Immobilization of arsenic in soils by stabilized nanoscale zero-valent iron, iron sulfide (FeS), and magnetite (Fe₃O₄) particles

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Arsenic is a widespread contaminant in soils and groundwater. While various iron-based materials have been studied for immobilizing arsenic in contaminated soils, the feasibility of stabilized iron-based nanoparticles has not been reported. This study investigates the effectiveness of using three types of starch-stabilized iron-based nanoparticles, including zero-valent iron (ZVI), iron sulfide (FeS), and magnetite (Fe₃O₄), for immobilization of arsenic in two representative As-contaminated soils (an orchard soil and a fire range soil). To test the effect of the nanoparticles on the arsenic leachability, As-contaminated soils were amended with the nanoparticles at various Fe/As molar ratios (5:1–100:1) and contact time (3 and 7 d). After three days' treatments of a field-contaminated sandy soil, the PBET-based bioaccessibility of As decreased from an initial (71.3±3.1)% (mean±SD) to (30.9±3.2)% with ZVI, (37.6±1.2)% with FeS, and (29.8±3.1)% with Fe₃O₄ at an Fe/As molar ratio of 100:1. The TCLP-based leachability of arsenic in a spiked fire range soil decreased from an initial (0.51±0.11)% to (0.24±0.03)%, (0.27±0.04)% and (0.17±0.04)% by ZVI, FeS, and Fe₃O₄ nanoparticles, respectively. The Fe₃O₄ nanoparticles appeared to be more effective (5% or more) than other nanoparticles for immobilizing arsenic. When the two soils were compared, the treatment is more effective on the orchard soil that has a lower iron content and higher initial leachability than on the range soil that already has a high iron content. These results suggest that these innocuous iron-based nanoparticles may serve as effective media for immobilization of As in iron-deficient soils, sediments or solid wastes.

arsenic, immobilization, iron, nanoparticle, soil pollution, soil remediation

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Various natural sources (e.g., natural geochemical reactions) and anthropogenic activities (e.g., mining, discharges of industrial wastes, military activities, and application of agricultural pesticides) can lead to arsenic (As) contamination of soils and groundwater. Arsenic is ranked the second most common inorganic pollutant in the U.S. superfund sites [1]. Arsenic-contaminated soils, sediments and waste slurry are major sources of arsenic in food and water. To mitigate the toxic effect on human health, the maximum contaminant

level (MCL) for arsenic in the U.S. drinking water was lowered from the previous 50 ppb to 10 ppb, effective in January 2006.

Arsenic is a redox active element, with As(V) or As(III) being the two most common stable oxidation states in soils [2]. In general, As(III) is more toxic than As(V), and inorganic arsenic is more toxic than organic arsenic [3], and arsenic in soils is less bioavailable and less bioaccessible than As in water due to soil adsorption effect [4].

Arsenate can strongly interact with soils, especially, iron (hydr)oxides. Adsorption of arsenate by iron (hydr)oxides

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have been widely studied [5–13]. These studies have focused on the adsorption and surface complexation of arsenic on the amorphous and crystalline iron oxide structures, such as ferrihydrite and goethite. The complexation between arsenate and iron (hydr)oxide surfaces has been known to be inner-sphere surface complexation as either monodentate corner sharing, bidentate corner sharing, or bidentate edge sharing complexes [11,14].

Laboratory-scale and field-scale studies have been reported on remediation of As-contaminated groundwater by granular or powder ZVI particles [15–17] and iron oxides [18]. They observed that ZVI can effectively reduce the concentration of As in aqueous phase.

In recent years, aggregated (or non-stabilized) ZVI particles were studied for potential environmental remediation uses [19–21]. Because of the small particle size, large surface area, and high reactivity, these nanoscale materials have shown great potential for treatment of contaminated soil and groundwater [22–24]. Cumbal and Sengupta [25] studied arsenic removal from water by hydrated iron oxides nanoparticles loaded on polymer-matrix, and the immobilized iron oxides displayed practically effective sorption capacity for both arsenite and arsenate.

