ENHANCED REDUCTIVE DECHLORINATION OF CARBON TETRACHLORIDE IN ACIDIC SOIL COLUMN MANIPULATED WITH Fe(II) AND HS^-

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Abstract

Column tests were conducted to investigate the effect of reductant type and pH on reductive dechlorination of carbon tetrachloride (CT) by soil manipulated with Fe(II) and HS^- in this study. The bed volumes (BV) to reach a breakthrough of CT in soil column without pH adjustment were 2.8 (control), 13.8 (Fe(II)), and 4.0 (HS^-), respectively. The column breakthrough for HS^- system with CaO was 9.5 BV and that for Fe(II) with CaO couldn't be determined until 28.5 BV, presenting capacity of Fe(II) was more enhanced as a reductant. Generally, Fe(II) treatment showed better removal of CT in the soil column with the addition of CaO than HS^- treatment did. The distribution of surface chemical species ($FeOH^+$, $Fe(OH)_4^-$, and FeS) was predicted by PHREEQC. This research can provide fundamental knowledge to properly apply the modified natural attenuation and in-situ redox manipulation.

Introduction

Chlorinated organic compounds are widespread soil and groundwater contaminants, which have been widely used in agricultural and industrial purposes for several decades[1]. The chemical compounds have been focused due to their carcinogenic and mutagenic characteristics[2] and persistence in natural environments[3]. They have been steadily observed in common engineered and natural systems. Carbon tetrachloride (CT) is one of the chemical compounds frequently shown in soil and groundwater at National Priority List Sites of the United States (US)[4]. CT is a dense non-aqueous phase liquid so that it can sink below water table and form a low-permeable layer[5]. Applying conventional technologies such as pump-and-treat and soil vapor extraction to the sites contaminated with CT has been proved to be ineffective[3].

Natural attenuation has been evaluated as an efficient and cost-effective remedial alternative to degrade chlorinated organic compounds without extensive changes in the contaminated sites. Reduced forms of iron and sulfur, i.e. Fe(II) and bisulfide (HS^-) contained in the soil minerals have been known to play a pivotal role for the reductive dechlorination[6-13]. Reductive capacity of soil can be significantly enhanced by manipulating the soil with Fe(II) and HS^- and it can be ultimately used to reductively degrade chlorinated compounds during natural attenuation. In practice, the soil has limited intrinsic reductive capacity for the degradation of chemical compounds[7], thereby adding the reductants to the soil can enhance its capacity and facilitate the degradation during the natural attenuation process.

In this study, we performed column tests to investigate the effect of reductant type and pH on the reductive dechlorination of CT by real acidic soil and to enhance its reductive capacity by a manipulation with Fe(II) and HS^-. CT and acidic soil were chosen as representative target compound and soil. CaO was added to acidic soil columns treated with the reductants to increase the pH of the soil and its reductive capacity.

Materials and Methods

An experimental procedure to obtain anaerobic environments has been well found everywhere[6,14]. Carbon tetrachloride (CT, 99.5%, Aldrich) and chloroform (CF, 99%, Aldrich) were used as a target compound and a potential by-product, respectively. $FeCl_2 \cdot 4H_2O$ (99%, Aldrich) and NaSH (Aldrich) were used as sources of Fe(II) and HS^-. Calcium oxide (98%, Junsei) was used to increase the pH of soil in the column. In addition, sodium bromide (99%, Junsei) was used as a tracer for column experiments and sodium carbonate (99.9%, Merck) was used to make an eluent for ion chromatograph analysis. Stock solutions of CT and CF were prepared by diluting them in methanol (99.9%, Merck). Normal hexane (n-hexane, 98.0%, Merck) was used as an extractant and 1,2-dibromopropane (1,2-DBP, 97%, Aldrich) was used as an internal standard for gas

chromatograph (GC) analysis.

Soil was taken from the top 10-20 cm on a hill near Korea Institute of Science and Technology. The soil was fully dried in the air for 14 d and screened with a 10 mesh to separate particles less than 2 mm. The soil samples were equilibrated with mixed gases (95% nitrogen and 5% hydrogen) for 2 d in an anaerobic chamber (Coy Laboratory Products Inc., Grass Lake, MI) before use. X-ray diffraction (XRD) analysis (RINT2000 Wide angle goniometer using Cu Kα radiation) showed that the soil is mainly composed of quartz (80%) and phyllosilicates (kaolinite and vermiculite, 20%). pH, iron content, and surface area of the soil were 4.0, 2%, and 14.9 m^2g^{-1}, respectively.

