



Chloroethene dehalogenation with ultrasonically produced air-stable nano iron

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ABSTRACT

Zerovalent iron (ZVI) has been demonstrated to be suitable for the dehalogenation of environmental pollutants such as chloroethenes. The construction of ZVI reactive barriers by conventional engineering measures is expensive and limited to shallow aquifers. The use of nanosized ZVI particles opens new opportunities to construct ZVI barriers with less invasive techniques. However, nanosized particles of pure ZVI are pyrophoric and react spontaneously with atmospheric oxygen.

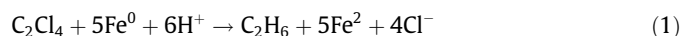
In this study, nanosized air-stable ZVI particles were produced by applying ultrasound to a solution of $\text{Fe}(\text{CO})_5$ in edible oil. The resulting iron nanoparticles were dispersed in a carbon matrix, and coated with a non-crystalline carbon layer of approx. 2.5 nm. Although, these nanoparticles are non-pyrophoric and stable in air, dechlorination of tetrachloroethene was demonstrated in synthetic aqueous medium and in polluted groundwater. Additionally, hydrogen was formed. Due to the larger surface area, significantly higher mass-normalized reaction rates of the novel carbon-coated nanoparticles were obtained as compared to conventional bulk ZVI material. Surface normalized pseudo-first-order-reaction rates of $k_{SA} = 3.49 \times 10^{-3} \text{ L h}^{-1} \text{ m}^{-2}$ and $2.33 \times 10^{-2} \text{ L h}^{-1} \text{ m}^{-2}$ were calculated for the nano-ZVI and the bulk ZVI, respectively. Dechlorination reaction products of the novel nano-ZVI were trichloroethene, cis-dichloroethene, vinyl chloride, ethene, and ethane.

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1. Introduction

Halogenated pollutants, such as chlorinated ethenes, are the most often found contaminants in subsurface environments. In recent years, it has been demonstrated that zerovalent iron (ZVI) can be used to dehalogenate chloroethenes. Permeable reactive barriers (PRBs) packed with ZVI have been shown to be an effective technology for the remediation of contaminated groundwaters, with elimination rates affected by contact time and hydrochemical groundwater composition [1–4].

Many halogenated hydrocarbons such as tetrachloroethene (perchloroethylene (PCE)), trichloroethene (TCE), and carbon tetrachloride can be reductively dechlorinated by ZVI [5,6]. TCE, dichloroethene (DCE), and vinyl chloride (VC) represent metabolites that might be formed during reductive dechlorination of PCE with ZVI. Complete reductive dechlorination of chlorinated ethenes leads to the formation of non-halogenated compounds [4,5,7,8]. The overall stoichiometric reaction is given in Eq. (1):



The construction of reactive barriers for groundwater remediation usually is done by the excavation of aquifer material followed by

refilling with reactive permeable material. The direct injection of nanosized materials into the subsurface might represent an alternative method that also is suitable for the treatment of source areas [9–11]. However, at present most of the research in the field of the removal of chlorinated ethenes was conducted using commercially available ZVI, which consists of micron size or even larger particles.

It has been shown that both the micro- and nanoscales of ZVI were capable of removing pollutants, but the higher removal efficiencies were by nanoscale ZVI because of the massive specific surface area [4,8]. However, pure nano-ZVI is pyrophoric and burns spontaneously in air. That is why many different ways to prevent iron nanoparticles from oxidation were developed. The various techniques include: embedding the iron in polymer matrices [12], passivation of iron nanoparticles with oxide shell [13], carburization of iron powder with methane to get on the surface a different content of iron carbide in a carbon matrix [14], or high temperature annealing mixtures of hematite and carbon powders [15], borohydride reduction of aqueous ferrous sulfate supported on hydrophobic polymer resin [16], preparing porous iron/silica composites through an aerosol-assisted process [17], or surface modification by triblock copolymers and surfactants in order also to improve mobility in the subsurface [18,19].

Recently, an effective synthesis method of highly magnetic air-stable iron–iron carbide nanocrystalline particles by ultrasound irradiation of iron pentacarbonyl was reported [20–22]. The

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process was carried out in the solution of diphenylmethane (DPhM), and the polymeric products of sonochemical decomposition of DPhM covered the surface of iron nanoparticles. The following annealing resulted in the formation of a protecting shell consisting of a mixture of Fe_3C and C. However, sonication in DPhM has some disadvantages, such as producing some toxic by-products during sonochemical decomposition of DPhM [23] and the high cost of this solvent. Therefore, recently DPhM was replaced by a cheap and green substitute – edible vegetable (rapeseed and corn) oils [24]. The sonication process yields at the end of the first stage metallic iron embedded in an unidentified polymeric shell. This as-prepared product is heated in argon at 750 °C. This annealing stage leads to the carbonization of the polymer. A carbon layer is formed around the iron atoms, and part of the carbons react with the iron forming the iron carbide. It should be noted that the valence state of the iron is not changed in the sonication and the annealing. It stays zero through the whole process.

The current study focussed on the dechlorination activity and surface structure of the novel sonochemically prepared ZVI nanoparticles. Activity studies were done in synthetic mineral medium and with groundwater taken at a chloroethene polluted field site.

2. Materials and methods

2.1. Ultrasonic preparation of air-stable nanostructured iron

Pure ZVI nanoparticles have no protective shell on the surface and hence they are not stable in contact with air. Therefore, a new sonochemical method was developed to prepare air-stable iron nanoparticles in the presence of commercial edible oils [24]. The oxidation shell was avoided by performing the reaction under argon. The polymer formed around the iron as well as the solvent prevented the formation of an oxide shell. Air-stability was demonstrated for several months. Every month (for six months) the samples underwent three measurements: magnetization loops, Mossbauer spectroscopy, and XRD. No changes were detected during the first six months.

