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Remediation of trichloroethylene by xanthan gum-coated microscale zero valent iron (XG-mZVI) in groundwater: Effects of geochemical constituents

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HIGHLIGHTS

- TCE removal by XG-mZVI was attributed to adsorption and chemical reduction.
- The effects of organic and inorganic geochemical constituents were investigated.
- In the co-presence of geochemical constituents, TCE adsorption was rarely affected.
- The presence of HA favored TCE reduction by XG-mZVI.
- TCE reduction was curbed in Ca/Mg-HCO_3-type water.

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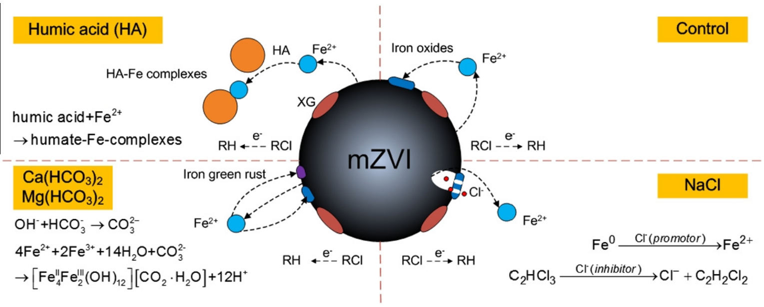
GRAPHICAL ABSTRACT



ABSTRACT

Xanthan gum-coated microscale zero valent iron (XG-mZVI) is potentially an inexpensive and effective material to promote the degradation of environmental contaminants. The effects of geochemical constituents (humic acid (HA), Ca^{2+}/Mg^{2+}-HCO_3^-, Na^+-Cl^-) on trichloroethylene (TCE) removal using XG-mZVI were investigated using batch experiments to evaluate the potential performance of XG-mZVI in field treatments. TCE was removed from groundwater by adsorption and chemical reduction. In the co-presence of geochemical constituents, TCE adsorption was not significantly impacted, while its reduction rate was increased by the presence of HA (5–20 mg L^{-1}), inhibited with increasing $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ concentrations (0.4–2 mM) and unaffected by NaCl in the range of 10–100 mM. The promotional effect of HA on TCE reduction was primarily due to the Fe-humate complexes in solution that delayed the formation of passivated precipitates. However, the presence of $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ exerted an opposite effect on TCE reduction by facilitating the formation of passivated precipitates, such as green iron rust. These findings provide insight into the impact mechanism of XG-mZVI reactivity by organic and inorganic geochemical constituents with particular implications for the XG-mZVI degradation of TCE in real groundwater.

1. Introduction

Due to its extensive use as an industrial solvent and detergent for dry cleaning in the past several decades, subsurface contamination associated with trichloroethylene (TCE) has been widely

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reported [1,2]. Because of its toxicity, bioaccumulation and suspected carcinogenicity [3], there is an urgent need to develop effective control and treatment methods to remediate TCE-contaminated aquifers [4].

In recent years, microscale zero-valent iron (mZVI) particles, which are less expensive, have a longer useful lifetime and pose less risk to human health [5], are considered a suitable and promising reduction agent to remediate chlorinated aliphatic hydrocarbons (CAHs) contaminated groundwater. To enhance its mobility and stability, mZVI particles have usually been modified with surface coatings, such as guar gum (GG) [6], xanthan gum (XG) [7], chitosan [8], and carboxymethylcellulose (CMC) [9]. To evaluate and improve its remediation performance, the effects of geochemical constituents on the modified-mZVI reactivity require significant study. Previous studies have shown that the reactivity and reaction mechanism in real groundwater treatment were significantly different from results involving synthetic contaminant solutions, due to various geochemical constituents in real environmental water samples [10,11]. Additionally, the complex interactions among mZVI particles, target contaminants and geochemical constituents in the presence or absence of surface modifiers are also dramatically different. Thus, the design and implementation of modified-mZVI-based in situ remediation should be improved. However, with bare ZVI particles usually being selected for testing as reducing agents, the reactivity of modified-mZVI under different geochemical conditions has been rarely explored.

