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A Study of Groundwater Matrix Effects for the Destruction of Trichloroethylene Using Fe/Pd Nanoaggregates

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Abstract

Iron nanoaggregates have been prepared using the sodium borohydride reduction method and post-coated with Pd using aqueous phase electro-deposition. The Fe/Pd nanoaggregates were used to examine dechlorination of trichloroethylene (TCE) with regard to matrix effects using materials representative of a potential zero-valent metal remediation site surrounding the Paducah gaseous diffusion plant in Paducah, KY. A surface-area-normalized first-order rate constant of $1.4 \times 10^{-1} \text{ L m}^{-2} \text{ h}^{-1}$ was obtained for the case of ideal dechlorination of 19.6 mg L^{-1} TCE at room temperature and pH 6.2 using 0.5 g L^{-1} Fe/Pd (0.42 wt % Pd) loading. This value decreases by an order of magnitude to $1.9 \times 10^{-2} \text{ L m}^{-2} \text{ h}^{-1}$ when the reaction is carried out in a realistic background matrix when the pH is high (8.8). For all variables tested, Pd content has the most impact on reaction rates. Circulating batch-column experiments are used to study dechlorination under flow conditions and demonstrate the ability of nonstabilized Fe/Pd nanoaggregates to remove significant amounts of TCE (80–90%) over a broad range of groundwater velocities (12.9–83 ft per day) using moderate metal loadings ($0.23\text{--}0.5 \text{ g L}^{-1}$).

Keywords

Fe/Pd nanoaggregates; TCE; circulated-column; matrix effect; remediation

INTRODUCTION

Trichloroethylene (TCE) is a volatile, halogenated organic compound that was once a widely used degreasing agent. Years of improper disposal have resulted in contamination of ground water throughout the United States, prompting the need for the development of treatment methods to safely remove and/or destroy this suspected carcinogen. Many remediation options are being explored, including steam injection/adsorption, reductive permeable reactive barriers using bulk metals, and chemical oxidation using free radical chemistry [1–3]. Perhaps the most promising method is the direct injection of zero-valent nanoscale metals into contaminated plumes to facilitate the *in situ* electrochemical reduction of TCE to its nonhalogenated form because of the environmentally benign nature of the treatment chemicals involved and their wide applicability with regard to chemical contaminants.

Zero-valent nanosized metals (characteristic length $< 100 \text{ nm}$) have been used to dechlorinate a wide range of chlorinated organics, including TCE, perchloroethylene (PCE), poly-

chlorinated biphenyls (PCBs), and chlorophenols, with minimal intermediate formation [4–8]. This is a key benefit given the often more toxic nature of the intermediates (vinyl chloride for example) of TCE dechlorination. The use of nanoscale iron has increased dechlorination reaction rates by one to two orders of magnitude when compared with bulk materials because it provides a much higher specific surface area and reactivity [4–8]. Typically, the iron nanoparticles are synthesized using modifications of the aqueous phase reduction of metal ions using sodium borohydride presented by Glavee *et al.* [9]. More recent methods include H₂ reduction and carbothermal reduction of supported zero-valent iron [10,11]. Zero-valent iron nanoparticles are capable of reducing TCE to harmless ethane through direct electron transfer using the following overall reaction sequence:



The preferred kinetic model for these systems has been developed for the reaction of the parent compound and suggests a pseudo first-order behavior:

$$C = C_0 e^{-k_{\text{obs}} t} \quad (2)$$

where k_{obs} is the observed pseudo first-order rate constant (h^{-1}), t is the reaction time (h), C is the aqueous phase concentration of TCE (typically mg L^{-1}), and C_0 is the initial concentration of TCE in solution. An in-depth treatment of the pseudo-first order model can be found in the work of Johnson *et al.* [12]. Based on their work, the use of a surface-area-normalized rate constant (k_{SA} , $\text{L m}^{-2} \text{h}^{-1}$) has become the accepted means by which to compare results amongst the various systems examined. For this parameter, the observed reaction rate constant is normalized using the metal surface area loading as follows:

$$k_{\text{SA}} = \frac{k_{\text{obs}}}{A_{\text{BET}} \rho_{\text{M}}} \quad (3)$$

where A_{BET} is the metal surface area ($\text{m}^2 \text{g}^{-1}$) determined using nitrogen adsorption and the Brunauer-Emmett-Teller method and ρ_{M} is the amount of Fe in solution (g L^{-1}) [12]. As a basis for comparison, the value of k_{SA} reported by Johnson *et al.* [12] based on data available from 12 studies of TCE dechlorination by bulk Fe is $(3.9 \pm 3.6) \times 10^{-4} \text{ L m}^{-2} \text{h}^{-1}$ using gram quantities of metal per liter of solution and represents a reaction time on the order of days.

Bimetallic Dechlorination

The rate of dechlorination can be further enhanced through the use of bimetallic particles, which are produced by doping a hydrogenation-promoting catalyst, such as Ni or Pd, onto the surface of the zero-valent iron nanoparticle. The presence of the hydrogenation catalyst is believed to alter the mechanism for dechlorination, promoting a faster hydrogenolysis reaction through the storage of active hydrogen (H^-) [13]. The value of k_{SA} reported by Schrick *et al.* [14] for aqueous-phase TCE dechlorination using Fe/Ni (3.4:1 Fe-to-Ni ratio) particles is $9.8 \times 10^{-2} \text{ L m}^{-2} \text{h}^{-1}$. This is an improvement of almost three orders of magnitude when compared with the rate of bulk Fe^0 , and one order of magnitude compared with most results for nanoscale Fe^0 .

Tee *et al.* [15] have examined the impact of particle composition on aqueous-phase TCE dechlorination using bimetallic nanoparticles. They were able to obtain the complete transformation of TCE (10 mg L^{-1}) to ethane in under 2 h using 2.5 g L^{-1} of metal with bimetallic ratios ranging from 15 to 20 wt % Ni. This corresponds to a first-order rate constant of $3.7 \times 10^{-2} \text{ L m}^{-2} \text{ h}^{-1}$. Studies by Tee *et al.* [15] varying the Ni composition from 0 to 100 wt % found that a maximum rate of dechlorination is achieved at 25 wt % Ni. The decrease in reaction rates as the Ni content is increased beyond this level can be attributed to high levels of Ni with respect to Fe at the particle edges, which hinders the ability of Fe to react with water, a source of hydrogen.

Pd-Coated Fe

Although Ni is effective for TCE dechlorination, its toxic nature makes it less favorable for remediation applications. A better choice is the use of a small Pd doping. Zhang and coworkers [5,8,16–18] have demonstrated the ability of both Fe and Fe/Pd nanoparticle systems to detoxify a wide range of compounds (TCE, PCE, PCBs, etc.) in only a matter of hours, including results for *in situ* remediation. Given the size and longevity of the nanoparticles, they are believed to have the potential to move with a plume, further increasing their effectiveness *in situ*. The current focus of research involving Fe/Pd particles for dechlorination is the use of stabilization either through capping or immobilization to prevent particle agglomeration and enhance particle reactivity [19–22]. In addition, capping is also believed to reduce particle-soil interactions and increase particle mobility within the ground after injection [20–22]. Xu and Bhattacharyya have used polyvinylidene fluoride microfiltration membranes functionalized with (poly)acrylic acid to capture ferrous (Fe^{2+}) ions from solution, which could then be reduced to form 30-nm Fe/Pd nanoaggregates (2 wt % Pd) [19]. The use of these materials for the dechlorination of 2,2'-dichlorobiphenyl to biphenyl resulted in approximately the same first-order rate constant for both batch-soaking and pressure-induced flow, which demonstrates the advantage of open-structured supports to fully utilize particle reactivity. When using starch as a capping stabilizer to prevent particle agglomeration in solution, He and Zhao found that 98% of the TCE in a 25.0 mg L^{-1} solution could be destroyed in less than 1 h using only 0.1 g L^{-1} of bimetallic Fe/Pd nanoparticles [20]. He *et al.* [22] have applied sodium carboxymethylcellulose as a stabilizer and found that 0.1 g L^{-1} of the stabilized nanoparticles (0.1 wt % Pd) could completely dechlorinate 50 mg L^{-1} TCE with a surface-area-normalized rate constant $1.56 \text{ L m}^{-2} \text{ h}^{-1}$. In addition to the order of magnitude increase in the reaction rate, the stabilized particles were more mobile during column elution tests.

