



## Ligand-assisted degradation of carbon tetrachloride by microscale zero-valent iron

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### ARTICLE INFO

#### Article history:

Received 9 February 2010

Received in revised form

3 October 2010

Accepted 23 December 2010

Available online 14 January 2011

#### Keywords:

Carbon tetrachloride

Dechlorination

Zero-valent iron

Organic ligands

### ABSTRACT

Degradation of carbon tetrachloride (CT) by microscale zero-valent iron (ZVI) was investigated in batch systems with or without organic ligands (ethylenediaminetetraacetic acid (EDTA), citric acid, tartaric acid, malic acid and oxalic acid) at pHs from 3.5 to 7.5. The results demonstrated that at 25 °C, the dechlorination of CT by microscale ZVI is slow in the absence of organic ligands, with a pseudo-first-order rate constant of 0.0217 h<sup>-1</sup> at pH 3.5 and being further dropped to 0.0052 h<sup>-1</sup> at pH 7.5. However, addition of organic ligands significantly enhanced the rates and the extents of CT removal, as indicated by the rate constant increases of 39, 31, 32, 28 and 18 times in the presence of EDTA, citric acid, tartaric acid, malic acid and oxalic acid, respectively, at pH 3.5 and 25 °C. The effect of EDTA was most significant; the dechlorination of CT at an initial concentration of 20 mg l<sup>-1</sup> increased from 16.3% (no ligands) to 89.1% (with EDTA) at the end of 8 h reaction. The enhanced CT degradation in the presence of organic ligands was primarily attributed to the elimination of a surface passivation layer of Fe(III) (hydr)oxides on the microscale ZVI through chelating of organic ligands with Fe(III), which maintained the exposure of active sites on ZVI surface to CT.

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### 1. Introduction

Extensive studies have shown that ZVI is effective at degrading many chlorinated organic compounds (COCs), such as chlorinated methanes (Matheson and Tratnyek, 1994; Lien and Zhang, 1999), trichloroethylene (Chen et al., 2001; Szecsody et al., 2004; Liu et al., 2006), trichloroethane (Su and Puls, 1999; Lookman et al., 2004), vinyl chloride (Deng et al., 1999), pentachlorophenol (Kim and Carraway, 2000), and atrazine (Dombek et al., 2001; Kim et al., 2007).

CT is a chlorinated compound widely used as a solvent for dry cleaning and degreasing in the past, resulting in numerous groundwater and soil contaminations. It is considered a priority pollutant by the United States Environmental Protection Agency due to its high toxicity and carcinogenicity. Reductive dechlorination is increasingly explored for its decomposition in the environment in recent years (Boopathy, 2002; Mariaa and Lizaberth, 2004; Choi et al., 2009). When ZVI was used as the reductant, the reduction of CT occurred through a complex pathway, involving formation of chloroform (CF) and dichloromethane (DCM) as intermediates (Feng and Lim, 2005). These intermediate species could accumulate in the aqueous system at the beginning of the reaction due to their low

degradation rates, although they were still degraded slowly (Feng and Lim, 2005; Wang et al., 2009).

Zero-valent iron is thermodynamically unstable in the presence of water and oxygen, and its corrosion can lead to an increase in solution pH and precipitation of iron oxides including Fe(OH)<sub>2</sub>, Fe(OH)<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub>. The formation of oxide coating on the surface of ZVI could cause a rapid decrease in dechlorination because the coating inhibits access of target COCs to the active iron surface, especially at a high pH (Matheson and Tratnyek, 1994; Agrawal et al., 2002; Kober et al., 2002).

