Nanoscale iron particles for complete reduction of chlorinated ethenes

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Abstract

This paper examines the potential for using laboratory synthesized nanoscale Pd/Fe bimetallic particles to reduce chlorinated ethenes. Rapid and complete dechlorination was achieved for six chlorinated ethenes: tetrachloroethene (PCE, C_2Cl_4), trichloroethene (TCE, C_2HCl_3), 1,1-dichloroethene (1,1-DCE, $C_2H_2Cl_2$), *cis*- and *trans*-1,2-dichloroethene (c-DCE, t-DCE, $C_2H_2Cl_2$), and vinyl chloride (VC, C_2H_3Cl). The chlorinated ethenes (20 mg l^{-1}) were completely reduced within 90 min at a metal loading of 5 g l^{-1}. Ethane was the primary product from these reactions, amount to 60–90% of the total carbon. Ethene (3–20%) was produced during the transformation of TCE, DCEs and VC. No chlorinated intermediates or final products were detected above the method detection limit (< 5 μg l^{-1}). The remarkable performance of the nanoscale particles can be attributed to: (1) High specific surface area of the nanoscale metal particles, approximately 35 m^2 g^{-1}, tens to hundreds of times higher than commercial grade micro- or milli-scale iron particles; (2) Increased reactivity per unit metal surface area, largely due to the presence of the noble metal (Pd) on the surface. Values of the surface-area-normalized rate coefficients (k_{SA}) were two orders of magnitude higher than those reported in the literature for larger iron particles. Due to their small particle size and high reactivity, the nanoscale bimetallic particles may be useful in a wide array of environmental applications including subsurface injection for groundwater treatment. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ground water; Iron; Nanoparticle; Palladium; Remediation; PCE; TCE; DCE; VC

1. Introduction

The rediscovery of zero-valent iron for the transformation of chlorinated organic compounds has led to the development and proliferation of a number of environmental applications, particularly in so far as groundwater remediation is concerned. Research in the past few years has demonstrated that metals such as iron and zinc can effectively reduce a broad array of organic compounds such as chlorinated aliphatics [1–6], nitro aromatics [7], polychlorinated biphenyls (PCBs) [8], pesticides and related compounds [9,10]. Applications of zero-valent iron for remediating contaminated soils, sediments and aquifers have received particular attention. An attractive

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feature is that it can be readily incorporated into reactive subsurface barriers via the 'funnel and gate' approach [11–13]. As contaminated water passes through the permeable wall of iron particles, organic contaminants react with iron to form primarily non-toxic end products such as hydrocarbons and chloride ion.

Bimetallic particles (e.g. Pd/Fe, Pd/Zn) have been shown to exhibit a high efficacy for the transformation of many chlorinated compounds. For example, palladized iron has been demonstrated to rapidly dechlorinate chlorinated ethenes such as PCE, TCE, 1,1-DCE, c-DCE, and t-DCE [14]. These compounds can be completely reduced to ethane in just a few minutes. The palladized iron was also noted for its effective transformation of PCBs [15]. Ni/Fe and Cu/Fe were used to transform 1,1,1-trichloroethane [16]. Other bimetals such as Pt/Fe, Pd/Zn have been reported for the degradation of chlorinated benzenes [17].

We reported using nanoscale metallic particles for transformation of TCE, chlorinated benzenes and polychlorinated biphenyls (PCBs) [18,19]. The nanoscale metallic particles, with diameter on the order of 1 to 100 nm, were synthesized in the laboratory. A small amount ($\sim 0.05\%$ wt.) of Pd was deposited on the iron surface to enhance the reactivity of the metal particles. Preliminary experimental results suggest that reactivity of Pd/Fe particles is significantly higher than that of commercial grade iron particles. Due to their small particle sizes and high reactivity, the nanoscale metal particles may be useful in a wide array of environmental applications. For example, the metal particles could be injected directly into contaminated soils, sediments and aquifers [20,21] for in situ treatment of chlorinated hydrocarbons, offering a relatively low-cost alternative to such conventional technology as pump and treat, air sparging or reactive barriers.