For arsenic removal in groundwater by iron-based nanoparticles, surface adsorption appears to be an important mechanism [26]. Compared with commercial iron powder or granular iron particles, ZVI nanoparticles offer much faster sorption kinetics and are more deliverable in the sub-surface. Consequently, iron nanoparticles hold great potential to immobilize arsenic *in situ* in contaminated soil and groundwater [20].

However, because of the high reactivity and inter-particle interactions, ZVI nanoparticles tend to agglomerate rapidly, resulting in the formation of much large (> microscale) aggregated particles and loss of reactivity and soil mobility. To prevent iron nanoparticle agglomeration, various particle stabilization strategies were reported [27–31]. He and Zhao [27,30–31] reported a new method for synthesizing stabilized iron nanoparticles by using some low-cost and environmentally benign starch and cellulose as a stabilizer. The stabilized nanoparticles displayed much improved physical stability, soil mobility, and reactivity compared with non-stabilized iron particles.

To quantify relative As mobility and leachability in soil, two operationally defined measures, bioaccessibility and TCLP (toxicity characteristic leaching procedure) leachability, have been commonly used. Bioaccessibility is quantified by a physiologically based extraction test (PBET), which mimics the conditions in human stomach and essentially reflects an *in vivo* accessibility of As [32]. TCLP is an EPA-defined standard method for measuring extractability of various chemicals from solid wastes. Earlier, a number of researchers [33–35] used TCLP tests to evaluate the leachability of As in contaminated soils.

Akhter et al. [33] concluded that higher iron content in

soil reduces the leachability of arsenic. Yang et al. [36] observed that high iron content reduced the bioaccessibility of arsenic in soil.

The overall goal of this study is to test the effectiveness of stabilized nanoparticles for reducing the bioaccessibility and TCLP leachability of arsenic in soils. Three types (ZVI, FeS, and Fe₃O₄) of stabilized nanoparticles were prepared using a water-soluble starch as a stabilizer, and then used for treating two representative soils in batch experiments. Effects of the Fe-to-As molar ratio and treatment time on the treatment effectiveness were examined.

1 Materials and methods

1.1 Materials

All chemicals used in this study were of analytical grade or above, and were obtained from Fisher Scientific (Pittsburgh, PA). All solutions were prepared with deionized water (18 MΩ cm).

An As-contaminated sandy soil (denoted as WAOS; As concentration = 315 mg/kg-dry-soil) was collected from a Washington Orchard (WA, USA), which was contaminated from application of As-based pesticides. In addition, a relatively clean red clay soil was collected near a small police fire range in east-central Alabama, USA. Both soils were first fractionated using standard sieves, and soil fractions of <250 μm were used in all experiments.

The WAOS soil has an iron content of nearly 52.4 g/kg and a soil pH of 6.75. The range soil has a higher iron content (122 g/kg) and a soil pH of 4.83. For subsequent arsenic immobilization tests, the range soil was first spiked with arsenic following the procedures by Yang et al. [36], which resulted in an arsenic concentration of 89 mg/kg.

1.2 Preparation of nanoparticles

The method developed by He and Zhao [27] was adopted for preparing starch-stabilized ZVI nanoparticles. In brief, a water-soluble starch (Alfa Aesar, Wall Hill, MA, USA) was used as a stabilizer in the preparation. The preparation was carried out in a 250 mL flask. Before use, deionized (DI) water and starch solution were purged with N₂ for 2 h to remove dissolved oxygen (DO). FeCl₃ stock solution was added to a starch solution (2.4%) through a burette, to give a final Fe concentration of 2.35 g/L, a starch concentration of 1.2%, and a solution pH of 8.1. Then, Fe³⁺ was reduced to Fe⁰ using stoichiometric amounts of sodium borohydride. To ensure efficient use of the reducing agent BH₄[−], the reactor system was operated in the absence of DO. The flask was shaken by hands during the reaction.

