Carbothermal Synthesis of Carbon-supported Nanoscale Zero-valent Iron Particles for the Remediation of Hexavalent Chromium

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Nanoscale, zero-valent iron is a promising reagent for in situ reduction of a variety of subsurface contaminants, but its utility in full-scale remediation projects is limited by material costs. Iron nanoparticles (20-100 nm diameter) supported on carbon (C-Fe⁰) were synthesized by reacting iron salts, adsorbed or impregnated from aqueous solutions onto 80 m²/g carbon black, at 600-800 °C under Ar. Similar products were obtained by heating the reactants under air in a covered alumina crucible. X-ray powder diffraction patterns show that Fe₃O₄ particles are formed at 300-500 °C in the initial stage of the reaction and that these particles are reduced to a mixture of α - and γ -Fe nanoparticles above 600 °C. When C-Fe⁰ was combined with carboxymethylcellulose in a 5:1 weight ratio in water, the resulting material had similar transport properties to previously optimized nanoiron/polyanion suspensions in water-saturated sand columns. At a 10:3 Fe/Cr mole ratio, C—Fe⁰ reduced a 10 ppm Cr(VI) solution to \sim 1 ppm within three days. The surface area normalized first-order Cr removal rate was 1.2 h⁻¹ m⁻² under these conditions. These results demonstrate that reactive nanoiron with good transport properties in water-saturated porous media can be made in a scalable process from inexpensive starting materials by carbothermal reduction.

Introduction

The contamination of soil and groundwater is a widespread environmental problem (1). Dense nonaqueous phase liquids (DNAPLs) such as chlorinated hydrocarbons and polychlorinated biphenyls (PCBs) are very long-lived in the subsurface environment, and the methods currently used to eliminate or detoxify these compounds can take decades to effectively remediate a contamination site (2). The in situ chemical reduction of contaminants by zero-valent iron nanoparticles, or nanoiron, represents a potentially more effective, lower cost alternative to remediation technologies such as pumpand-treat, flushing with solvents and surfactants, steam treatment, and natural attenuation via bio and phytoremediation (3–6). In addition to halogenated compounds (7, 8), pollutants such as nitroaromatics and a variety of metal ions including Cr(VI) and As(V) can also be remediated by nanoiron reduction (9-11).

Although nanoiron has been studied for over a decade as an environmentally benign chemical reducing agent for DNAPLs, nitroaromatics, perchlorate, hydrocarbons, and toxic metal ions in the subsurface, there are still serious technical challenges associated with its use (12-17). Until recently, the poor transport properties of nanoparticles in porous media such as soil and groundwater aquifers has made nanoiron relatively ineffective for in situ remediation. Recent studies have shown that the transport of nanoparticles can be improved dramatically by using microemulsions (18) or polymers as "delivery vehicles", (19-23) and this approach has now been field tested and commercialized (24, 25). Controlling the aggregation of nanoparticles (26), targeting them to contaminant source zones in the subsurface (27), and optimizing their reactivity and stability (28, 29) are some of the remaining technical challenges. Another important problem is the high materials cost associated with nanoiron remediation. Because contaminants are typically distributed over very large volumes of soil and groundwater, effectively treating them requires a large stoichiometric excess of iron. A typical full-scale remediation project may involve several thousand pounds of nanoiron (25). Although iron is inexpensive in bulk form or as microparticles, reactive nanoparticles are much more expensive because of the materials and processes needed to make them. The most reactive iron nanoparticles are made by borohydride reduction of aqueous iron(II) salts (30, 31). However, this process is not easily scalable because of the large volumes of hydrogen gas generated in the reaction, and borohydride salts are expensive reagents. An alternative process developed by Toda Kogyo, Ltd. uses hydrogen as a reducing agent for iron oxide nanoparticles at 350-600 °C (32). Although this process is scalable and has been commercialized, it involves a number of chemical processing steps to synthesize the oxide nanoparticles and then reduce them in a batch process. There is, thus, a high capital cost associated with producing large quantities of nanoiron by hydrogen reduction.

In this paper, we explore a simple, inexpensive process for making reactive iron nanoparticles by reacting soluble iron salts with carbon black. The carbothermal reduction process is analogous to that used in the production of iron and steel from iron ore. Because the reduction of iron oxides by carbon is endothermic and gives only gaseous byproducts, it is potentially scalable to large reactors and continuous processing. The use of excess carbon in the process also has the potential to provide a hydrophobic carbon support for the Fe⁰ nanoparticles. We report here the synthesis and characterization of these carbon-supported particles, as well as preliminary experiments to quantify their reactivity and transport behavior in sand-packed soil columns.

