Electrokinetic-enhanced permanganate delivery and remediation of contaminated low permeability porous media

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ABSTRACT

Back diffusion of contaminants from low permeability strata has inhibited site remediation and closure due to an inability to deliver remediants into these strata. This study demonstrates the potential of electrokinetics (EK) to significantly reduce back diffusion of chlorinated compounds from low permeability porous media. Experiments were conducted in a two-dimensional sandbox packed with vertical layers of coarse sand and silt contaminated with aqueous trichloroethene (TCE). Three experiments, each approximately 41 days in duration, compared EK-enhanced in situ chemical oxidation (EK-ISCO) to EK or ISCO alone. EK-ISCO successfully delivered the oxidant (permanganate, PM) throughout the silt cross-section while ISCO without EK resulted only in PM delivery to the edges of the silt layer fringes. EK-ISCO resulted in a 4.4-fold reduction in TCE concentrations in the coarse sand compared to a 3.5-fold reduction from ISCO alone. EK-ISCO with a 25 mA current was found to be more effective than with 300 mA current. Overall, this study suggests that electrokinetics coupled with an appropriate in situ remediation technique, such as ISCO, can enhance remediation of lower permeability strata and limit the extent of contaminant back diffusion.

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1. Introduction

Contaminant mass sequestered in low permeability zones (e.g., silt, clay) has recently been identified as an issue limiting site closure (Seyedabbasi et al., 2012). These zones can store significant contaminant mass, and this mass can diffuse into adjacent permeable zones (termed 'back diffusion'), acting as a long term source of contamination (Ball et al., 1997; Chapman and Parker, 2005; Liu and Ball, 2002; Parker et al., 2008; Sale et al., 2007; Seyedabbasi et al., 2012). Remediating both high and low permeability zones is therefore recognized as necessary to prevent contaminant concentration rebound at sites and ensure compliance with regulatory standards (Sale et al., 2013).

A range of technologies have been developed to target contaminant mass in permeable zones, including injection of oxidants (e.g., permanganate) (Baciocchi et al., 2014; Siegrist et al., 2011). Use of permanganate (PM) as an in-situ chemical oxidation (ISCO) remediation technology has garnered significant interest due to its high oxidation-reduction potential (+1.7 V), stability in aqueous solution, reactivity over a wide range of pH (3.5–12), ability to work without an activator, and production of non-toxic by-products after reaction with chlorinated solvents (Kao et al., 2008; Petri et al., 2011; Siegrist et al., 2011; Waldemer and Tratnyek, 2005). Although oxidants hold significant promise successful delivery of oxidants (or any remediant) into low permeability zones or uniformly throughout heterogeneous zones, is an unresolved challenge (Sale et al., 2013; Yeung, 2011).

This challenge was clearly shown in a series of 2D laboratory experiments by Sale et al. (2013). In this study, ISCO was applied to tanks characterized by alternating 5 cm vertical strips of coarse sand (K = 200 m/d) and silt (K = 0.2 m/d) flooded with aqueous TCE (1300 mg/L) for 52 d (17 pore volumes, PV). PM (2000 mg/L) was flooded through the permeable zones for 27 d (9 PV) and TCE concentrations were measured at the tank effluent for the

following 82 d (27 PV). During the PM injection period, TCE was non-detect at the outlet due to destruction of TCE diffusing out of the silt by PM in the permeable zones. However, TCE concentrations rebounded as soon as PM injection stopped; this occurred because back-diffusion continued while PM was swept out of the system by continuing groundwater flow. At the end of the post-PM treatment period the final TCE concentration was reduced by 3.1 orders of magnitude from the initial concentration, showing some improvements on the 2.6-fold reduction observed in the no-treatment control. PM only penetrated a maximum of 1.3 cm into the edges of the silt layers, underscoring that remediation of the silt itself was ineffective. Consistent with many field and modelling studies (Ball et al., 1997; Chapman and Parker, 2005; Gerhard et al., 2014; Liu and Ball, 2002; Parker et al., 2008; Seyedabbasi et al., 2012), this study suggested that remediants must be effectively delivered into contaminated low permeability zones in order for remediation efforts to ultimately be successful.

Numerous studies are exploring how to achieve this goal. For example, xanthan and sodium hexametaphosphate added to PM was shown to penetrate into a low permeability soil embedded within a transmissive sand layer (Chokejaroenrat et al., 2014). Electrokinetics (EK) is another promising avenue for increasing the effectiveness of remediant (nano-scale zero valent iron, permanganate, persulfate) delivery into low permeability soils (Chowdhury et al., 2012; Hodges et al., 2013; Reynolds et al., 2008; Roach and Reddy, 2006; Robertson, 2009). EK involves the application of a low voltage direct current (DC) across two or more electrodes (positive/anode and negative/cathode) (Acar and Alshawabkeh, 1993). Electromigration (EM), an EK-migration mechanism, results in the transport of ionic species in the bulk solution. For negative ions (e.g., PM) they migrate from cathode to anode. Since EM is independent of intrinsic permeability, EK has significant potential for delivering ionic remediants into low permeability zones (Hodges et al., 2013; Reynolds et al., 2008; Robertson, 2009).

