Degradation of Trichloroethene with a Novel Fe-C Nanocomposite

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Abstract

Nanoscale zero-valent iron (NZVI) is effective in reductively degrading dense non-aqueous phase liquids (DNAPLs), such as trichloroethene (TCE), although the NZVI technology itself still suffers from high material costs and inability to target hydrophobic contaminants in source zones. To address these problems, we developed a novel, inexpensive iron-carbon (Fe-C) nanocomposite material by simultaneously milling micron-size iron and activated carbon powder. Microscopic and X-ray diffraction (XRD) characterization of the composite material revealed that nanoparticles of Fe were dispersed in activated carbon and a new iron carbide phase was formed. Bench-scale studies showed that this material instantaneously sorbed >90% of TCE from aqueous solutions and subsequently decomposed TCE into non-chlorinated products. Compared to milled Fe, Fe-C nanocomposite dechlorinated TCE at a slightly slower rate and favored the production of ethene over other TCE degradation products such as C₃-C₆ compounds. When placed in hexane-water mixture, the Fe-C nanocomposite materials are preferentially partitioned into the organic phase, indicating the ability of the composite materials to target DNAPL for enhanced degradation.

Keywords: Activated carbon; ball mill; dechlorination; groundwater remediation; zero-valent iron nanoparticles

1. Introduction

In recent years, injection of nanoscale zero-valent iron (NZVI) to chemically reduce chlorinated solvents has been proposed as a potentially simple, cost-effective, and environmentally benign method to remediate dense non-aqueous phase liquids (DNAPLs) [1-4]. Complete dechlorination by Fe^0 converts chlorinated solvents to innocuous species (e.g., TCE to ethane) [5, 6].

Currently, three general approaches to NZVI manufacturing exist: solution-based precipitation, solid-based grinding, and gas-phase reduction of iron oxide nanoparticles. Solution-based methods mostly involve the reduction of ferrous or ferric iron by borohydride to precipitate Fe^0 nanoparticles [7-9]. Solid-based grinding (i.e., ball milling), on the other hand, uses a mechanical process to break macro-scale ZVI down to nanoscale particles [10]. This method of obtaining NZVI is relatively cost-effective and scalable. The third method involves reduction of iron oxide nanoparticles at high temperature in the presence of either hydrogen gas or elemental carbon [8, 11].

However, major challenges still remain unresolved for field applications of NZVI. First, due to their high surface energies and intrinsic magnetic interactions, NZVI particles aggregate into large clusters that impede their subsurface transport [12, 13]. Second, NZVI particles are oxidized spontaneously when exposed to molecular oxygen, resulting in significant decrease in reactivity [14]. Third, NZVI has a short lifetime in the subsurface due to its high reactivity with water [2]. Finally, the intrinsic hydrophilic properties of NZVI make the particles non-specific for treating hydrophobic contaminants in source zones [15].

Significant efforts have been made to address these challenges. For example, in order to minimize aggregation and increase mobility of NZVI particles, surfactants and polymers have been used to modify the surface of the nanoparticles [16-19]. NZVI has also been attached to matrices, such as carbon and silica, to achieve the same goal [20-22]. Among these support/stabilizing materials, carbon is thought to be the most viable because of its low cost, its sorptive property that enhances contaminant attachment to NZVI for reduction [23, 24], and its hydrophobicity that is specific for DNAPLs [22].

Several methods have been used to form Fe-C composite materials in recent years. One approach is to use borohydride to reduce iron salts that have been loaded onto activated carbon by wet impregnation or an adsorption process, thereby producing NZVI on surface and in the confined pores of carbon [16, 24, 25]. The Fe-C composites obtained were used to treat a variety of contaminants including PCBs [26], hexachlorobenzene [27], and TCE [24, 28]. Another method is carbothermal reduction, which involves saturating carbon black or activated carbon particles with iron salts, followed by heating the mixture at 600-800°C to produce Fe-C composites [20, 29]. Additional techniques are required to make the Fe-C composite small enough to be mobile in the subsurface. For example, hydrothermal and aerosol-based methods have been explored to produce carbon microspheres (0.1 -1 µm) from sugar, which were used as carbon supports to produce colloidal Fe-C composites through a variety of processes [22, 30-32]. Such colloidal Fe-C composites with sizes that favor subsurface transport were not only reactive to chlorinated solvents such as TCE (with rapid adsorption followed by continuous degradation), but also able to partition into DNAPLs. Alternatively, Fe-C composites were synthesized by doping milled activated carbon ($D_{50}= 0.8 \mu\text{m}$) with iron salts using wet impregnation, followed by transforming

