

Synthesizing Nanoscale Iron Particles for Rapid and Complete Dechlorination of TCE and PCBs

CHUAN-BAO WANG AND
WEI-XIAN ZHANG*

Department of Civil and Environmental Engineering, Lehigh University, Bethlehem, Pennsylvania 18015

Transformation of halogenated organic compounds (HOCs) by zero-valent iron represents one of the latest innovative technologies for environmental remediation. For example, iron can be used to construct a reactive wall in the path of a contaminated groundwater plume to degrade HOCs. In this paper, an efficient method of synthesizing nanoscale (1–100 nm) iron and palladized iron particles is presented. Nanoscale particles are characterized by high surface area to volume ratios and high reactivities. BET specific surface area of the synthesized metal particles is 33.5 m²/g. In comparison, a commercially available Fe powder (<10 μm) has a specific surface area of just 0.9 m²/g. Batch studies demonstrated that these nanoscale particles can quickly and completely dechlorinate several chlorinated aliphatic compounds and a mixture of PCBs at relatively low metal to solution ratio (2–5 g/100 mL). Surface-area-normalized rate constants (k_{SA}) are calculated to be 10–100 times higher than those of commercially available iron particles. The approach presented offers unique opportunities for both fundamental research and technological applications of zero-valent metals. For example, a potential application of the nanoscale particles is to inject the metal particles directly into contaminated aquifers instead of building iron walls.

Introduction

Destruction of halogenated organic compounds (HOCs) by zero-valent iron represents one of the latest innovative technologies for environmental remediation (1, 2). Laboratory research in the past few years has shown that granular iron can degrade many HOCs, including chlorinated aliphatics (3), chlorinated aromatics (4), and polychlorinated biphenyls (PCBs; 5). Prospect for field application also looks promising. Granular iron can be adapted in the “funnel and gate” treatment system (1, 6), in which a porous wall of granular iron is constructed in the path of a contaminated groundwater plume. As contaminated water passes through the reactive barrier, HOCs react with the surface of iron and form mostly benign compounds such as hydrocarbons, chloride, and water.

Implementation of the zero-valent iron technology still faces several challenges (7): (i) production and accumulation

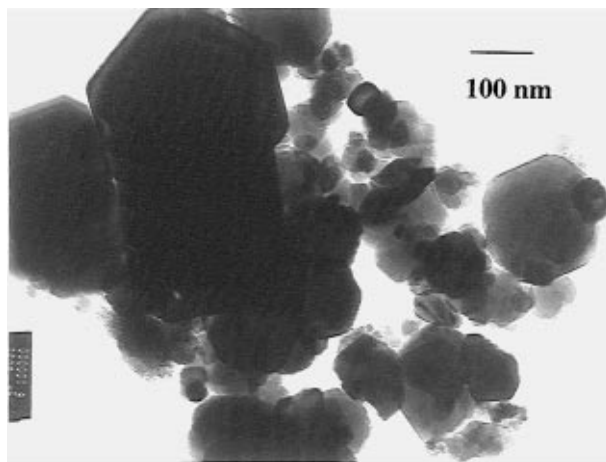


FIGURE 1. Transmission electron microscopy image of nanoscale Fe particles.

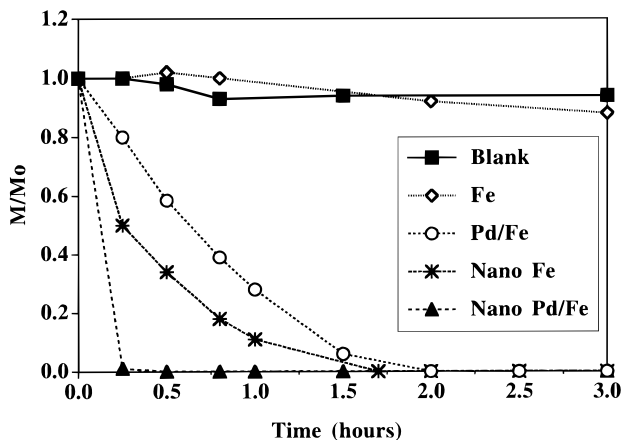


FIGURE 2. Reactions of TCE with commercial Fe powders (Fe), Pd-modified commercial Fe powders (Pd/Fe), nanoscale Fe particles (Nano Fe), and nanoscale Pd/Fe particles (nano Pd/Fe). Initial TCE concentration was 20 mg/L. Metal to solution ratio was 2 g/100 mL.

