Integration of emulsified nanoiron injection with the electrokinetic process for remediation of trichloroethylene in saturated soil

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1. Introduction

Trichloroethylene (TCE) is used primarily as a degreasing agent, extractant, as a feedstock for manufacturing organic chemicals, etc. Industrial processes are the main sources of TCE in the environment. TCE has a density higher than water. Therefore, it is a typical dense nonaqueous phase liquid (DNAPL). When it is released into the ground, it can sink through the vadose zone by gravity and capillary forces until it reaches a confining layer, at which point forms a pool. Since chlorinated DNAPLs will gradually dissolve in water, they provide long-term sources of groundwater contamination. It can pose a great threat to soil and groundwater resources.

Like other DNAPL compounds, TCE has such a low solubility in water. Conventional methods (e.g., pump and treat) that only treat the dissolved-phase contamination require long periods of operation to achieve overall levels that are safe for human health and the environment. This would result in a rather costly and time-consuming process. Therefore, the issue of TCE contamination and its treatment or remediation has received much attention from public and private sectors and academia. Among others, Zhang [1] has reported the use of nanoscale zero-valent iron (NZVI; also known as nanoiron) for in situ remediation of TCE-contaminated groundwater. However, studies have shown that aggregation of nanoiron and deposition of nanoiron onto the soil grains limit the delivery of nanoiron in water-saturated porous media [2–5]. Thus, efforts to enhance the delivery and transport of reactive iron nanoparticles in the subsurface have been made by many researchers using various approaches mainly focusing on the stabilization of aqueous-based nanoiron suspensions [4–9]. Encapsulation of nanoiron within an oil-in-water (O/W) emulsion is one of the approaches employed.

Emulsified zero-valent iron (EZVI) is a surfactant-stabilized, biodegradable emulsion that forms droplets consisting of a liquid-oil membrane surrounding zero-valent iron (ZVI) particles in water. Methods and materials for preparing oil-based EZVI and their remediation applications have been reported by several authors [9–17]. Although NZVI can be injected into DNAPL source zone, the iron nanoparticles still require water in the surrounding for the degradation reactions to take place. With respect to subsurface remediation, the technology of injecting EZVI and/or stabilized NZVI was designed for the in situ treatment of DNAPLs and is one of the few methods that can treat the DNAPL source itself rather than dissolved-phase contamination only. Due to the hydrophobicity of the exterior oil membrane of the emulsion particles, the emulsion is miscible with the DNAPL. Therefore, the TCE, for example, dissolves and diffuses into the aqueous droplet containing ZVI that resides within the oil emulsion droplet. The reductive dechlorination occurs. EZVI also overcomes limitations of current...
DNAPL treatment technologies by providing a method that is quick, effective, and cost-competitive. EZVI was originally developed by researchers at NASA and the University of Central Florida to treat chlorinated-solvent contamination at KSC’s Launch Complex 34 [18]. A field demonstration of DNAPL dehalogenation using emulsified zero-valent iron was first reported by Quinn et al. [11]. The field-scale demonstration evaluated the performance of EZVI containing nanoscale zero-valent iron when applied to TCE in the saturated zone. Results of the field demonstration indicate substantial reductions in TCE soil concentrations (>80%) at all but two soil boring locations and significant reductions in TCE groundwater concentrations (e.g., 60–100%) at all depths targeted with EZVI. In the subsequent years, several pilot- and field-scale cleanup projects for various contaminants using EZVI have been reported [12–17]. Recently, a more comprehensive review of field applications of using NZVI and its bimetallic particles for environmental applications in the U.S. was reported by Quinn et al. [19].

Although ENZVI offers several advantages over its counterpart without emulsification, the delivery and transport of the concerned O/W emulsions in the subsurface is another issue and problem to many remediation engineers and researchers. Indeed, the relevant velocity and distance of transport of ENZVI in the subsurface are highly depending on soil texture, hydrogeology, and others. Normally, subsurface remediation using ENZVI and otherwise stabilized NZVI is suitable for sandy porous media, but not for low permeability soils (e.g., clay and silt). As a result of a rather slow groundwater velocity in general, a long remediation period and high remediation cost would be of major concerns to site owners. To overcome these problems, a patented, novel technology for transporting nanomaterials in the porous media has been developed by the primary author of the present study [20,21]. When used for subsurface remediation, this integrated technology basically combines NZVI injection and the electrokinetic (EK) process. Researches in this regard have been reported by Yang group and others [22–28]. During the past few years, researches conducted by Yang group have focused on preparation of NZVI slurries (including the slurry of palladized nanoiron) and their integration with the EK process for degradation of various contaminants (e.g., TCE and nitrate). In addition to NZVI, injection of nanoscale Fe₃O₄ slurry coupled with the EK process for remediation of NO₃⁻ in contaminated soil was reported by Yang group as well [29]. The objectives of this work were two-fold: (1) to prepare O/W emulsified NZVI using NZVI synthesized from two industrial-grade precursors, and (2) to evaluate the performance of combining the injection of thus-prepared ENZVI and the EK process for remediation of TCE-contaminated soil.

