Published in final edited form as:

Environ Sci Technol. 2010 June 1; 44(11): 4258–4263. doi:10.1021/es903801r.

Synthesis of Highly Reactive Subnano-sized Zero-valent Iron using Smectite Clay Templates

Cheng Gu, Hanzhang Jia, Hui Li, Brian J. Teppen, and Stephen A. Boyd*

Department of Crop and Soil Sciences, Michigan State University, East Lansing, Michigan 48824, USA.

Abstract

A novel method was developed for synthesizing subnano-sized zero-valent iron (ZVI) using smectite clay layers as templates. Exchangeable Fe(III) cations compensating the structural negative charges of smectites were reduced with NaBH₄, resulting in the formation of ZVI. The unique structure of smectite clay, in which isolated exchangeable Fe(III) cations reside near the sites of structural negative charges, inhibited the agglomeration of ZVI resulting in the formation of discrete regions of subnanoscale ZVI particles in the smectite interlayer regions. X-ray diffraction revealed an interlayer spacing of ~ 5 Å. The non-structural iron content of this clay yields a calculated ratio of two atoms of ZVI per three cation exchange sites, in full agreement with the XRD results since the diameter of elemental Fe is 2.5 Å. The clay-templated ZVI showed superior reactivity and efficiency compared to other previously reported forms of ZVI as indicated by the reduction of nitrobenzene; structural Fe within the aluminosilicate layers was nonreactive. At a 1:3 molar ratio of nitrobenzene:non-structural Fe, a reaction efficiency of 83% was achieved, and over 80% of the nitrobenzene was reduced within one minute. These results confirm that non-structural Fe from Fe (III)-smectite was reduced predominantly to ZVI which was responsible for the reduction of nitrobenzene to aniline. This new form of subnano-scale ZVI may find utility in the development of remediation technologies for persistent environmental contaminants, e.g. as components of constructed reactive domains such as reactive caps for contaminated sediments.

Introduction

Zero valent iron (ZVI) has been extensively studied as a strong reductant for the environmental remediation of a wide variety of organic and inorganic contaminants including nitroaromatic compounds (1), uranium (VI) (2), chromate (VI) (3) and chlorinated organic solvents (4). In recent years nanoscale ZVI has gained considerable attention due to its enhanced reactivity compared to bulk or microscale iron particles. Nanoscale ZVI is characterized by small particle size (10-100 nm) and high specific surface area, hence providing more reactive surface sites and enhanced reaction rates (5,6). In addition, iron nanoparticles have potential for both *in situ* and *ex situ* application because they can be directly injected as a slurry into contaminated subsurface zones (7,8), and can be incorporated with solid matrices such as granular activated carbon (9), palygorskite (10) and zeolite (11,12) to achieve simultaneous reduction and adsorption capabilities.

*To whom correspondence should be addressed. University Distinguished Professor Department of Crop and Soil Sciences Michigan State University 532 Plant and Soil Sciences Bldg East Lansing, MI 48824-1325 Phone: (517) 881-0579 Fax: (517) 355-0270 boyds@msu.edu .

Supporting Information Available Methodology (chemicals used and suppliers, and preparation of Fe(III)/Fe(II)-saturated SWy-2 clay) and results (Table S1. Total iron and sodium contents of montmorillonite (SWy-2) saturated with different exchangeable cations; Table S2. Comparison of reactivity of the clay-templated ZVI to different forms of reduced iron). This material is available free of charge via the internet at <http://pubs.acs.org>.

One of the major issues associated with nanoscale ZVI is that during the synthesis process iron particles tend to agglomerate rapidly resulting in diminished reactivity. To stabilize the synthesized iron nanoparticles, several strategies have been tested (12-16). Anionic hydrophilic carbon (13) and chitosan/silica (14) were successfully employed as supports to inhibit the aggregation of iron nanoparticles. Starch (15) and carboxymethyl cellulose (16) were used as stabilizers to increase particle dispersion and hence reaction performance. Huang et al. (17) immobilized iron nanoparticles onto supported polyelectrolyte multilayers to yield evenly distributed nanoparticles of uniform size (1 to 4 nm).

Smectites, including montmorillonite, are 2:1 layered aluminosilicate clay minerals that are widely distributed in soils, subsoils, sediments and pre-historic clay deposits (18). The size of the elementary platelets of smectites, ranging from a few tens to hundreds of nanometers wide and 1 to 1.8 nanometers thick, results in a natural material with typical surface areas of ~700 to 800 m²/g (19). Due to isomorphic substitution in the layers, smectites possess structural negative charges that are compensated by exchangeable cations that reside at or near the clay surfaces. Simple cation exchange reactions can be used to produce homoionic smectites (20). Smectites most commonly occur as assemblages of stacked layers, with the regions between layers termed interlayers. The interlayer spacing is typically in the range of ~2 to 8 Å and depends on the type and hydration properties of the interlayer cations. The average distance between adjacent exchangeable cations depends on the layer charge density and surface area of the clay, as well as the formal charge of the cation, and ranges from ~6 to 10 Å (21). The distinct structure and properties of smectite clays suggest their use as templates for synthesizing nano- or subnanosized ZVI particles on clay surfaces including the interlayer domains. Conceivably, single-atom ZVI could be formed via reduction of Fe(III) present as an exchangeable cation on smectite clay.