In this paper, systematic laboratory studies applying the nanoscale bimetallic particles for transformation of chlorinated ethenes (PCE, TCE, t-DCE, c-DCE, 1,1-DCE, VC) are presented. These compounds are among the most prevalent contaminants in soils and aquifers [22,23]. They have been listed as priority pollutants by the US Environmental Protection Agency, and also on the Superfund National Priority List. These compounds are known or potential threats to public health and the environment so there is an urgent need to develop effective control methods. This study was aimed to: (1) characterize and quantify reaction intermediates and final products; (2) assess the stability of the nanoscale metal particles; and (3) examine their reactivity compared to larger commercial grade iron particles. This information is essential for exploring the possible environmental applications of the nanoscale metal particles.

2. Materials and methods

2.1. Preparation of nanoscale metal particles

Synthesis of nanoscale iron particles was achieved by adding 1:1 volume ratio of $NaBH_4$ (0.25 M) into $FeCl_3 \cdot 6H_2O$ (0.045 M) [17–19]. The solution was mixed vigorously under room temperature for 5 min (22 ± 1 °C). Ferric iron was reduced by borohydride according to the following reaction:

$$4Fe^{3+} + 3BH_4^- + 9H_2O$$
$$\rightarrow 4Fe^0 \downarrow + 3H_2BO_3^- + 12H^+ + 6H_2 \quad (1)$$
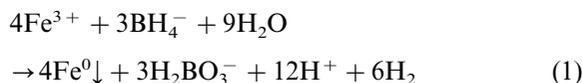
The borohydrate to ferric iron ratio added was 7.4 times of the stoichiometric requirement according to Equation 1. Excessive borohydrate was the key factor for rapid and uniform growth of iron crystals. The metal particles formed from the above reaction were then washed with large volume (> 100 ml g^{-1} iron) of Milli-Q water for at least three times. Air-dried particles from the above procedures have sizes generally < 0.1 μm (mostly between 10 and 100 nm). BET analysis gave a specific surface area of ~ 35 m^2 g^{-1}.

Palladized Fe particles were prepared by soaking freshly prepared nanoscale iron particles with an ethanol solution containing 0.1 wt.% of palladium acetate ($[Pd(C_2H_3O_2)_2]_3$). This caused the reduction and subsequent deposition of Pd on the Fe surface:

$$Pd^{2+} + Fe^0 \rightarrow Pd^0 + Fe^{2+} \quad (2)$$
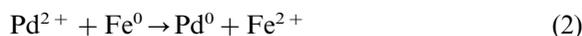
2.2. Batch experiments

Batch experiments were conducted in 150 ml serum bottles (Wheaton glass). In each batch bottle, 20 μl stock solution of a chlorinated ethene compound dissolved in methanol was spiked into 50 ml deionized water. Initial organic concentration was ∼ 20 mg l^{-1}. The solution contained 0.25 g of the nanoscale particles. The serum bottles were then capped with Teflon Mininert valves and mixed on a rotary shaker (30 rpm) at room temperature (22 ± 1 °C). Parallel experiments were also performed without the metal particles (control) and with commercial grade iron powders (Alrich, < 10 μm, < 0.9 m^2 g^{-1}). Analyses of organic mass in the control samples indicated that the total mass of parent chlorinated ethylenes in the batch bottles varied from 95 to 106% of the initial input after 24 h. Variability of organic concentrations in the control samples was largely due to errors in preparing the bottles and the gas chromatograph (GC) analyses. Most experiments reported in this work were completed within 3 h, it was therefore concluded that potential leak and/or loss should not be a concern.

2.3. Methods of analyses

At selected time intervals, 5 μl headspace gas aliquot was withdrawn with a gas-tight syringe for organic analyses. Concentrations of chlorinated ethenes were measured by a HP5890 GC equipped with a DB-624 capillary column (30 m × 0.32 mm) and an electron capture detector (ECD). Temperature conditions were programmed as follows: oven temperature at 50 °C for 1,1-DCE, c-DCE and t-DCE, 80 °C for PCE and TCE with a split ratio of 10; injection port temperature at 180 °C; and detector temperature at 300 °C. The carrier gas was ultra-pure nitrogen at a flow rate of 4.86 ml min^{-1}. Detection limits using this method were < 5 μg l^{-1} for the six chlorinated ethenes. The detection limits were determined according to the EPA procedures for method detection limit (MDL). Calibration curves for each model compound were made initially and the variability was checked daily before analysis (< 15%).

