Research article

Effect of carboxylic acids on the properties of zerovalent iron toward adsorption and degradation of trichloroethylene

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A B S T R A C T

Zerovalent iron (ZVI) based technology has been applied to remediate contaminated groundwater and has been paid great attention as an economic alternative. But it is still remains highly challenging to remove chlorinated pollutants such as trichloroethylene (TCE) with ZVI. Low molecular weight carboxylic ligands (formic acid (FA), oxalic acid (OA), and citric acid (CA)) were chosen to study the influence on the performance of ZVI in groundwater, including the morphology of Fe surface and the Fe dissolution. The removal rate of TCE with ZVI in the presence of 30 mM carboxylic groups followed an order of FA > OA > pure water $\cong$ CA. FA provides protons to promote the surface corrosion and generated more magnetite on the ZVI surface, which was further responsible for a high adsorption of TCE. With the strong complexing ability of OA and CA, passive layers could form dissoluble complexes via a ligand-promoted dissolution process. However, high concentration of OA resulted in Fe oxalate reprecipitated back onto the ZVI surface then inhibited the reactivity of ZVI. The Fe-ligand complexes also have ability to transform TCE depending on their redox properties. It is expected that effectiveness of carboxylic ligands on the ZVI: those low molecular weight carboxylic ligands in groundwater and soil may enhance the reaction efficiency of ZVI by altering the surface characteristics of ZVI. Therefore, the carboxylic ligands could increase the reactivity and the longevity of ZVI.

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1. Introduction

In the past decade, zerovalent iron (ZVI) has been elicited great interest in the dehalogenation of chlorinated pollutants (Arnold and Roberts, 2000; Farrell et al., 1999; Lowry and Johnson, 2004; Wang and Zhang, 1997). In-situ field studies demonstrate ZVI based permeable reactive barriers (ZVI-PRBs) remove polluted groundwater under environmentally relevant conditions (O'Hannesin and Gillham, 1998). Since 2003 over 70 field-scale PRBs were installed to degrade chlorinated hydrocarbons (Vikesland et al., 2003), but the performance of ZVI varies with different water parameters including pH, dissolved oxygen content, composite ions and ion strength (Mylon et al., 2004; Tang et al., 2012; Yang et al., 2007). One of the main factors that influence the overall efficiency of ZVI is the surface aging. ZVI is usually reported to have a core-shell structure that contains oxidized iron such as mostly magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) or

lepidocrocite (γ-FeOOH) (Díez-Pérez et al., 2006; Farrell et al., 1999; Reinsch et al., 2010). It is also expected that the interactions between Fe particles and common electrolytes form iron (hydro) oxides on the surface further cause a rapid decrease in the activity of ZVI (Agrawal et al., 2002; Kober et al., 2002). It also noted that the presence of high concentration of Fe^{2+} in carbonate-bearing water formed ferrous carbonates precipitate on Fe surface, which may block the reactive and attachment sites on the Fe surface and reduce its reactivity (Tso and Shih, 2015). Thus, a method for extending the long-term performance of ZVI is required to increase the effectiveness of ZVI application. The reactivity of ZVI was reported to be increased under mildly and weakly acidic solutions because of the corrosion effect on its surface (Bokare et al., 2008; Epolito et al., 2008; Liu and Lowry, 2006). Protons dissolve Fe (hydro)oxides that precipitates on the Fe surface exposing more fresh reactive sites (Shih et al., 2011a), it attributed mainly to the proton adsorption on metal (hydro)oxides depending to their surface groups and structures (Hiemstra and van Riemsdijk, 1990).

Besides the proton effect, the other important dissolution process of metal oxides in soil environments is related to activated surface metal-ligand complexes, which is referred as the ligand-

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promoted pathway (Furrer and Stumm, 1986). Organic ligands could form soluble surface complexes to induce the dissolution of metal oxides (Furrer and Sticher, 2014; Hamer et al., 2003). The major sources of protons and ligands in natural soil environments are commonly composed of carboxylic acids and aromatic acids, originating from the microbial degradation of humic substances, plant debris, and root exudation (Biver and Shotyk, 2012). Moreover, some organic ligands, such as catecholate, hydroxamate and organothiol, promote Fe^{2+} reactivity toward nitroaromatic compounds via complexation (Naka et al., 2006, 2008).

For the halogenated contaminant of concern, dense nonaqueous phase liquids (DNAPLs) such as chlorinated solvents have been an important issue because of their plume migration and toxicity. Chlorinated hydrocarbons like trichloroethylene (TCE) generally would pose great threats to the environment and human health because TCE is harmful to the human respiratory, the circulatory, and the central nervous systems and possible association to female breast cancer (Chang et al., 2003). In Taiwan, several TCE contaminate sites such as a leakage of a TCE storage tank in an industrial park site located in southern Taiwan was discovered in early 2005, which resulted in groundwater contamination with TCE (Kao et al., 2016). Until now, even though there have been a variety of technologies used to remediate sites contaminated with chlorinated hydrocarbons, it still remains highly challenging to remove or destroy DNAPLs in a timely and cost-effective manner owing to the magnitude and complexity of the problem. It is further be noted that the dechlorination of TCE using ZVI was very slow with a half-life of days or longer (Johnson et al., 1996; Sayles et al., 1997) and formed hazardous byproducts (Arnold and Roberts, 2000; Johnson et al., 1996).

