Immobilization of arsenate in a sandy loam soil using starch-stabilized magnetite nanoparticles

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HIGHLIGHTS

- First study on starched magnetite nanoparticles for *in situ* immobilization of As(V).
- A small dose of the nanoparticles in soil greatly enhances soil sorption of As(V).
- The stabilized nanoparticles are deliverable in soil under moderate pressure.
- The nanoparticles are effective for *in situ* immobilization of As(V) in a model soil.
- Delivered nanoparticles will not spread under natural groundwater flow conditions.

ARTICLE INFO

ABSTRACT

This study investigated effectiveness of starch-stabilized magnetite nanoparticles for *in situ* enhanced sorption and immobilization of arsenate, As(V), in a model sandy loam soil. Batch tests showed that the nanoparticles offered an As(V) distribution coefficient of 10,000 L/g, which is >3 orders of magnitude greater than that for the soil. Batch and column experimental results revealed that the nanoparticle treatment greatly reduced water-leachable As(V) and the leachability of As(V) remaining in the soil per TCLP (Toxicity Characteristic Leaching Procedure) analysis. Column tests showed that water-leachable As(V) from the As(V)-laden soil containing 31.45 mg/kg was reduced by ~93% and the TCLP leachability by >83% when the soil was treated with 34 pore volumes of a 0.1 g-Fe/L of the nanoparticle suspension. While the nanoparticles are deliverable in the soil, the effective travel distance of the nanoparticles can be manipulated by controlling the injection flow rate. Under natural groundwater flow conditions (velocity $\leq 2.4 \times 10^{-4}$ cm/s), the delivered nanoparticles are confined within a limited distance (<6.1 cm).

1. Introduction

Arsenic (As) has been widely detected in soil and groundwater worldwide, particularly in the Bengal Delta and western United States [1]. Based on analysis of 30,000 groundwater samples in the U.S., ~10% exceeded 10 μg/L [2]. Excessive levels of As were detected at over 1/3 of the National Priorities List sites [3]. Exposure to As in drinking water has been associated with development of cancers and non-carcinogenic effects [4,5]. To mitigate human exposure, U.S. EPA lowered the maximum contaminant level (MCL) of As in drinking water from 50 to 10 μg/L effective in 2006.

The predominant As species in groundwater are inorganic As(III) and As(V) [6,7]. Although both species can be adsorbed on soil, they also undergo slow desorption/dissolution in the subsurface, posing long-term threat to groundwater quality. Depending on the biogeochemical conditions, three principal mechanisms have been proposed for As mobilization: desorption in alkaline conditions, competitive sorption of co-ions, and reductive release [3]. Reducing As(V) to As(III) increases As in groundwater [8], and dissolution of iron oxyhydroxide minerals causes release of As(V) [9].

Iron oxides have been known to offer high adsorption affinity for both As(V) and As(III) [10–14]. Investigations using extended X-ray absorption fine structure (EXAFS) [15,16], energy dispersive analysis of X-rays (EDAX) [17], and Fourier Transform Infrared Spectroscopy (FTIR) [18] showed that As(V) forms strong inner-sphere Fe–O–As complexes at the mineral surface.

Over the past decade, nanoscale adsorbents have gained strong momentum in water and soil remediation engineering [19–23]. Compared to the bulk counterparts, nanoparticles offer much

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greater specific surface area and greater adsorption capacity. For example, iron oxide nanoparticles were found to offer 10 times greater sorption capacity than the micro-scale counterparts [10,18]. In addition, well dispersed/stabilized nanoparticles offer another unique advantage that the nanoparticles may be directly delivered into contaminated soil or deep aquifers to facilitate *in situ* immobilization of target contaminants. For example, Xiong et al. [24] developed a class of CMC (carboxymethyl cellulose) stabilized FeS nanoparticles and found that the nanoparticles were able to immobilize Hg^{2+} *in situ*. Xu and Zhao [25] demonstrated that CMC-stabilized ZVI nanoparticles were effective for *in situ* reductive immobilization of Cr(VI) in a sandy loam soil. Compared to conventional technologies (*e.g.*, permeable reactive barrier, pump-and-treat, and excavation), the *in situ* immobilization approach is not only potentially much more cost-effective, but is likely the only way to reach contaminant plumes in deep aquifers and sites that are not accessible by conventional technologies.

However, nanoparticles without a stabilizer tend to aggregate, thereby losing soil deliverability. For example, Shipley et al. [26] tested non-stabilized magnetite and hematite nanoparticles for arsenic immobilization in soil. Yet, physical mixing was required to deliver the particles into the soil, which greatly limited the feasibility for treating deep aquifers. Kanel et al. [27] tested surfactant-modified ZVI nanoparticles, which showed improved transportability when tested in sand-packed columns.

In our prior work, we synthesized a class of starch-stabilized magnetite nanoparticles, and preliminarily tested the nanoparticles for arsenate removal in simulated groundwater [23]. The starch-stabilized nanoparticles offered a 2.2 times greater As(V) uptake capacity than conventional non-stabilized magnetite particles. However, the effectiveness of the stabilized nanoparticles for treating soil-sorbed As and related particle transport issues remain unexplored.