Potential Site Application

The Paducah gaseous diffusion plant (PGDP) is an active uranium enrichment facility located ~10 miles west of Paducah, Kentucky, and 3.5 miles south of the Ohio River in the western part of McCracken County (see Figure 1). The plant is on a US Department of Energy (DOE) reservation and is surrounded by the West Kentucky Wildlife Management Area, a TVA power plant, and private properties. Following the discovery of contamination in nearby drinking wells in 1988, the facility was designated as an EPA superfund site. In addition to significant groundwater contamination by Technetium-99, several TCE plumes have migrated from the site north toward the Ohio River. The principal potential impact of the current groundwater contamination on the surface environment would be if contaminated groundwater was pumped to the surface and used for irrigation purposes or other commercial purposes. Such activities are currently prevented by restricting the use of contaminated groundwater. There is the potential, however, for contaminated groundwater to migrate to the surface under normal hydrostatic conditions. Ground-water from the regional groundwater aquifer (RGA) currently migrates to the surface and discharges at seeps in the lower reaches of the Little Bayou Creek. Concentrations of TCE associated with such discharges have been observed to be as high as $400 \text{ }\mu\text{g/L}^{-1}$. However, concentrations are below the TCE MCL of $5 \text{ }\mu\text{g/L}^{-1}$ within a mile

downstream of the seeps as TCE volatilizes. Nonetheless, this location provides at least one potential site in which to test the efficiency of the proposed technology.

As a potential means of treatment, the DOE, in collaboration with the Kentucky Research Consortium for Energy and the Environment (KRCEE), are interested in studying the performance of zero-valent metal nanoparticles in a matrix that is representative of actual field conditions. Therefore, the objectives of this work are: (1) synthesize Fe/Pd nanoaggregates using simple solution-phase techniques; (2) implement the room temperature dechlorination of TCE using batch studies to examine the impact of matrix and particle variability on dechlorination kinetics; and (3) use a circulated batch-column system to study dechlorination of TCE under simulated groundwater flow.

EXPERIMENTAL METHODS

Ferrous chloride, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (crystalline, reagent, Fisher Scientific), and potassium tetrachloropalladate (K_2PdCl_4) (Sigma-Aldrich, 99.99%) were obtained and used as sources of Fe/Pd in the bimetallic nanoparticle synthesis. Sodium borohydride (NaBH_4) (Aldrich, granules, 99.995%) was used as the metal reducing agent. TCE (Aldrich, 99.9%, A.C.S.) was obtained and used in dechlorination studies without further purification. Hexane (Aldrich, 99%, spectrophotometric), and 1,2-dibromoethane (EDB) (Aldrich, 99%) were acquired for use in analytical techniques. All water used in the experiments, unless otherwise specified, was deionized ultra-filtered (DIUF) water (Fisher Scientific). All pH adjustments were made using dilute (0.5 N) sulfuric acid. As part of this study, site-specific RGA aquifer materials were collected from a location identified by Sexton and Nelson as an outcrop of the Regional Gravel Aquifer (see Figure 2) [24]. Ground-water samples were collected from a local well outside of the TCE contaminant plumes from areas surrounding the PGDP and supplied by KRCEE in cooperation with the Kentucky Water Resources Research Institute (KWRRI). Groundwater and media samples were screened to ensure the absence of detectable technetium-99 activity. Two samples were provided and used during this work. Average water quality for the Paducah site based on 10 monitoring wells is shown in Table 1.

Synthesis of Fe/Pd Nanoaggregates

An aqueous 0.1 M FeCl_2 solution was prepared at a pH of 4.5 to prevent oxidation of the dissolved Fe^{2+} . An aqueous 0.5 M NaBH_4 solution was added drop-wise to reduce the ferrous ions to the zero-valent form with mixing at 300 rpm. Excess NaBH_4 was used (2.5 times) to ensure complete reduction because the borohydride will also react with water during the reduction step. The borohydride reaction was carried out under a N_2 atmosphere to prevent oxidation of freshly formed iron. The reduced Fe was allowed to settle before decanting off the excess solution. The remaining slurry was vacuum-filtered using continuous additions of ethanol to wash the aggregates while minimizing oxidation. The moist cake was recovered for Pd deposition by electroplating.

A potassium tetrachloropalladate (K_2PdCl_4) solution was prepared in 100 mL of a 90/10 (v/v) ethanol/water mixture for palladium deposition. The mass of Pd in solution was adjusted to give the desired Pd doping based on wt %. The moist Fe^0 aggregates were added to the Pd solution and mixed 2 h for electroplating to occur. The particles were again vacuum-filtered under ethanol and dried overnight under vacuum.

Scanning Electron Microscopy Analysis

Aggregate size was examined using a Hitachi S900 field emission scanning electron microscopy (SEM) for high magnification imaging. Samples were mounted on aluminum grids with carbon adhesive and coated in Au/Pd before analysis.

Surface Area Measurements by N₂ Sorption

A 1 g sample of nanoaggregates was prepared by out-gassing for 6 h at 120°C under N₂ refluxing. The N₂ adsorption and desorption isotherms at 77 K was then measured using a Micromeritics Tristar 3000 pore volume analyzer. The total surface area was calculated from this data using the Brunauer-Emmett-Teller method. The average pore size was also calculated from this data using the BJH method.

Pd Quantification by Atomic Absorption

The amount of Pd deposited during synthesis was determined using a Varian SpectrAA 220 Fast Sequential atomic absorption (AA) spectrometer equipped with a Fisher Scientific Pd data-coded hollow cathode lamp. A 50 mg sample of nanoaggregates was digested overnight using 20 mL of a 4 M nitric acid solution. Analysis of Pd was performed at a wavelength of 247.6 nm. The instrument was programmed to obtain readings in triplicate for each sample. An acidic (4 M nitric acid) blank was used between samples to avoid carry-over. The detector was calibrated over a range from 5 to 25 ppm Pd, with a linear trend existing over the entire calibration range. The sensitivity of the machine at this wavelength yields a reproducible lower limit of 1 ppm Pd. The upper calibration limit was selected based on the anticipated amount of Pd for a sample. Standards were prepared using the appropriate quantity of a known Pd standard for AA (Fisher) to produce the desired concentrations. Before analysis of digested samples, known samples were first prepared and analyzed to verify the accuracy of the AA machine. A 15 ppm known sample routinely gave errors of less than 5%. Digested samples were split in triplicate, with a 5 ppm Pd-spike added to one sample to verify the analysis by the method of standard addition. Recoveries for spiked samples were greater than 95%.

Batch TCE Dechlorination

For each time interval, a known quantity of Fe/Pd nanoaggregates was first placed in a dry 40 mL EPA-certified glass vial (nominal volume = 42 mL). Typically, a metal loading of 1 g L⁻¹ was used to provide adequate sampling size for the metal because this corresponded to ~40 mg of metal. Next, the vials were filled with 42 mL of DIUF water that had been previously adjusted to the desired pH. This volume was sufficient to guarantee no headspace for organic volatilization. For selected cases, the DIUF water was also de-oxygenated before use through ultra-high purity nitrogen aspiration. Finally, the reactor was spiked with a concentrated TCE solution in methanol and placed in an incubator-style shaker such that mixing occurred in the axial direction. For studies examining the impact of aquifer materials, sediment samples were washed and filtered to remove the silt and sand from the gravel because the corresponding column studies (see below) used only gravel as a packing material to avoid the need for a high-pressure flow system. A quantity of this gravel was then added to the 40 mL vials after the nanoaggregates based on a solid-to-liquid ratio of 500 g L⁻¹. For these experiments, the total liquid volume required to fill the vial was only 36 mL. Identical experiments were also conducted using water samples obtained from around the Paducah Superfund site. The only pretreatment applied pertained to pH adjustment and de-oxygenation when desired. For each set of experiments, a control for TCE loss was prepared without nanoaggregates using the same procedure. In a similar fashion, a background control for Cl⁻ was prepared without TCE.

The vial was removed from the shaker at the desired sampling interval. A 10 mL liquid sample (with nanoaggregates) was immediately removed using a gas-tight syringe and injected into a 20 mL vial containing 10 mL of hexane for TCE extraction. This vial was placed in the shaker for 24 h to allow for complete extraction. An additional 10 mL liquid sample was withdrawn for pH and Cl⁻ measurements and filtered using a filter syringe equipped with a 0.2 μm polypropylene membrane.

Circulating Batch-Column Studies

A circulating batch-column system was constructed to assess the reactivity of particles under flow conditions. A schematic of this system is shown in Figure 3. The column consisted of a 121.92 cm (4 ft) section of clear PVC piping with a 7.62 cm (3 in) inner diameter. The ends were capped with blind flanges that could be removed to allow access to fill the column. The end caps were drilled and fitted with 1/4" Teflon tubing attached to stop-cock valves as access points for liquid flow (see Figure 3). In addition, the column was drilled and fitted with seven ports consisting of the same 1/4" Teflon tubing attached to stop-cock valves. A pump could be attached to the system using any of the 10 Teflon ports. The system was set-up so that flow occurred vertically downward in the axial direction of the column with liquid re-circulated from 106.7 cm (3.5 ft) down the length of the column back to the top flange port (see Figure 3). For the present work, either a Masterflex peristaltic pump or Varian ProStar 220 solvent delivery module was used, allowing for flow rates ranging from 1 to 100 mL min⁻¹. The column was lined with a 120-mesh polypropylene screen to prevent clogging of ports. A nonuniform sampling of RGA aquifer gravel was washed using the same methods employed for batch testing and used to pack the column. The samples were nonuniform in that no control of size and type of rock was used. The liquid volume was reduced from 5.8 to 2.4 L after packing, corresponding to a porosity of ~41%.