The objective of this study was to synthesize a new highly reactive and efficient form of ZVI using smectite clay as a template. When smectites are exchanged with Fe(III), the cations are spatially dispersed near the various negatively charged sites on the external and interlayer clay surfaces. We hypothesize that this dispersed, mineral-templated distribution of exchangeable Fe(III) minimizes the aggregation of iron particles upon reduction, perhaps resulting in the formation of subnanoscale ZVI particles. Our results indicate that the reactivity and efficiency of such synthetic smectite clay-templated ZVI are significantly enhanced compared to other existing forms of ZVI.

Materials and Methods

Materials

Details on the chemicals used and suppliers, and preparation of Fe(III)/Fe(II)-saturated SWy-2 clay are included in the Supporting Information.

Preparation of Subnanoscale ZVI

Before reduction by NaBH₄, the pH of the Fe(III)-montmorillonite slurry was adjusted to ~2 using 1 M HCl. Upon addition of NaBH₄, the clay immediately turned to black color indicating that Fe(III) was reduced to Fe(0). The molar ratio of NaBH₄:Fe(III) (based on interlayer iron species) was adjusted from 1.5 to 35. To remove the excess of NaBH₄, the clay suspension was centrifuged and rinsed with water.

Characterization of Subnanoscale ZVI

The Fe and Na contents in clay were determined through acid digestion and inductively coupled plasma-optical emission spectrometry by Huffman Laboratories, Inc. (Golden, CO). Clay basal spacings were obtained by X-ray diffraction (XRD) analysis. All the samples were freeze-dried

and the reduced-clay powders were analyzed by XRD within one hour. The X-ray diffractometer was equipped with CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) and crystal graphite monochromator, operating at 45 kV and 100mA. The diffraction patterns were collected between 4 and 12° at a scanning rate of 1°/min. To confirm the reduction of Fe(III) to Fe(0), freeze-dried powder samples were also analyzed by X-ray photoelectron spectroscopy (XPS) (Perkin-Elmer Physical Electronics PHI5400 spectrometer) employed with a monochromatic Mg X-ray source operated at 30 kV and 300 W with an emission current of 20 mA.

Determination of Reduction Efficiency

The reaction efficiency of synthesized ZVI was studied using nitrobenzene as the probe molecule. The degradation experiments were carried out in 7-mL glass scintillation vials. To each vial, 0.02 mL of nitrobenzene methanol stock solution (0.4%) was added to freshly synthesized clay in aqueous suspension (5mL, clay content was 12.6 g/L based on dry weight) to obtain an initial nitrobenzene concentration of 2.1 mM. All water used in the experiment was deoxygenated by purging with N₂ for 1 hr. Reaction vials were then placed on a rotary shaker inside the anaerobic chamber. After 3 hrs, samples of the clay suspension were filtered immediately through 0.45 μm regenerated cellulose syringe filter (Whatman, Dassel, Germany). Nitrobenzene and other reaction products (nitrosobenzene, phenylhydroxylamine and aniline) were analyzed by a reverse-phase high-performance liquid chromatography (HPLC) system (Perkin-Elmer, Norwalk, CT) fitted with a 15 cm $\times$ 4.6 mm Discovery C18 column (Sigma-Aldrich/Supelco, Supelco Park, Bellefonte, PA). An isocratic mobile phase consisting of a mixture of acetonitrile/aqueous 20 mM Na₂HPO₄ (55:45, v/v) at pH = 7 was used at a flow rate of 1 mL min⁻¹. The UV wavelength for detection was 240 nm for aniline and phenylhydroxylamine, and 272 nm for nitrobenzene and nitrosobenzene. The experiments were conducted in triplicate at room temperature (~23 °C). Experimental controls consisted of Na⁺- and Ca²⁺-saturated montmorillonites. Fe(II) saturated SWy-2 was used to investigate the reactivity of surface and interlayer-bound Fe²⁺ species for the reduction of nitrobenzene.

Results and Discussion

Characterization of Subnanoscale ZVI

Two major types of iron species are associated with montmorillonite clay (22-24). Structural iron is present in the Al-O octahedral sheet of smectite due to isomorphic substitution (25). Adsorbed iron can be held either on (mostly) interlayer cation-exchange sites or at external edge sites. In this study the total iron contents in homoionic Na- and Ca-SWy-2 were used to define the structural iron content of the SWy-2 clay. The structural iron content in Na- and Ca-SWy-2 clay was ~2.6% (Table S1, Supporting Information), in agreement with previously reported results (23,24). In both Fe(III)- and Ca-SWy-2 negligible amounts of sodium were present. After Fe(III)-SWy-2 was reduced by NaBH₄ the sodium content increased significantly; as the NaBH₄:Fe(III) ratio increased from 1.5 to 35 the sodium content increased from 1.24 to 2.50% (Table S1). Addition of NaBH₄ caused reduction of Fe(III) to Fe(0), and concomitantly, the negative charges associated with the clay minerals became compensated by Na⁺ from the added NaBH₄ (26). The total iron content in Fe-SWy-2 was ~6%, which included 2.6% structural iron and ca. 3.3% non-structural iron. Based on the literature (27) we estimate a maximum sorption of Fe to smectite edges ~9 cmol Fe/kg clay (0.5% Fe by weight). This would leave about 2.8% Fe(III) to populate the CEC (82 cmol_c/kg) of SWy-2, indicating that interlayer Fe(III) atoms have hydrolyzed to an average charge of 1.6 before reduction. Previous studies (28-32) of iron speciation on the CEC of smectite clays show dependence on pH, temperature and time. Iron contents as high as 26 mmol/g clay with OH/Fe ratios of 2 have been observed (28). The pH of the 0.1 M FeCl₃ used in our preparation of homoionic Fe-SWy-2 was ~1.7, so it is unlikely that precipitation of Fe(III) occurred (32). However, during the washing steps the pH increased to 4.5, hence exchangeable Fe(III) may have formed small