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4 iron precursors to iron oxide/hydroxide by increasing pH, and then reducing the iron oxide to
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6 NZVI under H₂ at 450 to 520 °C, or under N₂ at 700 °C [33-35]. The Fe-C composites exhibited
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8 high reactivity toward TCE degradation ($k = 0.011\text{--}0.042 \text{ L hr}^{-1} \text{ g}^{-1}$) [34]. However, all these
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10 processes involve chemical reduction of oxidized iron, which inevitably increases the final cost
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12 of material synthesis.
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18 In this study, we explore the possibility of producing Fe-C nanocomposite in a single step. This
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20 is distinctly different from the concepts of milling micro-size iron to obtain NZVI (iron-based
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22 material only) [36], or milling carbon to obtain colloidal carbon as a support for chemically
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24 synthesized NZVI (involving multiple steps) [34]. Our approach employed a ball milling
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26 technique, in which micron-size Fe⁰ particles and activated carbon powders were ground
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28 together to produce a novel Fe-C nanocomposite material. It should be noted that the results
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30 achieved by ball-milling in this study are transferable for large-scale production-sized mills,
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32 which can process over 1000 kg of iron in each batch [36]. After synthesis, we systematically
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34 characterized the composite materials for particle size, morphology and distribution of chemical
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36 elements. Partitioning experiments were conducted to evaluate the effectiveness of the composite
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38 for targeting DNAPLs. The reactivity of the synthesized product was assessed by TCE
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40 dechlorination experiments.
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50 **2. Materials and Methods**

51 **2.1 Chemicals**

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53 Micron-size zero-valent iron (Hepure, iron content >95%, $d_{50} = \sim 44 \mu\text{m}$) and powdered activated
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55 carbon (Sigma Aldrich, St. Louis, MO) were used as the feed materials in ball-milling for
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4 composite material synthesis. Propylene glycol (99.5%, ACS Grade, Alfa Aesar) was used as a
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6 lubricant during Fe-C nanocomposite synthesis, and for maintaining reducing conditions. The
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8 following chemicals were used in TCE dechlorination studies. N-octane (99+%) was purchased
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10 from Sigma Aldrich (St. Louis, MO), and TCE (stabilized, J.T.Baker[®] ACS Reagent) from VWR
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12 (Suwanee, GA). Gaseous olefin standards (1000 ppm of ethene, propene, butene, pentene, and
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14 hexene) and paraffin standards (1000 ppm of methane, ethane, propane, butane, pentane, and
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16 hexane) were obtained from Matheson Tri-Gas (Twinsburg, OH). Gas calibration standards of
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18 acetylene (97.2 ppm), vinyl chloride (1000 ppm), chlorinated ethenes (1000 ppm of TCE, cis-
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20 1,2-dichloroethene, trans-1,2-dichloroethene, and 1,1-dichloroethene), and hydrogen (10.02%)
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22 were purchased from Air Liquide (Plumsteadville, PA). Ultrahigh purity helium and N₂ supplied
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24 by Air Liquide were used as carrier gases for gas chromatography.
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33 2.2 Ball milling for Fe-C nanocomposite production