Experimental Section

Preparation of C–Fe⁰ Particles. Compressed carbon black (Alfa Aesar), with a surface area of 80 m²/g, was combined with aqueous solutions of iron(II) or iron(III) salts, either by adsorption or by impregnation. In a typical adsorption procedure, 50 g of Fe(NO₃)₃•9H₂O (Sigma-Aldrich, FW 404.00) and 5 g of carbon black were mixed in 200 mL of deionized, nanopure water, with a resistivity of 18.2 MΩ cm. The supernatant solution was separated from the solid using a vacuum filtration flask with a 47 mm diameter nylon membrane filter, 0.2 μm, (Whatman). The solid was removed from the filter while still slightly damp and placed in a vacuum

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oven, without heating, overnight to dry. The solid was then placed in an alumina boat in a quartz tube inside a tube furnace and heated to 800 °C, ramp rate 4.5 °C/min, under Ar, flow rate 200 ccpm, and kept at that temperature for 3 h. The tube was purged with Ar for 1 h before heating began, and the sample was allowed to cool to ambient temperature and to remain under Ar for several hours before removing from the tube furnace. The resulting carbon-supported nanoiron (C–Fe⁰) particles were then handled in air for characterization and reactivity and transport measurements.

The minimum temperature of the carbothermal iron reduction was determined by dividing a sample of carbon black with adsorbed iron (from ferric nitrate solution) into 1 g portions; the first was heated to 200 °C under Ar at a ramp rate of 4.5 °C/min. Each subsequent sample was heated 100 °C higher than the previous one. The final sample was heated to 800 °C. The same 1 h purging time was used for each sample. Ambient temperature X-ray powder diffraction patterns were then obtained from each sample.

The impregnation synthesis of C–Fe⁰ particles differs slightly from the adsorption method described above. Instead of 5 g of carbon black, 0.5 g was used. The number of moles of iron in 5 g of Fe(NO₃)₃·9H₂O was calculated and was used to determine the amount of each iron salt, in order to keep the same ratio of iron to carbon in all experiments. These amounts were: 2.153 g of iron(II) acetate, anhydrous, packaged under Ar (Alfa Aesar); 2.994 g of iron(III) oxalate hexahydrate (Alfa Aesar); and 3.701 g of iron(III) citrate trihydrate (Alfa Aesar). Each compound was combined in a vial with 0.5 g of carbon black and 50 mL of deionized water, and the mixtures were stirred overnight. The vials were then attached to a rotary film evaporator (Evapotec), and the water was evaporated. The particles were then placed in the vacuum oven to fully dry. The procedure for heating the particles was the same as that described above.

A scaled-up synthesis of C-Fe⁰ particles followed the iron(III) nitrate adsorption method described above with slight modifications. A 40 g portion of carbon black and 400 g of iron(III) nitrate nonahydrate were combined by the adsorption method described above, and the solid was filtered and dried. The reduction was not performed under inert atmosphere. Instead, the sample was heated in a box furnace (Fisher Scientific) that had vents that were open to the air. The samples were placed in a 300 mL alumina crucible with a loosely fitting cover. Two experiments were carried out. In one, no attempt was made to control the atmosphere, that is, the atmosphere in the furnace was ambient air. In the other experiment, a partially deoxygenated atmosphere was achieved by pumping in N₂ gas into the box furnace. The furnace was purged for 1 h before the sample was heated. In this way, the partial pressure of oxygen in the furnace was reduced to approximately 0.1 atm, as determined by sampling the atmosphere and analyzing it with a Buck Scientific gas chromatograph, model 910, with a 60/80 molecular sieve, 5 Å stainless steel column (Supelco), 10 ft. \times 1/8 in., a thermal conductivity detector (Buck Scientific), and an ultra high purity Ar carrier gas. In both experiments, the particles were heated to 800 °C and were held at that temperature for 3 h; the ramp rate was not controlled but was approximately 40 °C/min.

