# Comparative study on oxidative treatments of NAPL containing chlorinated ethanes and ethenes using hydrogen peroxide and persulfate in soils

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## ARTICLE INFO

## ABSTRACT

The goal of this study was to assess the oxidation of NAPL in soil, 30% of which were composed of chlorinated ethanes and ethenes, using catalyzed hydrogen peroxide (CHP), activated persulfate (AP), and $H_2O_2$—persulfate (HP) co-amendment systems. Citrate, a buffer and iron ligand, was amended to the treatment system to enhance oxidative treatment. Four activation/catalysis methods were employed: (1) oxidant only, (2) oxidant-citrate, (3) oxidant-iron(II), and (4) oxidant-citrate—iron(II). The NAPL treatment effectiveness was the greatest in the CHP reactions, the second in HP, and the third in AP. The effective activation and catalysis methods depended on the oxidant types; oxidant only for CHP and HP and oxidant-citrate—iron for AP. The treatability trend of chlorinated ethanes and ethenes in the soil mixture was as follows: trichloroethene > tetrachloroethene > dichloroethane > trichloroethane > tetrachloroethane. A significant fraction of persulfate remained in the oxidation systems after the 2-day reaction period, especially in the citrate—iron(II) AP. In general, oxidation systems that included citrate maintained a post-treatment pH in the range of 7—9. A final pH of AP oxidation systems was acidic (pH 2—3), where a molar ratio of citrate—iron(II) was less than 1.8 and where no citrate was amended.

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## 1. Introduction

In-situ chemical oxidation (ISCO) involves the delivery of a chemical oxidant into the subsurface where oxidative reactions transform contaminants into less-toxic or non-hazardous compounds. Fenton's reagent involves the reaction between $H_2O_2$ and ferrous iron ($Fe^{2+}$), forming the hydroxyl radical ($\cdot OH$), a powerful non-specific oxidant intermediate (Walling, 1975). Other reactive intermediate oxygen species include perhydroxyl radicals ($\cdot HO_2$), superoxide radical anions ($\cdot O_2^-$), and hydroperoxide anions ($HO_2^-$) (Watts and Teel, 2005). Modified Fenton or catalyzed $H_2O_2$ propagations (CHP) reactions used for ISCO, generally involve higher concentrations (2—12%) of $H_2O_2$ than used in water treatment ($\sim 0.03\%$ $H_2O_2$) operations. A broad range of naturally occurring iron species exists in the subsurface to catalyze $H_2O_2$ reactions (Teel et al., 2001; Kwan and Veolker, 2002).

Persulfate ($S_2O_8^{2-}$) is also used in ISCO applications and is a strong oxidant ($E° = 2.1$ V). Persulfate is activated to generate a sulfate radical ($\cdot SO_4^-$) that is a stronger oxidant ($E° = 2.6$ V). Heat, iron, and chelated iron are known activators of persulfate (Tsitonaki et al., 2010 and references therein). Naturally occurring iron and manganese minerals are able to activate persulfate (Ahmad et al., 2010; Do et al., 2010). $H_2O_2$ has also been identified as a potential activator of persulfate (Block et al., 2004), but the reaction mechanism has not yet been fully investigated. Here, we propose that the $H_2O_2$ activation of persulfate involves several possible mechanisms including (1) Fe(II) formation during the Fenton reaction where it subsequently activates persulfate, and/or (2) persulfate activation by heat resulting from the exothermic $H_2O_2$ reaction. In this study, these two activation mechanisms are referred to as $H_2O_2$—persulfate co-amendment rather than $H_2O_2$ activated persulfate.