Column experiments were conducted using glass column reactors (2.44 cm inside diameter × 43.8 cm length) at room temperature (25 ± 0.5℃). The reactors were equilibrated with anaerobic atmosphere for 2 d and packed with the same acidic soil resulting in a uniform bulk density of 1.22 ± 0.05 g/cm^3 and total porosity of 0.45 ± 0.05. The column reactors were filled with glass wool, plugged with Teflon adapters at each end, and flushed with nitrogen to remove air pockets. The soil in the columns was then equilibrated with DDW at the flow of 0.07 mL/min for 5 d with a peristaltic pump in the anaerobic chamber. Fe(II) and HS^- solutions (200 mM) were then introduced into the DDW-saturated soil columns at the same flow rate for 4 bed volumes, respectively. Control column to check retardation due to sorption of CT was prepared by introducing DDW into column for 4 additional bed volumes instead of reductants. A non-reactive tracer, standard bromide solution, was prepared for tracer tests to investigate physical characteristics of soil columns. The reductive dechlorination of CT in the soil columns was initiated by introducing standard CT and bromide mixture to the column inlets at the same flow rate under the room temperature. The concentrations of CT and bromide in the reservoir were 1 mM, respectively. A self-collapsible Teflon bag was used as a feeding reservoir to prevent the partitioning of CT to its headspace. The effluents from outlets of control column and soil columns manipulated with Fe(II) and HS^- were collected at the regular sampling times to monitor the concentrations of target organic, transformation products, and tracer. All samples were prepared in duplicate. Reductive capacity of the soil for CT might be limited due to its acidity. In this research, we tried to enhance the reductive capacity by increasing the pH of the soil through the addition of CaO. CaO and soil were mixed at a mass ratio of 1:20 and the mixture was then transferred to the columns.

An aliquot of supernatant (100 μL) was transferred to an extractant (1.4 mL of n-hexane containing 50 μM of 1,2-DBP as an internal standard). It was shaken for 30 min using an orbital shaker at 200 rpm. Target compound and product were analyzed by a gas chromatograph with electron capture detector (GC/ECD, Hewlett Packard (HP) 5890) equipped with HP-5 column (30 m length, 0.32 mm i.d., 0.25 μm thickness). For the analysis of bromide, an aliquot of outlet sample filtrate by 0.2 μm membrane filter (Advantec., Japan) was introduced into the injection port of ion chromatograph (Dionex DX-120) equipped with Dionex AS9-HC column (250 × 4 mm i.d.) and suppressed conductivity detector.

Results and Discussion

1. Degradation of CT in soil columns treated by Fe(II) and HS^-

Figure 1 shows CT removal in soil columns with and without treatment of Fe(II) and HS^- under no pH adjustment. No color changed in soil column with Fe(II), while soil color changed to black in the column with HS^-, indicating the formation of iron sulfide. No XRD analysis has been conducted to confirm its formation. The bed volumes (BV) to reach a column breakthrough of CT assuming it to be the relative concentration (C/C_0) of 0.5 were 2.8 (control), 13.8 (Fe(II)), and 4.0 (HS^-), respectively, which indicates that the soil column treated with Fe(II) has the greatest reductive capacity for CT followed by column treated with HS^- and control. The removal of CT in control column (Figure 1(a)) is due mainly to the adsorption on the soil surfaces. The removal caused by intrinsic reduction capacity of the soil surfaces did not seem to play a pivotal role because no transformation products were observed during the control test. CT was reductively degraded to CF in the soil column treated with Fe(II) (Figure 1(b)), while CT was removed but CF was not detected under the detection limit in the column treated with HS^- (Figure 1(c)). The result indicates that CT was reductively degraded in the column treated with Fe(II). In the soil column treated with HS^-, CT may be reductively transformed to potential transformation products (CS_2, CO_2, CO, and $HCOO^-$) during the reductive dechlorination of CT by sulfides. We

did not measure the transformation products in this experiment.