A method used by Si et al. [37] was modified for synthesizing stabilized magnetite (Fe₃O₄) nanoparticles. First, 50 mL of an aqueous solution of FeCl₂·4H₂O (5.0 g/L as Fe)

was added dropwise to a 50 mL aqueous solution of 2.55% (w/v) starch solution under continuous shaking. The mixture was shaken for 30 min to allow for formation of homogeneous Fe^{2+} -starch solution. Then, the pH of the solution was then increased slowly to 11 by adding 0.5 mol/L NaOH solution. The reaction mixture was subsequently aged for 1 h with constant shaking, giving a final Fe concentration of 2.35 g/L and a starch concentration of 1.2%. Characterization of the nano-structured Fe_3O_4 can be found in reference [38].

The method by Xu and Akins [39] for preparing CdS nanoparticles was modified for preparing starch-stabilized FeS nanoparticles. First, deionized water and starch solution (3.6%) were purged with nitrogen to remove DO. Then, FeCl_2 solution was prepared and added into the starch solution to form Fe-starch complex (Fe: 3.525 g/L, Starch: 1.8% (w/w)). Na_2S solution (4.03 g/L as S) was added dropwise to the Fe-starch solution, resulting in the FeS nanoparticle suspension. The final Fe concentration was 2.35 g/L, starch concentration 1.2% (w/w), final pH 6.8. Equation 2 gives the reaction stoichiometry. Characterization of the nano-structured FeS can be found in reference [40].

1.3 Experimental design

A series of soil treatment tests were performed using 15 mL polypropylene centrifuge tubes (Fisher Scientific, Fair Lawn, NJ, USA). Typically, 2 g of an As-laden soil sample was mixed with a given mass of a nanoscale particle (ZVI, FeS, Fe_3O_4) suspension. To test the effect of iron dosage on arsenic immobilization effectiveness, a range of Fe:As molar ratios (5:1, 10:1, 25:1, 50:1, 75:1, 100:1) were tested. In all cases, the soil-to-solution ration was either 1 g:2 mL (for Fe:As molar ratios of 5:1, 10:1, or 25:1) or 1 g:5 mL (for Fe:As molar ratios of 50:1, 75:1, 100:1). In addition, control tests were carried out in parallel with 2 g of a soil with 4 mL and 10 mL, respectively, of 1.2% starch solution. After the mixtures were shaken thoroughly for 5 min, the tubes were placed on a rotator for 3 d or 7 d (previous kinetic experiment had shown that the adsorption reached equilibrium in 3 d). After the treatments, all samples were centrifuged with 6 kg force (Accuspri 400 centrifuger, Fisher Scientific). Arsenic and iron concentrations in the supernatants were analyzed after centrifuging of the mixtures. Upon removal of the supernatant, each soil sample was oven-dried at 70°C for 1 d. Then, 0.1 g of treated soils was sampled and subjected to the PBET procedure, 0.5 g to the TCLP tests, and 1.0 g of the soil was used for soil pH measurements. To ensure data quality, all tests were performed in duplicates.

1.4 PBET and TCLP extraction tests

The bioaccessibility of arsenic in the soils was quantified following a modified PBET method [36,41]. The PBET extraction solution was prepared using a 0.4 mol/L glycine solution adjusted to a pH of 1.5 using HCl solution. In each PBET test, 0.1 g of a dry soil sample was mixed with 10 mL of the extraction solution (i.e., solid-to-solution ratio = 1:100). During the 1-h extraction, water temperature was maintained at body temperature (37 ± 2)°C with a water bath. After the extraction, the samples were centrifuged at 1 kg force. The supernatant was then filtered using 0.45 μm filter (Fisher Scientific), and then analyzed for arsenic using a graphite AAS. To ensure QA/QC, NIST soil samples were also subjected to the same procedure.

TCLP tests were performed to evaluate the leaching potential of arsenic in the untreated and treated As-contaminated soils following the US. EPA protocol (Method SW-846). In brief, 0.5 g of a dried soil sample was mixed with the TCLP extraction solution at a solid-to-liquid ratio of 1:20. The mixtures were placed on a rotating shaker operated at 30 r/min. After 18 h extraction, the samples were centrifuged at 1 kg force, and the supernatants were separated by 0.45 μm filter. The soluble arsenic concentration in the filtrate was analyzed with AAS.