Experiments were carried out by first preparing 2.4 L of a 100 ppm TCE solution in DIUF water at pH 6–7. The large concentration of TCE was used to saturate the column with regard to TCE adsorption at the gravel surface. The feed solution was then added to the column and circulated at the desired flow rate for 24 h to stabilize the column. A sample of the circulated feed was collected and saved for organic analysis by extraction. A known quantity of Fe/Pd nanoaggregates was added to the top of the column through removal and resealing of the top flange. At desired sample intervals, 20 mL EPA vials were used to collect liquid samples at various lengths down the column. These samples were then subjected to the same sampling procedures for analysis of organics, pH, and Cl⁻ described above.

Organic Analysis

TCE was extracted with hexane and analyzed by GC/MS using a HP 5890 Series II GC with a Supelco 0.25 mm ID SPB-624 fused silica capillary column and a Series 6150 MS. A linear calibration curve was used over the range 1–40 mg L⁻¹ TCE. The calibration error based on analysis of a known sample was only 3%. Replicate analysis was 6% for this range. A 1 mL sample of the hexane phase was withdrawn using a syringe and placed in a 1 mL auto-sampler vial. A 10 µL spike of a 1002 ppm EDB solution was added to the vial as an internal standard. The vial was capped and mixed before a 1 µL aliquot was withdrawn by syringe and injected for analysis.

pH and Cl⁻ Measurements

Samples to determine pH were analyzed using an Accumet dual-electrode meter and AccuTupH double-junction silver/silver chloride pH electrode. The amount of Cl⁻ in each sample was determined using an Orion Model 9617BN combination ion-selective electrode manually calibrated for a working range of 1–100 mg L⁻¹ Cl⁻ with a standard deviation in mV response from 0.2 to 0.5 mV. Standards were prepared using a 100 ppm Cl⁻ solution (Orion). A 200 µL portion of 5 M sodium nitrate was added to each vial after pH measurements as an ionic strength adjustor. For every third sample analyzed, a standard addition of 5 mg L⁻¹ Cl⁻ was used to verify results. Recoveries were always greater than 90%.

RESULTS AND DISCUSSION

Material Characterization

The results for Pd analysis using AA are shown in Table 2. Differences between the targeted and actual amount of Pd deposited ranged from 8 to 32%, with an average difference of 18.4%. This is a favorable result when considering that deposition was carried out using simple aqueous phase electrochemistry as opposed to the more precise vapor deposition techniques that are available. The analysis also suggests that distribution of Pd is fairly uniform based on the similar differences obtained for the various samples.

The base particle size for typical nanoaggregates prepared using borohydride reduction was determined using SEM micrographs of the particles at 60,000 \times magnification (Figure 4a). At lower magnification (30,000 \times) it becomes clear that the nanoaggregates grow in a chain-like structure (Figure 4b). Using a population size of $n = 100$ particles, the average particle diameter is 100 ± 50 nm. The large standard deviation is the reason why the nanostructures in this study are referred to as nanoaggregates and not nanoparticles. Higher magnification (not shown) showed that larger “chunks” of material were really several smaller particles clustered on the surface of larger particles. The BET surface area for nanoaggregates prepared using this method was determined to be $30.7 \text{ m}^2 \text{ g}^{-1}$. This value is much larger than surface area values associated with bulk scale Fe that range from 0.005 to $4 \text{ m}^2 \text{ g}^{-1}$ [12]. An examination of N_2 adsorption as a function of relative pressure (see Figure 5) reveals a Type II multilayer adsorption. Based on the small maximum volume of N_2 adsorbed, one can conclude that the Fe-Pd material is primarily nonporous and accessible for adsorption at the external surface. This should be expected when considering that the material is aggregates of smaller nanoparticles. The average pore size of 8.8 nm can be taken as a rough measure of the intraparticle spacing within a single aggregate.

Batch TCE Dechlorination

Although the kinetics of TCE dechlorination using Fe/Pd nanoaggregates has received significant attention, the studies often represent an ideal system of de-oxygenated, de-ionized water at optimal pH. For comparison, the current study began with the same type of ideal system. Key parameters were then varied to gain a better understanding of how to gauge the potential of the Fe/Pd nanoaggregates for actual field remediation applications. The results for the dechlorination of a de-oxygenated solution containing 16.6 mg L^{-1} TCE at a pH of 6 using 1 g L^{-1} of FePd-1 (0.8 wt % Pd) nanoaggregates are shown in Figure 6. For the given conditions, complete removal of TCE is achieved within the first 30 min. Complete dechlorination of TCE and any intermediates based on chloride formation (see Figure 6) is not achieved until 1 h when the value of $[\text{Cl}^-]/[\text{Cl}^-]_{\text{MAX}}$ is 1. No intermediates were detected during the organic analysis throughout the experiment, which is expected given that bimetallic systems have been shown to eliminate the evolution of chlorinated intermediates from desorption at the particle surface [15]. The final hydrocarbon product of TCE dechlorination with nanoscale Fe is known to be ethane [4,7,14,15,25–27]. For this work, ethane was not specifically sampled for because analysis typically involves the use of a headspace in the reaction vessel to collect and concentrate the ethane for gas phase analysis [4,15,25–27]. These results represent rapid dechlorination when compared with traditional bulk-scale Fe, and are within an order of magnitude of the literature results presented by He and coworkers for capped Fe/Pd nanoparticles [12,22].

The first variation in experimental conditions was to change the background matrix from DIUF water to sample water from the Paducah area. For this experiment, the water sample 1 was used. These results are also shown in Figure 6. Using the same experimental conditions with regard to metal loading, organic concentration, de-oxygenation, and pH, the performance of

the FePd-1 nanoaggregates was unchanged, with complete removal of TCE also occurring within the first 15 min. These results were expected because the Paducah water was not known to have high concentrations of potential competitive species (natural organic matter, nitrate, etc.) based on results for sample well monitoring throughout the region. The only difference in the results was that the pH when using DIUF water shifted less than 1 unit to 6.5 over the course of the reaction while in the case of the sample water, the final pH was 9.

The next set of experiments examined the role of Pd-deposition and metal loading on dechlorination in de-oxygenated DIUF water. These results are shown in Figure 7. For all data, the initial concentration of TCE was 20.5 mg L^{-1} and the initial pH was 5. As before, complete removal of TCE was achieved within 30 min when using 1 g L^{-1} of Fe/Pd nanoaggregates (0.8 wt % Pd). When the loading of the same 0.8 wt % Pd particles was lowered to 0.24 g L^{-1} , the removal of TCE declined by 30% for the same reaction interval. The experiment was again repeated using 1 g L^{-1} of FePd-2 (0.48 wt % Pd). For this case, the decrease level of Pd yielded only a 38% removal of TCE during the first 30 min, with a total of 64% removed at 1 h. Of the two, the amount of Pd deposited has a more significant impact on dechlorination kinetics than the metal loading in solution.

Before column testing, a set of batch vial experiments was performed to determine if the RGA aquifer gravel to be used as column packing would impede the dechlorination process through potential TCE adsorption at the gravel surface. For this purpose, a 21 mg L^{-1} TCE solution was treated with 0.9 g L^{-1} of Fe/Pd nanoaggregates (0.5 wt % Pd; not included in Table 1) in the presence of 461 g L^{-1} aquifer gravel. Sample water from Paducah was also used without de-oxygenation to better simulate actual conditions in the field where the level of dissolved oxygen is ~ 17 ppm. The results for these experiments are shown in Figure 8. In all cases, a 100% removal of TCE was achieved by the first sample interval at 20 min. To account for the potential of adsorption, controls with no Fe/Pd indicated negligible loss of TCE from solution after 1 h. These results are encouraging with regard to the potential for TCE partitioning that would ultimately inhibit dechlorination using zero-valent metals. However, the gravel used in these tests had to be able to fit in the vial and do not reflect the potential for larger porous RGA material to trap TCE. The results also indicate that the reactivity of the Fe/Pd nanoaggregates is not affected by pH over the range of 6–8. Interestingly, the performance of the 0.5 wt % material is greatly enhanced when compared with the previous case involving no gravel and de-oxygenation. The reason for this enhancement is not understood at this time.

