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Investigating the efficiency of microscale zero valent iron-based in situ reactive zone (mZVI-IRZ) for TCE removal in fresh and saline groundwater

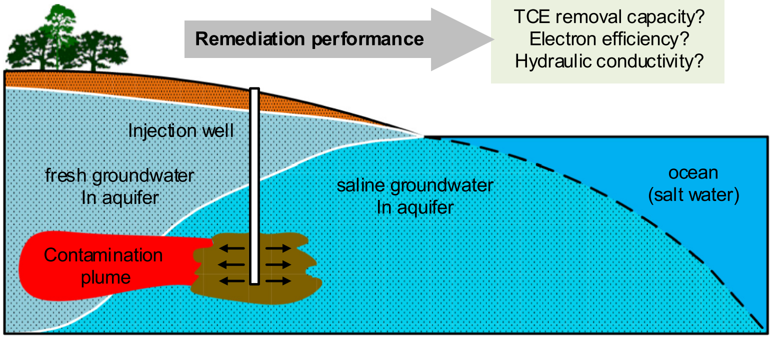
Jia Xin [a,*], Fenglin Tang [a], Jing Yan [b], Chenghong La [a], Xilai Zheng [a], Wei Liu [c,*]

[a] *Key Lab of Marine Environmental Science and Ecology, Ministry of Education, Shandong Provincial Key Laboratory of Marine Environment and Geological Engineering, College of Environmental Science and Engineering, Ocean University of China, Qingdao 266100, China*
[b] *North China Sea Maritime Engineering Prospecting Institute of State Oceanic Administration, Qingdao 266033, China*
[c] *School of Environmental Science and Engineering, Shandong University, Jinan 250100, China*

HIGHLIGHTS

- The remediation performance of mZVI in three media was investigated and compared.
- mZVI had the best TCE removal capacity but the worst EE in saline groundwater.
- The column containing saline groundwater experienced the greatest porosity loss.
- Both gas and precipitates could account for the porosity loss.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, long-term column experiments were conducted in three media (Milli-Q water, fresh groundwater and saline groundwater) to evaluate the trichloroethylene (TCE) removal performance, electron efficiency (EE), and permeability loss of a microscale zero valent iron-based in situ reactive zone (mZVI-IRZ) under different field conditions. A potential scenario of in situ contamination plume remediation was simulated by adding a TCE-containing influent to columns filled with mixed mZVI particles and silica sand at a flow rate of 4 mL h^{-1} for 6 months. Results showed that, over the course of 100 pore volumes (PV) for 6 months, mZVI displayed the lowest TCE breakthrough rate (0.0026 PV^{-1}) and highest TCE removal capacity (43.72 mg) but the poorest EE value (25–40%) in saline groundwater. Mineral characterization (SEM, XRD), ion concentration analysis, and geochemical modeling corroborated that different dominant solid precipitates (magnetite, siderite, dolomite/magnetite) were identified inside the three columns. The column containing saline groundwater experienced the greatest porosity loss, approximately 30.23 mL over the course of 100 PVs. This study illustrates that, to improve designs of mZVI-IRZs, EE as well as hydraulic conductivity should be taken into consideration for predictive evaluations.

1. Introduction

Nowadays, both inland and coastal land has been exploited extensively for agricultural, industrial, and urban use (Chatton et al., 2016;

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* Corresponding authors.
E-mail addresses: xinj15@ouc.edu.cn (J. Xin), wliu@sdu.edu.cn (W. Liu).

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Tian et al., 2016), with the uncontrolled industrial discharge resulting in the occurrence of groundwater contamination (Masciopinto, 2013; Zhou et al., 2009). Therefore, to screen the best available groundwater remediation methods for both inland and coastal industrial sites, the remediation efficiency and long-term remediation performance in engineering practice under different field conditions must be pre-evaluated.

Zero valent iron-based in situ reactive zone (ZVI-IRZ) formed by directly injecting finer (microscale and nanoscale) particles into subsurface water is a cost-effective and efficient solution for a number of complex and challenging groundwater remediation problems (Fagerlund et al., 2012; Qiu et al., 2013; Su et al. 2012b). In comparison with nanoscale particle, microscale zero valent iron (mZVI) particle displays better longevity, lower health risks and lower cost, making it a more suitable reduction agent for a ZVI-IRZ system (Comba et al., 2011; Lee et al., 2008). Different corrosion and fouling behaviors of ZVI as well as depassivation strategies in natural freshwater and seawater were previously investigated by researchers in the fields of cooling water system functions (Huttunen-Saarivirta et al., 2018), elemental cycling (Gunnars et al., 2002), or contaminant removal (Liu et al., 2013a). Our previous batch study presented the first report about the distinct mechanisms of surface passivation layer formation that mZVI may undergo when in contact with fresh groundwater and saline groundwater (Xin et al., 2016). After that, long-term remediation performance concerns motivate us to further determine the reactivity loss and hydraulic conductivity loss of an mZVI-based in situ reactive zone (mZVI-IRZ) in both fresh and saline groundwater. This has been previously discussed in some studies, but obtained controversial results, which would restrain this technology from being widely accepted.