Hydrocarbon products in the headspace were qualitatively identified with a Shimadzu QP5000 GC-MS and further quantified with GC analysis by comparing retention times and peak areas with standard gas samples (ethane, ethene, methane and carbon dioxide). The GC was equipped with a flame ionization detector (FID) and an AT-Q column (Alltech, 30 m × 0.32 mm). The oven temperature was set at 30 °C, injection port temperature at 250 °C, and detector temperature at 300 °C. The carrier gas was ultra-pure nitrogen. Before each analysis, the GC was calibrated with commercial gas standards. Detection limits were 22 μg l^{-1} for methane, 9 μg l^{-1} for ethene and 4.5 μg l^{-1} for ethane. Hydrocarbon products in the aqueous phase were calculated using Henry's law. Concentrations of hydrocarbons are expressed as molar ratios to the parent chlorinated compounds.

2.4. Chemicals

HPLC grade PCE (99.9 + %) and TCE (99 + %) were purchased from Aldrich. t-DCE, c-DCE, 1,1-DCE, VC were from Supelco. A standard gas mixture for GC analysis was obtained from Supelco, which included 1% of ethane, ethene, and methane. Single standard gases of 1.04% ethene and 1.04% methane were acquired from Aldrich. Sodium borohydride ($NaBH_4$, 98%) and ferric chloride ($FeCl_3 \cdot 6H_2O$, 98%) were from Aldrich. Palladium acetate ($[Pd(C_2H_3O_2)_2]_3$, Pd 47.4%) was from Alfa.