Several studies have examined the performance of organic ligands on reactivity of ZVI for groundwater treatments (Hou et al., 2009; Su and Puls, 2004); however, little is known about their related reaction mechanisms. Organic acids with low molecular weight may act as providers for both the proton and functional groups to affect the surface characteristic of Fe. Once Fe complexes form during ZVI treatments, they may further influence the degradation mechanism. The aim of this study is to investigate the effects of three simple carboxylic ligands including formic acid, oxalic acid and citric acid on the surface characteristics of ZVI were used to assess possible multi-reaction mechanisms between ZVI and ligand-Fe complexes. These findings can further be applied to forecast and predict the possibility of sequential treatments with Fe complexes in the presence of organic ligands.

2. Materials and experiments

2.1. Chemicals

All chemicals were of regent grade. TCE, ZVI (325 mesh, BET surface area of 0.17 m^2/g), citric acid (CA), oxalic acid (OA), and Ferrozine™ iron reagent were purchased from Acros. Formic acid (FA) was purchased from Sigma-Aldrich. Ferrous sulfate heptahydrate was provided by Merck. Sodium hydroxide, sodium chloride, ammonium acetate, hydrochloric acid, sodium bicarbonate, and sodium carbonate were obtained from J.T. Baker. All aqueous solutions employed to the experiments were prepared from deoxygenated and deionized water. The deionized water (18 MΩ/cm, Millipore) was deoxygenated by boiling for 30 min and then purging with nitrogen gas.

2.2. Removal kinetic of TCE by ZVI and Fe^{2+} in the presence of ligand

ZVI particles were pretreated with a HCl washing process to remove the passive film followed by soaking with 0.1 M HCl, then washed with deoxygenated DI water and dried at 70 °C overnight in the anoxic glovebox (Coy Lab Products, Inc.) under a H_2/N_2 atmosphere (95% N_2 and 5% H_2). TCE saturated stock solution was prepared by dissolving excess TCE in deoxygenated DI water. Three organic ligands, FA (pK_a = 3.75), OA (pK_{a1} = 1.25 and pK_{a2} = 4.27) and CA (pK_{a1} = 3.13, pK_{a2} = 4.76 and pK_{a3} = 6.40), were selected to investigate the enhancement on the reactivity of ZVI.

All preparations were performed in the glovebox. Batch experiments were performed in 110 mL anaerobic septum-sealed vials in triplicates. Each vial contains 50 mL of reactants and reagents including TCE stock solution, a ligand of interest, and acid-pretreated ZVI. The final ZVI dosage was 20 g/L and TCE initial concentration was 4.57 μM. Blank sets were run with the same conditions but in the absence of ZVI. HCl was applied as an inorganic ligand that could further compare to organic ligands. The effect of Fe^{2+}-ligand complexes on the removal kinetic of TCE was also investigated in this study. Fe^{2+} was applied with a concentration of 40 mM, which was higher than it released from the HCl system after 48 h. Fe^{2+} was mixed with carboxylic ligands and TCE stock solution under a same condition mentioned above. Reactors were mixed on an orbital shaker with 100 rpm at room temperature.

2.3. Characteristics of ZVI

The surface morphologies of ZVI were analyzed using a scanning electron microscope (SEM, JOEL JSM-7600F). A diluted ZVI sample was dropped on an acid-washed silicon wafer and heated at 120–150 °C for 15 min in an anaerobic condition. The atomic and molecular structures of the crystals of ZVI were determined using X-ray diffraction (XRD) (13A1 beamline of National Synchrotron Radiation Research Center (NSRRC), Taiwan). ZVI samples were prepared inside the glove box and sealed with plastic bags with original solutions. XRD scan range of 10–60° 2θ were acquired for iron and iron oxides with a scan speed of 2° min^{-1}.

Fe dissolution processes were calculated via the measurement of Fe^{2+}/Fe complex concentrations released from ZVI with time. Fe^{2+} and Fe complex concentrations were measured colorimetrically using the ferrozine method (Viollier et al., 2000). A ferrozine agent (10 mM) was prepared in an ammonium acetate solution of 100 mM. 1 mL of 0.22 μm-filtered sample (non-pyrogenic, Minisart) or standard was mixed to 100 μL of ferrozine agent. The absorbance was measured at the maximal absorption of Fe^{2+}-ferrozine complex of 562 nm.

2.4. Analysis of TCE

TCE was quantified using gas chromatography with a micro-electron capture detector (GC-μECD, Agilent 6890) equipped with a HP-5 column (30 m × 0.32 mm, 0.25 μm film). The injector and detector temperatures were 200 °C and 280 °C, respectively. The flow rate of column carrier gas was 1.0 mL/min. The oven temperature of 110 °C was held for 4.5 min. TCE concentrations in headspace of reaction bottles were monitored with time as our previous study (Su et al., 2013). As the adsorption of halogenated hydrocarbons on the Fe surface occurred in reactions (Shih et al., 2011b; Shih and Tai, 2010; Tso and Shih, 2015), Fe particles were separated from liquid phases using a magnet at the end of reactions. The Fe particles around 1 g were dried and extracted with 10 mL hexane on a vortex mixer for 30 min about three times at room temperature until there was no TCE residue in the extract. TCE concentration in the combined extract was quantified using GC-μECD as above. The anion concentrations in the solutions were monitored using ion chromatography (IC) (Metrohm, Switzerland) after filtering through a 0.22 μm filter.