1.5 Analytical methods

Aqueous samples were diluted as necessary and analyzed for aqueous As and Fe concentrations. A graphite-furnace atomic absorption spectrometer (GFAA) was used to analyze As concentration. Aqueous Fe concentrations in samples were analyzed using a flame atomic adsorption spectrometer (FLAA). Solution pH was measured with a pH meter (Thermo Orion, pH meter 410).

2 Results and discussion

2.1 Treatment effects on soluble arsenic removal and soil pH

As mentioned earlier, the nanoparticle amended soil samples were first centrifuged. To ensure mass balances for both the nanoparticles and arsenic in the systems, total Fe and As in the supernatants were analyzed. For the range soil samples treated with the three types of nanoparticles, iron concentration in the supernatant was less than 1% of total Fe added, and arsenic concentration was less than 0.5% total arsenic initially in the soils, which is about the same as that when no nanoparticles were added, indicating that addition of the nanoparticles will not mobilize soil-sorbed arsenic. These observations indicate that upon the high speed centrifuging, virtually all of the nanoparticles were removed from the aqueous phase, and nearly all soluble As was re-

moved upon addition of the nanoparticles. For the WAOS soil samples, 0.1%–1.1% of total iron and 1.1%–2.4% of arsenic remained in the supernatant when treated with Fe_3O_4 nanoparticles, whereas 1.5%–2.6% of total iron and 0.9%–2.7% of arsenic remained in the supernatants with ZVI nanoparticles; and 1.3%–3.9% of total iron and 0.3%–2.7% arsenic were in the supernatants with FeS nanoparticles. The soluble As level was again comparable to that when no nanoparticles were applied. These results again indicated that most of iron and soluble As were removed from the solution phase.

Table 1 gives the soil pH changes after each treatment. In all cases, the final soil pH was only slightly increased. For ZVI and FeS nanoparticle treatments, the soil pH remained nearly the same. Although Fe_3O_4 nanoparticles were applied at an initial pH of ~ 11 , the resultant pH for both soils increased only by <0.5 pH unit.

2.2 Reduction of PBET-bioaccessibility

Figure 1 presents the PBET-based bioaccessibility of arsenic for WAOS soil samples when the samples were treated for 3 d with the three types of nanoparticles. As the Fe/As molar ratio was increased, the bioaccessibility decreased progressively. At the Fe/As ratio 100:1, the bioaccessibility decreased from the initial ($71.3 \pm 3.1\%$) to ($30.9 \pm 3.2\%$)% for ZVI, and ($37.6 \pm 1.2\%$)% for FeS , and ($29.8 \pm 3.1\%$)% for Fe_3O_4 nanoparticles. Earlier, Subacz [42] studied the reduction of bioaccessibility of the same soil when it was amended with FeCl_3 at an Fe/As molar ratio of 100:1, and observed a bioaccessibility reduction of 33%.

For the As-spiked range soil, similar results were observed (Figure 2). After three days of treatments, the bioaccessibility of As decreased from an initial ($23.2 \pm 2.8\%$)% to ($11.7 \pm 1.4\%$)% for ZVI, ($16.1 \pm 0.8\%$)% for FeS , and ($10.4 \pm 1.5\%$)% for Fe_3O_4 at an Fe/As molar ratio of 100:1.

For both soils, Fe_3O_4 nanoparticles appear to be most effective for As immobilization. In addition to their better sorption characteristics, the superior performance of Fe_3O_4

Figure 1 Comparison of PBET-based As bioaccessibility for an orchard (WAOS) soil treated with three types of iron-based nanoparticles at various Fe/As molar ratios. Data plotted as mean of duplicates, relative errors are less than 3% in all cases.

Figure 2 Comparison of PBET-based As bioaccessibility for an As-spiked fire range soil treated with three types of iron-based nanoparticles at various Fe/As molar ratios. Data plotted as mean of duplicates, relative errors are less than 5% in all cases.