Physical Characterization. X-ray powder diffraction (XRD) was performed on a Phillips X'Pert MPD X-ray diffractometer, using Cu K α radiation at 40 kV and a step size of 0.03° 2 θ at 1.5 s/step. Nitrogen Brunauer–Emmet–Teller (BET) adsorption isotherms were obtained using a Micromeritics ASAP 2010 surface area analyzer. Transmission electron microscope (TEM) images were obtained at the Electron Microscopy Laboratory at the Pennsylvania State University using a JEOL 1200EXII microscope. The total iron content of samples was determined colorimetrically by the

phenanthroline complexation method (33), as described in detail elsewhere (19). The absorbance of solutions at 508 nm was measured with a Hewlett-Packard 8452A diode array spectrophotometer. Zero-valent iron content was measured by digesting 35 mg aliquots of the C-Fe⁰ sample in 1 mL of 12.1 M HCl (aq) in a sealed 125 mL Erlenmeyer flask (34). The flasks were purged with Ar for 30 min prior to addition of the HCl. After 5 h, 1.2 mL of 10 M NaOH (aq) was injected into the flask to neutralize the HCl and to eliminate the HCl vapors in the flask. The solution was then allowed to stand for 2 h, and a headspace sample was withdrawn using a gastight syringe. The gas sample was analyzed for H₂ by gas chromatography as described above, and the zero-valent iron content was calculated assuming that 1 mol of H₂ was produced per mole of zero-valent iron. A calibration experiment using granular Zn under similar conditions gave 80 \pm 5% of the theoretical yield of H_2 .

Analytical Measurements. A 10 ppm Cr(VI) stock solution was prepared by dissolving $19.2 \text{ mg of } \text{CrO}_3$ (Fisher Scientific), FW = 99.99, in 1000 mL of deionized water. A 70 mL portion of the Cr(VI) stock solution was added to aqueous zero-valent iron suspensions at a fixed Fe/Cr mole ratio of 10:3. These Fe–Cr and C–Fe–Cr suspensions were placed on a sample agitator and were allowed to react over one week. Measurements of the supernatant Cr(VI) concentrations were made 6-7 times, at varying intervals over the one-week period. Filtered solutions were analyzed for soluble Cr using a Shimadzu AA-6601F atomic absorption flame emission spectrophotometer with a VWR hollow cathode lamp, Cr 1.5 in. Air was used as the oxidant, and acetylene was used as the fuel source. Two different types of Fe⁰ were used as comparisons to C-Fe⁰ particles: RNIP, a reactive, microcrystalline α -iron with particle diameters ranging from 50 to 100 nm received as a 220 g of Fe/L aqueous suspension, which was combined with sodium polyacrylate (MW = 3500, supplied by Toda Kogyo) at a 10/1 Fe/polymer weight ratio; and HQ carbonyl iron powder (CIP) received from BASF, with an average particle diameter of 0.77 μ m. Carbon black with no added iron was used as a control. All Fe⁰-containing suspensions were prepared at a 1 mg/mL concentration of Fe⁰. To prepare the C–Fe⁰ suspensions, 82.7 mg of the powder was added to 21 mL of a carboxymethylcellulose (CMC) stock solution and sonicated for 15 min. The CMC solution was prepared by dissolving 17 mg of low viscosity carboxymethylcellulose sodium salt (Calbiochem) in 85 mL of deionized nanopure water. The HQ-CIP suspension was prepared by adding 21 mg of the iron powder to 21 mL of deionized nanopure water. To prepare the RNIP sample, a stock solution was made by taking 205 μ L of the RNIPpolyacrylate suspension and adding it to 45 mL of deionized nanopure water. The carbon black control suspension was prepared by adding 62 mg of carbon black to 21 mL of the CMC stock solution. The amount of carbon black in this control experiment was the same as the amount of carbon in the C–Fe⁰ suspension.

To test the transport behavior of the $C-Fe^{0}$ particles, 1.6 cm diameter glass buret columns were slurry-packed with 75 g of Ottawa sand (VWR, CAS 7631–86–9) to a height of 26 cm as described elsewhere (19). The column porosity was 42%. The sand was sieved through mesh screens to narrow grain size dispersity for sand-packed columns. The sand used was able to pass through a 40 mesh screen but was unable to pass the 60 mesh screen. The sand particles were measured to be $160 \pm 45 \,\mu$ m in diameter by an optical microscope. The columns were equipped with a two-way valve to set the flow rate at 18.0 mL/min, which corresponds to a Darcy flow rate of 0.152 cm/s. A small glass wool plug was placed at the tip of the column prior to the addition of the sand in order to prevent sand from draining out of the column. A 10 mL stock suspension was prepared containing 50 mg of C–Fe⁰ particles



FIGURE 1. TEM images of C-Fe⁰ particles synthesized by the adsorption method from ferric nitrate.