oligomers such as $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}_2(\text{OH})^{2+}$ and $\text{Fe}_3(\text{OH})_4^{5+}$ as observed by Tzou (29). This would account for the higher than expected iron loading on SWy-2 based on its CEC. The iron content in the synthesized ZVI-clay did not change significantly with an increase in the $\text{NaBH}_4\text{:Fe(III)}$ ratio used (Table S1). The total Na content (2.50%) of the Fe-SWy-2 after reduction at the higher level of NaBH_4 was nearly identical to that in the homoionic Na-SWy-2 (2.57%) indicating that Na^+ occupied the cation exchangeable sites in fully reduced Fe-SWy-2 clay.

Our preliminary results showed that when the pH of Fe-SWy-2 was > 4 , the NaBH_4 reduction reaction slowed significantly. Hence, the pH was adjusted to ~ 2 before the addition of NaBH_4 . A lower initial pH would risk dissolution of the clay as well as reaction of ZVI. The formation of ZVI from Fe(III) proceeds according to the following reactions:

Under acidic conditions, the low molecular weight hydroxyl-iron polymers, e.g. $\text{Fe}_3(\text{OH})_4^{5+}$ depolymerize and Fe(III) is then reduced to Fe(0) by NaBH_4 .

The XRD patterns of original and reduced Fe-SWy-2 (montmorillonite) clays, and Na-SWy-2, are shown in Figure 1. The basal spacing of air-dried Fe-SWy-2 was 13.4 Å (Fig. 1a), consistent with previous research (29,31). The interlayer space is expected to contain a monolayer of small iron oligomers, with each Fe atom octahedrally coordinated by water and hydroxyl ligands. The basal spacing of air-dried Na-SWy-2 was 11.2 Å (Fig. 1b). Sodium smectites generally hydrate with a monolayer of water (basal spacing ~ 12.5 Å) if the relative humidity is ~ 30 -70% and typically collapse to a 10 Å dehydrated state when the relative humidity is below 30% (21,33). Since this Na-SWy-2 was air-dried in a lab at relatively low humidity (typically 10% in winter), the observed basal spacing is consistent with a mix of these two different types of interlayer regions (33).

During the reduction of the Fe(III)-SWy-2 clay with NaBH_4 , we would expect that most Fe (III) oligomers that had previously satisfied cation-exchange sites on the clay would be replaced by Na^+ cations. This hypothesis is supported by the clay composition data (Table S1), which show that, as reduction increases, the exchangeable Na^+ content of the clay approaches that of the homoionic Na-SWy-2 clay. After reduction, the XRD peaks (Fig. 1c-f) for each clay occur at basal spacings significantly greater than 11.1 Å, indicating that Na^+ is not the only species remaining in the interlayer. At the lower $\text{NaBH}_4\text{:Fe(III)}$ molar ratios (5 and 10), the main XRD peaks are broad enough to allow the possibility that some Fe(III) still remains, but the partial collapse of the peak center to 12.6 Å (Fig. 1c, d) also indicates that Fe(III) no longer dominates the interlayer. The interlayer could plausibly consist of mixed Fe(III) species, reduced Fe species, and Na^+ (26). Even at higher $\text{NaBH}_4\text{:Fe(III)}$ ratios of 20 and 30, few clay interlayers would seem to contain only Na^+ , since no basal spacings near 11 Å are seen. Indeed, as the concentration of Na^+ (and of reductant) in the system increased, the dominant basal spacing actually increased to ~ 14.5 Å (Fig. 1e, f). Apparently, at least a portion of ZVI remains in the interlayer and inhibits collapse of the Na-SWy-2. It is also possible that some hydrated Fe(III) may remain in the interlayer and contribute to inhibiting collapse of the Na-clay after reduction. However, if this were significant, then we would expect the most Fe(III) to remain after the mildest reduction, yet the basal spacing after the mildest reduction was the smallest of any of the reduced systems. In addition, the interlayer expansion increased with increasing reduction and none of the XRD patterns for reduced systems are in the correct location nor look like the

XRD pattern for Fe(III)-SWy-2 clay. These results imply that neither Fe(III) nor Na^+ are controlling the basal spacings of the reduced clay systems.