As described previously, the accepted means of comparison when discussing dechlorination results is the use of the surface-area-normalized rate constant (k_{SA}) given in Eq. 3. Therefore, a final set of experiments was performed using much shorter sampling times to provide the necessary data for calculation of this parameter in order to compare the present system with those studied elsewhere. The reduction of a 19.6 mg L^{-1} TCE solution (no de-oxygenation) using 1.0 g L^{-1} of FePd-5 (0.42 wt % Pd) was carried out for both the ideal case (DIUF water at pH 6.2) and in Paducah sample water (water sample 2) with no pH adjustment (initial pH = 8.8). The results are shown in Figure 9. For the ideal case, a 29% removal of TCE occurs within the first 5 min (0.167 h). The overall performance after 30 min is much better than before, with 88% of the TCE removed when compared with 38% achieved previously using 0.48 wt % Pd. The results obtained using the Paducah sample water were much lower, with only 24% of the TCE removed after 30 min. These results are not surprising, though, considering the much higher pH of 8.8 which is more conducive to oxide formation at the Fe-water interface. The value of the observed first-order reaction rate constant (k_{obs}) needed for Eq. 3 can be obtained graphically for both sets of data using the linearized form of Eq. 2. A plot of this nature is shown in Figure 10 where the value of k_{obs} is equal to the slope of a linear fit of the data. The resulting values of k_{obs} for the DIUF water and Paducah sample water cases are 4.20 and 0.57 h^{-1} , respectively. This is approximately an order of magnitude difference in kinetics when

comparing the two cases and is consistent with literature results regarding pH effects in going from pH 6–9 [22]. Interestingly, both rates are much higher than would be expected based on results presented by Lien and Zhang [28] describing an optimal range of Pd coating between 1 and 5 wt %. When these values are inserted into Eq. 3 along with the BET surface area (A_{BET}) and metal loading (ρ_{M}) for each case, the resulting values of k_{SA} for the DIUF water and Paducah sample water cases are 1.4×10^{-1} and $1.9 \times 10^{-2} \text{ L m}^{-2} \text{ h}^{-1}$, respectively.

Circulating Column Studies

The final phase of this work involved dechlorination during simulated groundwater flow. Unfortunately, a limited volume of Paducah sample water prevented its use during column studies. Preliminary results were obtained while circulating the system at a flow rate of 100 mL min^{-1} . This corresponds to a linear velocity of 259 ft per day and is much faster than typical groundwater velocities. At this rate, the equivalent liquid column volume is passed through the column approximately every 20 min. Using 0.4 g L^{-1} of FePd-3 (0.37 wt % Pd), an average of 87% of TCE in a 46 mg L^{-1} TCE solution was removed in 4 h within a column depth of 2 ft. Using a single-point calculation of the observed rate, the value of k_{SA} for this run is $4.3 \times 10^{-2} \text{ L m}^{-2} \text{ h}^{-1}$, just 36% of the maximum rate obtained above for the ideal case during batch vial studies. However, the actual time required to achieve this removal may have been much shorter. Regardless, this is a substantial TCE removal using a small loading of metal.

Groundwater velocities within the TCE plume at Paducah are known to vary in areas between 10 and 100 ft per day. Therefore, column experiments were performed using flow rates to approximate both the upper and lower end of this range. The results for the dechlorination of a TCE solution ($C_0 = 16 \text{ mg L}^{-1}$) using a modest metal loading of 0.23 g L^{-1} of FePd-4 (0.43 wt % Pd) and a more rapid groundwater velocity of 73 ft per day are shown in Figure 11. After 24 h of circulation (1 equivalent bed volume every 1.3 h), the removal of TCE ranged from 56% at a column depth of 0.5 ft to 69% beyond 2 ft. The larger removal towards the bottom of the column is a reflection of metal migration through the column. The corresponding chloride went from 55% of the maximum possible at 0.5 ft to 42% at 3 ft. The Cl^- data indicates that the TCE reacted had been completely and rapidly dechlorinated, eliminating the concern for a build up of possible toxic intermediates. A sample obtained at a depth of 0.5 ft after 48 h indicated additional reaction had occurred, with a total TCE removal of 75%. A single-point calculation of k_{SA} using the average column concentration after 24 h and assuming the sample time is a good approximation of the reaction time produces a value of $6.3 \times 10^{-3} \text{ L m}^{-2} \text{ h}^{-1}$, only 5% of the maximum value. Again, these are still promising results based on the material usage.

The final results that will be presented represent two experiments that can be used to directly examine the issue of groundwater velocity because they both involve the dechlorination of TCE ($C_0 = \sim 16 \text{ mg L}^{-1}$ TCE) at similar pH (6.4 and 7) using 0.5 g L^{-1} of Fe/Pd nanoaggregates (0.4 wt % Pd) with only the column velocity varied (12.9 and 82 ft per day). The results are shown in Figure 12. For both experiments, $\sim 81\%$ of the TCE is removed throughout the entire column depth after 24 h. After 48 h, the removal of TCE is unchanged at the rapid flow rate while an additional 10% of the TCE is removed under slower flow conditions. The value of k_{SA} based on single-point calculations after 24 h is the same for both cases, $4.5 \times 10^{-3} \text{ L m}^{-2} \text{ h}^{-1}$, and is similar to the value obtained using half the metal loading. Based on these results, it is possible to conclude that groundwater velocity does not have a significant influence on dechlorination kinetics.

CONCLUSIONS

The application of Fe/Pd nanoaggregates to room temperature TCE dechlorination for the ideal case of de-oxygenated, deionized, ultrafiltered water yielded a surface-area normalized rate

constant of $1.4 \times 10^{-1} \text{ L m}^{-2} \text{ h}^{-1}$ that is comparable with results presented in literature. The application of these particles to batch TCE dechlorination in a matrix that is representative of actual remediation conditions suggested that the Pd content of the metal nanoaggregates is the most significant factor in driving reactivity within the system. Interestingly, materials with low levels of Pd coating performed better in oxygen environments. However, the reason for this is not yet understood. The presence of sediment material (gravel) did not have an effect on reaction kinetics. The influence of pH was only observed for values greater than 8. The use of a circulating column system for dechlorination demonstrated that sufficient removal of TCE could be achieved using moderate metal loadings of $0.23\text{--}0.5 \text{ g L}^{-1}$. The groundwater velocity does not suppress TCE removal over a fairly broad range of $12.9\text{--}83 \text{ ft per day}$. Single-point values of k_{SA} based on a 24 h reaction time showed a decrease in the rate by one to two orders of magnitude. These results support the need for further testing involving *in situ* application.

Acknowledgments

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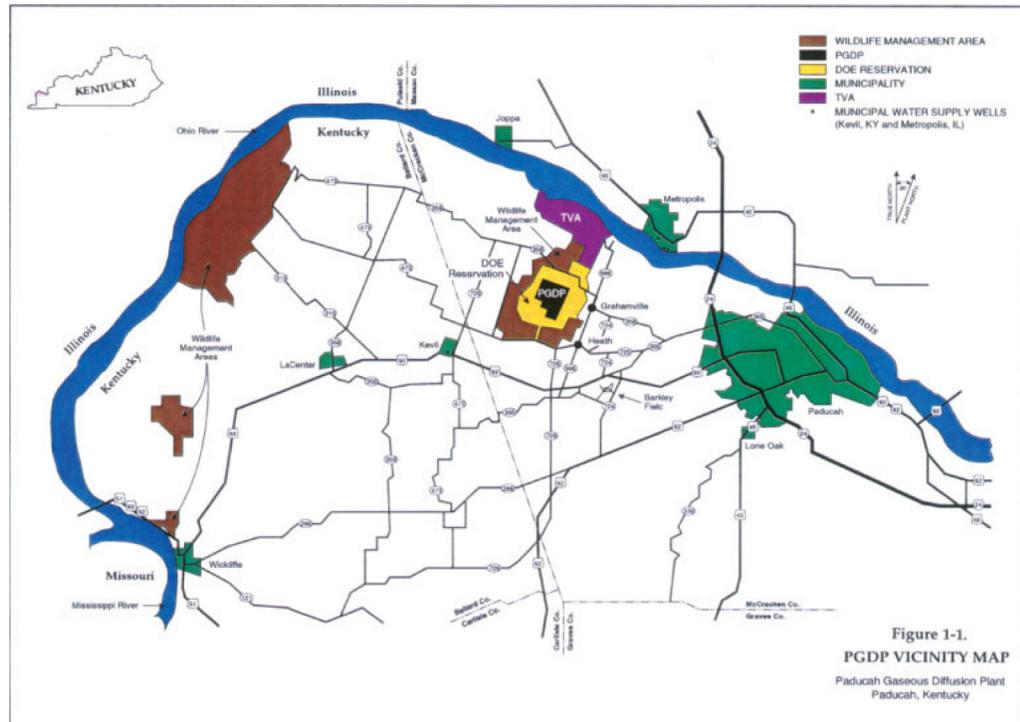


Figure 1.