3. Results and discussion

3.1. Reactions of chlorinated ethenes with nanoscale metallic particles

Reactions of the six chlorinated ethenes with the nanoscale Pd/Fe bimetallic particles are shown in Fig. 1(a–f). Concentrations in the figure are expressed as the molar ratio to initial organic concentrations. As shown in Fig. 1(a), 20 mg l^{-1} PCE was completely dechlorinated within 90 min. We observed the immediate appearance of ethane corresponding to the disappearance of PCE. Av-
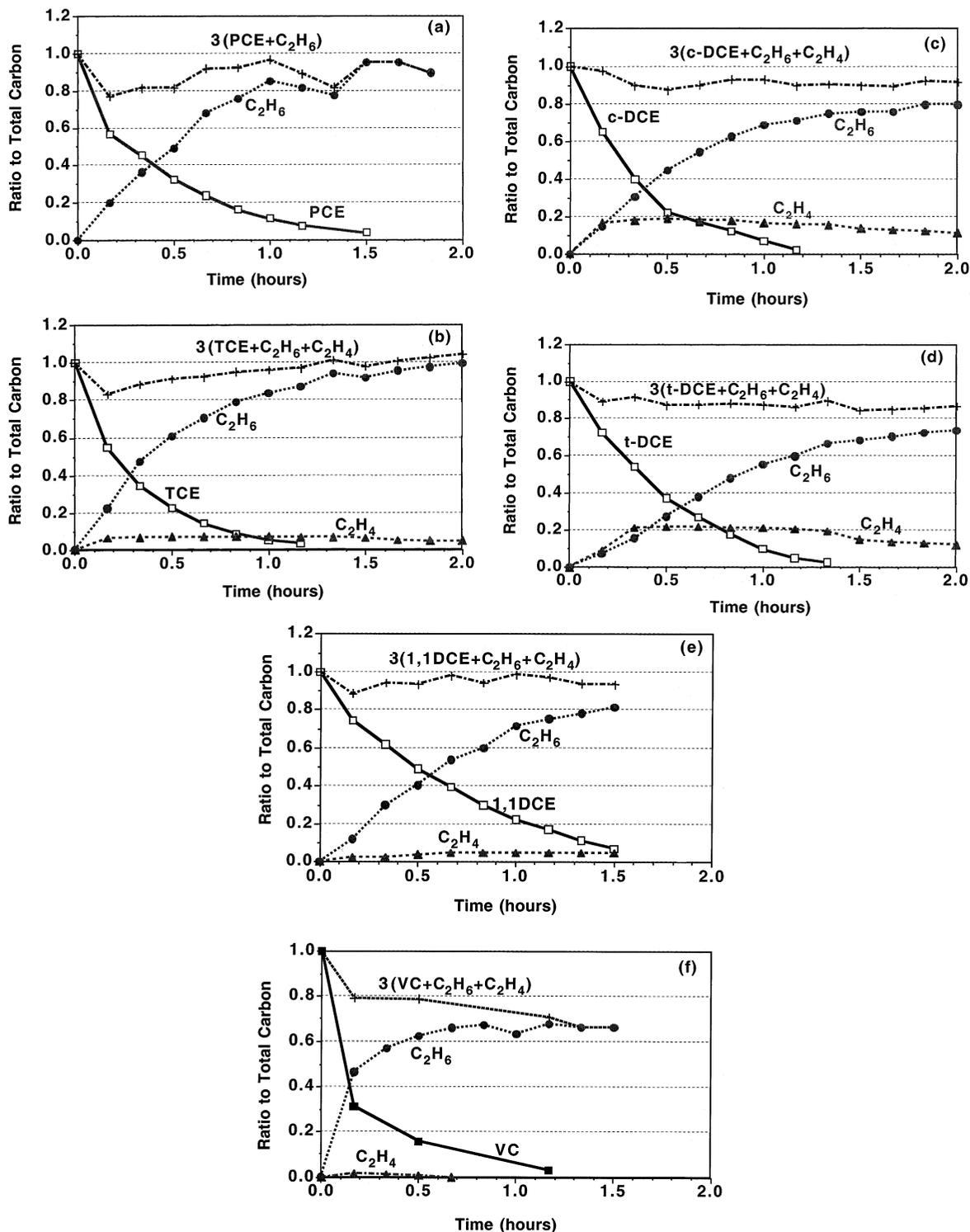
Fig. 1. Reactions of nanoscale Pd/Fe bimetallic particles with: (a) PCE; (b) TCE; (c) c-DCE; (d) t-DCE; (e) 1,1-DCE; and (f) VC. Initial organic concentration was 20 mg l^{-1}, and metal loading was 0.25 g 50 ml $^{-1}$ in all experiments. Concentrations are expressed as the molar ratio to initial organic concentration.

erage yield of ethane was 89% after 1 h. Trace amounts of TCE were detected briefly (< 1 h). The amount of TCE was near detection limit (~ 10 µg 1^{-1}). No other product was detected within a 3-h reaction time. PCE was essentially reduced completely to ethane in accordance with the following stoichiometry:

$$C_2Cl_4 + 5Fe + 6H^+ \rightarrow C_2H_6 + 5Fe^{2+} + 4Cl^-$$

(3)
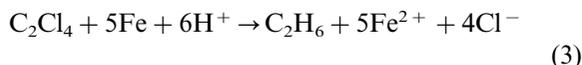
For the reaction with TCE (Fig. 1(b)), complete dechlorination was also achieved within 90 min. Ethane concentrations increased steadily during the entire reaction time. The yield of ethane from TCE was $\sim 87\%$. Unlike the PCE transformation where ethane was the only end-product, significant amounts of ethene were detected. Ethene concentrations remained relatively steady during the course of the experiment and amounted from 5.8 to 7.1% of the initial TCE carbon.

Transformation of c-DCE also paired with the instant accumulation of ethane in the headspace (Fig. 1(c)). Yield of ethane from c-DCE was $\sim 70\%$ initially. Meanwhile, much more ethene was detected. The yield of ethene from c-DCE was nearly 20% in the first hour. After the completion of c-DCE dechlorination, ethene concentrations in the headspace decreased slightly while the yield of ethane increased to $\sim 80\%$. The sum of ethane and ethene accounted for $> 90\%$ of the initial c-DCE carbon. Rapid transformations were also observed for t-DCE (Fig. 1(d)) and 1,1-DCE (Fig. 1(e)) in which complete dechlorination was also achieved within 90 min. Overall carbon mass balance was $\sim 90\%$ in all the experiments. Furthermore, no chlorinated intermediates or products such as VC were detected above the detection limit (< 5 µg 1^{-1}).