A plausible hypothesis that is consistent with all the XRD results is that reduction produced some Fe(0) that remained in the clay interlayer region. The milder reduction treatments may have produced some interlayer Fe(0) with unknown connectivity parallel to the clay layers, but no more than one atom thick in the direction perpendicular to the clay layers. The diameter of elemental Fe is $\sim 2.5 \text{ \AA}$ (34), and if such atoms remained in the interlayer it would explain why the Na-dominated clay no longer collapses to $11 \text{ \AA}$ (Fig. 1c, d). That is, the approximate thickness of a montmorillonite sheet alone is $9.6 \text{ \AA}$ (35), implying a basal spacing of at least $12 \text{ \AA}$ if Fe(0) were intercalated in the clay interlayer. The stronger reduction treatments of the clay may create Fe(0) clusters that are up to two atoms thick in the direction perpendicular to the clay layers, consistent with the $14.5\text{--}14.7 \text{ \AA}$ basal spacing that dominates these treatments (Fig. 1e, f). Such Fe(0) clusters would be 1–2 orders of magnitude smaller than nanoscale ZVI synthesized from conventional methods (5). The small shoulders at 12.3 and $12.9 \text{ \AA}$ in the XRD patterns of these samples (Fig. 1e, f) were similar to the peaks observed in samples where lower rates of $\text{NaBH}_4\text{:Fe(III)}$ were used (Fig. 1c, d). The lack of a peak at 2θ of 44.9° , which is the expected diffraction peak of crystalline phase of Fe(0) (36), suggests that there is no continuous Fe(0) phase present.

Due to the low iron content in Fe-SWy-2 smectite clay, the Fe 2p signals in the XPS spectra of both the original and reduced Fe-clay are relatively weak (Fig. 2). The peaks at binding energies of Fe $2p_{1/2} = 726 \text{ eV}$ and Fe $2p_{3/2} = 712 \text{ eV}$ represent the oxidized iron species, and two peaks at Fe $2p_{1/2} = 722 \text{ eV}$ and Fe $2p_{3/2} = 710 \text{ eV}$ (36,37) correspond to ZVI. Compared to the XPS spectra of original Na-SWy-2 and Fe-SWy-2 (Fig. 2a, b), the Fe(0) peaks in the spectra of reduced Fe-SWy-2 gradually become more intense as the increase of $\text{NaBH}_4\text{:Fe(III)}$ ratios, indicative of more ZVI present at higher level of reduction (Fig. 2c-f).

Reduction Efficiency of Subnano-sized ZVI in Clay

Previous studies showed that both structural and surface-bound iron species, present as Fe^{2+} after reduction, were active in the reductive transformation of nitroaromatic compounds (22–24,38). Our control experiments showed negligible reduction of nitrobenzene for the NaBH_4 -treated Ca- and Na-SWy-2 clays indicating that structural iron present in the aluminosilicate structure of the smectite clay used in this study, or residual BH_4^- , did not participate in the reduction of nitrobenzene. Furthermore, there was no detectable reduction of nitrobenzene in the presence of homoionic Fe(II)-SWy-2 (under N_2 atmosphere), indicating minimal contribution of exchangeable (non-structural) Fe^{2+} species to the reduction of nitrobenzene by our smectite clay-templated ZVI. These control experiments imply that the electron donor for the reduction of nitrobenzene to aniline in our experiments with NaBH_4 -reduced Fe-SWy-2 was: $\text{ZVI} \rightarrow \text{Fe}^{2+} 2\text{e}^-$.

The sorption of nitrobenzene and aniline by SWy-2 clays was insignificant ($< 5\%$) based on preliminary experiments and a previous study (39). This enabled us to estimate the reactivity and efficiency of ZVI reduction directly by measuring nitrobenzene and aniline concentrations. The reduction pathway of nitrobenzene has been well documented (1,38,40,41):

(3)

According to this pathway, nitrosobenzene and phenylhydroxylamine are partially reduced intermediates, and aniline is the final reduced product.

To evaluate the reduction efficiency of the NaBH_4 -reduced Fe-SWy-2, the initial concentration of nitrobenzene (2.1 mM) was set to the anticipated reduction capacity (i.e., two moles electrons per mole Fe) of the total non-structural iron content of the clay, i.e. a 1:3 molar ratio of nitrobenzene:non-structural Fe was used. By assuming that a) all the exchangeable iron was reduced to ZVI and available for reduction of nitrobenzene, b) that six electrons provided by this ZVI were required to reduce each molecule of nitrobenzene to aniline, and c) that reaction intermediates did not accumulate significantly, the amount of aniline found in solution could be used to measure the reduction efficiency of the synthesized ZVI. In the reaction mixture analyzed we observed four HPLC peaks which were attributed to nitrobenzene, nitrosobenzene, phenylhydroxylamine and aniline. Standards for these compounds were available except for phenylhydroxylamine, so its HPLC peak is purported, although the sequence of reduced intermediates is well established. Kinetic experiments indicated that the degradation of nitrobenzene occurred rapidly. Within the first one minute, ~80% of nitrobenzene had been reduced to phenylhydroxylamine and aniline. As the reaction proceeded, phenylhydroxylamine was reduced to aniline, which accumulated as the major reductive product. After two hours, the reaction reached equilibrium; most of the phenylhydroxylamine was converted to aniline (> 98% of its maximum concentration), and a small amount of nitrosobenzene (< 1% of the initial nitrobenzene on a molar basis) was observed. Thus, in this study of reduction efficiency a three-hour reaction time was used.