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While some soils exhibit significant buffer capacity, acidic pH in ground water and soil may result when using persulfate due to the highly acidic nature of the persulfate solution. Therefore, post-treatment pH can be an important factor in assessing the feasibility of persulfate oxidation as a treatment option. Citrate is a weak base and can be used as a buffer to keep pH levels near neutral. Citrate is also a natural organic chelating agent that is readily biodegradable and more environmentally friendly than other common iron chelators (e.g., ethylenediaminetetraacetic acid). Complexing agents, such as citrate–citric acid, enhanced desorption of hydrophobic organic compounds (e.g., polycyclic aromatic hydrocarbons) from soils and diffusion to the water interface (Yang et al., 2001). Citrate might enhance desorption and diffusion of some of hydrophobic organic contaminants that may be amenable to oxidative treatments, but have not been available to oxidants in the subsurface. Furthermore, the stability of oxidant in soils was enhanced in the presence of citrate (Watts et al., 2007).

Most studies focus on the treatment of single contaminants, such as TCE or PCE, even though a high percentage of sites contaminated with non-aqueous phase liquid (NAPL) are characterized as complex mixtures (USEPA, 2010). In this study, oxidative treatment of NAPL containing chlorinated ethanes and ethenes was performed, using catalyzed $H_2O_2$ propagation (CHP), activated persulfate (AP), and $H_2O_2$–persulfate (HP) co-amendment systems. The effect of citrate, amended as a buffer and ligand, on the oxidative treatment was also evaluated.

## 2. Materials and methods

### 2.1. Materials

In this study, sodium persulfate (>98.0%, Fisher chemical, ACS grade) and hydrogen peroxide (30%, Fisher chemical, ACS grade) were used as oxidants. Ferrous sulfate (>99.0%, heptahydrate, Fisher chemical, ACS grade) was used as a soluble ferrous iron source, and sodium citrate (>98.0%, dehydrate, Fisher chemical, ACS grade) as an iron chelating agent and buffer in persulfate and $H_2O_2$ oxidation systems. 1,4-dichlorobenzene-d$_4$ (1,4-DCB-d$_4$, 2000 µg/mL in methanol, Supelco) was used as an internal standard and 4-bromofluorobenzene (4-BFB, 2500 µg/mL in P&T grade methanol, Restek) as a surrogate and tuning standard for gas chromatography and mass spectroscopy (GC/MS) analysis. Standard solutions of 1,2-dichloroethane (DCA), trichloroethene (TCE), 1,1,2-trichloroethane (TCA), tetrachloroethene (PCE), and 1,1,2,2-tetrachloroethane (TeCA) (Restek) were purchased as 2000 µg/mL solutions in purge and trap (P&T) grade methanol. Methanol (>99.9%, Fisher chemical, HPLC grade) was used to extract the organic contaminants from soil slurry samples and to quench the oxidation reactions. Sulfuric acid (95.0–98.0%, Fisher chemical, ACS grade), ferrous ammonium sulfate (hexahydrate, 98.5–101.5%, Fisher chemical, ACS grade), and ammonium thiocyanate (>97.5%, Fisher chemical, ACS grade) were used to measure persulfate concentration. Hydrochloric acid (35.6–38.0%, Fisher chemical, certified ACS plus grade) was used to adjust pH. Water was de-ionized (>18 MΩ cm) using a Barnstead Nanopure system. De-ionized water (DIW) was used to prepare stock solutions of persulfate, citrate, and reagents for persulfate measurement. It was also used to dilute samples for chemical analyses, and to make up the final volume in batch reaction vials.