The rate of degradation of VC observed in this experiment was comparable to the results for PCE and TCE and DCEs (Fig. 1(f)). Twenty micrograms 1^{-1} of VC disappeared from the aqueous solution within 90 min. About 70% of the VC carbon was found as ethane, 10–20% less than the five compounds discussed above. Only trace levels of ethene ($< 1\%$) appeared briefly in the headspace.

Compared to results from published studies using commercial grade iron particles (mostly on the millimeter scale), the above results show some similarities in terms of product formation. For example, hydrocarbons such as ethane and ethene are the major products. Ethane ($\sim 15\%$) and ethene ($\sim 35\%$) were the major products for TCE reaction with iron [3]. In another study, it was noted that the ethene ($\sim 50\%$) was only final product from the reaction between VC and iron [24]. Formation of acetylene during PCE reaction with iron and zinc was also reported [5]. Interestingly, in a system containing Pd, the fraction of chlorinated ethene converted to ethane was much higher (55–85%) while the yield of ethene was $< 5\%$ [25]. It appears that reduction of chlorinated ethenes in the presence of palladium tends to be more complete with significantly higher yields of ethane.

The precise role of palladium for the quick and complete reduction in a bimetallic system is not fully understood. It was hypothesized that hydrogen gas intercalated in the palladium lattice may serve as a powerful reducing agent for the dechlorination reactions [26]. Studies using high-resolution X-ray photoemission spectroscopy indicate catalytic functions (i.e. chemosorption) of palladium surface. For example, adsorbed PCE and TCE are converted to Cl and C atoms [27,28]. Presence of palladium on the surface of iron certainly creates many galvanic (bimetallic) cells, thus promoting the electron release reactions of iron corrosion.

An advantage of the nanoscale bimetallic particles is that much less chlorinated intermediates or final products are generated. Numerous investigators have observed that lesser-chlorinated compounds such as DCEs and VC undergo dechlorination much slower than PCE and TCE. The reaction rates typically follow the trend of PCE > TCE > *cis*-DCE > VC [29]. As a result, partially dechlorinated intermediates and products have been observed to accumulate. For example, 3–3.5% of DCEs and VC were detected during TCE degradation with iron [3]. Similar results were also reported in several other studies [4,30,31]. In this study, no chlorinated intermediates or products such as VC were detected above the detection limit (< 5 µg 1^{-1}).

3.2. Reaction of PCE with microscale iron particles

To further investigate the differences between the nanoscale particles and commercial-grade iron particles, batch experiments with commercial grade iron powders were conducted under similar environmental conditions. Fig. 2 presents the results of the batch reaction between PCE and with the Aldrich iron powders (< 10 μm, 0.91 m^2 g^{-1}). Besides a much higher metal loading (20 g Fe/25 ml), other experimental conditions were identical to the experiments described above for nanoscale particles. Batch experiments using larger iron particles yielded much slower and incomplete reactions with the chlorinated ethenes. For example, after a 50 h contact time, 85% of the parent PCE (20 mg l^{-1}) remained in the solution, 70% after 90 h. Of the 30% PCE that disappeared, ~ 14% was found in the form of TCE. Measurable ethane and ethene did not appear until 106 h, and increased slowly after that. After 142 h, 38% PCE was removed from the solution. 13% of the original carbon was found in the form of TCE. 11% in the form of ethene, 4% in the form of ethane, and 10% unidentified (Fig. 2). This experiment confirmed that for the commercial-grade iron particles:

(1) the reaction rate was much slower; (2) a substantial fraction of PCE was converted to undesirable chlorinated products (e.g. TCE); and (3) the yield of ethene was higher than ethane.