The reduction efficiency was calculated as described above using the measured aniline concentration normalized to the non-structural Fe content (i.e. three equivalents of ZVI required for each equivalent of aniline produced). As the $\text{NaBH}_4\text{:Fe(III)}$ molar ratio increased from 1.5 to 25 the reduction efficiency reached a plateau, with a maximum efficiency of ca. 83% (Fig. 3). This very high reduction efficiency could only be achieved if essentially all of the non-structural Fe was reduced to ZVI. More oxidized forms of Fe, i.e. Fe^{2+} , could not have supplied enough electrons to account for the 83% reduction efficiency. Borohydride is the most commonly used reductant to synthesize nano-sized ZVI. Excessive borohydride has been identified as the crucial factor for rapid and uniform growth of synthesized iron particles (5, 42). Apparently, at lower $\text{NaBH}_4\text{:Fe(III)}$ ratios (≤ 10), incomplete reduction of exchangeable iron was achieved, which manifested lower reaction efficiencies. As more borohydride was used, more Fe(III) was presumably converted to ZVI. The hypothesis that increased reductant produced increased Fe(0) is supported by four self-consistent trends:

- First, the color of the clay material after reduction became progressively darker as the $\text{NaBH}_4\text{:Fe(III)}$ ratio increased.

- Second, the reactivity of the reduced clay material increased (Fig. 3). The observed stoichiometry implies that over 1.6 moles of electrons per mole Fe were captured for reducing nitrobenzene.
- Third, the Fe(0) peaks at 710 and 722 eV in the XPS spectra became more pronounced as the NaBH₄:Fe(III) ratio increased (Fig. 2).
- All three of these observations imply that some Fe is not fully reduced at low NaBH₄:Fe(III) ratio and that progressively more reduced Fe was created as the NaBH₄:Fe(III) ratio increases.
- A fourth observation supporting the hypothesis that increasing NaBH₄:Fe(III) ratio results in increasing Fe(0) production is the clay composition data (Table S1), which show that, as reduction increases, the exchangeable Na⁺ content of the clay approaches that of the homoionic Na-clay. This implies that the total charge attributable to Fe on the clay approaches zero at the highest levels of reduction. In turn, this implies that the Fe in the system is predominantly ZVI.

The ZVI formed in this system apparently exists as small iron clusters based on our XRD data (Fig. 1e, f). The maximum dimension of the clay-templated interlayer ZVI perpendicular to the clay sheets is ~5 Å; the corresponding Na-SWy-2, in the absence of ZVI, manifested an interlayer distance of ~2 Å (Fig. 1b). Thus, in the fully reduced Fe-SWy-2 clay, where Na⁺ fully occupies the cation exchangeable sites (Fig. 1e, f), the 5 Å interlayer distance is determined by the dimension of the ZVI. Taken together, our results indicate that the unique planar smectite layer structure with its dispersed negative charge sites inhibited the growth of large Fe(0) particles and facilitated the formation of very small discrete regions of ZVI, possibly approaching single atom dimensions (radius of atomic Fe is 1.25 Å (34)). As explained above, we estimate that there were an average of 1.9 interlayer Fe(III) atoms per three cation exchange sites before reduction. Assuming that the smectite clay layers are fully stacked, then the clay surface charge density (1.09 μmol/m²) implies that the average distance between adjacent Fe (III) is 11 Å, suggesting the possibility of near-single-atom forms of ZVI in the smectite clay interlayers after reduction. The extent of lateral clustering in the interlayer is unknown, but the XRD measurements indicate that these putative interlayer Fe(0) clusters are no more than two atoms thick in the direction perpendicular to the clay layer, even at the highest NaBH₄:Fe(III) molar ratios (since the interlayer distance was ~5 Å and the diameter of elemental Fe is 2.5 Å). Hence, the process seems to have produced ZVI intercalates in the sub-nanoscale range. Such small isolated regions of subnanoscale ZVI is consistent with the observed high reactivity, availability, and reduction efficiency.

Environmental Implications

In this study a new method was developed to synthesize highly reactive subnano-sized-ZVI. Smectite clay was used as a layer template and supporting matrix to synthesize subnanosized ZVI. Exchangeable Fe(III) exists as isolated species on smectite surface due to the distribution of fixed negative charge sites in the clay. We suggest that this clay surface serves as a template leading to the formation of small isolated regions of ZVI, consisting of a few atoms of Fe(0), when the Fe(III)-clay is reduced by NaBH₄. The significantly enhanced reactivity and high reduction efficiency of clay-templated ZVI compared to previously reported forms of ZVI, including nano-sized particles, is evidence of the very small size of the ZVI, and precludes Fe (II) as the reactive form of iron. Preliminary experiments showed that ~80% of the fresh ZVI reactivity was retained after freeze-drying. Further experiments to test the temporal stability of the synthesized ZVI have been undertaken.