A vicinity map of the Paducah gaseous diffusion plant (PGDP) [23]. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

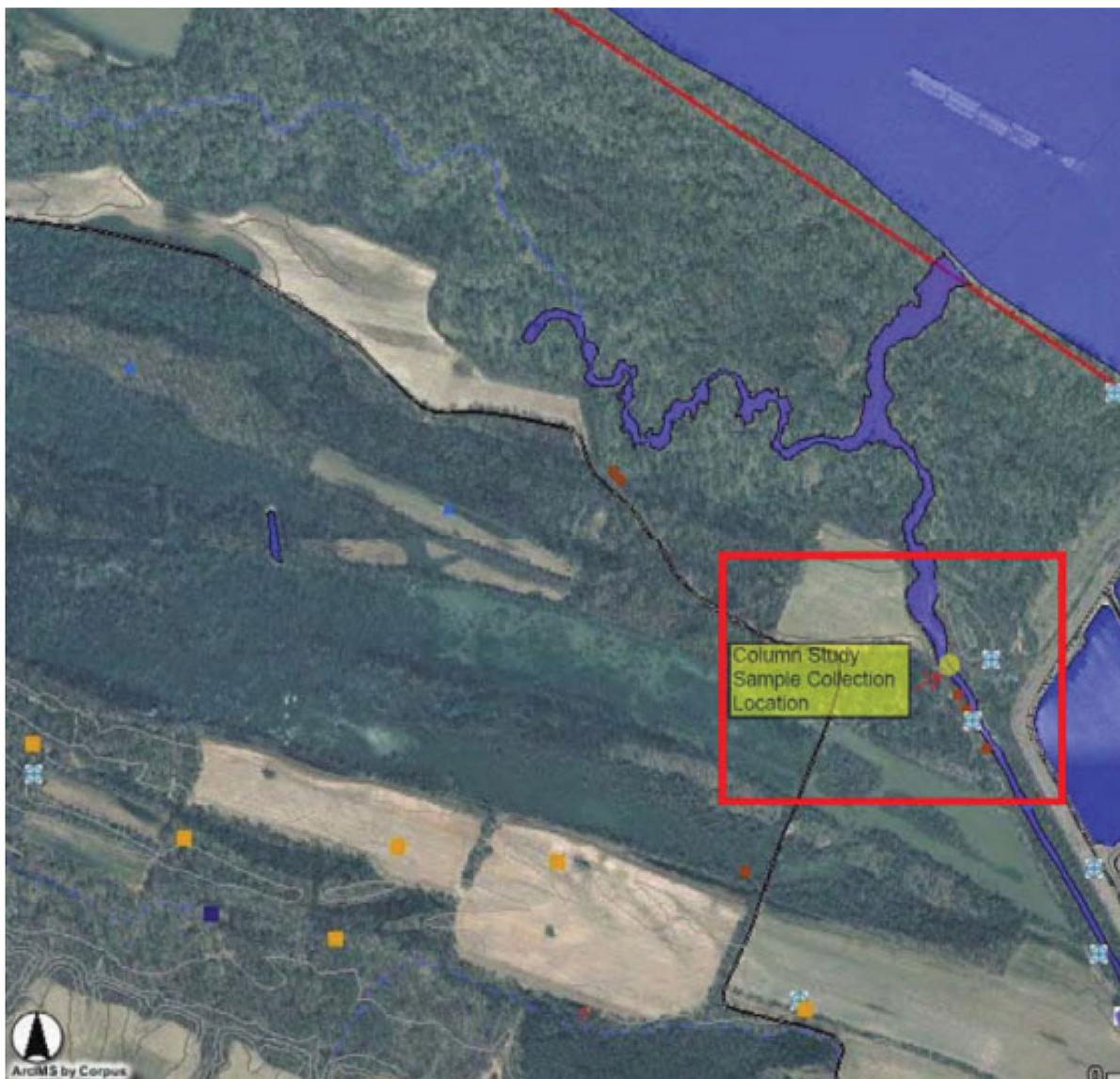


Figure 2. Sample location of RGA material used in batch and column tests. Ky State Plane E 752253.24, N 1957480.65. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

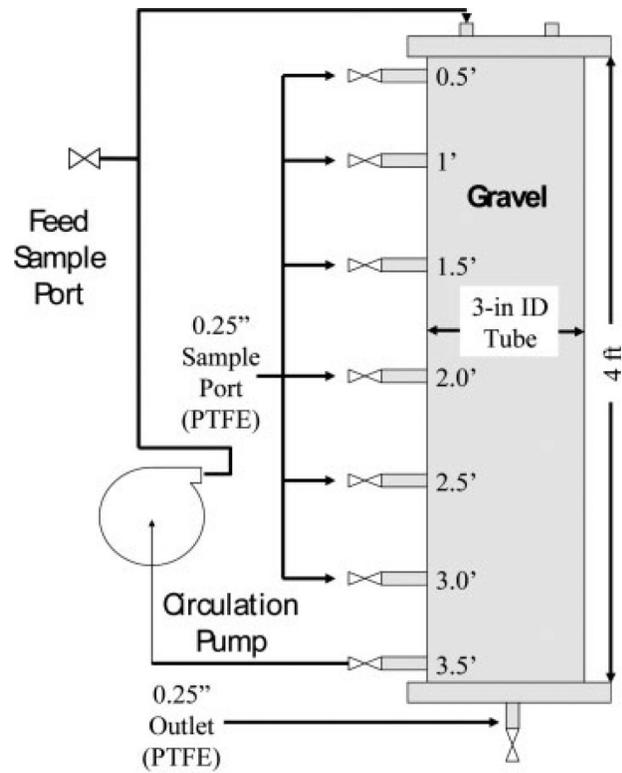


Figure 3. Schematic of the packed-column system used for simulated groundwater injection studies.

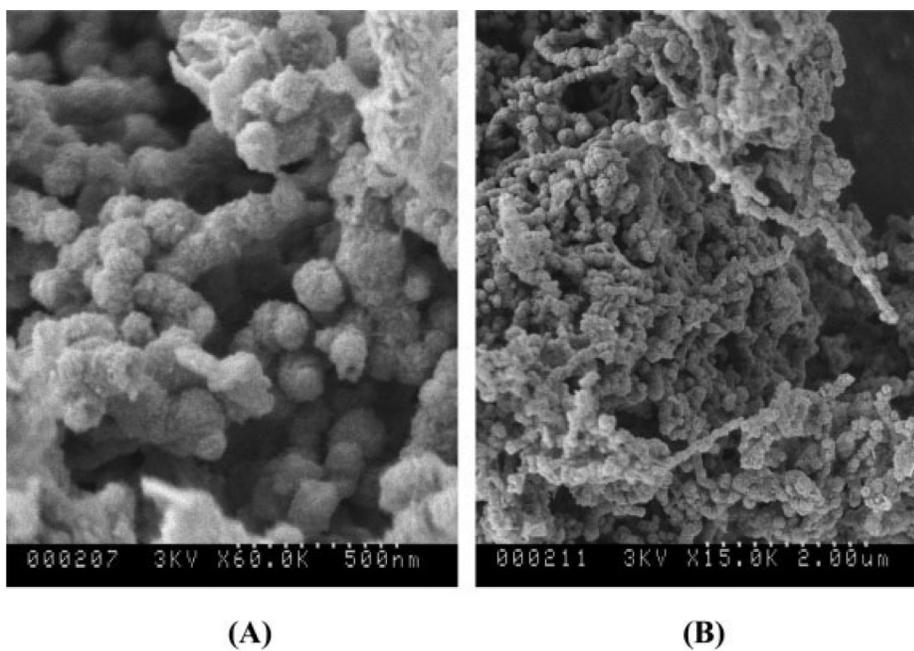


Figure 4. SEM micrographs of nanoaggregates prepared via borohydride reduction.