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35 A laboratory-use ball mill (MiniFer) was purchased from Netzsch (Exton, PA, USA) for making
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37 the Fe-C nanocomposite. To prepare the composite material, 140 mL of zirconia beads (diameter
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39 of 0.9–1.1 mm) were first loaded into the mill chamber as the grinding medium. Then, 36 g of
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41 micro-size ZVI and 4 g of activated carbon powders were mixed with 400 ml of lubricant,
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43 propylene glycol, in an open mixing vessel. Propylene glycol is non-reactive toward Fe⁰ and has
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45 low vapor pressure and therefore was selected to maintain the reduced iron and to avoid
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47 production of flammable or hazardous gases in the laboratory. Lower viscosity media such as
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49 water and ethanol could be used to decrease the milling resistance (thus decreasing the milling
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51 energy) but water would react with Fe⁰ to produce flammable H₂ and ethanol would generate
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53 hazardous/flammable ethanol vapors in the open vessel. The milling speed was set at 3000 rpm
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4 and the feed materials and lubricant were circulated in the milling chamber at a rate at 150 ml
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6 min^{-1} . After 4 hours of milling, the Fe-C nanocomposite samples were collected, centrifuged at
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8 5000 rpm, washed with ethanol three times, vacuum dried, and stored in a N_2 -filled glove box
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10 before use. In separate experiments, either 36 g of Fe or 4 g of activated carbon were milled
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12 separately under the same operating conditions, and the products were also washed, dried and
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14 stored for use. We note that the milling parameters were not optimized in this study and the
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16 selection of 4 h milling was only to ensure that a Fe-C composite was formed. Optimization of
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18 the milling process will be carried out in our future research.
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26 2.3 Characterization

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28 Transmission electron microscope (TEM) images of the milled Fe-C composite, Fe, and C
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30 particles were obtained with a Zeiss Libra 120 TEM. Fe mapping was conducted for Fe-C
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32 nanocomposite via electron energy loss spectroscopy (EELS), using the in-column Omega
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34 energy filter. The particles were also characterized for morphology and size with a scanning
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36 electron microscope (SEM) (Zeiss Merlin VP SEM/STEM) and for localized elemental
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38 composition using energy-dispersive X-ray spectroscopy (EDX) installed on the SEM. Surface
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40 areas were determined by BET N_2 adsorption analysis on a NOVA 2200 BET-surface area
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42 analyzer (Quantachrome, Boynton Beach, FL). The crystalline structure of the solids was
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44 examined using an X-ray diffractometer (XRD, PAD V, Scintag, Inc., Sunnyvale, CA) equipped
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46 with $\text{Cu-K}\alpha$ radiation at 45 kV/40 mA, with a scan rate of 2θ at $1^\circ\text{--}2^\circ/\text{min}$.
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55 The Fe^0 content of particles was determined by the amount of H_2 evolved during particle
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57 digestion in concentrated HCl [37]. H_2 was analyzed with an Agilent 7890 gas chromatograph
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(GC) with a thermal conductivity detector equipped with a HP-PLOT/U column (0.32 mm × 30 m × 10 μm, Agilent Technologies). After acid digestion, the iron content in solution was measured spectrophotometrically using 1,10-phenanthroline at the wavelength of 510 nm, and the total iron content of the particles was then calculated [38].

2.4 Adsorption and dechlorination experiments

Batch experiments were conducted in 40 mL amber glass vials capped with Teflon Mininert valves. Pre-determined amounts of Fe-C nanocomposite, milled Fe, or milled carbon were first placed in each vial, followed by addition of 20 ml of ~50 mg L⁻¹ TCE solution (diluted from a saturated TCE solution, and the initial concentration determined by GC using a blank sample) to the reactive materials in the vials in an anaerobic glove box. The saturated TCE solution was made by mixing excess TCE with N₂-purged water in a sealed container until a stable TCE concentration in water was achieved (~ 1000 mg L⁻¹). The container was maintained free of headspace and refilled with fresh water after each use. The vial reactors were capped and then transferred and placed on a shaker. The vial reactors were shaken at room temperature for up to 800 hrs. The initial pH of the solution was not modified and was around 7. The pH slightly increased (less than 1 unit) during the reaction for Fe-containing solutions. The reaction was monitored over time by sampling headspace of the reactors and analysis using an Agilent 7890 GC with a flame ionization detector (FID) equipped with a GS-Q column (0.53mm ×30 m, Agilent Technologies). The oven temperature was held at 75 °C for 2 min, ramped to 190 °C at a rate of 25 °C/min, and held at 190 °C for 10 min to separate TCE from other chlorinated and non-chlorinated degradation products.[39, 40] Aqueous concentrations of TCE and its reaction products were calculated using reported Henry's constants. Chloride (Cl⁻) concentration was

analyzed with an ion chromatograph (DX-120, Dionex, Sunnyvale, CA) equipped with a Dionex IonPac AS14 column (4 × 250 mm).