of chlorinated byproducts due to the low reactivity of iron powders toward lightly chlorinated hydrocarbons. For example, reduction of tetrachloroethene (PCE) and trichloroethene (TCE) by zero-valent iron has been observed to produce *cis*-1,2-dichloroethene (DCE) and vinyl chloride (VC; 3, 8). Both are of considerable toxicological concern; (ii) decrease of iron reactivity over time, probably due to the formation of surface passivation layers or due to the precipitation of metal hydroxides [e.g., Fe(OH)₂, Fe(OH)₃] and metal carbonates (e.g., FeCO₃) on the surface of iron; (iii) engineering difficulties for constructing metal wall in deep aquifers (e.g., >30 m).

Many other metals, particularly zinc and tin, can transform HOCs more rapidly than iron (9). Palladium, with its catalytic ability, produces dramatic results as well. For example, recent studies have demonstrated that palladized iron can completely dechlorinate many chlorinated aliphatic compounds to hydrocarbons (10). The Pd/Fe bimetallic complexes have also been found to degrade PCBs with all the chlorines replaced by hydrogen to yield biphenyl (11).

* To whom all correspondence should be addressed; phone: (610)-758-5318; fax: (610)758-6405; e-mail: wez3@lehigh.edu.

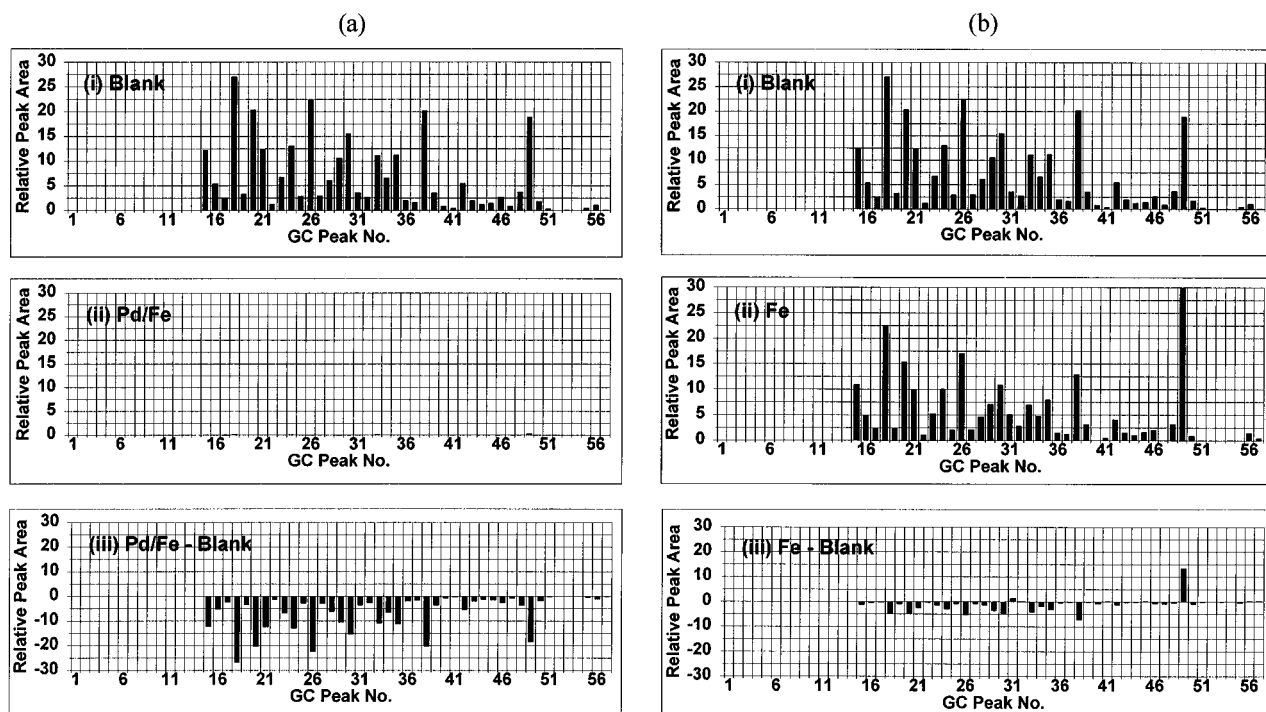
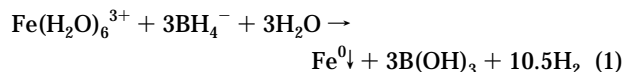