3.3. Rates of dechlorination reactions

The above descriptions of changes in concentrations of chlorinated ethylenes are system-specific. To better compare dechlorination rates observed for metal particles of various sizes, it is useful to normalize the reaction rate to the particle surface area. The rate of transformation for a chlorinated organic compound in a batch system can be described by the following Eq. [29]:

$$\frac{dC}{dt} = - k_{SA} a_s \rho_m C \qquad (4)$$

where C is the concentration of organic compound in the aqueous phase (mg l^{-1}), k_{SA} is the surface-area-normalized rate coefficient (l h^{-1} m^{-2}), a_s is the specific surface area of metal (m^2 g^{-1}), ρ_m is the mass concentration of metal (g l^{-1}), and t is time (h). For a specific system, k_{SA}, a_s and ρ_m are constants. The above equation therefore represents a pseudo-first-order kinetics.
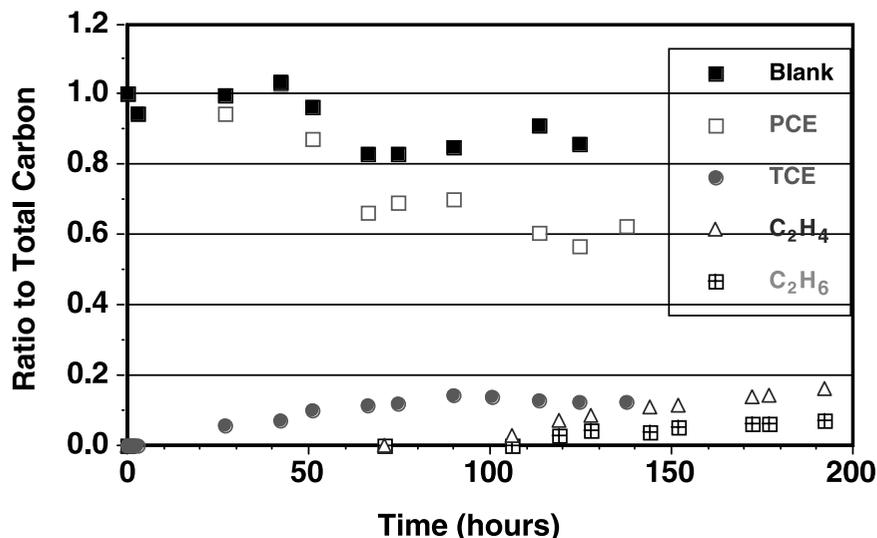
Fig. 2. Reactions of commercial grade iron particles (Aldrich, < 10 μm) with PCE. Initial PCE concentration was 20 mg l^{-1}. Metal loading was 40 g/50 ml.
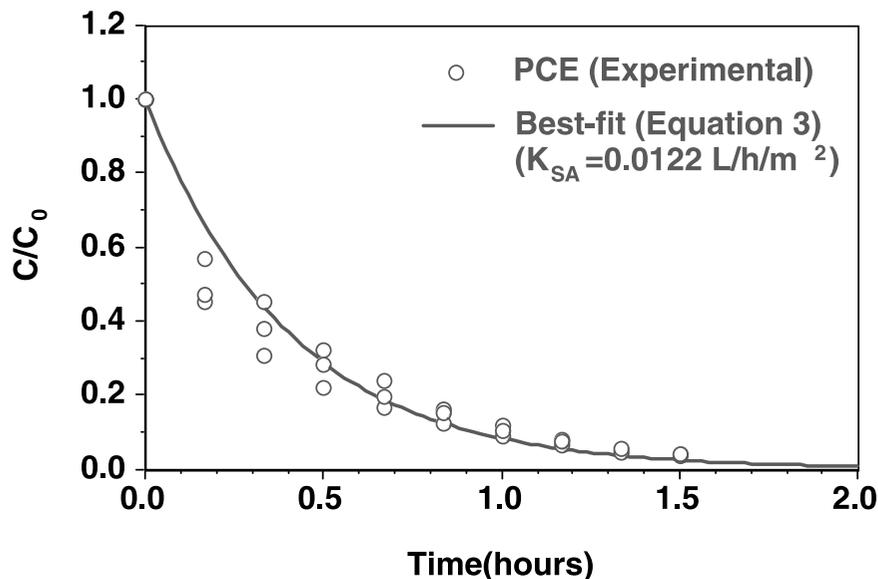
Fig. 3. Best-fit k_{SA} for PCE reaction with nanoscale Pd/Fe bimetallic particles.