2.5 Extraction

At the end of batch experiments, the solids were separated from the supernatant by centrifugation at 5000 relative centrifugal force (rcf) for 20 minutes, 3 ml of octane was added to the solids, and the mixture was sonicated for 10 minutes and further gently shaken for 20 minutes. The mixture was then centrifuged at 18000 rcf for 30 minutes and the supernatant was analyzed for TCE and daughter products on an Agilent 7890 GC with FID. TCE standards in liquid phase were prepared by serial dilution of TCE in octane. The extraction efficiencies of TCE from activated carbon control samples were approximately 98.6±9.8% (refer to Table 2).

3. Results and Discussion

3.1 Characterization of milled Fe, C, and Fe-C nanocomposite

Representative SEM images of milled Fe and C particles, as well as un-milled Fe and C particles, are shown in Figure S1. After 4-h ball milling, in addition to being smaller, the Fe and C particles showed noticeable differences in morphology, including major deformation, welding and fracturing due to collision and compaction with the milling beads [10, 41]. Consistent with previous reports, the final milling particles were mainly in the nanometer range and commonly formed micron-size loosely-structured agglomerates due to increased particle-particle interaction [42]. The Fe-C composites may also contain defects because of the large strain developed during milling [42].

Figure 1. (a) SEM image of an Fe-C composite aggregate (~4 μm across). (b) – (d) Elemental spot mapping of Fe (b), C (c), and O (d) respectively, measured by SEM-EDX in the rectangular area shown in (a). Fe and C are unevenly distributed within the Fe-C composite particle.

Figure 1 shows an SEM image of the milling-formed Fe-C nanocomposite and elemental spot mapping of Fe, C and O. The elemental mapping not only revealed the formation of Fe-C nanocomposite, but also the heterogeneous welding of Fe and C. This is not surprising given that milling is a solid-solid deformation/welding process. The X-ray maps of Fe and O match well in most areas as the surface of the unmilled Fe was already oxidized and consisted of significant amount of iron oxides (see details in later XRD results). However, some areas are much richer in Fe than O (Figure 1), indicating that milling detached iron oxide coatings from the metallic iron particles, exposing fresh Fe⁰. In order to study the substructure of the Fe-C nanocomposite, the particles were further analyzed using transmission electron microscopy-electron energy loss

spectroscopy (TEM-EELS). We observed the electron-dense Fe particles inside or on the surface of Fe-C nanocomposite, with their primary sizes less than 100 nm (Figure 2).

Figure 2. TEM (a) and EELS (b) images shown for an Fe-C composite particulate (~100 nm by 300 nm). Nano-sized Fe particles – dark spots in (a) and bright spots in (b) – are clearly heterogeneously imbedded in the composite.

Powder XRD patterns of the initial Fe and C particles and Fe-C nanocomposite are shown in Figure 3. Rietveld refinement with the High Score Plus technique was used to determine the solid phases present in the starting materials and Fe-C nanocomposite. For the starting Fe materials, coatings of Fe particles were composed of iron oxide mixtures of hematite and magnetite, with 15.0% and 11.9% Fe, respectively. The Fe^0 content was 73.1% of the total Fe, consistent with the results obtained from chemical analysis (71.2%, Table 1). After milling, the sizes of hematite, magnetite, and Fe^0 particles were reduced from 25.7, 19.5, and 22.8 nm to 9.6, 7.6, and 13.7 nm, respectively. For the Fe-C nanocomposite, Rietveld refinement of the XRD pattern indicates that a transitional iron carbide phase (i.e., martensite) was formed as a result of the milling, which accounts for 10.9% of the total iron. The notable presence of iron carbide

indicates that recrystallization of carbon material had occurred during milling, when energy was applied to the particles through impacts with the milling media and other particles. The formation of an iron carbide phase during milling of zero-valent iron and carbon materials (e.g., graphite) is well documented [43, 44], consistent with our results. The remaining iron phases were composed of 18.5% hematite, 39.9% magnetite, and 30.7% Fe⁰. The lower quantity of Fe⁰ in the Fe-C nanocomposite compared to that in the starting Fe particles reflects Fe⁰ oxidation during milling. By using organic solvent and avoiding water, we minimized, but could not completely eliminate, oxidation.