2. Experimental

2.1. Materials

Soil studied in this work was collected from a local construction site, where there has been no agricultural activity for years. After collection, soil was first air dried for several days, during which time plant roots and debris were removed. Then the soil was subjected to various characterization methods before it was spiked with TCE to become an artificially contaminated soil.

Grades of chemicals and materials used for various reaction purposes are given as follows: sodium borohydride (industrial grade; 95.5% in purity) from a Taiwanese local company; ferric chloride (industrial grade; 60.5% in purity from a Taiwanese local company); Span 80 (HLB = 4.3) from a Japanese chemical company; Tween 40 (HLB = 15.6) from a Japanese chemical company; soybean oil (food grade; 100% in purity) from Taiwan Sugar Company; and trichloroethylene (TCE; >99.0% in purity) from J.T. Baker. Unless otherwise specified, de-ionized (DI) water was used throughout this work.

Nanoscale zero-valent iron (nanoiron) was synthesized using the chemical reduction method reported by Glavee et al. [30] based on the following reaction equation:

\[
2\text{FeCl}_3 + 6\text{NaBH}_4 + 18\text{H}_2\text{O} \rightarrow 2\text{Fe} + 21\text{H}_2 + 6\text{B(OH)}_3 + 6\text{NaCl}
\]

(1)

Nanoparticles with a pulp density of 87 wt% was then added to the mixture of 10 wt% of soybean oil and 3 wt% of mixed surfactants (Span 80 and Tween 40) for the preparation of emulsified nanoscale zero-valent iron.

2.2. Preparation of the TCE-spiked soil specimen

The procedures for preparing the TCE-contaminated soil are given as follows: (1) weigh about 2 g of TCE and add to de-ionized water to attain a total volume of 500 mL; (2) agitate the mixture using a magnetic stirrer for 12 h, then let the mixture stand for 20 min to have layers of aqueous phase liquid and dense non-aqueous phase liquid; (3) take 150–200 mL of TCE-contaminated aqueous phase liquid from the upper layer of solution, then add it to 800 g of air-dried soil specimen having no stone, debris, tree leaves, and roots; and (4) mix the said TCE-contaminated aqueous phase liquid and soil specimen thoroughly so that the soil specimen would become saturated. The so-prepared TCE-contaminated soil specimen was immediately used for EK tests indicated in Section 2.3.

2.3. Methods

The schematic diagram of the experimental set-up for the EK remediation system used in this work is shown in Fig. 1. Basically, it was composed of a direct-current power supply, an assembly of Pyrex glass EK test compartments (including the anode compartment, soil compartment, and cathode compartment), and two graphite rod electrodes. The dimensions of the soil compartment are 20 cm in length and 5.5 cm in diameter, whereas the dimensions for electrode compartments are 5 cm in length and 7.5 cm in diameter.

The TCE-spiked soil specimen was fed into the soil compartment with compaction and aged for 12 h before it was subjected to EK testing. In all EK tests, both electrode compartments were filled with a simulated groundwater [5], and an electrical potential gradient of 1 V/cm was applied to the EK treatment system by a DC power supply for the entire test period. The treatment efficiency of combining ENZVI injection and EK processes in treating a sandy soil contaminated by TCE (95–119 mg/kg) was evaluated. Experimental conditions employed are given as follows: (1) soil specimens with...
### Table 1
Physicochemical properties of the soil specimen before testing.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil texture</td>
<td>Sand</td>
</tr>
<tr>
<td>Particle size distribution (%)</td>
<td>&lt;2 μm: 0.37</td>
</tr>
<tr>
<td></td>
<td>2–50 μm: 4.41</td>
</tr>
<tr>
<td></td>
<td>50–2000 μm: 92.79</td>
</tr>
<tr>
<td>pH</td>
<td>8.17</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>0.43</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>2.56</td>
</tr>
<tr>
<td>Organic matter content (%)</td>
<td>0.51</td>
</tr>
<tr>
<td>Cation exchange capacity (mequiv/100 g)</td>
<td>3.77</td>
</tr>
<tr>
<td>Total Fe (mg/kg)</td>
<td>78347.5</td>
</tr>
</tbody>
</table>

