



Carbon isotope fractionation of 1,1,1-trichloroethane during base-catalyzed persulfate treatment

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HIGHLIGHTS

- Treatability and C fractionation of 1,1,1-TCA by base-catalyzed $S_2O_8^{2-}$ was studied.
- The rate of degradation of 1,1,1-TCA increased with a higher $OH^-:S_2O_8^{2-}$ ratio.
- Base-catalyzed $S_2O_8^{2-}$ can potentially treat recalcitrant compound like 1,1,1-TCA.
- An enrichment factor of -7.0% independent of the $OH^-:S_2O_8^{2-}$ ratio was obtained.
- Carbon isotope can potentially be used to estimate the ISCO treatment efficacy.

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ABSTRACT

The extent of carbon isotope fractionation during degradation of 1,1,1-trichloroethane (1,1,1-TCA) by a base-catalyzed persulfate ($S_2O_8^{2-}$) treatment system was investigated. Significant destruction of 1,1,1-TCA was observed at a pH of ~ 12 . An increase in the $NaOH:S_2O_8^{2-}$ molar ratio from 0.2:1 to 8:1 enhanced the reaction rate of 1,1,1-TCA by a factor of ~ 5 to yield complete ($>99.9\%$) destruction. An average carbon isotope enrichment fractionation factor which was independent of the $NaOH:S_2O_8^{2-}$ molar ratio of $-7.0 \pm 0.2\%$ was obtained. This significant carbon isotope fractionation and the lack of dependence on changes in the $NaOH:S_2O_8^{2-}$ molar ratio demonstrates that carbon isotope analysis can potentially be used *in situ* as a performance assessment tool to estimate the degradation effectiveness of 1,1,1-TCA by a base-catalyzed persulfate system.

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1. Introduction

1,1,1-Trichloroethane (1,1,1-TCA, $C_2H_3Cl_3$) is a common chlorinated organic compound found in soil and groundwater, and has been identified at more than 50% of the hazardous waste sites identified on the EPA National Priorities List (NPL) [1]. It frequently co-exists at contaminated sites with chlorinated ethenes (e.g., trichloroethene (TCE)) since its industrial use is similar [2]. However, 1,1,1-TCA is more recalcitrant than common chlorinated ethenes due to the presence a single C–C bond [3].

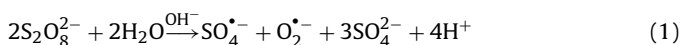
One potential remediation technology is *in situ* chemical oxidation (ISCO) which involves the injection or release of a chemical reagent into the subsurface with the capability to degrade the target organic compound(s). Among the numerous oxidants and activation systems available, the emergence of persulfate ($S_2O_8^{2-}$) and its novel activation strategies has created the potential for treatment of chlorinated methanes and ethanes (like 1,1,1-TCA) [4]. Gates-Anderson et al. [5] observed very little degradation of 1,1,1-TCA with either peroxide or permanganate while Huang et al. [4] and Liang et al. [6] found that thermally activated persulfate ($>40^\circ C$) completely degraded chlorinated solvent compounds like 1,1,1-TCA. Numerous methods are available to activate persulfate such the use transition metals, peroxide, and heat, or establishing alkaline conditions. The most frequently applied activation method is base-catalyzed persulfate (pH > 11) which has been used at $\sim 60\%$ of the sites where persulfate has been employed [7]. Base-catalyzed persulfate treatment consists of establishing high pH conditions

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by adding a strong base (e.g., sodium hydroxide) to the subsurface along with persulfate. Block et al. [8] and Brown et al. [9] suggested that some chlorinated methanes and ethanes can be destroyed using base-catalyzed persulfate.

Furman et al. [10,11] investigated the base activation mechanism and the effect of alkalinity on persulfate reactivity and showed complete degradation of the probe compound hexachloroethane. Furman et al. [10] reported that the base activation mechanism for persulfate starts with the base-catalyzed hydrolysis of a persulfate molecule to generate the hydroperoxide anion, a reducing species (HO_2^- , $E_h = -0.9\text{ V}$). The hydroperoxide anion then reduces another persulfate molecule generating the sulfate radical ($\text{SO}_4^{\bullet-}$) and the hydroperoxide anion is oxidized to the superoxide radical ($\text{O}_2^{\bullet-}$, $E_h = -2.4\text{ V}$), another strong reducing species. The overall reaction is given by [10]:



The production of these reducing species is what enables the base-catalyzed persulfate system to degrade highly oxidized organic compounds [10,11]. Furman et al. [11] also demonstrated that the generation of these reducing species was highly dependent on the base to persulfate molar ratio employed, indicating that for base to persulfate molar ratios above 3:1 the production of reducing species increased considerably.

The evaluation of ISCO performance for organic compounds following conventional concentration or mass-based estimates is generally difficult and prone to numerous uncertainties [12]. For chlorinated organic compounds, estimation of destruction effectiveness is usually based on the decrease in concentration (or mass load) of the target contaminant and/or an increase in chloride (Cl^-) concentration at a monitoring network downgradient of the source zone. However, changes in the organic compound concentrations between the target source zone and monitoring locations can also occur through non-chemical oxidation/reduction processes (e.g., displacement of contaminated groundwater by the injected oxidant solution). Furthermore, even though oxidation/reduction of the target contaminant may have extensively occurred, the concentration may still remain elevated due to the continuous dissolution from residual non-aqueous phase liquids (i.e., rebound [13]). Interpretation of Cl^- data may also be ambiguous in the presence of high background concentration levels, and, in the case of persulfate, Cl^- can react with the sulfate radical [14]. Hence, the use of concentration data alone may be insufficient to evaluate the effectiveness of an ISCO system [15].