Table 1
k_{SA} values for reactions of chlorinated ethenes with metal particles

Metal particles	PCE	TCE	t-DCE	c-DCE	1,1-DCE
Nanoscale Pd/Fe (l h^{-1} m^{-2})	(12.2 ± 0.36) $\times 10^{-3}$	(18.2 ± 1.18) $\times 10^{-3}$	(15.1 ± 2.08) $\times 10^{-3}$	(17.6 ± 1.34) $\times 10^{-3}$	(11.5 ± 1.25) $\times 10^{-3}$
Commercial grade Fe [a] (l h^{-1} m^{-2})	(2.1 ± 2.7) $\times 10^{-3}$	(3.9 ± 3.6) $\times 10^{-4}$	(1.2 ± 0.4) $\times 10^{-4}$	$(4.1 \pm 1.7) \times 10^{-5}$	$(6.4 \pm 5.5) \times 10^{-5}$
Ratio[b]	5.80	46.67	125.8	429.2	179.6

[a] From Johnson et al. (1996).
[b] Ratio = k_{SA}(Nanoscale Pd/Fe)/k_{SA}(Commercial Grade Fe).

Data presented in Fig. 1 can be fitted well to this pseudo-first-order model ($R^2 > 0.97$). An example is given in Fig. 3 in which the best-fit k_{SA} value of PCE reaction with the nanoscale Pd/Fe particles was calculated to be 0.0122 l h^{-1} m^{-2}. Values of k_{SA} for other compounds are given in Table 1. Table 1 also lists literature k_{SA} values for commercial grade iron particles [29]. Three observations can be made: (1) k_{SA} values for the nanoscale metal particles were much (5.8–429 times) higher than the commercial-grade iron particles. The results for nanoscale bimetallic iron particles are consistent with experimental observations for palladized iron (40 mesh), which was found more than an order of magnitude faster

than zero-valent iron for the transformation of TCE [31]. Several factors may contribute to this rate enhancement. Laboratory synthesized nanoscale iron surface may have a 'fresher' metal surface due to less surface oxidation and/or surface contamination. Mass transfer resistance in the batch system could also be less significant. It was observed that the Aldrich iron particles were settled at the bottom of the batch bottle while most of the nanoscale iron particles were suspended in solution. Therefore, slow transport or diffusion of chlorinated ethenes to the settled Aldrich iron surfaces may have contributed to the slower reaction for the commercial-grade iron particles. (2) Discrepancies of the k_{SA} values of

the nanoparticles toward the chlorinated ethenes are quite small (max/min = 1.50), compared to orders of magnitudes for the larger iron particles. (3) Since both a_s and k_{SA} are tens to hundreds of times higher than those of commercial-grade iron particles, overall performance of a nanoscale metal system could be potentially thousands of times better according to Eq. (4). This is especially important for injection of the iron particles into groundwater. To avoid clogging, it is beneficial to inject only a small of amount of highly reactive metal particles.

3.4. Stability of the nanoscale metal particles

One of most frequently asked question for the nanoparticle technology is the long-term performance and reactivity. Due to their small size and large surface area, the nanoparticles react very rapidly with a wide variety of oxidants in groundwater including dissolved oxygen, natural organic matter and water. It is speculated that nanoparti-

cles may have limited life time in the subsurface environment. Previous experiments conducted in my laboratory have demonstrated excellent reactivity up to 6 months in batch soil–water slurries. In experiments with nanoscale iron particles (no Pd), significant surface oxidation was observed in very short time periods. Freshly synthesized iron particles exhibit a characteristic dark color. The observed color tends to change to light brown in a few hours and reddish-brown within a few days, indicating extensive surface rusting or oxidation. Batch experiments further showed that the reactivity of nanoscale iron particles for the transformation of PCE and TCE declined substantially (> 80%) after exposed to air for a few days.