FIGURE 3. Changes in GC relative peak areas of an Aroclor 1254 solution in 17 h with (a) nanoscale Pd/Fe particles and (b) nanoscale Fe particles. GC peaks in (i) were from blank samples. Peaks in (ii) were from samples containing the nanoscale Fe or Pd/Fe particles. Peaks in (iii) were the difference between (ii) and (i) and represented the net degradation. Initial PCB concentration was 5 mg/L. Metal to solution ratio was 5 g/100 mL.

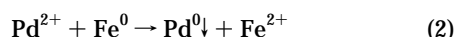
We report here an efficient method of synthesizing nanoscale iron and palladized iron particles and the results of using these metal particles for transformation of TCE and PCBs. Nanoscale metal particles, with diameter in the range of 1–100 nm (10^{-9} to 10^{-7} m), are characterized by high surface area to volume ratios, high levels of stepped surface, and high surface energies (12, 13). Instead of building metal walls, nanoscale metal particles may be applied through direct injection of metal particle suspensions to contaminated sediments and aquifers (14). Freshly prepared metal particles free of surface contamination and with very high reactivities also provide ideal tools for elucidating fundamental mechanisms of dechlorination at the metal–solution interface. Furthermore, nanoscale metal particles can be anchored on solid supports such as activated carbon, zeolite, and silica for ex-situ treatment of contaminated water and industrial effluent.

Experimental Methods

Methods for Synthesis. Nanoscale Fe particles were produced by adding 1.6 M NaBH_4 (98%, Aldrich) aqueous solution dropwise to a 1.0 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (98%, Aldrich) aqueous solution at ambient temperature with magnetic stirring. Ferric iron (Fe^{3+}) was reduced according to the following reaction (15):



The wet Fe precipitates were coated with a thin layer of palladium by saturating the above precipitates with an ethanol solution of $[\text{Pd}(\text{C}_2\text{H}_3\text{O}_2)_2]_3$ (47.5%, Alfa Aesar). This caused the reduction and subsequent deposition of Pd on the Fe surface through the following reaction (11):



Similar procedures were also employed to coat Pd on commercial iron powders (Aldrich, >99.9%, <10 μm).

Characterization of Synthesized Metal Particles. Surface areas (BET area) of the synthesized particles were measured using the nitrogen adsorption method with a Gemini 2360 surface analyzer. Prior to the measurements, dry Fe and Pd/Fe particles were obtained by washing the wet precipitates with acetone and drying them at 110 °C for 6 h under a flow of N_2 . Morphology of the particles was observed with a Phillips EM 400T transmission electron microscopy (TEM) at 120 kV to characterize the size and size distribution of the metal particles. Crystal structures were examined with an APD 1700 automated powder X-ray diffractometer (XRD) with nickel-filtered $\text{CuK}\alpha$ radiation ($\lambda = 0.1542$ nm).

Batch Experiments with TCE. Batch experiments were conducted to investigate reactivity of the synthesized particles for dechlorination of TCE. A 50-mL sample of 20 mg/L TCE aqueous solution and 1.0 g of the Fe or Pd/Fe particles were charged into a 50-mL serum bottle capped with a Teflon Mininert valve. The bottle was mixed on a rotary shaker (30 rpm) at ambient temperature (22 ± 1 °C). Parallel experiments were also performed without metal particles (blank) or commercial Fe powders (Aldrich, >99.9%, <10 μm). Periodically, 0.5 mL of the aqueous solution was withdrawn by a 1-mL gas-tight syringe into a 2-mL vial and extracted with 0.5 mL of pentane. Concentration of TCE was analyzed with a Hewlett-Packard Model 5890 GC equipped with an electron capture detector (ECD) and a BD-624 capillary column (Alltech Associates, Inc.). Hydrocarbon products in the headspace were identified with a Hewlett-Packard 5970 GC/MS.

