Science of the Total Environment 548–549 (2016) 1–5

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Variability in carbon isotope fractionation of trichloroethene during degradation by persulfate activated with zero-valent iron: Effects of inorganic anions

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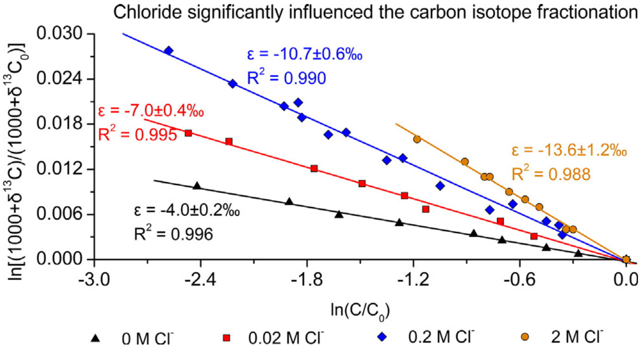
HIGHLIGHTS

- Significant C isotope fractionation for TCE degradation by Fe^0 activated persulfate.
- The enrichment factors was independent of Fe^0, SO_4^{2-}, or HCO_3^- concentration.
- Cl^- significantly influenced the carbon isotope fractionation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 September 2015
Received in revised form 3 January 2016
Accepted 3 January 2016
Available online xxxx

Editor: D. Barcelo

Keyword:
In situ chemical oxidation (ISCO)
Activated persulfate
Carbon isotope fractionation
Bicarbonate
Chloride

ABSTRACT

Stable carbon isotope analysis has the potential to be used for assessing the performance of *in situ* remediation of organic contaminants. Successful application of this isotope technique requires understanding the magnitude and variability in carbon isotope fractionation associated with the reactions under consideration. This study investigated the influence of inorganic anions (sulfate, bicarbonate, and chloride) on carbon isotope fractionation of trichloroethene (TCE) during its degradation by persulfate activated with zero-valent iron. The results demonstrated that the significant carbon isotope fractionation (enrichment factors ε ranging from -3.4 ± 0.3 to -4.3 ± 0.3 ‰) was independent on the zero-iron dosage, sulfate concentration, and bicarbonate concentration. However, the ε values (ranging from -7.0 ± 0.4 to -13.6 ± 1.2 ‰) were dependent on the chloride concentration, indicating that chloride could significantly affect carbon isotope fractionation during TCE degradation by persulfate activated with zero-valent iron. The dependence of ε values on chloride concentration, indicated that TCE degradation mechanisms may be different from the degradation mechanism caused by sulfate radical ($SO_4{\bullet}^-$). Ignoring the effect of chloride on ε value may cause numerous uncertainties in quantitative assessment of the performance of the *in situ* chemical oxidation (ISCO).

1. Introduction

Stable carbon isotope analysis offers a potential tool for assessing the performance of *in situ* remediation at sites contaminated with organic contaminants (Braeckevelt et al., 2012; Meckenstock et al., 2004;

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http://dx.doi.org/10.1016/j.scitotenv.2016.01.011

Thullner et al., 2012). The application of this isotope technique relies on the Rayleigh equation, which associates isotope fractionation of the contaminant with its concentration change due to specific transformation mechanisms (Mariotti et al., 1981). Generally, the extent of contaminant transformation (B [%]) can be calculated using the modified Rayleigh equation (Thullner et al., 2012):

$$B[\%] = \left(1 - \frac{C}{C_0}\right) \cdot 100 = \left[1 - \left(\frac{1000 + \delta^{13}C}{1000 + \delta^{13}C_0}\right)^{\frac{1000}{\varepsilon}}\right] \cdot 100$$

where $\delta^{13}C$ is the carbon isotope ratio of the substrate at any given fraction of remaining substrate (C/C_0), $\delta^{13}C_0$ is the initial value, and ε is isotope enrichment factor. Using measured $\delta^{13}C$ and $\delta^{13}C_0$ values, and the ε value obtained from laboratory studies, the calculated extent of contaminant transformation (B [%]) can then be used to quantitatively assess the performance of the *in situ* remediation (Thullner et al., 2012). Because the Rayleigh-based quantitative assessment is based on the ε value, the variation of ε value may cause uncertainty of the quantitative assessment. Therefore, the Rayleigh-based quantitative assessment of contaminant degradation should be used with caution.

Successful application of stable carbon isotope analysis for quantitative assessment of the *in situ* remediation performance requires understanding the magnitude and variability in carbon isotope fractionation associated with the reaction under consideration (Fletcher et al., 2011; Lee et al., 2007). To date, significant attention has been focused on the magnitude and variability of isotope fractionation associated with transformation of organic contaminants by different processes under various environmental conditions (Cichocka et al., 2007, 2008; Dong et al., 2011; Hofstetter et al., 2007).

As a popular *in situ* chemical oxidation (ISCO) technique, persulfate ($S_2O_8^{2-}$) is activated to generate sulfate radical ($SO_4^{\bullet-}$) to degrade organic contaminants (Johnson et al., 2008; Liang et al., 2008; Oh et al., 2010; Tsitonaki et al., 2010). The carbon isotope fractionation of chlorinated organic compound was independent on the concentration of persulfate and its activators such as Fe^{2+} and alkaline solution (Marchesi et al., 2012, 2013). However, the effect of inorganic anions on the isotope fractionation associated with organic compound degradation by activated persulfate has not been investigated. Previous studies showed that the pathway, kinetics, and efficiency of the activation of persulfate and the degradation of organic contaminants can be influenced by (bi)carbonate and chloride ions, which act as radical scavengers and metal complexing agents and are naturally present in the subsurface or introduced through anthropogenic activities (Bennedsen et al., 2012; Liang et al., 2006).