initial TCE concentrations in the range of 95–119 mg/kg; (2) an electric potential gradient of 1 V/cm; (3) a daily one-time injection of 20 mL ENZVI (i.e., nanoiron dose = 0.75 g/L) into the anode reservoir (in test 1) or cathode reservoir (in test 2); and (4) a treatment time of 10 days. For comparison purposes, an EK-alone test (i.e., test 3) and a control test without application of an electric field and injection of ENZVI (i.e., test 4) were also conducted. During each EK test, the cumulative electroosmotic (EO) flow quantity and residual TCE concentrations in relevant electrode reservoirs were determined. After the test, the soil specimen was sliced into four equal fractions along the longitudinal direction. The residual TCE concentration in each soil fraction was determined. In this work, TCE concentrations were determined by gas chromatography with a μ-ECD (Agilent; 6890(Plus+) series) and a HP-5 separation column of 30 m.

#### 3. Results and discussion

##### 3.1. Characterization of the soil specimen

The soil specimen was determined to be of a sand texture (see Table 1). Its pH, organic matter content, and total iron were 8.17, 0.51%, and 78347.5 mg/kg, respectively. Results of previous EK studies in this lab have shown there is a 3–10% deviation in cumulative quantity of electroosmotic flow depending on the soil texture and test conditions. Generally, a data deviation of less than 5% would be determined for sandy soil with low organic matter content. Thus, no replication EK test was carried out in this work.

##### 3.2. Characterization of the prepared nanoiron and ENZVI

The synthesized nanoparticles contained elemental iron and iron oxide as determined from the pattern of X-ray diffraction (see Fig. 2). Micrographs of FE-SEM (field emission scanning electron microscopy) have shown that a majority of iron nanoparticles were in the size range of 30–50 nm. Iron nanoparticles were also found in aggregate forms (see Fig. 3).

The results of dynamic light scattering indicated that the said soybean oil/surfactant emulsion droplets used in preparing ENZVI had a monodisperse distribution of emulsion droplets having an average size of 3.28 μm. However, the size of ENZVI would vary if different molar ratios of ferric chloride and sodium borohydride were used in preparing nanoiron, while the formulation ratios for preparing ENZVI were kept constant. More specifically, the images of optical microscopy illustrated that the concerned emulsion droplets became bigger if the dose of NZVI formed a greater fraction of ENZVI. Fig. 4 shows the optical microscope image of a few droplets of ENZVI in de-ionized water. Apparently, iron nanoparticles aggregated (due to magnetic attraction and electrostatic attraction) becoming larger particles and appeared at the interface of emulsion droplets and water. Due to the ENZVI specimen was diluted in de-ionized water prior to microscopic examination, the concerned microscope image also showed some “free” or unemulsified iron nanoparticles. Presumably, this is an image artifact. In fact, the concerned ENZVI was an oil-in-water emulsion having a HLB (hydrophile–lipophile balance) number of 8 and good kinetic stability as compared with other formulations tested for preparing ENZVI in this work.

![Fig. 2. X-ray diffraction pattern of the synthesized iron nanoparticles.](image)

![Fig. 3. SEM image of the synthesized iron nanoparticles.](image)

![Fig. 4. Optical microscope image of emulsified nanoscale zero-valent iron droplets in de-ionized water.](image)
3.3. Influence of the injection point of ENZVI on various EK observations and their implications

As indicated above, tests 1 and 2 represented EK coupled with the injection of ENZVI into the anode reservoir and cathode reservoir, respectively. Test 3 was an EK-alone test, whereas test 4 was a control test without application of an electric field and injection of ENZVI.

3.3.1. Variation in reservoir pH

Normally, due to the electrolysis of water in the neighborhood of electrodes in an electrochemical reactor, the final solution pH values would approach about 2 and 12 near the anode and cathode, respectively. There was no exception for tests 1–3 in this study (see Fig. 5). After one day of EK treatment, the reservoir pHs of concern reached about 2 and 12, respectively, and remained close to these values throughout the test period. In test 4, since there was no application of an electric field, the pH values of both electrode reservoirs slightly increased to 7.5. This might be due to the diffusion of OH− from the soil compartment, as the starting pH of the soil was 8.7.