Figure 3. XRD patterns of un-milled C (shown as GAC in blue), un-milled Fe (black), and Fe-C composite materials (red). Iron signals are dominating in the Fe-C composite materials.

Other physiochemical properties of un-milled and milled Fe and C and Fe-C nanocomposite particles are shown in Table 1. Milling significantly reduced the BET surface area of activated carbon, from 895.3 to 94.3 m² g⁻¹, probably by destroying its porous structure as the pore volume was reduced from 0.46 to 0.047 cm³ g⁻¹. The surface areas of Fe particles increased more than 3-fold, from 1.6 to 6.9 m² g⁻¹, due to Fe particle size reduction. The BET surface area of the Fe-C nanocomposite was 100.3 m² g⁻¹; the majority of the surface is clearly from the carbon component.

Table 1. Physiochemical properties of reactive materials used in the study, including un-milled Fe and milled Fe, un-milled and milled C, and Fe-C composite.

Sample	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Total Fe content (wt %)	Total Fe ⁰ content (wt %)
Un-milled Fe	1.6	0.0080	98.3	71.2
Un-milled C	895.3	0.46	<0.01	<0.01
Milled Fe	6.9	0.0034	95.9	67.5
Milled C	94.3	0.047	<0.01	<0.01
Fe-C composite	100.3	0.050	62.0	31.4

The total Fe and Fe⁰ contents are summarized in Table 1 for un-milled and milled Fe, C, and Fe-C nanocomposite particles obtained from chemical digestion. Fe⁰ contents were approximately 71.2% and 67.5% in un-milled and milled Fe, respectively, indicating oxidation of the Fe particles during milling. Total Fe content in the Fe-C nanocomposite particles was 62.0%, and the iron mineral phase distribution is known from XRD analysis (i.e., 10.9% iron carbide, 18.5%

hematite, 39.9% magnetite, and 30.7% Fe^0). Thus, the O content can be calculated, and the C content is then estimated to be about 23.7%, which is substantially higher (by a factor of 2) than the starting mixture, in which iron carbon ratio of 9:1 (i.e., C content 10%). This loss of Fe is probably due to Fe particles being much heavier than C, thus they tend to remain in the dead zone of the mixing vessel. Additional loss of Fe may occur in the pumping lines connected to the grinding chamber. Consequently, part of the iron was not delivered to the grinding chamber to form Fe-C nanocomposite. Fe^0 content was 31.4% in the Fe-C nanocomposite (or 50.6% of the total Fe since Fe is 62% of the Fe-C nanocomposite) based on chemical analysis, which is higher than that obtained from XRD analysis (41.6% of total Fe, including 30.7% Fe^0 and 10.9% iron carbide).

Figure 4. Partitioning of Fe-C composite in a water/hexane system. After shaking for a few seconds by hands, Fe-C composite preferentially partitioned into hexane and remained in hexane for up to weeks, demonstrating the material is hydrophobic.

The partitioning properties of the Fe-C particles were tested by introducing an organic solvent (hexane) into a stable Fe-C aqueous suspension (Figure 4). We observed that when mixed with

hexane by shaking by hand, the composite material in the aqueous phase was partitioned into the organic phase in seconds and remained at the oil/water interface for at least several weeks. This may be accounted for by the hydrophobicity of the carbon in the composite. Close examination of the oil phase using an optical microscope revealed the formation of water-in-oil emulsions stabilized by Fe-C composite particles (Figure 4). The tendency to partition into hydrophobic solvents makes the Fe-C nanocomposite an ideal material to enhance attachment to DNAPLs, and for chemical degradation of contaminants [22].

3.2 TCE adsorption and dechlorination

TCE adsorption and dechlorination experiments were performed using four different materials, (1) milled Fe, (2) milled C, (3) a mixture of separately milled Fe and C (Fe&C), and (4) Fe-C nanocomposite particles (Figure 5). In each of the samples containing Fe, approximately 10 g L^{-1} of total Fe was present. C concentration was maintained at approximately 3.8 g L^{-1} (based on the Fe:C ratio in the Fe-C nanocomposite estimated by XRD) for the samples containing C particles. A TCE solution, without any reactive materials, was used as a control.

