Mechanism insights into enhanced trichloroethylene removal using xanthan gum-modified microscale zero-valent iron particles

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ABSTRACT

This report focuses on the enhancement in trichloroethylene (TCE) removal from contaminated groundwater using xanthan gum (XG)-modified, microscale, zero-valent iron (mZVI). Compared with bare mZVI, XG-coated mZVI increased the TCE removal efficiency by 30.37% over a 480-h experimental period. Because the TCE removal is attributed to both sorption and reduction processes, the contributions from sorption and reduction were separately investigated to determine the mechanism of XG on TCE removal using mZVI. The results showed that the TCE sorption capacity of mZVI was lower in the presence of XG, whereas the TCE reduction capacity was significantly increased. The FTIR spectra confirmed that XG, which is rich in hydrophilic functional groups, was adsorbed onto the iron surface through intermolecular hydrogen bonds, which competitively repelled the sorption and mass transfer of TCE toward reactive sites. The variations in the pH, Eh, and Fe^{2+} concentration as functions of the reaction time were recorded and indicated that XG buffered the solution pH, inhibited surface passivation, and promoted TCE reduction by mZVI. Overall, the XG-modified mZVI was considered to be potentially effective for the in-situ remediation of TCE contaminated groundwater due to its high stability and dechlorination reactivity.

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1. Introduction

Trichloroethylene (TCE) has been extensively used as industrial solvent and detergent for dry cleaning (Junko et al., 2005). Due to its dense non-aqueous phase liquid characteristics, TCE moves downward in the soil by replacing water from the soil pores and eventually reaching groundwater. Since it has relatively high solubility (1100 mg L^{-1} in water), while migrating it leaves behind residual pockets that can dissolve and contribute to its long-term persistence in groundwater (Öztürk et al., 2012). TCE is one of the most frequently detected organic compounds in groundwater (Moran et al., 2006; Ma et al., 2012). Considering its high toxicity, bioaccumulation property, suspected carcinogenicity (Tabrez and Ahmad, 2009) and the current high production capacity of TCE in China (Zhang and Zhao, 2010), it is urgently needed to develop effective controls and treatment methods to remediate TCE contaminated aquifers (Huang and Cheng, 2012).

The use of zero-valent iron (ZVI) as a nontoxic reduction agent has been shown to be a promising technique for the in-situ degradation of chlorinated aliphatic hydrocarbons (CAHs) via abiotic reductive dechlorination (Matheson and Tratnyek, 1994; Orth and Gillham, 1995). Granular ZVI particles were originally used in subsurface permeable reactive barriers (PRB) (Tratnyek et al., 1997). Recently, there has been growing interest in the in-situ remediation of CAHs via the direct injection of finer ZVI particles (microscale and nanoscale) into subsurface water supplies (Cunningham and Reinhard, 2002). The in-situ injection technology can not only effectively remediate contaminant plumes in the source zone, but also substantially reduce the remediation cost and time (Gillham, 2003). In comparison with nanoscale zero-valent iron (nZVI), microscale zero-valent iron (mZVI) particles are less expensive and have a longer lifetime in field-scale remediation projects (Comba et al., 2011). In addition, they pose less risk for human health (Lee et al., 2008). Therefore, mZVI is a more suitable and promising reduction agent for the remediation of contaminated groundwater.

However, the application of mZVI is usually complicated by its sedimentation process prior to and during injection, which is

caused by the high density and size of the particles (Gastone et al., 2014). To overcome this issue, mZVI particles have been modified with surface coatings, such as guar gum (GG) (Tiraferri and Sethi, 2009), xanthan gum (XG) (Vecchia et al., 2009), carboxymethyl cellulose (CMC) (Krol et al., 2013), and polyacrylic acid (PAA) (Hydutsky et al., 2007). Previous studies have shown that surface modifiers enhance the stability of mZVI and nZVI by providing steric repulsion among the particles and increasing the viscosity of the suspension and facilitate particle transport through porous media due to their shear thinning properties (Xue and Sethi, 2012). Nevertheless, in addition to enhancing the suspension stability and mobility of the iron particles, the surface modifiers exert a synergistic influence on the dechlorination reactivity and removal efficiency of the iron particles, which is critical for remediation performance and improvement, but these have received markedly less attention.