FIGURE 2. Iron nanoparticle diameters, showing best fits to log-normal distributions, as a function of the precursor salt used. The nitrate sample was made by adsorption and the others by the impregnation method.

and 10 mg of CMC. Two milliliters of this suspension was introduced to the top of the sand column. After allowing the sample to flow into the column, deionized water was added to maintain the flow through the column. A 200 mL portion of the eluted suspension was collected and was analyzed for iron content by the phenanthroline colorimetric method. The results were compared to the iron content of the original stock solution to determine the percent of total iron eluted through the columns.

Results and Discussion

Nanoparticle Synthesis and Characterization. Ferrous and ferric salts were combined with carbon black, either by adsorption or by impregnation from aqueous solutions, and then reacted at 800 °C under Ar to produce $C-Fe^0$ composites. This carbothermal reduction, using either adsorbed or impregnated iron salts, results in the formation of iron nanoparticles supported on residual carbon. In Figure 1, TEM images show that the $C-Fe^0$ aggregates consist of roughly spherical iron particles, ~20 to 150 nm in diameter, associated with aggregated carbon platelets, which are mostly ~20 nm in diameter. Figure 2 shows the distribution of iron particle diameters, with fits to log-normal distributions, from TEM images of $C-Fe^0$ composites prepared from different iron salt precursors. The three samples prepared by impregnation from oxalate, citrate, and acetate salts contain mostly small



FIGURE 3. XRD patterns of C-Fe samples heated in Ar to different temperatures. Peaks are color-coded according to phases identified. Miller indices are indicated in parentheses.

particles (<50 nm diameter), whereas the peak in the distribution is about 70 nm for C–Fe⁰ made by adsorption of Fe(III) from the nitrate salt. TEM images at intermediate stages of the reaction (see Supporting Information) show that the nitrate salt adsorption method leads to larger Fe₃O₄ particles, which in turn form larger Fe⁰ particles. In representative TEM images of each sample we found no iron particles that were not associated with residual carbon particles.

The nitrogen-BET surface areas of $C-Fe^0$ prepared by adsorption, using the ferric nitrate salt (130 m²/g), was higher than that of the carbon starting material, which had a surface area of 80 m²/g. The three samples prepared by impregnation had somewhat lower surface areas. The ferric oxalate, ferric citrate, and ferrous acetate samples had a surface areas of 64, 95, and 38 m²/g, respectively. These changes in surface area most likely reflect changes in the residual amount and the porosity of the carbon support, because the specific surface area associated with 50 nm spherical particles of Fe⁰ should be in the range of ~10 m²/g.

X-ray diffraction patterns of ferric nitrate-adsorbed carbon black heated to progressively higher temperatures (Figure 3) show that the threshold for the carbothermal reduction of iron is about 600 °C. In the first sample, heated to 200 °C, the only peaks that are clearly observable are aluminum peaks from the sample holder and a broad peak centered at 26° 2 θ (d = 3.4Å), corresponding to the 002 graphite-like reflection



FIGURE 4. Comparison of percent zero-valent iron, total iron, and theoretical iron content of $C{-}Fe^0$ samples.

of carbon black. At this stage, no peaks in the pattern can be attributed to iron-containing phases. For samples heated to 300–500 °C, magnetite peaks dominate the patterns (*35*), indicating that the adsorbed iron ions and/or salts have decomposed to form Fe₃O₄ nanoparticles. Based on a line-shape analysis of the diffraction patterns of the 300 and 400 °C samples, the diameter of the magnetite particles is 10 ± 3 nm.

Between 500 and 600 °C, the magnetite peaks essentially disappear and are replaced by peaks corresponding to elemental iron. Samples prepared at or above this temperature contain predominantly body-centered cubic α -Fe (*36*), along with a smaller amount of face-centered cubic γ -Fe, as expected in a carbon-rich environment. Interestingly, small γ -Fe peaks are present at temperatures as low as 500°, even though the γ phase is not thermodynamically stable below 723 °C in the Fe–C phase diagram (*37*). The progression of XRD patterns in Figure 3 strongly suggests that it is the solid-state reaction of carbon with Fe₃O₄ that gives the final Fe⁰ product. This observation implies that other "green" aqueous chemical routes or dry milling processes to make iron oxide nanoparticles could lead to similar final products in a reaction with high surface area carbons.