In all three experiments containing C materials (i.e., C, Fe&C, and Fe-C), TCE concentration decreased by more than 90% in 3 minutes, as a result of rapid adsorption of TCE onto the carbon component (Figure 5(a)). In contrast, the milled Fe (without C) achieved 90% TCE removal after more than 400 hours. We note that C can adsorb but not degrade TCE, which would be required for in-situ groundwater remediation. Formation of the degradation products with time in the presence of Fe, Fe&C, and Fe-C nanocomposite materials is illustrated in Figure 5(b). For comparative purposes, all gas products (almost all completely dechlorinated hydrocarbons) were

summed on a mole basis of carbon (M_C) for each time point, and then normalized by Fe^0 concentration ($M_{C/Fe}$ in Figure 5(b)). In general, the observed dechlorination rates by reactive materials follow the trend: milled Fe > Fe-C nanocomposite > Fe&C mixture.

Figure 5. (a) TCE removal from solution (C/C_0 is the fraction of the original TCE remaining, C here is the molar concentration). (b) Time dependent formation of the degradation products, which are shown as the total moles of all the gas products (in terms of carbon) normalized by the

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4 mass concentration of Fe^0 ($M_{\text{C/Fe}}$, $\text{nmol-C g}^{-1}\text{-Fe}^0\text{ L}$) for milled Fe, Fe-C composite, and Fe&C
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6 mixture. Experiments were conducted at room temperature of $\sim 23^\circ\text{C}$ with initial TCE, C_0 at 50
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8 mg/L. Error bars represent the error of duplicated runs.
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11 Further analysis of the degradation product data, by plotting $\ln(M_{\text{C}}/M_{\text{C0}})$ versus time (M_{C0} is the
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13 initial moles of TCE as carbon, Figure S3), revealed that the initial TCE degradation followed
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15 pseudo-first-order kinetics. The data further show three phases of reaction for each reactant
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17 throughout the duration of the experiment (up to 650 hours), including a rapid reaction stage for
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19 the first 8 hours, a reduced reductive rate for the next ~ 100 hours, and a slow reaction stage for
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21 the final ~ 550 hours. Prolonged reaction of Fe^0 in water promotes growth of the iron oxide
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23 coating [6, 45], which inhibits TCE dechlorination by hindering electron and/or hydrogen atom
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25 transfer between Fe^0 and TCE molecules [37, 46]. The reaction rates normalized by Fe^0 content
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27 during the first 8 hours for the three milled Fe materials are between 0.029 and $0.037\text{ L hr}^{-1}\text{ g}^{-1}$.
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29 In the literature, the reported reaction rates for NZVI, synthesized by borohydride reduction,
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31 range widely, from 0.0026 [47] to $0.511\text{ L hr}^{-1}\text{ g}^{-1}$ [37], which makes comparison difficult.
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33 Nevertheless, Li, et al. [10] reported that under the same reaction conditions the milled NZVI
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35 showed superior chemical reactivity to TCE over chemically produced NZVI. Since a large
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37 number of defects may be formed on the Fe particle surfaces during milling (Section 3.1),
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39 increased surface roughness could have contributed to the high reactivity of milled NZVI. Our
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41 milled Fe-C nanocomposite also has an initial reactivity toward TCE comparable with that of the
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43 reported Fe/C composite (with first order reaction rate in the range of $0.011\text{--}0.042\text{ L h}^{-1}\text{ g}^{-1}$) [34],
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45 which was prepared from impregnation of milled activated carbon with iron precursors followed
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47 by hydrogen/carbothermal reduction. We note that although the particle reactivity decreased after
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49 the initial 8 hours, this does not prevent the Fe-C nanocomposite (whether synthesized by
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mechanical processes or chemical methods) from being a promising remediation material, since the TCE has already been sequestered by carbon and can be continuously degraded.

Table 2. Mass balance of C and Cl as a % of added TCE after degradation in the presence of reactive materials of Fe, Fe-C composite and Fe&C mixtures, determined by octane extraction and ion chromatography analysis respectively. The data were obtained at the ends of batch experiments (626, 486 and 646 h for Fe, Fe-C composite and Fe&C, respectively).