We compared the reactivity (for reduction of nitrobenzene) of the clay-templated ZVI described herein to different forms of reduced iron reported in the literature (summarized in

Table S2, Supporting Information). Agrawal and Tratnyek (1) studied the reduction of nitrobenzene by microscale ($\sim 1 \mu\text{m}$) ZVI, and reported that with an iron concentration of 33.3 g/L, and an initial nitrobenzene concentration 0.015 mM, 90% of nitrobenzene was reduced in about one hour. Choe et al. (43) investigated the reactivity of nanoscale (1 to $\sim 200 \text{ nm}$) ZVI, which was synthesized by reducing FeCl_3 with NaBH_4 ; the concentrations of iron and nitrobenzene were 5 g/L and 0.0812 mM respectively, and most nitrobenzene was degraded within five minutes. The reactivity of structural iron (Fe(II)) in smectite clay was also evaluated using nitrobenzene as the kinetic probe (24). About 90% of 2-acetylnitrobenzene (initial concentration of 0.05 mM) was converted to 2-acetylaniline in 2 hours with structural Fe(II) concentration of 0.35 g/L. Compared with the results from these studies, the smectite clay-templated ZVI described in this study demonstrated much higher reactivity in the view of the fact that the iron concentration was 0.33 g/L and the initial nitrobenzene concentration was 2.1 mM. The estimated portion of ZVI in the clay assemblages that reacted with nitrobenzene was $\sim 83\%$ (at the $\text{NaBH}_4\text{:Fe(III)}$ ratio of 30, and assuming that all exchangeable Fe(III) was reduced to Fe(0) and available to react with nitrobenzene). The high reduction efficiency of the clay-templated ZVI is plausibly attributable to the discrete distribution of Fe(0) on the surfaces of SWy-2 in which the individual reactive Fe(0) domains are isolated and very small (sub-nanosized). It also demonstrates that less reduced forms of Fe, i.e. Fe^{2+} , could not be the predominant form of reduced Fe species in our clay-templated samples.

Smectite clays have been shown to intercalate many inorganic and organic contaminants such as Cr(VI) (44), nitroaromatic energetics and herbicides (39,45), trichloroethene (46) and dioxins (47). It seems plausible *a priori* that smectite-intercalated subnano-sized ZVI, as described herein, could further enhance the reduction of these contaminants because of increased contact probability between ZVI and the contaminants in clay interlayers. Montmorillonite clays are commonly used as hydraulic barriers at waste disposal sites, and the clay-templated ZVI could be added as a component of such barriers to create a reactive cap or wall. Similarly, such reactive caps could be used to contain and remediate contaminated sediments. These applications could potentially harness several advantageous properties of smectite clays including their ability to function as hydraulic barriers, adsorbents, and to degrade contaminants via reduction with ZVI. Thus, the clay-templated ZVI described here could find utility as a component of reactive barriers to degrade chlorinated solvents, nitrobenzene and other persistent environmental contaminants in a variety of settings. The clay-templated ZVI also provides (sub)nanoscale ZVI while avoiding any potential environmental concerns or problems associated with nanoparticles themselves.

Brief: Smectite was used as a template to synthesize very small isolated regions of zero-valent iron (ZVI) on clay surfaces that displays superior reactivity and efficiency compared to other known forms of ZVI.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

The project described was supported by grant number P42 ES004911 from the National Institute of Environmental Health Sciences (NIEHS), NIH and its contents are solely the responsibility of the authors and do not necessarily represent the official views of the NIEHS, NIH.