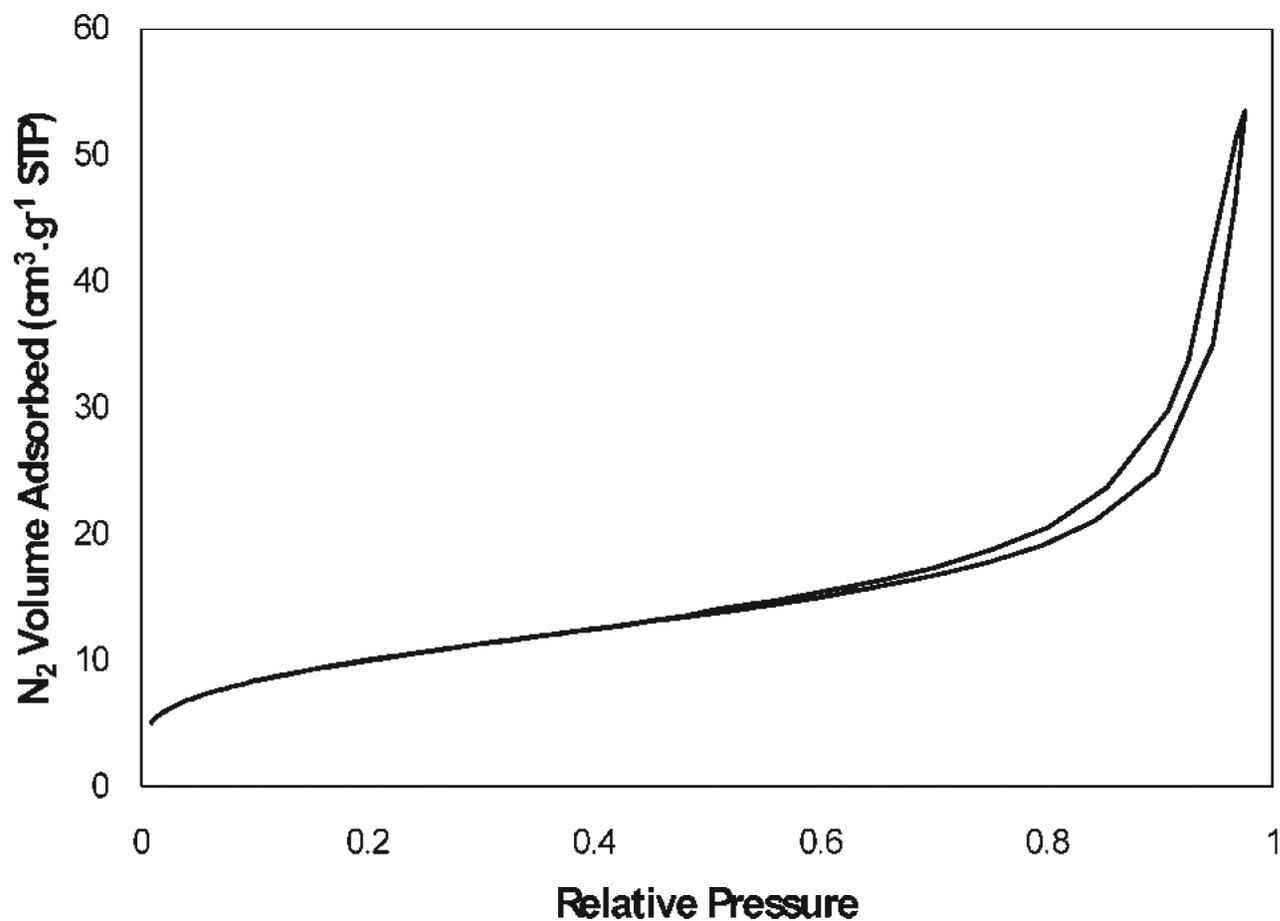


Figure 5. Nitrogen adsorption as a function of relative pressure for typical Fe/Pd nanoaggregates exhibiting a Type-II isotherm and lack of microporous area. Average pore size was 8.8 nm.

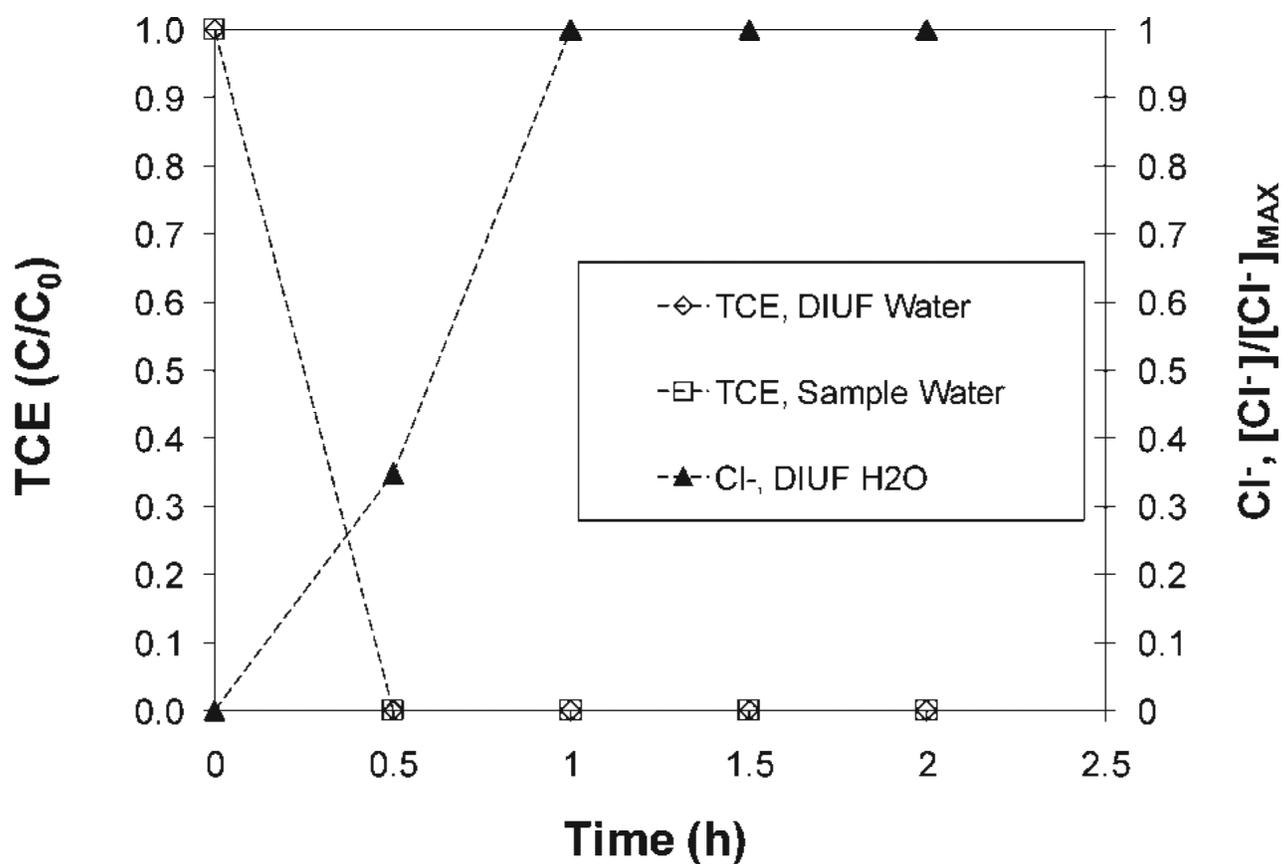


Figure 6. Evaluation of Fe/Pd nanoaggregates (0.8 wt % Pd) for the ideal dechlorination of 16.6 mg L⁻¹ TCE at pH 6 using 1.0 g L⁻¹ metal loading. The sample water used was from sample 1. The maximum chloride, [Cl⁻]_{MAX}, is 13.4 mg L⁻¹ and corresponds to the complete removal of Cl⁻ from TCE to form ethylene. The ethylene is subsequently converted to ethane through reaction with Fe/Pd nanoaggregates.

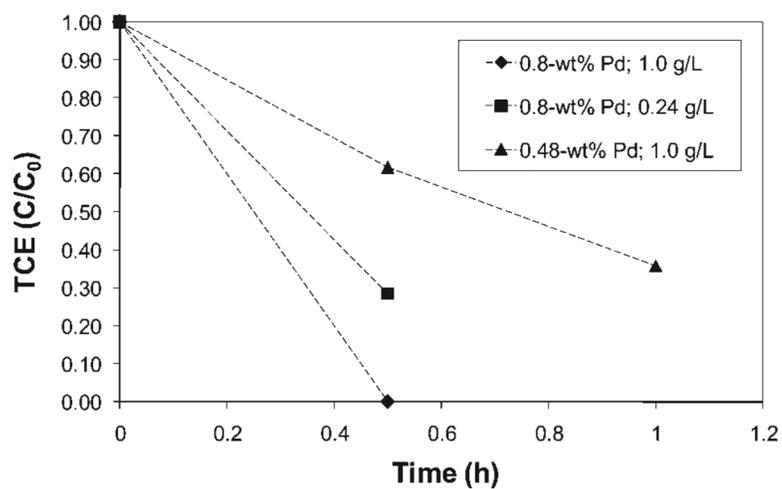


Figure 7. Examination of the effects of metal loading and Pd-deposition on the dechlorination of 20.5 mg L^{-1} TCE in de-oxygenated DIUF water at pH 5.