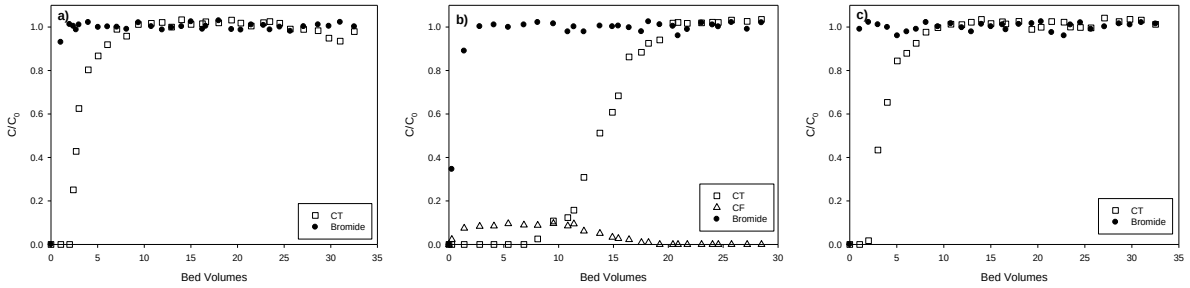


Figure 1. CT degradation in acidic soil columns filled with soil (a), soil treated with Fe(II) (b), and soil treated with HS^- (c). No pH adjustment.

2. Degradation of CT in soil columns treated by Fe(II) and HS^- under pH adjustment

Figure 2 shows the reductive dechlorination of CT in the treated soil columns with pH adjustment with CaO. Relative concentration (C/C_0) of CT for the soil column treated with Fe(II) under pH adjustment was almost zero and that of CF increased to 0.65 at the BV of 28.5 indicating no significant loss in its full reductive capacity during the column test. The relative concentration for the soil column treated with HS^- reached 1 at BV of 20.9 and the amount of CF produced in HS^- system was much smaller than that in Fe(II) system. The results obtained from pH adjustment tests are quite different to those under no pH adjustment (Figure 5(b) and (c)), i.e. the BV of HS^- system under pH adjustment with CaO to reach at C/C_0 = 1 was twice longer than that under no pH adjustment. The column breakthrough for HS^- system with CaO was 9.5 BV and that for Fe(II) with CaO cannot be determined until 28.5 BV. CaO, initially added into soil column to buffer the acidic soil, was reported to catalyze the formation of reactive soil minerals such as sulfate green rust ($Fe^{II}_4Fe^{III}_2(OH)_{12}SO_4 \cdot yH_2O$) crystals in hematite/Fe(II) system[15]. Breakthrough curves of bromide and CT observed in the control and reduced soil columns showed that retardation occurred during the degradation of CT in the columns.