Although the effects of groundwater geochemical constituents on the removal of organic contaminants by bare iron particles have been investigated in several studies, most explored the influences on iron reactivity only by comparing removal kinetic constants and providing speculative explanations for the net effects. As a result, conflicting results have been reported by different investigators. Considering natural organic matter (NOM) as an example, Hwang and Shin [12] found a negative effect of humic acid (HA) on nZVI reactivity towards nitrate and attributed it to the competitive adsorption, whereas Wang et al. [13] suggested that NOM promoted ZVI reactivity through being involved into complexations with ferrous ions to form soluble Fe-humate complexes and suppressing iron precipitation in ZVI systems. In addition, Liu et al. [14] reported that two different contaminants Cr(VI) and As(V) were observed to be subject to different effects induced by co-existing HA, which originated from their distinct removal mechanisms by ZVI. Therefore, to fully and clearly understand the effects of geochemical constituents on modified-mZVI reactivity, a study should address the involved removal mechanism, rather than merely focusing on removal kinetics. In addition, no previous study has explored the varied mZVI reactivity in groundwater of different salinities.

In this study, the objective was to determine the mechanism by which the geochemical constituents affected TCE removal by modified-mZVI. In ZVI treatment systems, the removal mechanisms of TCE are believed to involve instantaneous adsorption of TCE on ZVI surface and TCE chemical reduction. As a result, geochemical constituents might influence TCE removal in the following ways: (1) by affecting TCE diffusion towards the reactive sites and adsorption onto iron surfaces; and (2) by affecting TCE reduction through influencing iron surface passivation and electron transfer. To verify the above hypothesis, one biopolymer (XG) that is non-toxic, inexpensive, hydrophilic, stable, and biodegradable, was employed as a surface modifier to stabilize the mZVI particles. Organic (HA) and inorganic (Ca^{2+}/Mg^{2+}-HCO_3^- and Na^+-Cl^-) components were employed as model geochemical constituents to explore their effects on TCE removal reactivity by XG-mZVI particles.

2. Materials and methods

2.1. Chemicals

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. (Shanghai, China). Its molecular structure is displayed in Supplementary data, Table S1. 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 other chemicals used in the study were of at least reagent grade.

2.2. Batch experiments

The effects of geochemical constituents were investigated in this study. Batch experiments were performed in 40-mL amber-colored glass vials capped with Teflon-lined cap. Each vial was filled with 0.06 g XG, 0.2 g mZVI particles and 20 mL degassed Milli-Q water/synthetic solutes to obtain 10 g L^{-1} XG-mZVI suspensions. Suspensions were immediately homogenized by being strongly shaken. Experiments were initiated by injection of 100 μL TCE stock solution (2 g L^{-1} in methanol). Various concentrations of HA ranging from 5 to 20 mg L^{-1} as dissolved organic carbon (DOC) were used to investigate the effects of NOM on the system [15]. Ca^{2+}/Mg^{2+}-HCO_3^--type groundwater with low salinity and Na^+-Cl^--type groundwater with high salinity were used to represent major inorganic geochemical constituents in aquifers.

The Ca^{2+}-HCO_3^--type groundwater was prepared by using $CaCl_2$ and $NaHCO_3$ dissolved in Milli-Q water. In the synthetic water, the $[HCO_3^-]/[Ca^{2+}]$ molar ratio was kept at 2 and was labeled as $Ca(HCO_3)_2$ for simplicity in the following sections. Ca^{2+} concentrations were 0.4, 1.0 and 2.0 mM, corresponding to soft, moderately hard, and hard waters, respectively [16]. Correspondingly, HCO_3^- concentrations were set as 0.8, 2.0, 4.0 mM in each set. The Mg^{2+}-HCO_3^--type groundwater was prepared in the same way with Ca^{2+}-HCO_3^--type groundwater by using $MgCl_2$ and $NaHCO_3$ dissolved in Milli-Q water. For Na^+-Cl^--type groundwater, NaCl concentrations were varied over the range of 10–100 mM. No pH adjustment was made during the experiments.

Each vial was incubated near 12 °C while stirring on a rotary shaker at 120 rpm. Blank experiments without mZVI were conducted in XG solution and in Milli-Q water according to the same procedures. Three replicates were done for each experimental setup. The concentrations of TCE in aqueous and solid phases were

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.