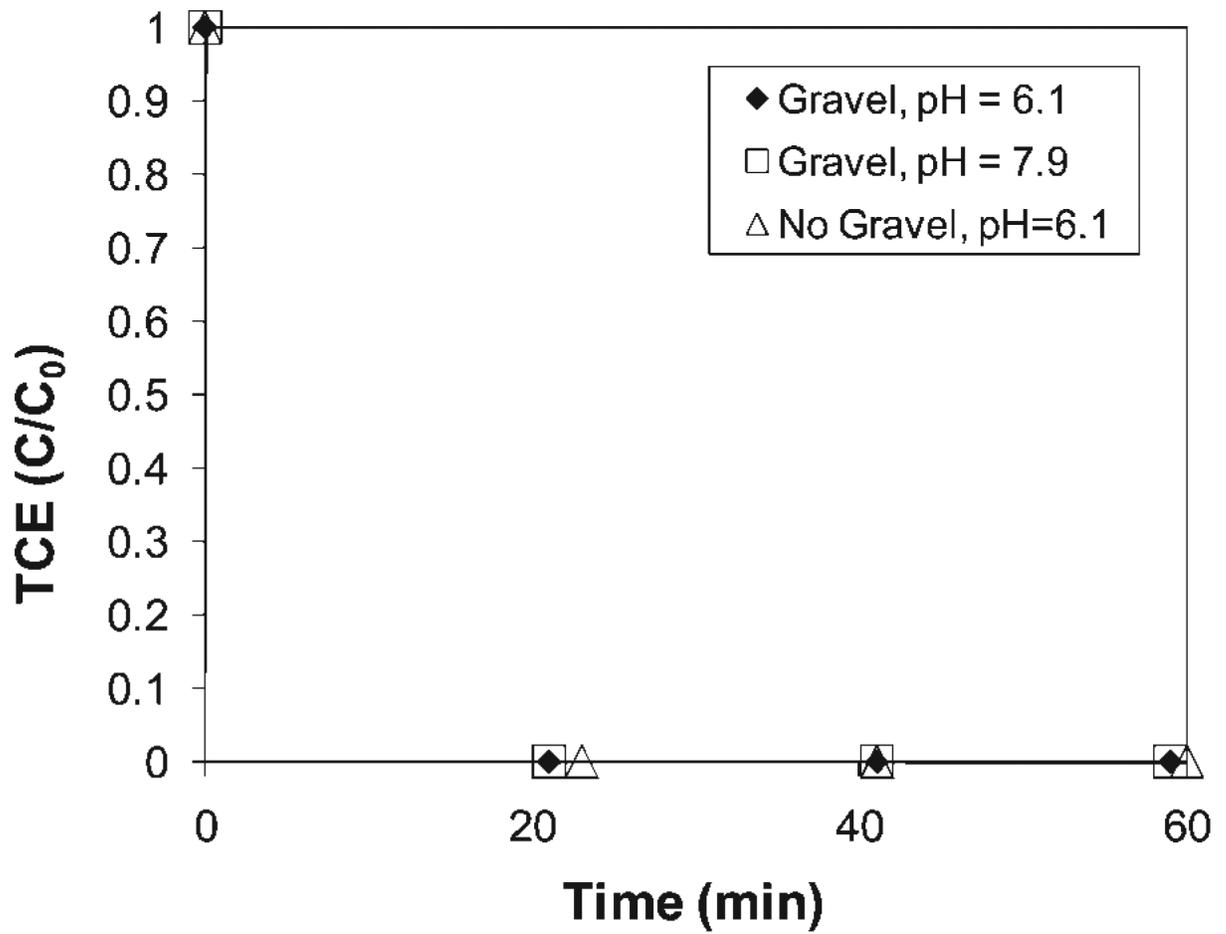


Figure 8. Reduction of a 21.1 mg L^{-1} TCE solution in Paducah sample water under aerobic conditions in the presence of aquifer gravel using 0.9 g L^{-1} of Fe/Pd nanoaggregates (0.5 wt % Pd).

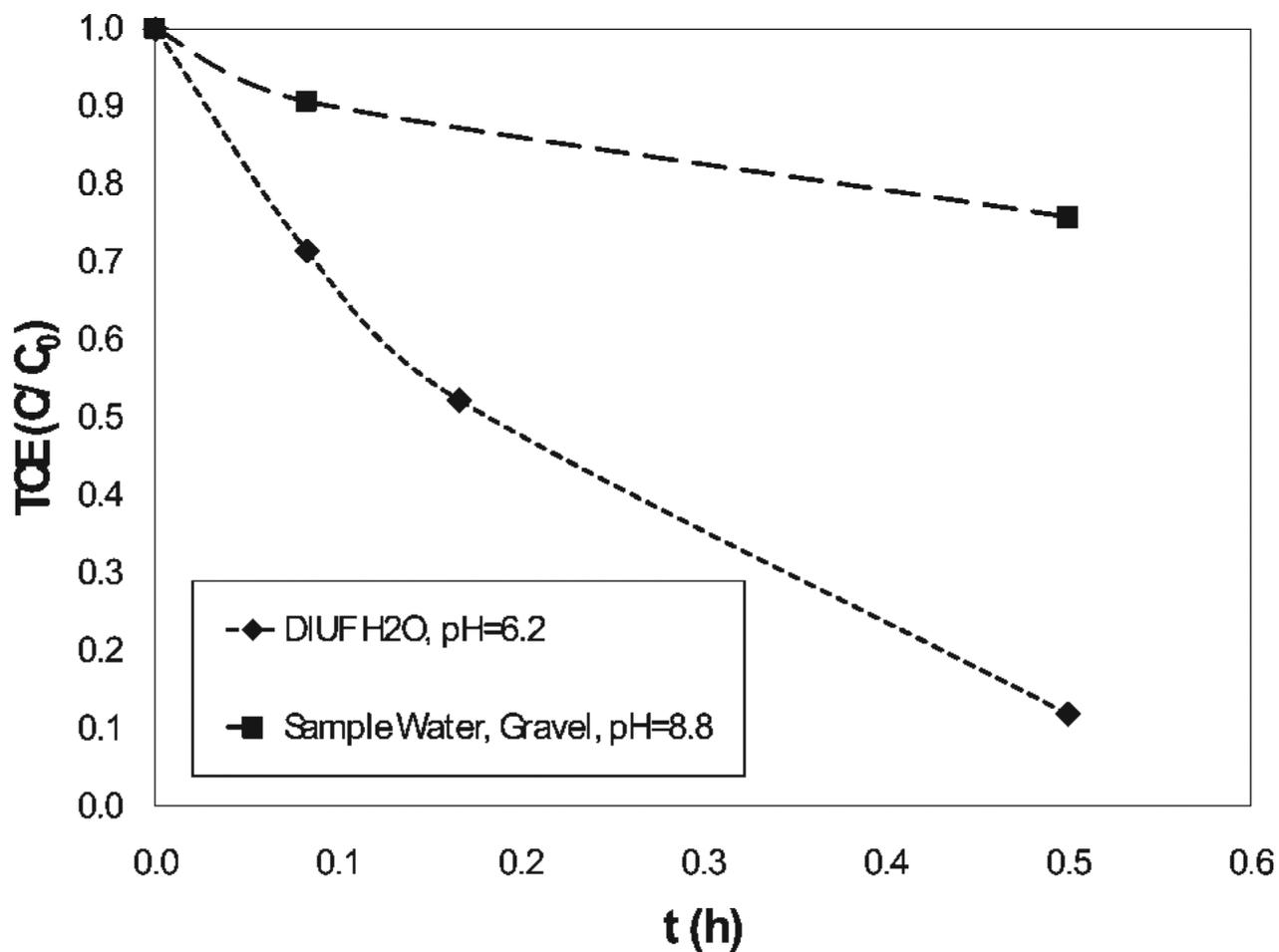


Figure 9. Reduction of a 19.6 mg L^{-1} TCE solution under aerobic conditions in the presence of aquifer gravel using 1.0 g L^{-1} Fe/Pd nanoaggregates (0.42 wt % Pd). The water sample used was from sample 2.