3.3.2. Variation in current density

Fig. 6 shows the variation of current density (i.e., electric current divided by the cross-sectional area) over the course of the test period for tests 1–3. Apparently, it would take 2–3 days for the EK remediation system to reach a stable current density. After day 7, a drop in current density was noted in all tests of interest. This phenomenon was ascribed to electrode polarization, resulting in an increase in electrical resistance and a lower current density. Inevitably, this would cause a slower reaction rate. Further, it was noticed that the magnitude of electric current (and of course the current density) of test 1 was slightly greater than that of test 2. This finding could be explained as follows: when nanoiron in ENZVI was injected into the anode reservoir as in test 1, the strongly acidic and oxidizing environment would cause a rapid corrosion of nanoiron. In contrast, slow corrosion occurred when ENZVI was injected into the cathode reservoir; hence, the magnitude of electric current in test 2 was ascribed to the same reasons given previously.

3.3.3. Variation in cumulative electroosmotic (EO) flow quantity

In this work the direction of EO flow was found to be from the anode end toward the cathode end in all tests. The 10-day cumulative EO flow quantities for tests 1–3 were found to be 219 mL, 189 mL, and 190 mL, respectively (see Fig. 7). To compare with the 6-day treatment performance of TCE by a similar remediation system including the injection of PNI (palladized nanoiron) slurry and the employment of the EK process [27], the 6-day cumulative EO flow quantities in Fig. 7 were determined to be 184 mL, 164 mL, and 150 mL, respectively. It was found that the 6-day cumulative EO flow quantities in the present study were slightly smaller. In addition, both studies found that a greater cumulative EO flow quantity was obtained for the case of injecting NZVI slurry into the anode compartment than that of its counterpart. Perhaps a very high concentration of total iron (78347.5 mg/kg) in native soil was responsible for the lower EO flow. As indicated above, the pH of the cathode reservoir would reach a value of about 12. There also would be a base front moving from the cathode end toward the anode end. Thus, the soil fraction near the cathode end would also have a high pH value, as was observed by its rise from pH 8.17 to about 11.50. A very high total iron content in soil would yield Fe3+ and Fe2+, which would react with OH− forming precipitates of Fe(OH)3 and Fe(OH)2. These precipitates would occupy some extent of the interstitial space among soil particles in the neighborhood, thereby hampering EO flow. Another factor possibly responsible for a low EO flow could be a great affinity between emulsion droplets and TCE adsorbed onto the soil particles. This might further jeopardize the already poor situation of EO flow. Greater EO flow in test 1 as compared with that of test 2 was ascribed to the same reasons given in the discussion of current density.
3.3.4. Analysis of electroosmotic permeability coefficient

Based on cumulative EO flow quantities, the corresponding EO permeability coefficients for tests 1–3 were calculated to be similar in magnitude, namely $1.19 \times 10^{-5}$ cm$^2$/Vs, $1.03 \times 10^{-5}$ cm$^2$/Vs, and $1.04 \times 10^{-5}$ cm$^2$/Vs, respectively. These values are comparable with that reported by other researchers [31,32] for soil with a sand texture, but are an order of magnitude greater than that of other studies (e.g., Ref. [28]). It has also been reported that the practical range of electroosmotic permeability coefficients lies between $1 \times 10^{-9}$ to $1 \times 10^{-5}$ m$^2$/Vs for a large panel of soils from clay to sand [33–35]. Further comparing the results obtained in Ref. [27], their values of EO permeability coefficients were found to be very close to each other based on the 6-day cumulative EO flow quantities for the corresponding tests.

3.3.5. Variation in residual TCE concentrations in electrode reservoirs

Before the discussion on residual TCE concentrations in electrode reservoirs, it is important to know the initial TCE concentration in the soil compartment in each test. They were 95.1 mg/kg, 96.8 mg/kg, 111.2 mg/kg, and 118.6 mg/kg for tests 1–4, respectively.

For the ease of discussion, the right reservoir in test 4 represents the location equivalent to the cathode reservoir in tests 1–3, whereas the left reservoir represents the location equivalent to the anode reservoir. Fig. 8 shows the residual TCE concentrations in the cathode/right reservoir as a function of treatment time for tests 1–4. As shown in Fig. 7, substantial amounts of EO flow were seen in tests 1–3. It would be reasonable to expect that TCE desorbed from the soil matrix would be carried over to the cathode reservoir, as exemplified by the result of test 3 (the EK-alone test). In test 3, a TCE concentration of 15.7 mg/L was observed in the cathode reservoir on day 2. As the treatment time elapsed, more TCE would be transported by EO flow to the cathode reservoir. Due to its high vapor pressure, however, TCE is easily vaporized at ambient temperature, resulting in an irregular pattern of concentration variations. It was noted that the residual TCE concentration of concern was lower in test 2 than in test 1. This is due to the implement of injecting ENZVI into the cathode reservoir, which caused immediate degradation of TCE when they were brought into intimate contact. In the control test, the residual TCE concentration in the right reservoir increased as time elapsed. Overall, it was noticed that during the test period of the practice of ENZVI injection into the either electrode compartment, the residual TCE concentrations in the cathode reservoir were reduced to less than 2 mg/L at the end of 10-day treatment. By comparing the residual TCE concentration in the cathode reservoir as reported in Ref. [27], it was found that the performance of ENZVI was much better than that of nanoscale Pd/Fe bimetals. This finding is in good agreement with the original concept of the employment of injecting oil-based emulsions of nanoiron rather than injecting water-based nanoiron slurry for the remediation of DNAPLs such as TCE.