Given the great potential of the starch-stabilized magnetite nanoparticles for in situ immobilization of arsenic in soil and groundwater, this study aimed to: (1) probe the effectiveness of the stabilized nanoparticles for *in situ* immobilization of soil-sorbed As(V) through batch and column experiments; and (2) test and model the soil deliverability and transport behavior of the stabilized nanoparticles.

2. Materials and methods

2.1. Chemicals

A potato starch (hydrolyzed for electrophoresis) and ferrous sulfate heptahydrate ($FeSO_4·7H_2O$) were obtained from Acros Organics (Pittsburgh, PA, USA). Sodium arsenate heptahydrate ($Na_2HAsO_4·7H_2O$) was purchased from Sigma–Aldrich (St. Louis, MO, USA). Ferric chloride ($FeCl_3$) and sodium hydroxide (NaOH) were obtained from Fisher Scientific (Pittsburgh, PA, USA). Hydrochloric acid and nitric acid were purchased from Mallinckrodt Chemical (St. Louis, MO, USA). All chemicals are of the ACS reagent grade.

2.2. Preparation of starch-stabilized magnetite nanoparticles

Starch-stabilized magnetite nanoparticles were prepared following the co-precipitation approach [23], and is described in *Section 1* of the Supplementary Materials (SM). Typically, the nanoparticle suspension was prepared at 0.10 g-Fe/L, which was stabilized with 0.04 wt.% of starch. Our previous study indicated that the TEM-based particle size and DLS-based hydrodynamic diameter were 75 ± 17 nm and 129 nm, respectively, for the nanoparticles stabilized with 0.1 wt.% of starch [23]. For

comparison, the nanoparticle suspension was also prepared at 0.50 g-Fe/L with 0.4 wt.% of starch.

2.3. Preparation of As(V)-spiked soil and soil analysis

A sandy loam soil was obtained from the E.V. Smith Research Center (EVSRC) in Shorter, AL, Before use, the soil was sieved through a standard sieve of 2 mm opening, and then washed with tap water to remove suspended colloids and water soluble compositions. The washed soil can be completely separated from water through centrifugation at 400 g-force. The soil was then air-dried and stored in a sealed glass bottle. Soil analyses were performed by the Soil Testing Laboratory at Auburn University. Table SM-1 (Supplementary Materials) provides pertinent physical and chemical properties of the soil and the corresponding analytical methods [28]. The pH at the point of zero salt effect (PZSE) was determined to be 6.0 following the potentiometric titration method [29] (Details and the titration curves are provided in SM, *Section 2*).

As(V) was loaded to the soil following the batch adsorption procedure by Yang et al. [30] and is described in SM, *Section 3*. The arsenic loading on the soil was determined to be 31.45 mg/kg by measuring the difference between the initial and final As(V) concentrations in the aqueous phase. The adsorbed arsenic was further verified via acid digestion of the soil per USEPA Method 3050B [31] and the difference was <5%. The As loading falls in the typical range of <0.1–97 mg/kg in U.S. soil according to the ToxGuide for Arsenic by the Agency for Toxic Substances and Disease Registry. The As(V) spiked soil was then air-dried for subsequent experimental uses.

2.4. Immobilization of As(V) in soil: batch kinetic tests

Batch kinetic tests of As(V) leaching from the As(V)-laden soil were carried out in the presence and absence of the starch-stabilized nanoparticles. The tests were conducted using a batch of Corning plastic (polyethylene tetraphthalate or PET) centrifuge tubes (53 mL). Typically, 5.3 g or 21.2 g of the As(V)-laden soil was added to the centrifuge tubes each containing 53 mL of the nanoparticle suspension containing 0.5 g-Fe/L of the nanoparticles (with 0.4 wt.% starch), resulting in a soil-to-liquid ratio (SLR) of 0.1 and 0.4 (g/mL), respectively. The tubes were then capped and equilibrated on an end-to-end rotator operated at 50 rpm at room temperature ($22.0 \pm 0.1\ °C$). The solution pH was kept at 6.8 ± 0.4 through intermittent adjustment. At pre-determined times, the tubes were sacrificially sampled by centrifuging the mixtures at 400 g-force for 20 min. The supernatants were then passed through the 25 nm Millipore membrane filters, and the filtrates acidified to pH < 2.0 with 0.1 N HNO_3 and then analyzed for total As. The membrane was able to completely remove the nanoparticles, but did not remove soluble As. All tests were conducted in duplicate.

To determine the As(V) sorption capacity of the soil, arsenate sorption isotherms were constructed for the soil through batch equilibrium experiments (Supplementary Materials, *Section 4*).

2.5. Toxicity characteristic leaching procedure (TCLP) tests

TCLP tests were performed following U.S. EPA Method 1311 [32] to determine the leachability of As(V) in the soil, and the test procedures are provided in Supplementary Materials (*Section 5*).

2.6. Soil sorption and transport of starch-stabilized Fe_3O_4 nanoparticles

Interactions between the soil particles and starch-stabilized magnetite nanoparticles were investigated through batch sorption kinetic experiments (Supplementary Materials, *Section 6*).