Literature Cited

- (1). Agrawal A, Tratnyek PG. Reduction of nitro aromatic compounds by zero-valent iron metal. *Environ. Sci. Technol* 1996;30:153–160.
- (2). Gu B, Liang L, Dickey MJ, Yin X, Dai S. Reductive precipitation of uranium(VI) by zero-valent iron. *Environ. Sci. Technol* 1998;32:3366–3373.
- (3). Puls RW, Paul CJ, Powell RM. The application of in situ permeable reactive (zero-valent iron) barrier technology for the remediation of chromate-contaminated groundwater: a field test. *Appl. Geochem* 1999;14:989–1000.
- (4). Farrell J, Melitas N, Kason M, Li T. Electrochemical and column investigation of iron-mediated reductive dechlorination of trichloroethylene and perchloroethylene. *Environ. Sci. Technol* 2000;34:2549–2556.
- (5). Zhang WX. Nanoscale iron particles for environmental remediation: An overview. *J. Nanopart. Res* 2003;5:323–332.
- (6). Cundy AB, Hopkinson L, Whitby RLD. Use of iron-based technologies in contaminated land and groundwater remediation: A review. *Sci. Total Environ* 2008;400:42–51. [PubMed: 18692221]
- (7). Elliott DW, Zhang WX. Field assessment of nanoscale biometallic particles for groundwater treatment. *Environ. Sci. Technol* 2001;35:4922–4926. [PubMed: 11775172]
- (8). Quinn J, Geiger C, Clausen C, Brooks K, Coon C, O'Hara S, Krug T, Major D, Yoon WS, Gavaskar A, Holdsworth T. Field demonstration of DNAPL dehalogenation using emulsified zero-valent iron. *Environ. Sci. Technol* 2005;39:1309–1318. [PubMed: 15787371]
- (9). Choi H, Al-Abed SR, Agarwal S, Dionysiou DD. Synthesis of reactive nano-Fe/Pd bimetallic system-impregnated activated carbon for the simultaneous adsorption and dechlorination of PCBs. *Chem. Mat* 2008;20:3649–3655.
- (10). Frost RL, Xi YF, He HP. Synthesis, characterization of palygorskite supported zero-valent iron and its application for methylene blue adsorption. *J. Colloid Interface Sci* 2010;341:153–161. [PubMed: 19850299]
- (11). Lee S, Lee K, Park J. Simultaneous removal of Cd and Cr(VI) using Fe-loaded zeolite. *J. Environ. Eng.-ASCE* 2006;132:445–450.
- (12). Lee S, Lee K, Rhee S, Park J. Development of a new zero-valent iron zeolite material to reduce nitrate without ammonium release. *J. Environ. Eng.-ASCE* 2007;133:6–12.
- (13). Schrick B, Hydutsky BW, Blough JL, Mallouk TE. Delivery vehicles for zerovalent metal nanoparticles in soil and groundwater. *Chem. Mat* 2004;16:2187–2193.
- (14). Zhu BW, Lim TT, Feng J. Reductive dechlorination of 1,2,4-trichlorobenzene with palladized nanoscale Fe-0 particles supported on chitosan and silica. *Chemosphere* 2006;65:1137–1145. [PubMed: 16735054]
- (15). Chen CC, Lei PX, Ji HW, Ma WH, Zhao JC, Hidaka H, Serpone N. Photocatalysis by titanium dioxide and polyoxometalate/TiO₂ cocatalysts. Intermediates and mechanistic study. *Environ. Sci. Technol* 2004;38:329–337. [PubMed: 14740755]
- (16). He F, Zhao DY, Liu JC, Roberts CB. Stabilization of Fe-Pd nanoparticles with sodium carboxymethyl cellulose for enhanced transport and dechlorination of trichloroethylene in soil and groundwater. *Ind. Eng. Chem. Res* 2007;46:29–34.
- (17). Huang QG, Shi XY, Pinto RA, Petersen EJ, Weber WJ. Tunable synthesis and immobilization of zero-valent iron nanoparticles for environmental applications. *Environ. Sci. Technol* 2008;42:8884–8889. [PubMed: 19192813]
- (18). Allen, BL.; Hajek, BF. Mineral occurrence in soil environments. In: Dixon, JB.; Weed, SB., editors. *Minerals in Soil Environments*. 2nd ed. Soil Science Society of America; Madison, WI: 1989. p. 199-278.
- (19). Schoonheydt RA. Smectite-type clay minerals as nanomaterials. *Clays Clay Miner* 2002;50:411–420.
- (20). Danganan CE, Ye RW, Daubaras DL, Xun LI, Chakrabarty AM. Nucleotide sequence and functional analysis of the genes encoding 2,4,5-trichlorophenoxyacetic acid oxygenase in *Pseudomonas cepacia* Ac1100. *Appl. Environ. Microbiol* 1994;60:4100–4106. [PubMed: 7527626]