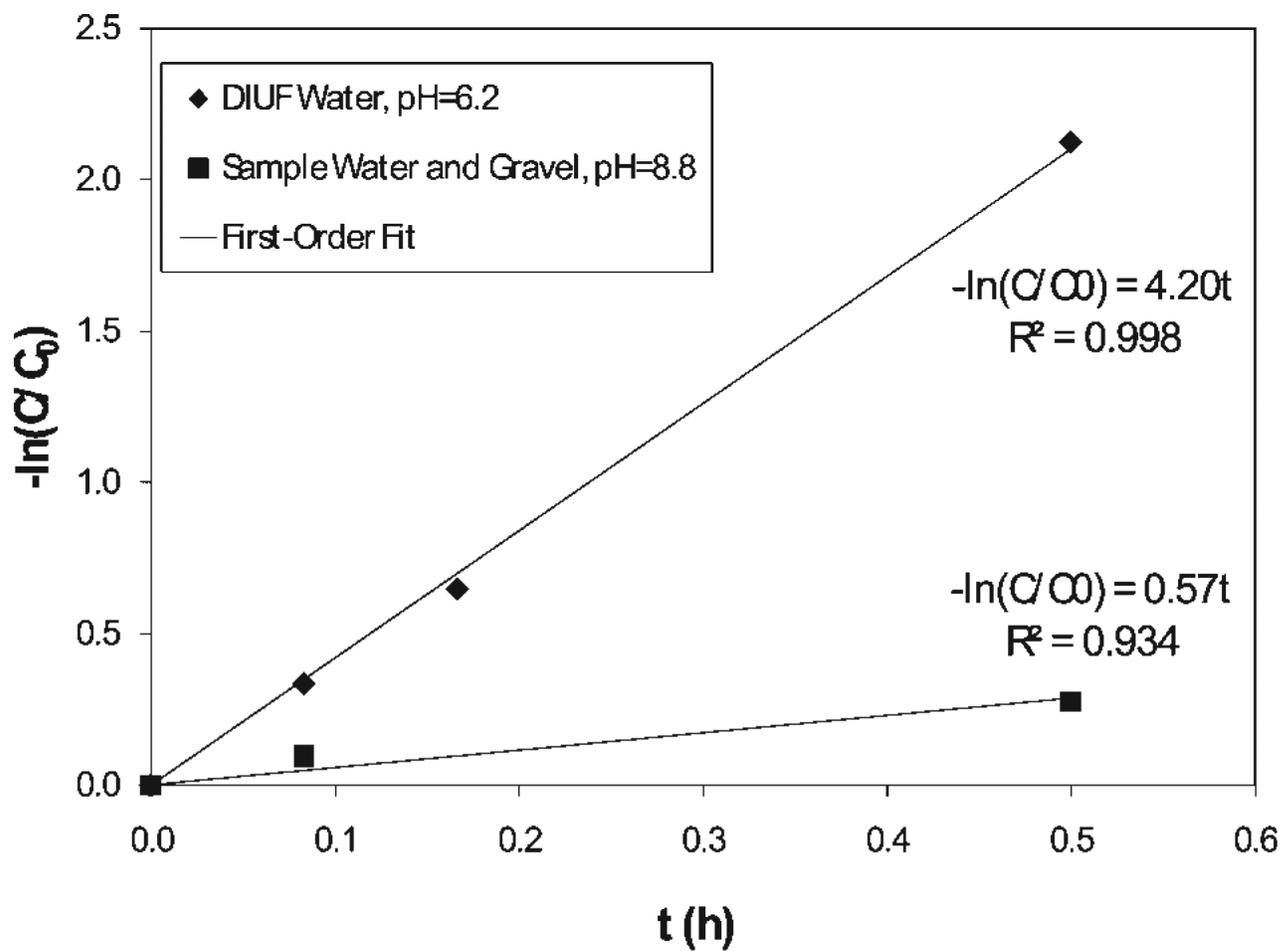


Figure 10. Determination of the observed first-order reaction rate constant (k_{obs}) from a fit of experimental data where the value of k_{obs} is equal to the slope of the graph.

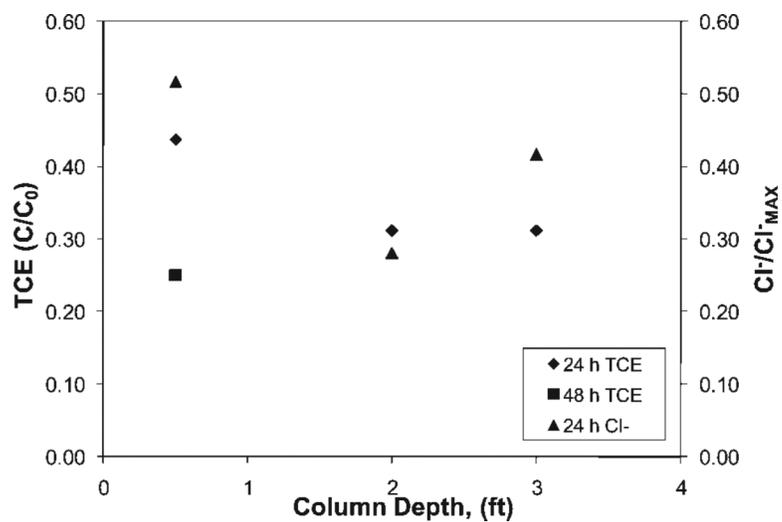


Figure 11. Results for circulating column dechlorination of TCE ($C_0 = 16 \text{ mg L}^{-1}$ TCE) at pH 7 using 0.23 g L^{-1} of Fe/Pd nanoaggregates (0.43 wt % Pd) and an equivalent groundwater velocity of 73 ft per day. The maximum chloride, $[\text{Cl}^-]_{\text{MAX}}$, is 13 mg L^{-1} .

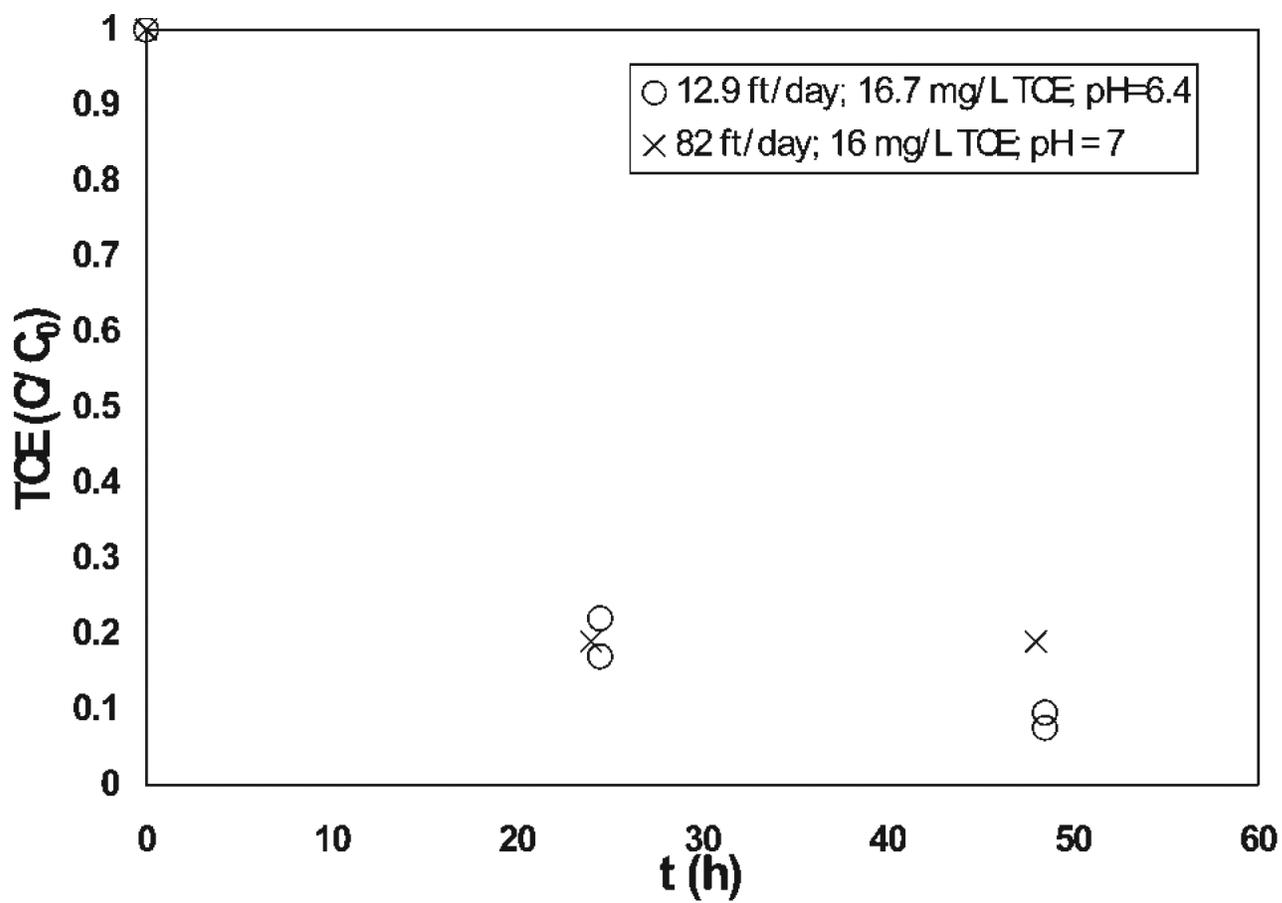


Figure 12. Results for circulating column dechlorination of TCE ($C_0 = \sim 16 \text{ mg L}^{-1}$ TCE) at pH 6.4–7 using 0.5 g L^{-1} of Fe/Pd nanoaggregates (0.4 wt % Pd) showing the negligible effects of groundwater velocity over the range of 12.9–82 ft per day.

Table 1

Average quality of water at the Paducah site based on 10 monitoring wells.

Alkalinity	82	mg L ⁻¹
Ca ²⁺	24	mg L ⁻¹
Cl ⁻	55	mg L ⁻¹
Conductivity	417	µmho cm ⁻¹
Dissolved oxygen (DO)	3	mg L ⁻¹
Fe ²⁺	0.3	mg L ⁻¹
NO ₃ ⁻	3	mg L ⁻¹
PO ₄ ³⁻	2	mg L ⁻¹
SO ₄ ²⁻	13	mg L ⁻¹
Total dissolved solids (TDS)	293	mg L ⁻¹
Total organic carbon (TOC)	1.2	mg L ⁻¹
Turbidity	21	NTU

Table 2

Analysis of Pd deposition using atomic absorption.

Sample	Target Pd (wt %)	Pd by AA (wt %)	% Difference
FePd-1	1.0%	0.8 ± 0.1%	20.0%
FePd-2	0.5%	0.46 ± 0.03%	8.0%
FePd-3	0.5%	0.34 ± 0.06%	32.0%
FePd-4	0.5%	0.42 ± 0.03%	16.0%
FePd-5	0.5%	0.42 ± 0.07%	16.0%