Although, the detailed synthetic description was reported elsewhere [24] it will be repeated here in brief. Commercial refined rapeseed or corn oils were used as purchased. $\text{Fe}(\text{CO})_5$ (99.5% STREM) was used without additional purification. One molar solution of $\text{Fe}(\text{CO})_5$ in oil was sonicated by means of a “Sonics and Materials” ultrasonic device with a direct immersion titanium horn (working frequency –20 kHz, electric power of generator –600 W, irradiation surface area of the horn –1 cm²). The volume of the sonicated solution was 100 mL. Absorbed acoustic power, measured by the thermal probe method [21] was found to be equal to 0.45 W/mL. Temperature was kept constant during sonication by cooler “Julabo FT-901”. As a rule, sonolysis has been performed for 3 h at 0–10 °C. The black solid product of sonication was removed by centrifugation, washed three times with pentane inside a N_2 -filled glove box and dried under vacuum at room temperature. Annealing of the solids was performed at 750 °C for 3.5 h in an argon flow (99.996%).

2.2. Batch tests on chloroethene degradation

The batch activity tests were performed in 10 mL vials capped with teflon coated septa. 100 mg nano-ZVI or 1000 mg conventional bulk ZVI (FG 0300/200 GG, Gotthard Maier Metallpulver GmbH) were filled into the vials. The open vials were transferred into an anaerobic chamber with nitrogen atmosphere. In the chamber, 5 mL synthetic medium with 5–10 mg/L PCE or 5 mL groundwater with approx. 1 mg/L PCE were added into the vials. The vials were capped immediately, and analysed after different incubation

periods with respect to chloroethenes and dehalogenated reaction products. In one series of experiments, also the formation of hydrogen was analysed.

The synthetic medium [25], suitable for subsequent microbiological incubation, contained the following mineral salts (analytical grade or higher) per L of demineralized water: 1.05 g of $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, 0.2 g of KH_2PO_4 , 0.1 g of NH_4NO_3 , 0.04 g of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.023 g of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and 1 mL of trace element solution (per L of demineralized water: 500 mg of EDTA–Na, 10 mg of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 200 mg of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 3 mg of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 30 mg H_3BO_3 , 20 mg of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 10 mg of $\text{CuSO}_4 \cdot 2\text{H}_2\text{O}$, 6 mg of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 3 mg of $\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$).

The groundwater was sampled at a chloroethene-contaminated site located in Karlsruhe, Germany [26,27]. Hydrochemical parameters were typical for anaerobic areas of a polluted groundwater plume: ORP 120 mV, oxygen < 0.5 mg/L, ammonium: 10 mg/L, nitrate < 1 mg/L, Fe(II): 6 mg/L, sulfide < 0.1 mg/L, methane: 0.5 mg/L. Control experiments without the addition of ZVI were performed with the groundwater. Since microorganisms capable of reductive chloroethene degradation were present in the groundwater, also control experiments were performed after inhibition of microbial activity by adjusting the pH to 2 by the addition of H_3PO_4 . In both sets of controls, a formation of metabolites was not observed and the recovery of PCE was >90%. The loss of up to 10% PCE most probably was due to volatilisation during transfer into the vials.

2.3. Chemical analysis

Analysis of PCE, TCE, cis-DCE, trans-DCE, VC, ethene, ethane, and methane was performed by a gas chromatograph from Hewlett Packard (Series II 5980) equipped with a headspace autosampler (HP 19395 A, 70 °C), flame ionization detector (FID) and electron capture detector (ECD). Separation was accomplished in a 50 m-capillary column (HP PONA, 0.21 mm inside diameter, 0.5 μm methyl silicon film). Helium was used as a carrier gas at a flow rate of 0.7 mL/min. The injector and detector temperatures were 180 °C and 220 °C, respectively, and the following temperature program was applied: 15 min at 35 °C, increased to 60 °C (1.5 °C min⁻¹), increased to 130 °C (15 °C min⁻¹), increased to 200 °C (30 °C min⁻¹), held for 5 min. Concentrations were determined using external standards with a linear calibration. Samples were taken by the autosampler directly from the reaction vials after equilibration for 3 h with the reactions proceeding during this period.

Analysis of hydrogen was performed by a gas chromatograph (Agilent 6890 N) equipped with a Poraplot-/Molesieve-column and a thermal conductivity detector. Nitrogen was used as carrier gas (29.5 mL/min) with isothermal operation at 120 °C. In the degradation tests with the synthetic mineral medium, 1 mL of gas phase was sampled with a gas-tight syringe for H_2 analysis before performing the chloroethene and related compounds analysis by headspace GC.

2.4. Surface area measurements and image analysis

N_2 adsorption–desorption isotherms at 77 K were measured with a Micromeritics Gemini 2375 system using static adsorption procedures. Samples were outgassed at 473 K at ambient pressure under nitrogen for 1 h prior to analysis. The BET surface area was calculated using the nitrogen adsorption data in the relative pressure (P/P_0) range 0.1–0.3.

Low resolution TEM image of an annealed sample of the product of the sonication of corn oil were obtained using a JEOL-JEM100SX electron microscope with 80–100 kV accelerating voltage. High resolution TEM (HR TEM) image for the same sample was obtained by employing a JEOL-2010 device with 200 kV accelerating voltage.

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