However, a much slower color change was noticed for the nanoscale Fe/Pd particles. Fig. 4 shows an example of an experiment of t-DCE reactions with 2-week old Pd/Fe particles (exposed to air). The major objectives of this experiment were to examine the stability of the metal particles under circumstances of repeated spikes
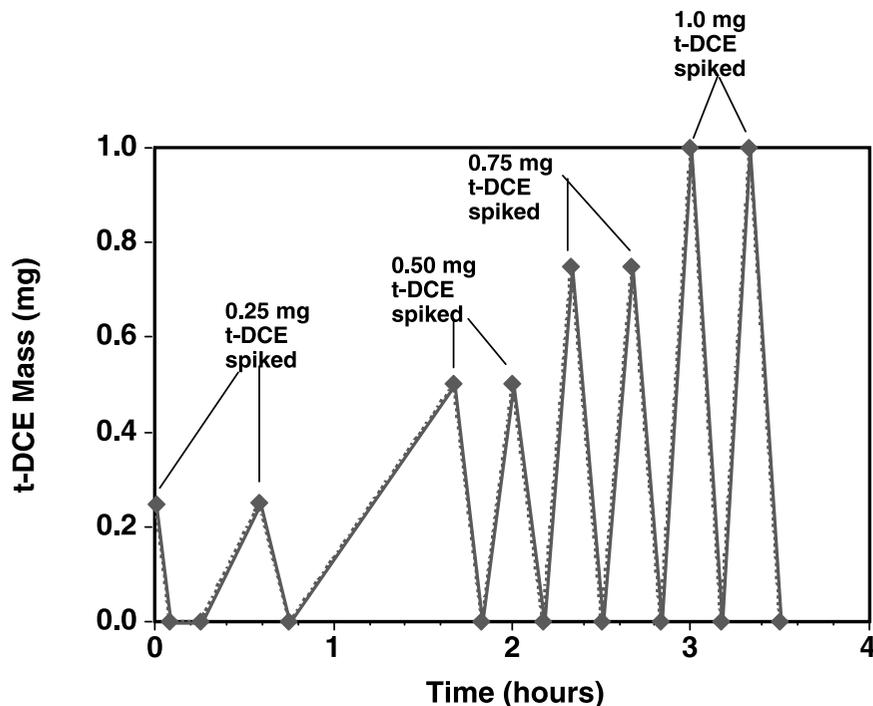
Fig. 4. Reactions of nanoscale Pd/Fe bimetallic particles with t-DCE. t-DCE was spiked into a 5 ml solution containing 0.5 g nano-Pd/Fe particles.

of contaminants and evaluate possible product inhibition for the dechlorination reactions. During this experiment, increasing doses of t-DCE were spiked into a 5 ml solution containing 0.5 g of nanoscale Pd/Fe particles. The dosage of t-DCE increased from 0.25 mg (or 50 mg l^{-1}) to 0.5, 0.75 and finally 1.0 mg (200 mg l^{-1}). As shown in Fig. 4, complete reduction of the spiked t-DCE in each cycle took ~ 20–30 min. Similar results were also observed for reactions with PCE and TCE [4].

In summary, the nanoscale Pd/Fe bimetallic particles have been shown to be very effective for the complete dechlorination of chlorinated ethenes. Advantages of the nanoscale iron system for treatment of chlorinated organic pollutants include: (1) High specific surface area; and (2) High surface reactivity. We have demonstrated that surface-area-normalized reactivity for the transformation of chlorinated ethenes (PCE, TCE, DCEs and VC) is one to two orders of magnitude higher than those reported in the literature for commercial grade iron particles; (3) Elimination of toxic chlorinated byproducts. Experiments with PCE, TCE, DCEs and VC suggest that there is no accumulation of chlorinated intermediate or toxic end products; and (4) Stability. The laboratory-synthesized nanoscale particles have been shown to be quite stable under ambient conditions. It is expected that the nanoparticles can remain reactive for extended periods of time in the subsurface environment.

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