Although long-term performance of mZVI-IRZ system has rarely been investigated, researches on the long-term performance of iron-based permeable reactive barrier (PRB) systems have been conducted before. For instance, Klausen et al. (2003) found the trichloroethylene (TCE) reaction rate constant declined exponentially over three years and Liu and Lowry (2006) also showed a first order decrease in the Fe^0 corrosion reactivity over 200 days. Based on these cases, the reaction rate constant k, representing the speed of Fe^0-based reactions, has attracted much research interest and been considered as the dominant indicator to evaluate the efficiency of a Fe^0-based system. However, usually in addition to the reaction between iron and target contaminants, reactions between iron and non-target oxidants (such as O_2, H_2O, NO_3^-, etc.) would occur simultaneously and affect the contaminant removal efficiency in the following different ways: 1) if the produced Fe(II) or H_2 could not be efficiently used as secondary electron donor, reactions between iron and non-target oxidants would divert the direction of electron transfer, resulting in unwanted extra chemical consumption of Fe^0 materials, and decreasing the contaminant removal efficiency (Noubactep, 2009); 2) if the released Fe(II) or H_2 from all iron corrosion processes could serve as secondary electron donors for target contaminant reduction, the target contaminant removal efficiency will be affected by co-existing oxidants in a less negative or even positive way (Noubactep, 2009); 3) if reduction is not the only mechanism for contaminant removal, the reactions between iron and non-target oxidants would promote the formation of iron hydroxide, which would simultaneously negatively and positively affect the decontamination efficiency by accelerating surface passivation and facilitating co-precipitation/adsorption respectively (Furukawa et al., 2002; Gheju and Balcu, 2011; Noubactep, 2011). Recently, Liu et al. (2013b) proposed electron efficiency (EE) as the ratio of electrons that could be transferred to the target contaminants through direct (iron as the reducing agent) or indirect (H_2 as the reducing agent) ways. Although the EE factor was based on several simplifications and could not accurately reflect the complicated effects of co-exiting oxidants on contaminant removal efficiency, it helps us to take a step forward in this field. Therefore, a more systematic evaluation of remediation performance should include both reaction rate and EE, and more efforts should be made to deepen the understanding of EE under different hydrochemical conditions.

In addition, besides the reactivity loss, permeability loss caused by geochemical reactions can also negatively impact the long-term performance of an iron-based system, possibly leading to failure (Ghauch, 2015; Noubactep, 2016; Wanner et al., 2012). Domga et al. (2015) proposed several main causes of clogging of field Fe^0 filters (e.g. Fe^0 PRBs): (i) precipitation of foreign species (e.g. $CaCO_3$), (ii) precipitation of iron species (e.g. FeOOH, Fe_2O_3, Fe_3O_4, green rust), (iii) accumulation of gas (e.g. H_2, N_2). When gas production and mineral precipitation are both considered, hydraulic conductivity reduction is, in some cases, mostly attributed to gas formation (Henderson and Demond, 2011), while, in other cases, it is mostly attributed to mineral precipitation (Bartzas and Komnitsas, 2010; Huang and Zhang, 2005; Westerhoff and James, 2003). This mismatch could be mostly attributable to the possible differences in the extent of solids and gas formation due to the dissimilar conditions (e.g. flow rate and chemical composition of groundwater, oxic/anoxic conditions) of the PRB systems considered in the different studies (Moraci et al., 2016). Therefore, further understanding of the potential for hydraulic conductivity loss and possible causes in fresh groundwater and saline groundwater could contribute to more efficient designs and more effective management of iron-based systems.

In this study, TCE was used as the model contaminant to assess the long-term performance of an mZVI-IRZ groundwater remediation system in fresh groundwater and saline groundwater. The specific research objectives were to (i) quantify the TCE removal rates and capacities of mZVI particles under different groundwater conditions (Milli-Q water, fresh groundwater, and saline groundwater), (ii) explore H_2 evolution and its effect on EE value, and (iii) examine the reduction of permeability under different groundwater conditions.

2. Materials and methods

2.1. Materials

The column was filled with a homogenous mixture of sand/mZVI ($5\%W_{Fe}/W_{Sand}$). The mZVI used in this study was carbonyl iron powder (certified by BASF as >97.9% Fe) obtained from BASF Chemistry Co., Ltd. (Germany). The iron particles were approximately 7 μm in diameter with a Brunauer–Emmet–Teller (BET) surface area of 0.1 m^2/g. The quartz sand (0.5–1.0 mm) was obtained from Wanchuan Company (China). Prior to use, the quartz sand was washed with 1 M HCl for 24 h, then rinsed to neutral with deionized water, and finally air-dried. The materials were prepared the same day that the column experiments were initiated.

2.2. Column experimental design

To evaluate their distinct TCE removal performance and system porosity changes, three columns (C1, C2, C3) were filled with barrier material and fed with different solutions (Milli-Q water, fresh groundwater, and saline groundwater) spiked with 3 mg/L of TCE. The components of the three influent solutions are provided in Table 1.

Fig. 1 illustrates the setup of the column experiments. The solution was fed into up-flow PVC columns at a flow rate of 4 mL h^{-1} (Lai and Lo, 2008). Columns (22 cm in length and 5.0 cm in diameter) were packed with barrier material inside an anaerobic chamber, resulting in a porosity of 0.42. Experiments were conducted at 25 ± 2 °C over a period of about 6 months. Groundwater samples 3–4 mL were collected from the outlet sampling port every 5–15 PVs for pH, oxidation

Table 1
Composition of the water samples used in the column experiments.

	NaCl (mM)	$MgSO_4$ (mM)	$CaCl_2$ (mM)	$NaHCO_3$ (mM)
Milli-Q water	0	0	0	0
Fresh groundwater	1	0.5	1	0.5
Saline groundwater	500	50	10	2