Hydrous Ferric Oxide Incorporated Diatomite for Remediation of Arsenic Contaminated Groundwater

MIN JANG,, SOO-HONG MIN,†
JAE KWANG PARK, AND
ERIC J. TLACHAC

Introduction

Human activities and natural phenomena have caused releases of arsenic into groundwater and surface water, creating potentially serious environmental problems for humans and other living organisms. Since arsenic contamination is a health risk for many countries around the world, there is an urgent demand for a highly effective, reliable, and economical technique for the removal of arsenic from groundwater.

Permeable reactive barrier (PRB) technology may be a practical and economical alternative to conventional groundwater remediation systems for treating arsenic contaminated groundwater. PRBs involve the placement or formation of a reactive treatment zone in the path of a dissolved contaminant plume with the objective of passively removing target contaminants or altering them by physical, chemical, and/or biological processes to reduce their toxicity and/or mobility in the subsurface. PRBs have been successfully applied to many organic compounds such as chlorinated ethenes, including trichloroethylene and tetrachloroethylene, and inorganic contaminants such as chromium, uranium, arsenic, and other dissolved metals in groundwater (*1-5*). PRBs have become increasingly popular because the operation and maintenance costs are significantly less expensive than the traditional "pump and treat" method. Many materials have been used as a reactive medium in pilot-scale PRBs, including recycled foundry waste, zerovalent iron (Fe^0), activated alumina, and ferric oxide. Among them, Fe^0 has been extensively utilized as a reactive medium in PRBs because it has been shown to be effective in removing anionic metals, such as Cr(VI), Cr(III), As(V), and As(III), as well as halogenated organic compounds by means of coprecipitation and reductive

dehalogenation (*6-8*). Several forms of Fe_0 with good structural and hydrodynamic properties are also commercially available. However, Fe_0 can potentially elevate pH and Fe(II) concentration in groundwater due to a corrosion reaction with dissolved oxygen. This reaction will change groundwater conditions, resulting in potentially undesirable chemical reactions and a reduction in oxidation potential. In addition, due to relatively slow adsorption kinetics and competition effects of other anions such as silicate or phosphate, it is necessary to design a PRB with an extra thickness of Fe_0 materials (*9*). To overcome these drawbacks of Fe_0, an effective and economical adsorptive medium has been developed in our previous study for the removal of arsenic from water (*10*).

Previous research has shown that amorphous hydrous ferric oxide (HFO) incorporated into porous, naturally occurring aluminum silicate diatomite [designated as Fe (25%)-diatomite] was more efficient than the conventional medium, AAFS-50, for arsenite and arsenate removal, and that the increase in efficiency was particularly pronounced with respect to arsenite (*10*). Diatomite (or diatomaceous earth) is a lightweight sedimentary rockcomposedprincipally of silica microfossils of aquatic unicellular algae having a variety of pore structures with up to 80-90%voids. Diatomite has not only been approved as a food-grade material by the Food and Drug Administration (FDA), but it is also stable in the liquid phase since it originated and is produced from a sea or lake. These properties will result in good stability in a saturated environment, such as a PRB, as well as environmental friendliness. Meanwhile, amorphous HFO has been widely studied as a promising adsorptive material for removing both arsenate and arsenite (*11*) due to its high selectivity for arsenic species. An incipient wetness impregnation method using a vortexing device was developed to disperse and incorporate anHFOprecursor homogeneously on the pore surfaces of diatomite. Since a large volume of precursor solution is not needed or wasted, this technique is simple, economical, and environmentally friendly.

In this study, two reactive media [Fe_0 and Fe(25%)-diatomite] were tested with groundwater from a hazardous waste site in northern Wisconsin containing high concentrations of both organic and inorganic species of arsenic, as well as other toxic or carcinogenic VOC/SVOCs. Granular activated carbon (GAC) was also included in this study as a reactive media since a PRB at the subject site would need to

address the hazardous VOC/SVOC contaminations as well as arsenic. Adsorption with GAC is a common, proven technology for removal of VOC/SVOC compounds from water. The VOC/SVOC removal was characterized in the large scale column tests as described below to determine the effect of simultaneous arsenic adsorption with both media. In an attempt to discover another purpose for the use of GAC, we tried to find some synergetic effects of GAC on the arsenic removal performance of Fe (25%)-diatomite by removing natural organic matters (NOMs) in groundwater, which have ubiquitous presence in natural aquatic systems and significant effects on the arsenic mobility due to their redox and complexation capabilities. Since NOMs have negatively charged functional groups such as carboxylic, phenolic, quinone, amino, sulfhydryl, nitroso, and hydroxyl functional groups (*12*) at a neutral pH, they could give not only significant inhibitory effects on the arsenic removal performance of Fe (25%)-diatomite, but also desorption effects that are comparative to phosphate (*13*). Fisher Fe_0, Fe (25%)-diatomite, and GAC were first subjected to kinetics tests to determine arsenic adsorption rates and capacities with actual groundwater and synthetic solutions. Fisher Fe_0 showed not only the highest arsenic removal speeds, but also the highest arsenic sorption capacities among the other commercialized Fe_0 products (*7*). Then, the Fe_0/sand (50/50, w/w) mixture and GAC preloaded Fe (25%)-diatomite were tested in small scale column tests with a fast flow rate. Finally, these two reactive media were tested in large-scale columns to determine breakthroughs with actual groundwater flow conditions at the subject site. All testing utilized groundwater from the subject site. The objectives of this study were (1) to investigate the arsenic removal efficiences of Fe (25%)-diatomite compared with Fe_0, (2) to evaluate the enhancement of arsenic removal performance with the addition of GAC, and (3) to find out the applicabilities of dual media [GAC preloaded Fe (25%)-diatomite] for actual high concentrations of organic and inorganic arsenic, as well as VOC/SVOC contaminated groundwaters through different sizes of column tests.

