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Sorption and speciation of arsenic by zero-valent iron

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ABSTRACT

Sorption and speciation of arsenic in groundwater remediation using zero-valent iron (ZVI) was investigated by batch and column experiments. In batch tests, arsenite was oxidized to arsenate which was favorably immobilized by co-precipitation with Fe(III)-bearing compounds as corrosion products, leading to the dominant surface species of As(V). In column materials after introducing influent with arsenite for 22 pore volumes(pvs), As(III) was predominant on the surface of ZVI in all segments of column, while intense oxidation of arsenite to arsenate was observed especially near the inlet. It is considered that the surface of ZVI granules was already uniformed and corrosion products are the most accumulated on ZVI granules near the inlet because ZVI has been contacted with high concentrations of arsenite for the longest time in the most bottom parts. This was also supported by the experimental results of XPS that relative intensity of O 1s peak assigned to oxide was the largest in the most bottom segment. Also XPS results revealed that arsenic was immobilized on ZVI granules mainly as arsenite and to a lesser extent arsenate. These observations suggest that the retention mechanism is primarily sorption rather than reduction. The results of geochemical calculations along with the SEM-EDX suggest that arsenite and arsenate were co-precipitated with mainly Fe(III)-bearing minerals and carbonates.

1. Introduction

The speciation of arsenic in natural waters is controlled by reduction, oxidation, and methylation reactions that affect its solubility, transport, bioavailability and toxicity [1]. Inorganic speciation is important since the varying protonation and charge of the arsenic species present at different oxidation states has a strong effect on their behavior in natural and anthropological processes. Sorption and co-precipitation are important processes to reduce the concentrations of inorganic contaminants in groundwaters. Permeable reactive barriers (PRBs) have been developed as passive and *in situ* groundwater remediation technique for more than 15 years and constructed as modern practice for reduction of a variety of inorganic contaminants, as well as organics [2,3].

In groundwaters the ratio of arsenite and arsenate can vary greatly depending upon the abundance of redox-active solids (especially organic carbon), the activity of microorganisms, and the input of oxygen from the atmosphere. Arsenic(III) typically dominates in strongly reducing aquifers in which Fe(III) and sulfate reduction are taking place. For example, the ratio of $As(III)/As_{Total}$ in reducing groundwaters from Inner Mongolia is typically 0.6–0.9 [4].

There have been numerous investigations on the removal of arsenic from groundwater using zero-valent iron (ZVI), typically in the form of iron fillings [5-7]. Zero-valent iron is a powerful reductant with a reduction potential of −0.44 V for the reaction of $Fe = Fe^{2+} + 2H^+$, and is reactive with many environmental contaminants [8]. Since the net cell potential is $E^\circ = 0.499$ V for the reaction of $HAsO_4^{2-} + 7H^+ + 5e^- = As(0) + 4H_2O$, reduction of arsenate to arsenic(0) by zero-valent iron is thermodynamically possible. Iron media may also remove arsenate species by adsorption onto iron corrosion products. In some cases, adsorption of arsenate to Fe(II, III) compounds, which are usually observed on the original surface of ZVI granules, may be irreversible due to formation of stable solid phases.

The purpose of the present work is to understand the immobilization mechanism of arsenite by ZVI and to determine the capacity of the material to retain arsenic in a PRB.

2. Experimental

2.1. Reactive materials

Zero-valent iron in the form of iron fillings was provided by Connelly Ltd., Chicago, IL, USA. The elemental composition was as follows: Fe 89.82%, C 2.85%, Mn 0.6%, S 0.107%, P 0.132%, Si 1.85%, Ni 0.05–0.21%, Cr 0.03–0.17%, Mo 0.15%, Ti 0.004%, Cu 0.15–0.20%. The

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Table 1
Characteristics of iron fillings from Connelly-GPM Inc. (Chicago, IL, USA).

Parameters	Data
Grain size range	2–0.25 mm (−8 to +50 mesh)
Bulk density	2.4 g/cm^3
Specific surface area	1.8 m^2/g
Hydraulic conductivity	5 × 10^{-2} cm/s
Current cost	US$ 700/ton