Sample	C Mass Balance (%)	Cl Mass Balance (%)
C	98.6 ± 9.8	99.1 ± 9.3
Fe	103.4 ± 17.8	115.4 ± 14.7
Fe-C	94.0	88.8
Fe&C	98.6 ± 2.5	99.7 ± 0.5

Carbon mass balance was calculated by summing the final TCE and its completely dechlorinated hydrocarbon products against the initial carbon mass of the added TCE. Carbon mass balances of 94-103% were obtained for all treatments (Table 2), indicating that the measured gas products (without including any chlorinated intermediates) are the major products formed during TCE reductive dechlorination. To further verify this, a chlorine mass balance was made by summing the equivalent Cl in TCE remaining in solution (determined by GC-FID) and the measured chloride that had been produced from the dechlorination reaction (determined by IC). A good agreement was achieved, with 88.8-115% mass recovery (Table 2). This result is consistent with the above finding, i.e., no significant formation of chlorinated intermediates in the reaction.

Control experiments, without the reactive materials, showed only a 10% loss of TCE after approximately 2 weeks (~30% loss of TCE occurred after about 4 weeks, but no reaction products were detected).

In addition to the difference in reaction rates, particle composition and properties also led to different TCE degradation pathways. Reduction of TCE by ZVI filings has been shown to occur mainly via a sequence involving reductive β -elimination to chloroacetylene, followed by the hydrogenolysis of chloroacetylene to produce acetylene [5] (Figure S4). The hydrogenation of acetylene produces ethylene and then ethane as a primary pathway in the presence of Fe^0 , whereas the coupling of acetylene produces minor amounts of C_4 compounds. Because both chloroacetylene and acetylene are extremely reactive, these products were not accumulated sufficiently to reach detectable levels in previous studies [5]. As shown in Figure 6, the major final products (ethene and ethane) in our study are consistent with TCE dechlorination by Fe^0 , suggesting that TCE dechlorination by milled Fe particles (either used alone or as a composite with C) comes from reaction with Fe^0 . For milled Fe particles, trace acetylene was detected in the first few days and then gradually disappeared (data not shown) confirming that dechlorination by milled Fe followed reductive β -elimination [5]. However, unlike iron filings [5], the coupling reactions to produce C_3 - C_6 compounds are more pronounced for our milled Fe particles. In the presence of C, as in the Fe&C and Fe-C systems, the C_3 - C_6 intermediate products were less pronounced and more ethene was generated, indicating that hydrogenation of acetylene is favored and that the coupling reactions were inhibited by the presence of C. No acetylene was observed with Fe&C and Fe-C particles, consistent with hydrogenation of acetylene proceeding more rapidly than the coupling reactions. The mechanism behind the change in the distribution

of hydrocarbon products in the presence of C is not clear. Based on our experimental results that extraction of Fe&C and Fe-C particles after reaction showed almost no hydrocarbons, the adsorption of reaction products by C is not a major factor. Furthermore, approximately 0.1% of 1,1-DCE was produced after 650 hours of reaction with Fe, whereas no chlorinated intermediates were detected in Fe&C and Fe-C (in both aqueous phase and solid phase, data not shown), implying strong adsorption of 1,1-DCE by carbon and a possible α -elimination pathway (Figure S4) that converts 1,1-DCE to ethene for Fe&C and Fe-C prior to the desorption of 1,1-DCE from the carbon matrix.

Figure 6. Fractional distribution of final reaction products at the end of the reaction (650 hours) - see Figure 5 - in the presence of milled Fe, Fe-C composite and Fe&C mixtures. Ethene is the dominant final product in all three reactive materials.

TCE can undergo reductive dechlorination either via direct electron transfer or via atomic hydrogen (from iron corrosion) [48]. As an electron or hydrogen conductor [49, 50], activated

carbon could transport electrons and/or atomic hydrogen from ZVI particles to the adsorbed TCE molecules and thus enable reductive dechlorination of TCE. Tang, et al. [23] determined that the electrical conductivity of GAC is 0.25 S m^{-1} , which is substantially smaller than that of Fe ($1.044 \times 10^7 \text{ S m}^{-1}$) and iron oxides (e.g., magnetite: $10^3\text{-}10^5 \text{ S m}^{-1}$) [51]. Accordingly, transfer of atomic hydrogen should also be slower for C than Fe if dechlorination is via atomic hydrogen [49]. This could explain why Fe alone showed a higher dechlorination rate than Fe-C and Fe&C, since electron or atomic hydrogen does not have to transfer through additional C layers in the sole Fe materials. It is worth noting that the difference in dechlorination rate between Fe-C and Fe&C particles and that of Fe is much less significant than the difference in the electronic conductivity between C and Fe or Fe oxide. We attribute this to the enrichment of TCE on the C matrices ($>90\%$ adsorption in 3 minutes), which enhances the electron utilization efficiency and thus dechlorination rates.