Similarly, Fig. 9 shows variations in residual TCE concentration in the anode/left reservoir for tests 1–4. It was found that test 4 (i.e., control test) yielded the highest residual TCE concentration in the left reservoir as compared with other tests. In further comparisons between the residual TCE concentrations in the two electrode reservoirs, no significant difference was found. From the result of test 3, only a small amount of TCE was observed in the anode reservoir. This finding might explain why tests 1–3 had a similar variation pattern of TCE concentration over the course of the test period.

In summary, injection of ENZVI into the cathode reservoir would enhance the degradation of TCE therein. On the other hand, injection of ENZVI into the anode reservoir yielded a slightly worse performance. In both cases, however, the residual TCE concentrations in the electrode reservoirs were all higher than Taiwan EPA’s Pollution Control Standard of 0.050 mg/L for TCE in Type II Groundwater. Noting that TCE was only treated for 10 days in this work, a prolonged treatment time would be needed to meet with the regulatory threshold.

3.3.6. Variation in residual TCE concentration in soil compartment

The above experimental results have shown that TCE in the soil compartment is transported by EO flow from the anode end toward the cathode end. This statement was verified by the distribution of residual TCE concentrations in different fractions of the soil specimen removed from the soil compartment after each test (see Fig. 10). In all tests, the residual TCE concentrations in soil fractions near the anode were always the lowest as compared with other soil fractions. The residual TCE concentrations in the soil specimens for tests 1–3 (28.5 mg/kg, 32.5 mg/kg, and 52.2 mg/kg, respectively) were all below Taiwan EPA’s Pollution Control Standard of 60 mg/kg for TCE. In test 4, the residual TCE concentration in soil remained over 110 mg/kg. Further calculations showed that the respective TCE removal efficiencies for soil were 70.1%, 66.4%, 53.0%, and 6.4% for tests 1–4. Further comparing the residual TCE concentration in soil as reported in Ref. [27], it was found
that the performance of ENZVI was inferior to nanoscale Pd/Fe bimetallic. The corresponding TCE removal efficiencies for the latter (with a treatment time of 6 days only) were 92.44%, 70.96%, 71.06%, and 2.09%, respectively. The residual TCE concentrations in the soil specimens were 7.90 mg/kg, 33.49 mg/kg and 22.07 mg/kg, respectively for corresponding tests 1–3. Moreover, in the case of PNI injection, the soil fraction near the anode reservoir contained nearly no residual TCE.

4. Conclusions

In this work nanoscale zero-valent iron (NZVI) was synthesized using industrial-grade precursors. Oil-in-water encapsulated NZVI (i.e., ENZVI) was further prepared using mixed surfactants (Span 80 and Tween 40) and soybean oil. An integrated technology combining the injection of thus-prepared ENZVI and the EK process has been tested for remediation of sand artificially contaminated by TCE for a period of 10 days. The major findings are given as follows:

(1) The chemicals and ingredients used were found to meet the needs of this study.

(2) Electrokinetics was found to be capable of enhancing the transport of oil-in-water encapsulated NZVI in the porous media.

(3) The cathode compartment was determined to be a better injection spot than its counterpart in terms of residual TCE concentration therein. However, a slightly greater TCE removal efficiency in soil was obtained for injecting ENZVI into the anode compartment.

(4) Using a similar integrated remediation system for TCE, ENZVI outperformed palladized nanonion (PNI) slurry in terms of residual TCE concentrations in electrode compartments. However, ENZVI was found to inferior to PNI slurry in removing TCE from soil.

(5) Under the conditions employed in this work, the residual TCE concentration in soil met Taiwan EPA’s Soil Pollution Control Standard of 70 mg/kg for TCE. However, the residual TCE concentrations in both electrode reservoirs were still higher than Taiwan EPA’s Control Standard of 0.050 mg/L for TCE in Type II Groundwater. Further optimization is needed to make this integrated technology viable to put into practice.

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