A number of new approaches have been explored to enhance the extent and rate of COC dechlorination. One way is to use nanoscale ZVI with large specific surface area that facilitates COC degradation (Zhang et al., 1998; Feng and Lim, 2005; Song and Carraway, 2006). Feng and Lim (2005) demonstrated that nanoscale ZVI particles significantly enhanced the removal rate of CT as compared with commercial microscale iron powder. Another approach is to deposit a second zero-valent metals such as Al, Ni, Pt, Cu, or Pd onto the iron surface as a catalyst (Lien and Zhang, 2002; Lee et al., 2006; Zhu et al., 2006; Li et al., 2008). For example, the catalytic Fe–Cu process is shown to be superior to Master Builders' iron in treating CT-containing water (Xu and Gao, 2007). The presence of zero-valent aluminum also prevented formation of a passive layer on the iron surface so the reactivity of iron could be maintained (Chen et al.,

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2008). Among bimetallic particles, Pd/Fe is considered to be most effective for the degradation of chlorinated methanes, which was ascribed to the Pd-facilitated hydrogen adsorption and subsequent contaminant reduction (Wang et al., 2009).

Although nanoscale iron and bimetallic particles are capable of degrading COCs in the environment, the cost of preparing single/bimetallic nanoscale particles is high. Since it is known that decreases in the removal efficiency of CT by ZVI result primarily from a formation of surface passive film, we hypothesize that any methods capable of inhibiting/removing the Fe(III) (hydr)oxides films on ZVI surface would facilitate the removal of CT. Organic ligands may form strong complexes with Fe(III) and thus could eliminate iron (hydr)oxides precipitates on ZVI surface. It has been reported that organic ligands accelerated the nitrate reduction by ZVI (Su and Puls, 2004) and Cr(VI) reduction by pyrite (Zhou et al., 2008). There is, however, no report examining the impact of organic ligands on the dechlorination of CT by microscale ZVI.

This study aimed at investigating ligand-assisted dechlorination of CT by microscale iron powder, using EDTA, citric acid, tartaric acid, malic acid, and oxalic acid as representative ligands and under various initial ligand concentrations and solution pH. The surface of ZVI before and after the reaction was characterized by the analyses of elemental composition and morphology.

## 2. Materials and methods

### 2.1. Materials

Microscale ZVI particles were purchased from the Development Center of Kemiou Chemical Reagent, Tianjin, China. Carbon tetrachloride (99.5%), EDTA (99%), citric acid (99.5%), tartaric acid (99.5%), malic acid (99.5%), oxalic acid (99.5%), hexane (95%, chromatographically pure) and AgNO<sub>3</sub> (99.5%) were obtained from Shanghai Chemical Reagent. All other chemicals used in the study were at least of reagent grade.

All glassware used in the experiments were cleaned by soaking in 1 M HCl for 24 h and thoroughly rinsed sequentially with tap water and deionized water.

### 2.2. Pretreatment of ZVI

To remove oil film and oxides on the ZVI surface that may affect the removal of CT, ZVI particles were cleaned by briefly reacting with 0.1 M NaOH and 0.1 M H<sub>2</sub>SO<sub>4</sub> sequentially, then rinsed with deionized water five to six times to remove any residual H<sub>2</sub>SO<sub>4</sub>. The cleaned iron particles were dried in a vacuum chamber at 60 °C for 2 h and then stored in a desiccator under the protection of N<sub>2</sub> prior to use.

### 2.3. Characterization of ZVI

Specific surface area of the cleaned iron particles was measured by N<sub>2</sub> gas adsorption on a JW-004 surface area analyzer (Beijing Jing Wei Gao Bo) and calculated by the Brunauer–Emmet–Teller (BET) isotherm. The surface morphological and elemental analyses of ZVI before and after the reaction were performed on an environmental scanning electron microscope (ESEM) with a Philips XL30 microscope and capability of energy-dispersive X-ray analysis (EDXA, Kevex) at a 20 kV beam potential.