Batch Experiments with PCBs. A 50- μL sample of 200 $\mu\text{g/mL}$ Aroclor 1254 was combined with 0.1 g of the wet Fe or Pd/Fe particles and 2 mL of ethanol/water solution (volume ratio = 1:9), followed by mixing on a rotary shaker (30 rpm) for 17 h. Analytical methods were similar to those described above for TCE experiments. A 0.5-mL sample PCB solution was extracted by 0.5 mL of pentane and analyzed with GC-ECD.

Results

Figure 1 shows a transmission electron microscopy image of the synthesized Fe particles. More than 90% of the particles were in the size range of 1–100 nm. BET specific surface area of the particles was 33.5 m²/g. In comparison, a commercially available fine iron powder (Aldrich, >99.9%, <10 μm) has a specific surface area of about 0.9 m²/g, or 37 times less than that of the synthesized particles. XRD analysis further revealed the periodic lattice arrangement of iron atoms, indicating crystalline structure of the nanoscale particles.

Degradation of TCE by various metal particles is presented in Figure 2. In all experiments, initial TCE concentration was 20 mg/L. Metal to solution ratio was 2 g/100 mL. The amounts of TCE in blank samples (without metal particles) and in the commercial Fe solution (Fe) remained relatively constant within a period of 3 h. TCE was completely dechlorinated by palladized commercial Fe powders (Pd/Fe) within 2 h, by the synthesized nanoscale Fe particles within 1.7 h, and by the synthesized nanoscale Pd/Fe bimetallic particles within less than 0.25 h (the soonest our measurement had been made). In the solutions containing the nanoscale particles, no chlorinated byproduct (i.e., DCEs, and VC) was detected. Final reaction products in the headspace of nanoscale particle solutions were identified to be hydrocarbons, including ethene, ethane, propene, propane, butene, butane, and pentane.

Degradation of a PCB mixture (Aroclor 1254) solution by nanoscale Pd/Fe and Fe particles at ambient temperature (22 ± 1 °C) is shown in Figure 3. Initial PCB concentration was 5 mg/L. Metal to solution ratio was 5 g/100 mL. GC peaks in (i) were from blank samples. Peaks in (ii) were from samples containing the nanoscale Fe or Pd/Fe particles. Peaks in (iii) were the difference between (ii) and (i) and represented the net degradation within 17 h. Few changes were observed for GC peaks in the blank samples over a period of 17 h (data not shown), indicating no natural degradation of PCBs in the absence of the metal particles. In the presence of synthesized nanoscale Pd/Fe particles (Figure 3a), GC peaks disappeared completely within 17 h, suggesting complete dechlorination of PCB congeners of Aroclor 1254 by the nanoscale Pd/Fe particles at ambient temperature. In solution containing the nanoscale Fe particles (Figure 3b), only partial PCB reduction (<25% of the total mass) was observed within the same time period. Accumulation of biphenyl was confirmed by GC/MS in both solutions. In contrast, little degradation of PCBs was observed with the commercial iron powders under the same experimental conditions.

In summary, freshly synthesized nanoscale Fe particles were more reactive than the commercial Fe powders, likely due to the high specific surface area and higher surface reactivity. Surface-area-normalized rate constants (K_{SA} ; 16) for the synthesized nanoscale particles (nano Fe) are calculated to be $3.0 \times 10^{-3} \text{ L hr}^{-1} \text{ m}^{-2}$. In comparison, values of K_{SA} for commercially available iron particles are generally below $1.0 \times 10^{-3} \text{ L hr}^{-1} \text{ m}^{-2}$ (16). Nanoscale Pd/Fe bimetallic particles (nano Pd/Fe) were even more reactive than the pure

Fe. K_{SA} for the synthesized nanoscale Pd/Fe particles is about $0.1 \text{ L hr}^{-1} \text{ m}^{-2}$, much higher than those of pure iron particles. Palladium could promote dechlorination reactions by serving as a catalyst accelerating the dissociation of chlorinated hydrocarbons (17). Palladium could also promote the dechlorination reactions by preventing the formation of iron oxides. Experiments have confirmed that the nanoscale Fe particles exposed to air reacted much more slowly with PCE and TCE than the freshly prepared iron particles. Addition of Pd onto Fe surface significantly reduced the oxidation of iron, thus preserving the reactivity of the zero-valent iron (17). We believe that the approach outlined here offers opportunities for both fundamental research and technological applications of zero-valent metals. Further studies are needed to delineate the underlying mechanistic steps of dechlorination on metal surfaces and to expand the scope of this synthesis method to other metals.

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