Stable carbon isotope analysis has been increasingly applied as a complementary tool to monitor the *in situ* efficacy of abiotic and biotic treatment systems (e.g., Refs. [15] and [16]). This technique is based on changes in the isotopic composition of the target contaminant and its degradation products. Due to mass-dependent differences in activation energies of the different isotopes ^{13}C and ^{12}C , the lighter isotope (^{12}C) reacts faster than the heavier isotope (^{13}C), leading to fractionation and an enrichment of heavy isotopes in the residual contaminant as the reaction proceeds [17]. Consequently the use of stable carbon isotope analysis to complement the concentration data can be very helpful in distinguishing between chemical oxidation and non-oxidation processes, and therefore in appropriately quantifying the effectiveness of chemical oxidation [15]. In order to test the carbon isotope approach as a potential tool to assess ISCO performance at the field scale, a series of bench-scale experiments were designed in this study. The experimental objectives were (a) to evaluate the carbon isotope fractionation factor, and (b) to assess whether the use of different initial hydroxide to persulfate molar ratios results in differences in the carbon isotopic fractionation and also in 1,1,1-TCA degradation rates.

2. Experimental methodology

2.1. Materials and experimental conditions

To determine the treatability and isotopic fractionation of 1,1,1-TCA, a series of aqueous batch experiments were conducted. Persulfate and 1,1,1-TCA concentrations, along with pH were monitored to evaluate the extent of degradation and to obtain kinetic information. The isotopic composition of 1,1,1-TCA was also quantified, and used to calculate the carbon isotope fractionation factor and to investigate its dependence upon treatment conditions.

All chemicals used were reagent grade: 1,1,1-TCA (99.9% purity, Fisher Scientific); sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, 98%, Alfa Aesar) and sodium hydroxide (NaOH , 99.5%, Alfa Aesar). A 1,1,1-TCA stock solution was prepared to a concentration of 25 mg/L (0.19 mM). This 1,1,1-TCA stock solution was mixed successively with a pre-determined amount of persulfate to obtain a final persulfate concentration of 100 mM ($\sim 16\text{ g/L}$), and in turn with different amounts of NaOH to obtain 0.2:1, 0.5:1, 2:1, and 8:1 $\text{NaOH}:\text{S}_2\text{O}_8^{2-}$ molar ratio solutions. Nominal 40 mL reactors capped with Teflon septa were used and were stored in the dark at ambient room temperature (i.e., 20°C). Reactors were completely filled (no headspace) to minimize volatilization. The initial concentration in the reactors was 20, 50, 200 and 800 mM for NaOH , and 0.15 mM (20 mg/L) for 1,1,1-TCA. Triplicate reactors were prepared for all experimental trials. The influence of the $\text{S}_2\text{O}_8^{2-}:1,1,1\text{-TCA}$ molar ratio on treatment effectiveness was not investigated here since the persulfate concentration used was considered to be in excess (the approximate $\text{S}_2\text{O}_8^{2-}:1,1,1\text{-TCA}$ initial molar ratio was $>600:1$).

Preliminary experiments indicated that a three-week long reaction period was necessary to obtain $\sim 90\%$ destruction of 1,1,1-TCA. Sampling was performed at Day 1, 3, 8, 15, and 22. The reactors were sacrificed and quenched in an ice bath, and then aliquots were taken for: persulfate analysis (1 mL), $\delta^{13}\text{C}$ determination (22 mL), quantification of 1,1,1-TCA concentration and potential degradation products (2 mL), and to measure pH. Preliminary experiments showed that the use of the ice bath was adequate to essentially stop the reaction over a 1–2 day period, since no significant variation in 1,1,1-TCA concentration was observed over this time frame (data not shown). All analyses were conducted within 24 h of sampling.

Based on previous studies [8], minimal degradation of 1,1,1-TCA was expected for the $\text{NaOH}:\text{S}_2\text{O}_8^{2-}$ molar ratio of 0.2:1 trial and hence isotopic analyses were not performed. The purpose of this trial was to investigate the effectiveness of the base-catalyzed persulfate system at a lower $\text{NaOH}:\text{S}_2\text{O}_8^{2-}$ molar ratio than the recommended ratio of 0.4:1 [8].

Aside from chemical degradation by the reducing species generated in the base-catalyzed persulfate system, destruction of 1,1,1-TCA may occur by hydrolysis [18]. For example, 1,1,1-TCA may react with OH^- to partially degrade into chloroethene which can then be completely mineralized in the presence of activated persulfate [8,14]. Myamoto and Urano [19] observed significant degradation of 1,1,1-TCA at neutral pH at 80°C ; however, the half-life at 15 and 20°C estimated by using the Arrhenius equation is between 2 and 5 years [19]. To investigate the role of hydrolysis over the 22-day reaction period, another series of experiments (controls) were run at an initial pH of 7, 9, 11, and 13 without any persulfate added.

2.2. Analytical methods

The concentration of 1,1,1-TCA and potential chlorinated degradation products (e.g., 1,1-dichloroethane and chloroethane) was determined by pentane extraction (2 mL sample to 2 mL pentane) and subsequent analysis on a Hewlett-Packard 6890 Plus gas chromatograph (GC) equipped with an HP-624 column

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