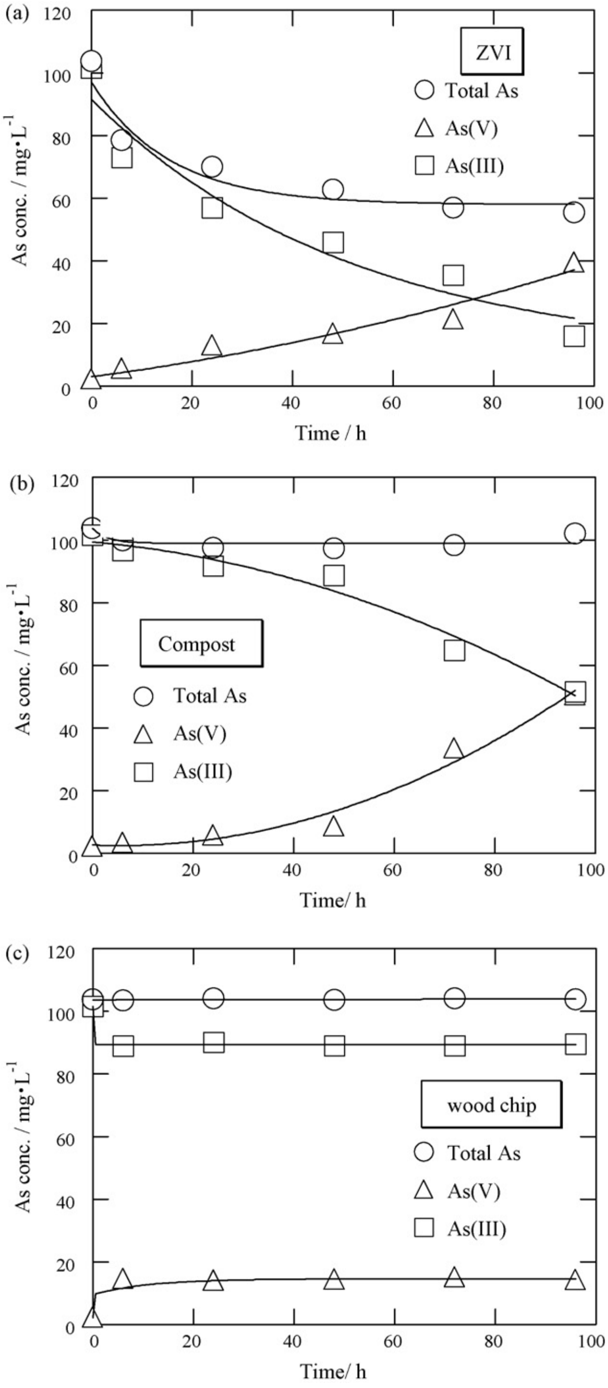

Fig. 1. Time courses of arsenite and arsenate in the reaction of arsenite with (a) ZVI, (b) compost, and (c) wood chips.

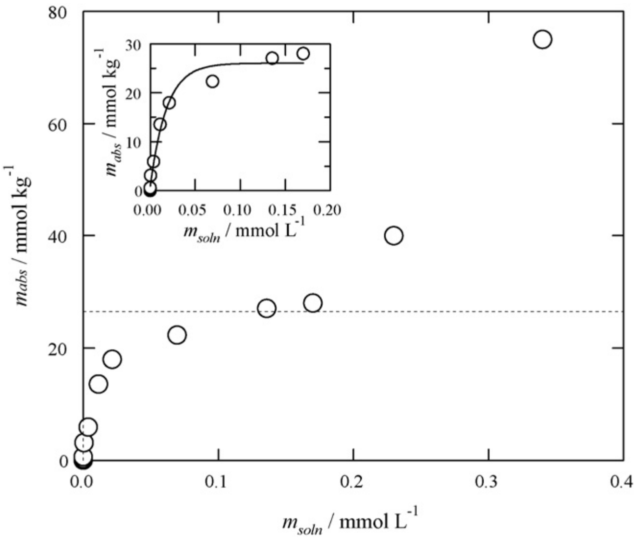

Fig. 2. Time courses of arsenic in sorption of arsenite onto ZVI from Connelly and the obtained isotherm. 5% (v/v) ZVI was loaded in 0.25 dm^3 of solutions containing the required amounts of arsenite in the presence of 0.1 mmol dm^{-3} KNO$_3$.

physical characteristics are summarized in Table 1. The leaching test recommended by the Environmental Ministry of Japan (Notification No. 46 of the Ministry of Environment, Japan) showed no toxic species above the maximum concentration limit (MCL). Compost

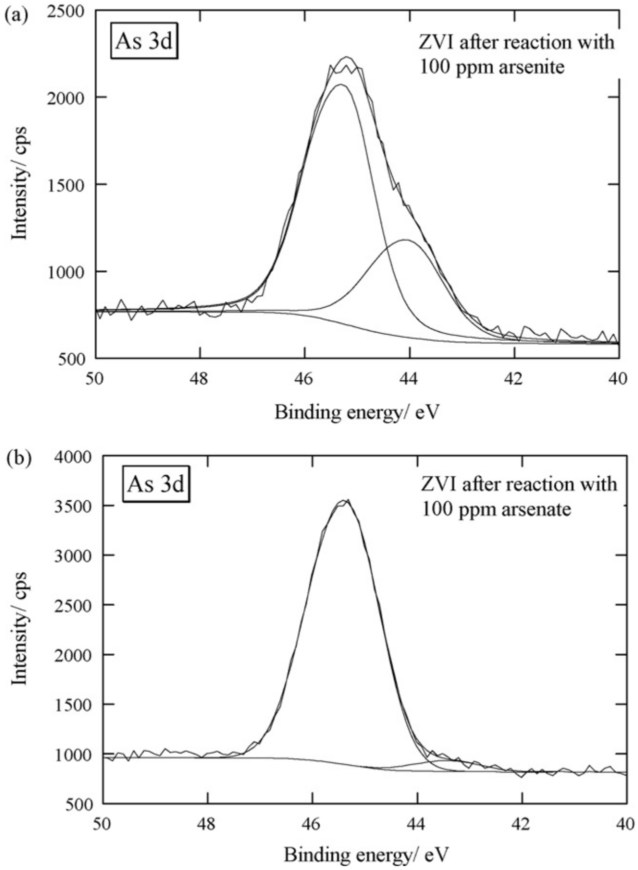

Fig. 3. XP spectra of As 3d for residual iron fillings after contacting with (a) arsenate and (b) arsenite. 1.08 g of washed iron fillings was contacted with 100 mg dm^{-3} arsenate and 100 mg dm^{-3} arsenite for 48 h at 25 °C. Initial pHs were 9 for both and final pHs were and 10.55 and 10.63.