The XRD patterns of C–Fe⁰ particles prepared at 600 °C or above do not show any evidence of residual oxide phases, and this was confirmed by comparing the total amount of iron (determined by the phenanthroline method) to the amount of zero-valent iron (determined from the amount of H₂ evolved in acid) in each sample. The results are summarized in Figure 4. Within experimental error, the amount of zero-valent and total iron are the same for the three samples prepared by adsorption of ferric nitrate. For the three samples made by impregnation, approximately 70–80% of the iron in the sample is zero-valent.

The theoretical iron content was estimated for the samples prepared by impregnation from the stoichiometry of overall reactions 1-3. Reaction 4 represents the reaction of magnetite (which forms as an intermediate with ferric nitrate-adsorbed carbon) to produce Fe⁰. It was assumed that iron was retained quantitatively in the sample. Consistent with this assumption, there was no visual evidence for loss of iron, such as deposition of material on the walls of the reaction tube or furnace. Determination of the theoretical iron content was complicated by the fact that the distribution of gaseous products (and hence the amount of carbon volatilized in the reaction) was unknown. From reaction 1, the theoretical Fe⁰ content of C-Fe⁰ from iron(III) oxalate was 58 wt %. Theoretical values from the citrate and acetate precursors were 62 and 66 wt % iron, respectively. These values are 15% higher, on average, than the total iron measured by colorimetric analysis. The difference may be due to several factors. Adsorption of water from the air may add mass to the C-Fe⁰ samples. It is also possible that some of the iron in the sample is fully encapsulated by carbon and is not released by acid dissolution in the analysis. In reactions 2 and 3, a lower analytical percent iron (i.e., higher than theoretical percent carbon) in the samples would result if more oxidized volatile products (e.g., CO_2 and H_2O , rather than CO, C_3H_6O , and CH_2CO) were released in the reaction (*38*).

$$\operatorname{Fe}_{2}(\operatorname{C}_{2}\operatorname{O}_{4})_{3} \cdot 6\operatorname{H}_{2}\operatorname{O} \rightarrow 2\operatorname{Fe} + 6\operatorname{CO}_{2} + 6\operatorname{H}_{2}\operatorname{O}$$
(1)

$$2Fe(C_6H_5O7) \cdot 3H_2O + C \rightarrow$$

$$2Fe + 2C_2H_2O + 6CO_2 + CO + 5H_2O \quad (2)$$

$$Fe(C_2H_3O_2)_2 + C \rightarrow Fe + 2CH_2CO + CO + H_2O$$
 (3)

$$Fe_3O_4 + 2C \rightarrow 3Fe + 2CO_2 \tag{4}$$

In the case of ferric nitrate adsorption, UV–visible absorption data showed that approximately 35% of the Fe^{3+} ions in solution adsorbed to the carbon; however, the amount adsorbed is somewhat variable from sample to sample. For this reason we did not attempt to compare theoretical and analytical iron contents for C–Fe⁰ made by adsorption of Fe(III) nitrate.

Because reactions 1-4 are all endothermic; they should be readily scalable to larger batch syntheses or to continuous processes. The last two entries in Figure 4 show the results from scale-up of the reaction, using the adsorption method and ferric nitrate as the source of iron. In these cases, the iron-carbon precursor material was heated to 800 °C in a box furnace in a covered alumina crucible. In the "N2" sample, the furnace was first purged with nitrogen, but analysis of the atmosphere showed that it still contained oxygen at a partial pressure of approximately 0.1 atm. In the second case, ambient air was used as the atmosphere. The resulting ratio of zero-valent to total iron is high in both cases, which indicates that the product gases in the crucible are sufficient to prevent air oxidation of the iron in the product. Because both reaction 4 and the analogous reaction that produces CO_2 are endothermic, it appears that this reaction can be easily scaled up without concerns about autothermal heating. In the case of our experiments, the scale of these reactions was simply limited by the size of the crucibles and furnaces available in our laboratory. The solid products of these reactions may be handled in air, and we have not observed any obvious reaction of C-Fe⁰ with air. In contrast, some preparations of nanoiron by the borohydride method yield pyrophoric materials unless special precautions are taken to passivate the surface of the particles (39)

Reactivity with Cr(VI). Figure 5 compares the reactivity of $C-Fe^{0}$ (made from adsorbed ferric nitrate) and other samples of nano- and microiron with aqueous Cr(VI). To mimic the conditions of in situ remediation more closely, the two kinds of nanoiron ($C-Fe^{0}$ and Toda RNIP) used in the transport experiments described below were combined with anionic polyelectrolytes (carboxymethylcellulose (CMC) and polyacrylate (PAA) respectively).