Only a limited amount of studies have explored the effects of surface modifiers on the reactivity of mZVI; nevertheless, inconsistent and even contradictory conclusions have often been drawn. He and Zhao (2007) found that nZVI synthesized with CMC as a stabilizer results in 17-fold faster TCE degradation rate than bare nZVI. These researchers attributed the increased reaction rate to the reduced particle size and the enhanced specific surface areas of CMC-stabilized nZVI. However, Velimirovic et al. (2012) showed a contradictory result: the stabilization of mZVI particles using the green polymer GG decreased the reactivity of the iron particles toward CAHs by one- to eight-fold. The authors suggested that the decreased reactivity was attributed to the inhibited diffusion of TCE molecules to the active sites on the mZVI surface by the adsorbed modifiers. In addition, different surface modifiers with varying surface structures and functional groups may impact the dechlorination rate of iron particles through different methods (Shin et al., 2008). However, these previous works only compared the removal kinetic constants and provided speculation for a one-sided potential influence mechanism, but the comprehensive and multi-involved impact pathways have rarely been considered. A systematic mechanistic understanding of how adsorbed modifiers affect the TCE removal rate is greatly needed to aid the design of surface modifiers that enhance mZVI mobility without negatively impacting its reactivity.

The objective of this study was to determine the mechanism through which the surface modifier affects TCE removal by mZVI. Because TCE removal by mZVI is attributed to both adsorption and reduction processes, surface modifiers may impact TCE removal in the following ways: (1) by affecting TCE diffusion toward the reactive sites and adsorption onto the iron surface and (2) by affecting TCE reduction by influencing variations in pH and iron surface passivation. To verify the above hypothesis, the biopolymer XG, which is non-toxic, inexpensive, hydrophilic, stable, and biodegradable, was employed as a surface modifier to stabilize mZVI particles. The measured Fourier transform infrared (FTIR) spectral properties of XG and XG-coated mZVI, the sorption and degradation contributions to TCE removal and the hydrochemical parameters (pH, redox potential (Eh), Fe^{2+}) were interpreted to gain insights on the effects of XG-related site blocking, pH buffering and surface passivation retardation on the observed rate of TCE removal.

2. Materials and methods

2.1. Chemicals and materials

mZVI particles were purchased from the Baidatongkuang Chemical Reagent Company (Hebei, China). The characteristics of the particles are given in Table 1. XG was purchased from Saifu Ltd.

Table 1
Characterization of the tested mZVI.[a]

	C%[b]	N%[b]	H%[b]	BET ($m^2 \ g^{-1}$)[c]	PSD[d] D_{10}, D_{50}, D_{90} (μm)
mZVI	0.65 ± 0.03	0.40 ± 0.02	0.82 ± 0.02	0.136 ± 0.024	27.49 ± 1.25, 88.65 ± 2.34, 217.91 ± 4.32

[a] Values are given as mean ± standard deviation for duplicate measurements.
[b] The bulk concentration of C, H, and N in the iron powder.
[c] BET: specific surface area according to Brunauer–Emmett–Teller (seven point measurement).
[d] Particle size distribution.

(Shanghai, China), and its molecular structure is displayed in Table 2. The chemical TCE (>99%) was supplied by Accustandard Company (USA). n-Hexane (95%, chromatographically pure) was obtained from J.T. Baker Chemical Reagent Company (USA). All of the other chemicals used in this study were of at least reagent grade.

2.2. Preparation of XG solution and mZVI suspension

A Milli-Q water solution of XG was stirred to achieve a final polymer concentration of 3 g L^{-1}. The concentration of 3 g L^{-1} was chosen based on the results of preliminary experiments, which showed that this concentration could efficiently prevent the settling of mZVI without triggering serious emulsification during the TCE analysis. The XG solution was then degassed using an N_2 stream to remove air bubbles and maintained for 12 h at room temperature to facilitate complete dissolution and hydration. To prepare mZVI suspensions using the XG solution, 0.2 g of the mZVI particles was dispersed directly in 20 mL of degassed XG solution in 40-mL amber glass vials, and the suspensions were immediately homogenized via strong shaking.

2.3. FTIR characterization of XG, bare mZVI and XG-coated mZVI

The structural information for the tested samples was determined through FTIR spectroscopy (Spectrum BX, PerkinElmer Inc., USA) in the absorption mode. Three types of samples, namely (1) mZVI, (2) XG, and (3) XG-coated mZVI, were measured in the solid state. The samples were collected and then freeze-dried prior to the

Table 2
Molecular structures of xanthan gum (XG).

Biopolymer	Molecular structure
XG	