### 2.4. Experimental procedures

The 2000 mg l<sup>-1</sup> CT stock solution was prepared by dissolving CT in methanol, and then stored in a brown bottle. All batch experiments for CT dechlorination were conducted in 250 ml glass bottles. Firstly, a desired amount of organic ligand was dissolved in

about 90 ml deionized water. The initial pH values were adjusted with dilute NaOH and H<sub>2</sub>SO<sub>4</sub>. A 1 ml aliquot of CT stock solution was then spiked into the organic ligand solution. The total volume of solution was 100 ml with an initial CT concentration of 20 mg l<sup>-1</sup>. Finally, 0.5 g pre-cleaned ZVI was rapidly introduced into the system to initiate the reaction. The molar ratio of organic ligand to ZVI in the reaction system was 1:1 for most of the batch experiments. These bottles were immediately sealed with medical rubber plugs with polytetrafluoroethylene membranes and placed on a water bath (SIM BS-31) at 25 ± 0.1 °C and shaken at 180 rpm. Control experiments (no ligands) were also performed under the same conditions. The pHs at the end of the reactions were measured. The study was conducted in the presence of dissolved O<sub>2</sub> and 150 ml headspace of air, so the effect of Fe(III) (hydr)oxide coating formation on the reaction could be evaluated.

### 2.5. Analytical methods

To monitor the degradation kinetics of CT, about 3 ml of sample was drawn from the suspension at pre-determined time intervals with a gastight syringe and immediately filtered through a 0.45 μm membrane filter to a clean and dry glass tube. A 2 ml of filtered sample was taken out with a pipette and extracted via liquid–liquid extraction process with 5 ml hexane, and then the organic phase was transferred into another clean and dry glass tube. A 0.2 ml aliquot of sample was withdrawn from the glass tube and added to a 10 ml volumetric flask containing 0.3 mg l<sup>-1</sup> γ-666 as an internal standard. Finally, the total volume was diluted to 10 ml with hexane. About 0.3 μl of the sample was injected into a gas chromatograph (Agilent 6820 with DB-1701 column) equipped with an electron capture detector (ECD) to determine the concentrations of CT. Nitrogen was used as a carrier gas with a pressure of 0.05 MPa, and temperature values of the oven, the inlet and the detector were set at 45, 280, and 300 °C, respectively.

The intermediates, CF and DCM, were measured following the processes below. Firstly, 1 ml aliquot of filtrate was diluted with deionized water to 10 ml. Then, 2 ml diluted sample solution was rapidly transferred to a 20 ml headspace autosampler, where the samples were equilibrated for 30 min at 60 °C (carrier gas pressure was 0.06 MPa). Finally, 1 ml headspace samples were withdrawn from the vial for determination of CF and DCM concentrations on an Agilent 6820 gas chromatograph equipped with a DB-MAX column and an electron capture detector in splitless mode. Nitrogen was used as the carrier gas with a pressure of 0.05 MPa. The temperatures of the injection port, detector, and column were 200, 300, and 40 °C, respectively. Peak areas were converted to aqueous concentrations by the external standard method.

Chloride was measured by an established turbidimetry method (Wang et al., 2007) with some modifications to obtain optimal results. After 2 ml aliquot of filtered sample was transferred to a 10 ml volumetric flask, 3 ml of 7.5 M HNO<sub>3</sub> and 2 ml of 0.1 M AgNO<sub>3</sub> were added, followed by deionized water dilution to 10 ml. The suspension was magnetically stirred for 5 min and then kept still for 45 min prior to the absorbance measurement at 440 nm, using a UV-9100 spectrophotometer (Beijing RuiLi Corp) with 1-cm cell. All standard curves were linear with correlation coefficients ( $R^2$ ) > 0.995, and the detection limit was 0.030 mg l<sup>-1</sup>.

The adsorption of chloride by iron particles in the presence of organic ligands was minimal and negligible. Without organic ligands, however, a passive Fe(III) (hydr)oxide film developed with time on the pre-cleaned ZVI surface, which could adsorb or occlude a portion of the released chloride. To measure the adsorbed amounts, residual iron particles from a parallel test were reacted with 10 ml of 1.0 M nitric acid for 240 min and rinsed 5 times with deionized water to remove chloride and residual COCs. Then, the

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