In this reaction, chromium is removed from the solution as insoluble Cr(III) compounds (40). The RNIP sample reduced the Cr(VI) concentration from 10 ppm to ~1 ppm most rapidly, within about one day. The C–Fe⁰ particles reacted less rapidly, but after three days the level of Cr(VI) removal was similar to that found with RNIP. Carbon black combined with CMC was used as a control. This sample removed ~3 ppm of Cr(VI) from the solution essentially upon mixing, but the concentration remained constant for the next 7 days. It is likely that adsorption of Cr(VI) onto the carbon surface occurs. The HQ CIP sample also reduced the level of soluble chromium to ~7.5 ppm; this may be due in part to adsorption, but HQ-CIP has a very low surface area, on the order of 1 m²/g. It is also possible that a small amount



FIGURE 5. Removal of Cr(VI) from 10 mM aqueous solutions by $C-Fe^0/CMC$, RNIP/PAA, BASF HQ carbonyl iron powder, and carbon black. For each iron-containing sample, a 10:3 Fe/Cr mole ratio was used.

TABLE 1. Percent Iron in C-Fe 0 CMC Suspensions Eluted from 26 cm Water-saturated Sand Columns and Particle Zeta Potentials^a

iron salt precursor	% iron eluted	zeta potential (mV)
ferric nitrate ferric oxalate ferric citrate ferrous acetate	$\begin{array}{c} 40 \pm 2\% \\ 55 \pm 1\% \\ 16 \pm 0.5\% \\ 66 \pm 2\% \end{array}$	-83 -78 -73 -84

^a Each entry represents the average of 4 elution experiments (except for the last entry, which was done twice).

of reactive Fe⁰ at the surface of the micron-size particles reduces some of the Cr(VI) to insoluble Cr(III) hydroxides.

Transport of Polymer-Modified Fe Nanoparticles in Saturated Sand Columns. Table 1 compares the fraction of iron in C-Fe⁰ samples eluted from water-saturated sand columns under conditions previously optimized for HQ-CIP/ PAA and RNIP/PAA suspensions (19). In each case, a 2 mL sample of the carbon-supported nanoiron (10 mg/mL) stabilized with CMC (2 mg/mL) was eluted through a 26 cm column at 18 mL/min by using 200 mL of water. Under similar conditions, RNIP stabilized by an optimized polyelectrolyte mixture elutes to the extent of \sim 65%. There was substantial variation with precursor and synthetic method in the elution of C-Fe⁰ samples. High and low values (66 and 16% elution) were obtained with samples made from ferrous acetate and ferric citrate, respectively. C-Fe⁰ made from ferric oxalate and ferric nitrate samples had elution values of 55 and 40% respectively, comparable to RNIP/PAA samples (19). Zeta potential measurements gave similar values for all samples (-73 to -84 mV). The samples with the most negative zeta potentials had the highest percentage elution. This is consistent with the idea that negative charge lowers the particle sticking coefficient (19). However, other factors such as aggregate size are likely to play an important role as well (26).

These reactivity and transport data confirm the expectation (from microscopy data, Figure 1) that the $C-Fe^0$ composite particles are in a size range that can provide both rapid remediation of Cr(VI) and good transport through saturated soils. Nanoiron/carbon composites have been shown to have synergistic properties in remediation reactions, with the hydrophobic carbon surface adsorbing hydrophobic reagents such as trichloroethylene for reduction by nanoiron (20). The sorption and reactivity of these particles with chlorinated organic contaminants will be studied in future experiments.

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Supporting Information Available

Additional electron micrographs of $C-Fe^0$ at various stages of the reaction, comparing adsorbed and impregnated materials, and experimental details of the zeta potential measurements are provided. These materials are available free of charge at http://pubs.acs.org.

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