EM-induced migration of PM has been examined in a number of laboratory studies (Cang et al., 2013; Hodges et al., 2013; Reynolds et al., 2008; Roach and Reddy, 2006; Thepsithar and Roberts, 2006). Overall these studies confirmed that PM penetration into low permeability zones could be enhanced with EK. With the exception of two, these studies were conducted in the absence of contaminants. Cang et al. (2013) reported that PM degraded 52% of pyrene after 336 h of EK+PM (9 g/L) application. Thepsithar and Roberts (2006) reported 91% of phenol was removed during 120 h of EK+PM (9 g/L) compared to 64% in the control (EK only) experiment suggesting that phenol removal was primarily due to electroosmotic sweeping (i.e., bulk fluid movement) and not from oxidation. These two studies suggest that PM penetrated into low permeability zones due to EK application, but the extent of PM penetration was small therefore limiting contaminant destruction. Sale and McWhorter (2001) suggests that removing most of the contaminant mass in low permeability zones is required to achieve remedial objectives. No studies have examined EK-enhanced oxidation of chlorinated solvents and none have quantified the impact on solvent concentration rebound in permeable zones, which ultimately dictates the degree of success of the treatment.

The goals of this work are to assess the ability of EK to enhance PM migration into TCE-contaminated silt layers and to quantify the extent to which this reduced TCE back diffusion to the adjacent coarse layers. This was achieved by conducting a suite of experiments in a heterogeneously packed 2D experimental apparatus contaminated with aqueous TCE. Experiments conducted included a hydraulic flushing experiment to quantify back diffusion under ambient conditions (i.e., no remediation), PM experiment in the absence of EK to assess the extent of back diffusion when TCE contamination in the silt layers is not specifically targeted, and an EK-enhanced PM experiment. This suite of experiments is further supported by six additional experiments as discussed in the supplementary information section. Although TCE mass destruction in the silt could not be directly quantified, extensive quantification of TCE in the coarse sand as well as image analysis examining PM penetration of the silt is included. This study represents a major step forward in our understanding of the ability for EK-ISCO to limit back diffusion from low permeability zones and provides valuable information for pilot field trials as the next step for this innovative remediation approach.

2. Materials and Methods

2.1. Experimental setup

All experiments were conducted in a custom built 2D sandbox (working area of 50 cm × 35.5 cm × 1.75 cm) made of aluminum with a 1.2 cm thick front glass panel (Fig. 1a). The metal back plate was covered with chemical resistant Viton glue (Pelseal® 2078: Zero-VOC, Pelseal Technologies, LLC, Bensalem, PA, USA) to avoid current short circuiting. Nine sampling ports with luer lock valves were installed on the back plate to collect water samples from the coarse sand (Fig. 1a–b). In addition, the sandbox contained one inlet and one effluent port arranged so that advective flow was vertically upwards (Fig. 1, a–b).

The sandbox was carefully packed (in 1 cm, individually compacted lifts) with coarse sand (F32, Barco Silica sand, $d_{50} = 0.475$ mm, K = 42 m/day) and fine silt (Sil-Co-Sil 106, US Silica, $d_{50} = 0.045$ mm, K = 0.2 m/day). The heterogeneity pattern consisted of alternate vertical layers of the sand (27.5 cm long x 6.5 cm wide, porosity = 0.29, bulk density = 1890 kg/m³) and the silt (27.5 cm long x 8 cm wide, porosity = 0.36, bulk density = 1690 kg/m³) (Fig. 1a–b). The left and right silt layers are referred to as Silt-1 and Silt-2 hereafter, and the three vertical coarse sand channels are referred to as Channel 1, Channel 2, and Channel 3 from left to right (Fig. 1a–b). The setup was conceptually similar to that used by Sale et al. (2013). Sampling ports P1, P4 and P7 were located in Channel 1, P2, P5, P8 in Channel 2, and P3, P6, P9 were in Channel 3 (Fig. 1b).

Gradational horizontal layers at the inlet and outlet locations ensured that injected fluid was well distributed across the width and advective flow was primarily vertically upwards. The inlet was located within a horizontal layer of glass beads (2.75 cm layer thickness; 1.5 mm diameter, VWR International, Canada) followed by a coarse sand (layer thickness 2.5 cm) and a fine sand (thickness 2 cm; $d_{50} = 0.12$ mm, K = 4.8 m/day, F110, Barco Silica sand) layers. The outlet was located within a coarse sand horizontal layer (5.5 cm) above a fine sand layer (2 cm; Fig. 1a–b). The upper, open end of the sandbox was sealed with a layer of kaolinite clay (5 cm; PSH, Oakville, Ontario, Canada). Two mixed metal oxide (MMO) anode electrodes (Titanium Electrode Products Inc, Stafford, Texas) were inserted into the left and right coarse sand channels while one MMO cathode electrode was inserted into the middle coarse sand channel (Fig. 1a). The distance between each anode-cathode pair was 14 cm. The electrodes were connected to a DC power supply (BK Precision–1623A, USA). The current and voltage measurements were directly taken from the power supply.

2.2. Experimental methodology

A summary of all nine experiments performed is presented in Tables SI–1. This paper focuses on the three main experiments (Table 1): Hydraulic Flushing (no PM, no EK), ISCO in which 30 g/L PM was injected (no EK), and EK+ISCO in which 25 mA direct current (DC) was applied during PM injection. The Supporting