Materials and Methods

Sample Collection and Characterization. The bulk groundwater sample was collected from a monitoring well at the subject site. This particular location was selected based upon analytical data from previous characterization work. The bulk

sample was collected utilizing low-flow methods (*14*) to minimize aeration of the groundwater during sample collection. This was done to minimize changes in arsenic speciation and loss of VOC/SVOC compounds which can occur during sample aeration. The bulk sample was filtered during collection with a 0.45-μm inline disposable groundwater filter to remove suspended solids that could interfere with laboratory chemical analysis and testing. Following filtration, the bulk sample was preserved in a refrigerator (4 °C) during long-term storage and handling, then pumped directly into 19 L Tedlar and/or Teflon bags to minimize aeration for column tests. The arsenite oxidation processes and microbial arsenic transformations considered for these procedures were negligible.

The total arsenic concentrations of groundwater or synthetic solutions were analyzed with an inductively coupled plasma atomic emission spectrometer (ICP-AES, Jobin Yyon Inc., Edison, NJ) for samples having arsenic concentrations larger than 1 mg L$_{-1}$. An atomic absorption spectrophotometer (AAS, Varian AA-975) and a GTA-95 graphite tube atomizer with a programmable sample dispenser (Palo Alto, California) were also used for samples having arsenic concentrations lower than 1mg L$_{-1}$. In this case, a 50mg L$_{-1}$ nickel solution was used as a matrix modifier. The detection limits of ICP-AES and AAS-graphite were 0.033 and 0.0006 μmol L$_{-1}$ for arsenic, respectively. Ion chromatography and inductively coupled plasma mass spectrometry (IC-ICPMS) were used to quantify arsenic species in groundwater samples. The chromatographic separation of arsenic species was achieved using gradient elution with dilute sodium hydroxide on a high-capacity anion exchange column. A DX-500 ion chromatograph (Dionex) and an Elan 6000 ICP-MS (Perkin-Elmer) were used for arsenic speciation analysis. The groundwater sample also contained 2-3 mg L$_{-1}$ volatile organic compounds (VOCs) and 3-4 mg L$_{-1}$ semi-volatile organic compounds (SVOCs). VOC/SVOC compounds were identified and quantified by gas chromatography and mass spectrometry (GC-S) following USEPA methods SW846-8260B (VOCs) and 8270B (SVOCs). Analytical testing for chemical composition and VOC/SVOC compounds of the groundwater was conducted at TestAmerica Analytical Testing Corporation (Watertown, WI). Preparation of Fe (25%)-diatomite is described in the Supporting Information.

Batch Kinetic Study. A groundwater sample of 300 mL was utilized for each kinetic of Fe (25%)-diatomite, Fe$_0$, GAC,

or mixed media[GACandFe (25%)-diatomite]. These samples were purged with nitrogen gas for 24 h to remove the VOC/ SVOCcompounds prior to kinetics. Except Fe_0 (half volume), masses of media were predetermined to have the same volume (Table S3 in the Supporting Information). Most cases of the column studies showed the mixture of Fe_0 with sand at the condition of 50/50 (w/w) to avoid a significant clogging effect. An aliquot of 1.5 mL of suspension was withdrawn at 10-60 min intervals and centrifuged at a speed of 10 000 rpm for 5 min. A 1-mL sample of the suspension was diluted with 19 mL of 1% HNO_3 solution prepared with deionized water. These samples were then analyzed for total arsenic utilizing an ICP-AES (Jobin Yyon Inc., Edison, NJ).

pH-Controlled Differential Column Batch Reactors (DCBRs). The pH-controlled DCBR tests were conducted not only to estimate the removal kinetics of different arsenic species on Fe (25%)-diatomite, but also to find the NOM addition effectonarsenite andMMAAthat were the dominant arsenic species of groundwater. Figure S1 in the Supporting Information shows the schematics of pH-controlled DCBRs. The most important reason to use pH-controlled DCBR is to control thepHcondition of feeding arsenic solution because pH is one of the most significant parameters in affecting arsenic species and active surface sites of metal oxide (*10*). For the evaluation of the effect ofNOMonthe arsenic removal for Fe (25%)-diatomite, humic acid (sodium salt, Sigma-Aldrich) was used as a representative of NOM species in groundwater (*15*, *16*). Arsenite standard solution for ICP (arsenic trioxide, Sigma-Aldrich), sodium arsenate heptahydrate $(Na_2HAsO_4·7H_2O)$,monosodiumacidmethanearsonate $(Na_2HAsNaO_3$,ChemService), and cacodylic acid $(C_2H_7AsO_2$, Sigma-Aldrich) were used to prepare 1000 mg L_{-1} stock solutions of arsenite, arsenate, MMAA, and DMAA, respectively. The pH-controlled DCBR tests were run with the following conditions: media mass (1 g), pH (6.8), empty bed contact time (EBCT) (3.3 min), arsenic (10 mg as As L_{-1}), and humic acid (100 mg L_{-1}, 50.3-65.3 mg C L_{-1}). For arsenic kinetic results, a pseudo second-order kinetic equation was found to fit well for many chemisorption processes using heterogeneous materials (*17*). Therefore, all of the kinetic data from our experiments were fit with a pseudo secondorder kinetic model in estimating the rate constants, initial sorption rates, and adsorption capacities for total arsenic. Ho et al. described the pseudo second-order kinetic rate equation (*18*, *19*). The pseudo-second-order kinetic model

can be solved with the following equations. The kinetic rate equation is expressed as follows (*17-20*):

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