Table 1 Values of pH for soils treated with various nanoparticles and at various Fe/As molar ratios

Fe/As molar ratio	Initial pH	Control ^{a)}	5	10	25	50	75	100
WAOS-ZVI			6.74	6.71	6.73	6.82	6.79	6.89
WAOS-FeS	6.75	6.73–6.89	6.64	6.71	6.67	6.78	6.86	6.95
WAOS-Fe ₃ O ₄			7.03	7.15	7.17	7.19	7.26	7.37
Range soil-ZVI			4.78	4.86	4.82	4.91	4.89	5.02
Range soil-FeS	4.83	4.83–4.93	4.81	4.91	4.89	4.87	4.94	5.03
Range soil-Fe ₃ O ₄			4.96	5.03	5.04	5.12	5.17	5.35

a) Control samples: Starch solution only at various soil/solution ratios.

nanoparticles is also attributed to the elevated soil pH upon the treatment. Earlier, Yang et al. [36] reported that bioaccessibility decreases with increasing soil pH. The treatment was more effective for the WAOS soil, which has a >2 times lower than iron content and >3 times greater than As content. Separate tests revealed that $>80\%$ of the nanoparticles became associated with the soil grains. Evidently, the addition of the nanoparticles resulted in elevated iron content, which enhanced the arsenic sorption capacity and affinity. Yang et al. [36] also reported that the bioaccessibility of soil arsenic decreased with increasing iron content of soil.

2.3 Reduction of TCLP-leachability

The initial TCLP leachability for both of the soils was quite low, as shown in Figures 3 and 4. TCLP leachability is defined as the percentage As in the leachate vs. the total As

Figure 3 Comparison of TCLP-based As leachability for an orchard (WAOS) soil treated with three types of iron-based nanoparticles at various Fe/As molar ratios. Data plotted as mean of duplicates, relative errors are less than 5% in all cases.

Figure 4 Comparison of TCLP-based As leachability for an As-spiked fire range soil treated with three types of iron-based nanoparticles at various Fe/As molar ratios. Data plotted as mean of duplicates, relative errors are less than 3% in all cases.

content. The initial TCLP leachability was 3.28% for the untreated WAOS soil and 0.51% for the untreated range soil. This result was in accord with those reported by Akhter et al. [33], who studied As-contaminated soils from various industrial sites. In all cases, the TCLP concentration was below 5 mg/L, which is the EPA threshold for a hazardous waste. When the soils were treated at an Fe/As molar ratio of 100/1, the TCLP leachability of arsenic in the WAOS soil decreased from the initial (3.28±0.78)% to (1.83±0.06)% for ZVI, (1.73±0.17)% for FeS and (1.63±0.16)% for Fe₃O₄; whereas the leachability for the range soil decreased from the initial (0.51±0.11)% to (0.17±0.04)% by Fe₃O₄, (0.24±0.03)% by ZVI, (0.27±0.04)% by FeS nanoparticles. For both soils, Fe₃O₄ nanoparticles were again most effective in reducing the As leachability. Miller et al. [35] also observed that the TCLP leachability of As in an As-contaminated soil was reduced from 1.42 to 0.26 mg/L when the soil was treated with soluble FeSO₄. The reduced TCLP leachability is again attributed to the added iron content and sorption capac-

ity for As. Akhter et al. [33] reported that there exists a correlation between the TCLP leachability of As in contaminated soils and iron content.

2.4 Effects of treatment time

Figures 5 and 6 compare the TCLP and PBET leachabilities when the soils were treated for 3 d and 7 d. It is evident from the results that the bioaccessibility and leachability of As, when the soils were treated at a 100:1 Fe/As molar ratio for 3 or 7 d, are quite comparable. A Student's *t*-test reveals that there is no significant difference between the results from the two treatment time. Earlier, Subacz [42] observed that the bioaccessibility of contaminated soils amended with FeCl₃ for 3 and 7 d differed significantly. These results suggest that the stabilized nanoparticles offer rather fast mass transfer and reaction kinetics, and equilibrium was reached within 3 d in all cases. Earlier, Kanel et al. [26] reported that most (~99%) of the arsenate uptake occurred in 1 h when non-stabilized ZVI nanoparticles were used to remove As from a groundwater, and the As adsorption reaction on nanoscale NVI were quicker than that on micron ZVI.