- (21). Sato T, Watanabe T, Otsuka R. Effects of layer charge, charge location, and energy change on expansion properties of dioctahedral smectites. *Clays Clay Miner* 1992;40:103–113.
- (22). Hofstetter TB, Schwarzenbach RP, Haderlein SB. Reactivity of Fe(II) species associated with clay minerals. *Environ. Sci. Technol* 2003;37:519–528. [PubMed: 12630467]
- (23). Hofstetter TB, Neumann A, Schwarzenbach RP. Reduction of nitroaromatic compounds by Fe(II) species associated with iron-rich smectites. *Environ. Sci. Technol* 2006;40:235–242. [PubMed: 16433357]
- (24). Neumann A, Hofstetter TB, Lussi M, Cirpka OA, Petit S, Schwarzenbach RP. Assessing the redox reactivity of structural iron in smectites using nitroaromatic compounds as kinetic probes. *Environ. Sci. Technol* 2008;42:8381–8387. [PubMed: 19068821]
- (25). Vantelon D, Montarges-Pelletier E, Michot LJ, Briois V, Pelletier M, Thomas F. Iron distribution in the octahedral sheet of dioctahedral smectites. An FeK-edge X-ray absorption spectroscopy study. *Phys. Chem. Miner* 2003;30:44–53.
- (26). Zhou P, Yan H, Gu BH. Competitive complexation of metal ions with humic substances. *Chemosphere* 2005;58:1327–1337. [PubMed: 15686750]
- (27). Baeyens B, Bradbury MH. A mechanistic description of Ni and Zn sorption on Namontmorillonite. 1. Titration and sorption measurements. *J. Contam. Hydrol* 1997;27:199–222.
- (28). Herrera, R.; Peech, M. Reaction of Montmorillonite with Iron (Iii); 1970. p. 740
- (29). Tzou, MS. Ph.D. Dissertation. Michigan State University; East Lansing, MI: 1983. Clay catalysts pillared by metal hydroxy polymers.
- (30). Klopogge JT. Synthesis of smectites and porous pillared clay catalysts: A review. *J. Porous Mat* 1998;5:5–41.
- (31). Akcay M. The surface acidity and characterization of Fe-montmorillonite probed by in situ FT-IR spectroscopy of adsorbed pyridine. *Appl. Catal. A-Gen* 2005;294:156–160.
- (32). Manjanna J, Kozaki T, Sato S. Fe(III)-montmorillonite: Basic properties and diffusion of tracers relevant to alteration of bentonite in deep geological disposal. *Appl. Clay Sci* 2009;43:208–217.
- (33). Berend I, Cases JM, Francois M, Uriot JP, Michot L, Masion A, Thomas F. Mechanism of adsorption and desorption of water-vapor by homoionic montmorillonites. 2. The Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺-exchanged forms. *Clays Clay Miner* 1995;43:324–336.
- (34). Pauling L. Atomic radii and interatomic distances in metals. *J. Am. Chem. Soc* 1947;69:542–553.
- (35). Johnson ID, Werpy TA, Pinnavaia TJ. Tubular Silicate-Layered Silicate Intercalation Compounds - a new family of pillared clays. *J. Am. Chem. Soc* 1988;110:8545–8547.
- (36). Sun YP, Li XQ, Cao JS, Zhang WX, Wang HP. Characterization of zero-valent iron nanoparticles. *Adv. Colloid Interface Sci* 2006;120:47–56. [PubMed: 16697345]
- (37). Zhu BW, Lim TT. Catalytic reduction of chlorobenzenes with Pd/Fe nanoparticles: reactive sites, catalyst stability, particle aging, and regeneration. *Environ. Sci. Technol* 2007;41:7523–7529. [PubMed: 18044536]
- (38). Elsner M, Schwarzenbach RP, Haderlein SB. Reactivity of Fe(II)-bearing minerals toward reductive transformation of organic contaminants. *Environ. Sci. Technol* 2004;38:799–807. [PubMed: 14968867]
- (39). Boyd SA, Sheng GY, Teppen BJ, Johnston CJ. Mechanisms for the adsorption of substituted nitrobenzenes by smectite clays. *Environ. Sci. Technol* 2001;35:4227–4234. [PubMed: 11718335]
- (40). Dunnivant FM, Schwarzenbach RP, Macalady DL. Reduction of substituted nitrobenzenes in aqueous-solutions containing natural organic-matter. *Environ. Sci. Technol* 1992;26:2133–2141.
- (41). Klausen J, Trober SP, Haderlein SB, Schwarzenbach RP. Reduction of substituted nitrobenzenes by Fe(II) in aqueous mineral suspensions. *Environ. Sci. Technol* 1995;29:2396–2404.
- (42). Lien HL, Zhang WX. Nanoscale iron particles for complete reduction of chlorinated ethenes. *Colloid Surf. A-Physicochem. Eng. Asp* 2001;191:97–105.
- (43). Choe S, Lee SH, Chang YY, Hwang KY, Khim J. Rapid reductive destruction of hazardous organic compounds by nanoscale Fe-0. *Chemosphere* 2001;42:367–372. [PubMed: 11100787]
- (44). Arnfalk P, Wasay SA, Tokunaga S. A comparative study of Cd, Cr(III), Cr(VI), Hg, and Pb uptake by minerals and soil materials. *Water Air Soil Pollut* 1996;87:131–148.

- (45). Johnston CT, Sheng G, Teppen BJ, Boyd SA, De Oliveira MF. Spectroscopic study of dinitrophenol herbicide sorption on smectite. *Environ. Sci. Technol* 2002;36:5067–5074. [PubMed: 12523422]
- (46). Aggarwal V, Li H, Boyd SA, Teppen BJ. Enhanced sorption of trichloroethene by smectite clay exchanged with Cs⁺ *Environ. Sci. Technol* 2006;40:894–899. [PubMed: 16509334]
- (47). Liu C, Li H, Teppen BJ, Johnston CT, Boyd SA. Mechanisms associated with the high adsorption of dibenzo-p-dioxin from water by smectite clays. *Environ. Sci. Technol* 2009;43:2777–2783. [PubMed: 19475949]

Figure 1. X-ray diffraction patterns of a) Fe-SWy-2, b) Na-SWy-2, c), d), e), f) Fe-SWy-2 after reduction by NaBH₄ at NaBH₄:Fe(III) ratio of 5, 10, 20 and 30 respectively. SWy-2 is a reference montmorillonite clay. Two Theta represents the diffracted angle relative to the incident X-ray beam.

Figure 2.

X-ray photoelectron spectra of a) Na-SWy-2, b) Fe-SWy-2, and reduced Fe-SWy-2 at $\text{NaBH}_4\text{:Fe(III)}$ ratios of c) 5, d) 10, e) 20 f) 30. SWy-2 is a reference montmorillonite clay.

Figure 3. Reduction efficiency of smectite clay-templated zero valent iron at different NaBH₄:Fe(III) molar ratios. Experimental conditions: initial nitrobenzene, clay and interlayer iron concentrations of 2.1 mM, 12.6 and 0.33 g/L, respectively. Error bars are the standard deviations of triplicate analyses. Molarity is normalized to maximum reduction achievable assuming all non-structural Fe is present as ZVI.