The contaminant site was a former fire training area. The geologic setting at the site includes three different aquifers, at discrete vertical intervals, each separated by low permeability strata. The base of the shallow sand aquifer is underlain by a clayey silt layer and a clay layer. ISCO treatment focused on the shallowest aquifer only because dense NAPL (DNAPL) has been observed to accumulate on top of this low permeable confining layer. The NAPL used in these experiments was obtained from a ground water monitoring well (4 m of depth) at this site, and soil was acquired from the same site. Soil used in this experiment was collected by excavation and was composed of slightly moist medium-coarse sand and shell fragments. The source and surrounding areas contain a variety of NAPL, adsorbed, and high-levels of dissolved phase organic compounds. Due to usage of fire suppression during the training, perfluoroocatane sulfonate (PFOS) (~15 µg/L) and perfluorooctanoate (PFOA) (~6.5 µg/L) were detected at the monitoring well. The concentration of PFOS and PFOA was much less than NAPL's (>hundreds mg/L), therefore, it was assumed that the effect of PFOS and PFOA on ISCO treatment of NAPL would be negligible. The NAPL contamination includes dense (DNAPL) and light (LNAPL) fractions with discrete horizontal and vertical extents. The organic constituents include chlorinated ethenes (i.e., PCE, TCE, 1,2-DCE, vinyl chloride, and others), chlorinated ethanes (i.e., TeCA, TCA, 1,1-DCA, 1,2-DCA, chloroethane, and others), chlorinated methanes (i.e., chloroform), chlorinated aromatics (i.e., chlorobenzene), and petroleum compounds (i.e., BTEX and TPH). The DNAPL density is close to water (1.08).

A set of five representative chlorinated volatile organic compounds (CVOCs) (DCA, TCE, TCA, PCE, and TeCA) were quantified. The average concentration of the CVOCs in the NAPL ($n = 11$) was $320 \pm 19$ mg L$^{-1}$ DCA; $84 \pm 6$ mg L$^{-1}$ TCE; $566 \pm 32$ mg L$^{-1}$ TCA; $87 \pm 7$ mg L$^{-1}$ PCE; and $171 \pm 13$ mg L$^{-1}$ TeCA. A majority of the CVOCs was present in ground water (i.e., ~90% of chlorinated ethanes and ~70% of chlorinated ethenes). Based on the GC peak area measurements, approximately 30% of the NAPL was composed of these 5 CVOCs, while ~70% was composed of chlorinated aliphatic organics, chlorinated aromatics, benzene, toluene, ethylbenzene, xylene (BTEX), styrene, petroleum hydrocarbons, and unidentified compounds. The NAPL pH was slightly alkaline (pH 8.1–8.2).

### 2.2. Analytical methods

Persulfate concentrations were measured via UV–vis spectrophotometer (HACH DR 5000) ($\lambda = 450$ nm) (Huang et al., 2002) and the calibration range was 100–1800 mg/L. $H_2O_2$ concentrations were measured with a HACH $H_2O_2$ test kit (model HYP-1). Other oxidants will positively interfere with $H_2O_2$ measurement since the test kit is designed for the sample only containing $H_2O_2$. Because of this, only persulfate concentrations were measured in the $H_2O_2$–persulfate co-amendment experiments. The solution pH was measured (APHA, 1997) using an Orion pH Micro-Electrode Combination.

The 5 CVOCs (DCA, TCE, TCA, PCE, and TeCA) were quantified using a GC (Varian 3900 equipped with Rtx-5MS column of 30 m × 0.25 mm inner diameter × 0.25 µm film thickness) and MS (Ion Trap Varian Saturn 2100T). Organic compounds were introduced to the GC/MS using P&T (OI analytical Eclipse model 4600) and a water/soil autosampler (OI model 4552). The analytical method for GC/MS and P&T analysis was developed based on EPA SW 846 methods 8260C and 5030C, respectively. Contaminant extraction by methanol was based on EPA SW 846 method 5035A (USEPA, 1996). Methanol (33 mL) added to the vial also served to quench the oxidation reaction ($k_{MeOH, \bullet OH} = 9.7 \times 10^8$ M$^{-1}$ s$^{-1}$ (Buxton et al., 1988); $k_{MeOH, \bullet SO_4} = 3.2 \times 10^6$ M$^{-1}$ s$^{-1}$ (Nata et al., 1988). The methanol soil-slurry samples were heated (45.5 °C) in a water bath (2 h) and shaken (2 days). After extraction was completed, the mixtures were centrifuged (2000 rpm, 5 min) to separate the liquid and solid phases.