2.5 Mechanisms of arsenic immobilization by iron-based nanoparticles

The mechanisms for arsenic sorption by iron oxides have been extensively studied [10,12,13,18,43]. According to Waychunas et al. [43], who studied the contaminant sorption mechanisms of nanoscale iron oxides in soils and sediments, surface complexation is the key mechanism for As uptake by nanoscale iron oxides, and the greater surface area of nanoparticles greatly improved the sorption capacity compared with micro-scale or larger particles. Gao and Mucci [44] also stated that surface complexation is the main reaction mechanism for arsenic uptake by iron oxides, and proposed the following surface ion exchange reactions:

Apparently, the solution pH can affect the surface charge and arsenic speciation, and thus the sorption capacity and affinity.

Ponder et al. [28] and Cornell and Schwertmann [45] reported that ZVI nanoparticles can react with both contaminants, DO and water (eqs. (8)–(11)). As a result, a layer of passivating iron oxides is formed at the surface of ZVI par-

Figure 5 Comparison of PBET-based As bioaccessibility (a) and TCLP-based As leachability (b) for an orchard (WAOS) soil treated with various iron-based nanoparticles for 3 and 7 d.

Figure 6 Comparison of PBET-based As bioaccessibility (a) and TCLP-based As leachability (b) for an As-spiked fire-range soil treated with various iron-based nanoparticles for 3 and 7 d.

ticles. Jegadeesan et al. [20] also proposed that adsorption of arsenic on the corroded iron surface is the main mechanism of arsenite removal by nanoscale NVI from groundwater. Kanel et al. [26] reported that 81% of non-stabilized ZVI particles were iron oxides, and they confirmed that the shell iron oxides adsorbed arsenate through inner-sphere surface complexation. Therefore, the arsenic sorption and immobilization are actually facilitated by the shell iron oxides. Given the rather labile properties and higher cost of ZVI, ZVI nanoparticles do not appear to offer any advantages over common iron oxide particles such as the magnetite. It was widely reported that both arsenite and arsenate can be adsorbed on iron oxides [15–17]. Bang et al. [46] claimed that arsenic can also be removed by Fe^0 through reducing arsenite and arsenate to element arsenic, which is insoluble in water. However, this mechanism was not observed when stabilized ZVI nanoparticles were tested in our lab (data not shown), and mass balance calculation and As speciation tests reveal that nearly all As species were present as As(V) after the ZVI treatment.

Bostick et al. [47,48] reported that FeS minerals in soils and sediments can adsorb arsenate and arsenite under anoxic conditions. As surface complexation is the key mechanism for arsenate removal, researchers also proposed that eq. (12) can be an important reaction for arsenite removal by FeS.

3 Conclusions

The preliminary results of this investigation indicate that the stabilized iron-based (especially the magnetite) nanoparticles can effectively decrease As bioaccessibility and leachability in soils, and thus mitigating the potential of toxicity of arsenic. The bioaccessibility and leachability were reduced progressively with increasing Fe/As molar ratio. After three days of treatments using Fe_3O_4 at Fe/As = 100:1, the bioaccessibility of As was decreased by 58% (from $71.3 \pm 3.1\%$ to $29.8 \pm 3.1\%$) for an orchard soil, and 67% for a fire-range soil (from $0.51 \pm 0.11\%$ to $0.17 \pm 0.04\%$). While ZVI and FeS nanoparticles also demonstrated various degrees of arsenic sorption capacities, they do not appear to offer superior advantages over Fe_3O_4 nanoparticles, which are cheaper and innocuous. No significant difference in the effectiveness was evident between 3 d and 7 d of treatments. When the two soils are compared, the treatment appeared to

be more suitable for the orchard soil, owing to its lower iron content and higher initial As leachability. In addition to the high As sorption capacity, the stabilized nanoparticles also offer the advantages of easy *in situ* deliverability and controlled transport [49]. These results suggest that stabilized nanoparticles may serve as alternative media for *in situ* immobilization of arsenic in soils, especially soils with high As concentration and low Fe content.

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