The objective of this study was to investigate the variability in the carbon isotope fractionation of trichloroethene (TCE) during degradation by persulfate activated with zero-valent iron in the presence of inorganic anions (sulfate, (bi)carbonate, and chloride). Ignoring the potential effect of inorganic ion on carbon isotope fractionation may cause numerous uncertainties in application of stable carbon analysis to assess the performance of the *in situ* chemical oxidation (ISCO). This study can be used to help assess the potential for stable carbon isotope analysis to be employed as a tool to estimate the ISCO remediation performance.

2. Material and methods

2.1. Batch experiments

A series of batch experiments were conducted at room temperature to determine the magnitude and variability in carbon isotope fractionation associated with trichloroethene (TCE) degradation by persulfate activated with zero-valent iron in the presence of sulfate, bicarbonate or chloride.

All experiments were prepared following the procedure described below and by adjusting factors to the exact conditions specified in Table 1. All batch experiments were performed in nominal 40 mL vials capped with PTFE/Silicone septa. The vials were filled with an appropriate amount of zero-iron (commercially available iron wire without any treatment) as shown in Table 1 and 40 mL deionized water or salt solution (e.g. Na_2SO_4, $NaHCO_3$ or NaCl solution, Table 1) adjusted to pH 2.5 by sulfuric acid (H_2SO_4, 98%; Sinopharm Chemical Reagent Co., Ltd., Shanghai, China). A volume of 3 μL neat trichloroethene (TCE, 99.0%; Tianjin Hengxing Chemical Reagent Co., Ltd., Tanjin, China) was spiked by gastight micro-syringe into each vial. The reaction was then initiated by adding 476 mg persulfate ($Na_2S_2O_8$, 98%; Sinopharm Chemical Reagent Co., Ltd., Shanghai, China). Each vial was sacrificed in order to analyze the TCE concentrations and $\delta^{13}C$ value at different reaction time. Preliminary experimental controls were prepared similarly, but without addition of persulfate, showing no loss in TCE concentration (<7%) and no variation in the $\delta^{13}C$ TCE value (<0.5 ‰) throughout the experimental period, which indicated that TCE reduction by zero-valent iron and physical losses were not significant.

2.2. Analysis methods

Aqueous TCE concentrations and $\delta^{13}C$ values were determined by solid-phase microextraction (SPME) on a TRACE GC Ultra gas chromatograph via a combustion interface (940 °C) to a Finnigan MAT253 isotope ratio mass spectrometer (GC-C-IRMS) (Elsner et al., 2004; Liu et al., 2013; Poulson and Naraoka, 2002). At each sampling time, aqueous sample (100–500 μL) was withdrawn by gastight micro-syringe and introduced to 2 ml vial with a final volume of 0.5 mL water. The vial was immediately sealed with open screw cup and PTFE/silicone septum. Subsequently, the SPME fiber (coated with 100 μm polydimethylsiloxane, PDMS; Supelco, Bellefonte, PA, USA) was exposed to the headspace (1.5 mL) for 5 min. After the extraction, the analytes were thermally desorbed from the SPME fiber for 2 min in the GC injector (230 °C). The GC was equipped with a DB-5 capillary column (30 m, 0.25 mm inside diameter, 0.25 μm film thickness; J&W Scientific, Folsom, CA, USA). The temperature program used for the GC was 35 °C for 1.5 min, 10 °C/min to 50 °C, 30 °C/min to 140 °C, 140 °C for 1 min. The flow rate of the carrier gas (helium) was 1.5 mL/min. $\delta^{13}C$ value for TCE was automatically determined relative to a CO_2 reference gas, with a typical reproducibility of 0.5 ‰. Aqueous TCE concentration was quantified with the signal intensity ($m/z = 44$) based on the calibration curve ($R^2 = 0.999$) between TCE concentrations and signal intensities ($m/z = 44$), with a reproducibility of 7%.

3. Results and discussion

3.1. Carbon isotope fractionation of TCE during degradation by persulfate activated with zero-valent iron

To determine the magnitude in carbon isotope fractionation, enrichment factors (ε values) were obtained by plotting $\ln(C/C_0)$ vs $\ln[(1000 + \delta^{13}C)/(1000 + \delta^{13}C_0)]$ and determining the slope (m) with least-squares regression, where $m = \varepsilon$ (Thullner et al.,

Table 1
Pseudo first-order rate constants (k_{obs}) and isotope enrichment factors (ε) for TCE degradation by persulfate activated with zero-valent iron.

Zero-iron (g)	Initial solution	k_{obs} (h^{-1})	CI [a]	R^2 [b]	E (‰)	CI[a]	R^2[b]
1.72	Deionized water	1.045	0.126	0.982	−4.0	0.2	0.996
0.34	Deionized water	0.256	0.040	0.981	−3.7	0.2	0.998
1.72	1 M SO_4^{2-}	0.967	0.073	0.997	−4.0	0.3	0.997
1.72	10 mM HCO_3^-	0.808	0.122	0.972	−4.3	0.3	0.994
1.72	100 mM HCO_3^-	0.034	0.005	0.974	−3.4	0.3	0.990
1.72	0.02 M Cl^-	0.921	0.124	0.978	−7.0	0.4	0.995
1.72	0.2 M Cl^-	0.700	0.037	0.991	−10.7	0.6	0.990
1.72	2 M Cl^-	0.099	0.018	0.953	−13.6	1.2	0.988

[a] CI is 95% confidence intervals (CI) of the regression.

[b] R^2 is the multiple correlation coefficient in linear regression.