chromatograms revealed no peaks for halogenated daughter compounds, with confirmation standards of cis and trans dichloroethylene (DCE) run for verification. Oxygen peaks were observed, with increasing peak heights correlating to increasing peroxide addition (Figure 5). This may be viewed as a measure of inefficiency, since oxygen formation implies off-gasing rather than oxidation. As shown in Figure 6, volumes of off-gas collected matched well with stoichiometrically-predicted values, based on equation 2.

This suggests that either oxygen off-gasing is the predominant chemical reaction, or the general oxidation of organic matter produces off-gas in a stoichiometric ratio similar to that of oxygen and hydrogen peroxide in this equation.

SUMMARY AND CONCLUSIONS

Hydrogen peroxide is capable of removing TCE from soil systems through volatilization and chemical oxidation. It appears that soil organic matter plays a role in the peroxidation process and may preclude the feasible hydrogen peroxide treatment of soils with high organic matter content due to the occurrence of oxidation reactions which consume hydrogen peroxide.

Halocarbon decay daughters of TCE, including vinyl chloride and dichloroethylene monomers, were not detected by GC analysis following hydrogen peroxide treatment. This suggests that hydrogen peroxide may be used to reduce toxicity of TCE contaminated soils without forming these hazardous by-products.

Off-gas produced by the application of hydrogen peroxide to soil can be accurately estimated by computing the volume of oxygen gas produced from the decomposition of hydrogen peroxide to oxygen and water.

Figure 5. Headspace oxygen as a function of hydrogen peroxide loading.

Figure 6. Comparison of measured and calculated off-gas production volumes for 2 ml hydrogen peroxide solutions.

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