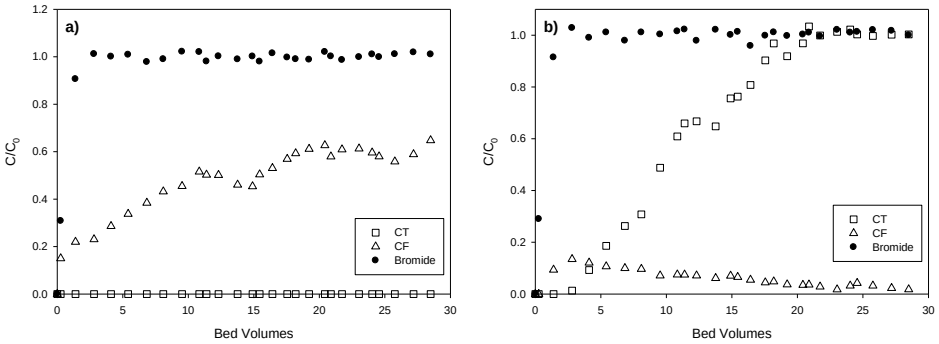
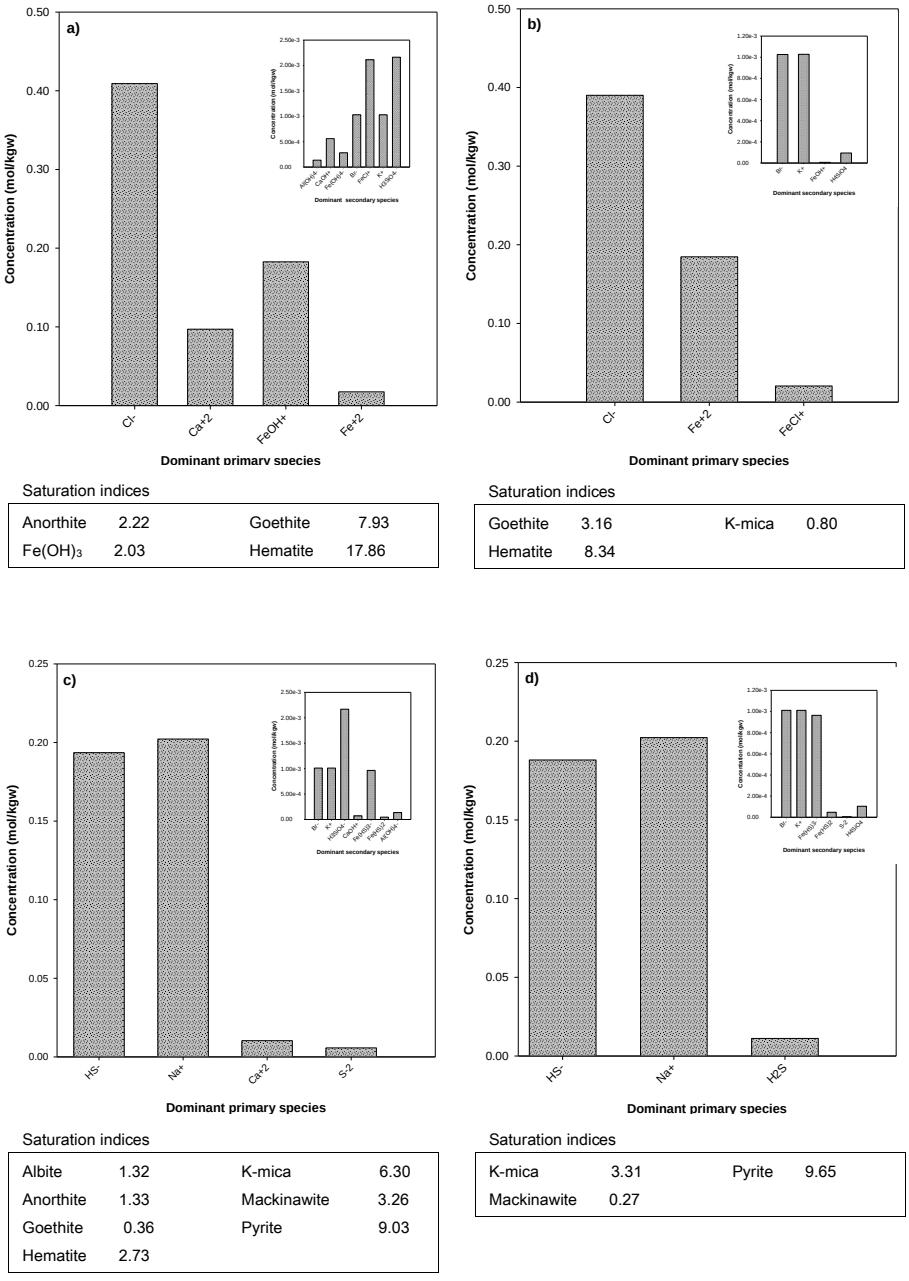


Figure 2. CT degradation in soil column treated with Fe(II) (a) and HS^- (b) under pH adjustment.

Figure 3 shows the distribution of surface chemical species predicted by PHREEQC. Figure 3(a) shows that $FeOH^+$ and $Fe(OH)_4^-$ complexes on the soil surfaces formed by the decrease of Fe(II) were dominant reactive surface species contributing to the enhancement of reductive capacity of soil treated with Fe(II) under pH adjustment for the reductive dechlorination of CT. However, the soil column without pH adjustment contained very low content of iron hydroxide species, which did not significantly affect the acceleration of the dechlorination kinetics (Figure 3(b)). We also estimated the contents of iron sulfide complexes (i.e., $Fe(HS)_2$ and $Fe(HS)_3^-$) and reactive precipitates such as FeS formed on the soil surfaces in the columns treated with HS^- with and without pH adjustment. The contents of iron sulfide complexes in each column were very low and similar but the column with pH adjustment had twelve times higher content of FeS than that without pH adjustment,

explaining the faster reaction kinetics of the column with pH adjustment (Figure 3(c) and (d)). This indicates that the pH adjustment with CaO is a very significant treatment to enhance the degradation kinetics for the reductive dechlorination of CT by forming reactive metal hydroxide species in the acidic soil column treated with reductants.



Saturation indices

Anorthite	2.22	Goethite	7.93
$Fe(OH)_3$	2.03	Hematite	17.86

Saturation indices

Goethite	3.16	K-mica	0.80
Hematite	8.34		

Saturation indices

Albite	1.32	K-mica	6.30
Anorthite	1.33	Mackinawite	3.26
Goethite	0.36	Pyrite	9.03
Hematite	2.73		

Saturation indices

K-mica	3.31	Pyrite	9.65
Mackinawite	0.27		

Figure 3. Distribution of dominant (primary and secondary) chemical species on the soil surfaces predicted by PHREEQC. Fe(II) system with (a) and without pH adjustment (b); HS^- system with (c) and without pH adjustment (d).

Acknowledgements

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