Figure 7. Schematic illustration of hypothesized mechanisms of reductive dechlorination of TCE by (a) Fe&C mixed materials and (b) Fe-C composite materials, using electron transfer as an example.

In the Fe&C reaction system, electrons or atomic hydrogens have to be transferred to the adsorbed TCE on C matrices for reductive dechlorination to occur. This may only happen when Fe and C have direct contact during mixing (Figure 7(a)). After the first few hours of reaction, the rate rapidly slowed. This is expected since TCE molecules gradually diffusing into C micropores, the electrons or atomic hydrogens encounter greater barriers to reach TCE. In addition, for groundwater remediation, the injection of Fe&C mixture would cause separation of Fe from C particles in the soil pores as a result of their large density difference, which would render the Fe&C mixture an ineffective remediation method. In the Fe-C nanocomposite, however, the Fe and C have constant and direct contact, permitting electrons or atomic hydrogens to transfer continuously from the Fe⁰ through any oxide coatings to C, thereby reducing the TCE molecules (Figure 7(b)). Even at later reaction stages, when TCE diffuses deeper into C micropores, electrons from Fe⁰ may still be able to reach TCE, since Fe particles are embedded in the Fe-C nanocomposite. These hypothesized events would account for the higher reactivity of Fe-C nanocomposite over Fe&C, especially during later reaction stages. Further investigations are required to elucidate these inferred mechanisms.

4. Conclusions

Novel, inexpensive Fe-C nanocomposite, synthesized from ball milling, has the combined advantages of containing both iron and carbon as reactive materials. When applied to remediation of groundwater contaminated by chlorinated solvents, this nanocomposite could rapidly sorb the contaminants due to the carbon component, effectively cutting off the migration of contaminant plumes. Subsequently, the iron component can continuously degrade the sorbed contaminants and liberate the carbon-sites for further contaminant sorption. When applied in the

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4 source zone, the nanocomposite could attach to the DNAPL/water interface, and thus enhance
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6 removal efficiency. It should be noted that NZVI produced by the ball milling method has been
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8 the leading NZVI in large scale field deployment in recent years due to its lower cost [8].
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10 Compared to milling pure Fe alone to produce NZVI, the milling of Fe and inexpensive C
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12 together to produce Fe-C nanocomposite does not add significantly to the cost of the final
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14 product. Therefore, Fe-C nanocomposite has significant potential application as either a reactive
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16 barrier or as a hot-spot destruction technology for groundwater remediation.
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23 **Supporting Information**

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26 SEM images of un-milled and milled Fe and C, respectively; three stage pseudo-first-order
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28 degradation kinetics of TCE by iron systems; possible reaction pathways of TCE dechlorination
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30 by ZVI.
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Nanoscale zero-valent iron (NZVI) is effective in reductively degrading dense non-aqueous phase liquids (DNAPLs), such as trichloroethene (TCE), although the NZVI technology itself still suffers from high material costs and inability to target hydrophobic contaminants in source zones. To address these problems, we developed a novel, inexpensive iron-carbon (Fe-C) nanocomposite material by simultaneously milling micron-size iron and activated carbon powder. Microscopic and X-ray diffraction (XRD) characterization of the composite material revealed that nanoparticles of Fe were dispersed in activated carbon and a new iron carbide phase was formed. Bench-scale studies showed that this material instantaneously sorbed >90% of TCE from aqueous solutions and subsequently decomposed TCE into non-chlorinated products. Compared to milled Fe, Fe-C nanocomposite dechlorinated TCE at a slightly slower rate and favored the production of ethene over other TCE degradation products such as C₃-C₆ compounds. When placed in hexane-water mixture, the Fe-C nanocomposite materials are preferentially partitioned into the organic phase, indicating the ability of the composite materials to target DNAPL for enhanced degradation.