

Monitoring of Arsenite and Arsenate by Flow Injection-Hydride Generation-Atomic Fluorescence Spectrometry II: Investigation of Leaching from Contaminated Sediments

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Abstract

The leaching of arsenic from contaminated sediments was investigated using flow injection-hydride generation-atomic fluorescence spectrometry as reported in the previous paper of this journal. Leached arsenite (As(III)) and arsenate (As(V)) were monitored with high time resolution (2 min), low sample consumption (120 μ L) and high sensitivity. Investigations were carried out using contaminated sediments sampled along a river near an old arsenic mine to characterize the kinetic behavior of arsenic leaching. The effect of phosphate was also examined under aerobic conditions at neutral pH. The obtained results indicated that the leaching of arsenate increased with phosphate addition in the suspension until equilibrium was reached. Leaching processes were characterized according to kinetic investigations. As(V) leaching was slower, but the amount of leaching was much higher compared with that of As(III).

Keywords Arsenite, arsenate, phosphate, leaching, kinetics

1. Introduction

Arsenic toxicity and its carcinogenicity are of serious environmental concern worldwide. Drinking water contaminated with arsenic is the principal cause of chronic arsenic poisoning in humans. Arsenic forms two oxyanions with two oxidation states, arsenite As(III) and arsenate As(V). In aerated soils or sediments, As(III) can be oxidized easily to As(V). The leaching of arsenic from soil or sediments poses a potential risk for surface and groundwater contamination.

Arsenate is a phosphate analog; both have similar electron configuration and form triprotic acids with similar dissociation constants [1]. In contaminated soil, phosphate is used to immobilize heavy metals such as Pb, Zn and Cd [2,3] and convert contaminants to their low leachability metal phosphates. However, phosphate addition to contaminated soils to immobilize heavy metals has the negative effect of mobilizing arsenic to groundwater. Investigations by Theodoratos *et al.* [4] revealed that when the phosphate dose to contaminated soils increased, the concentration of Pb and Cd metals in the leachate decreased with respect to the phosphate concentration but the arsenic concentration increased. Smith *et al.* [5] reported that the presence of phosphate in solution increased the amount of As(III) and As(V) sorption sites on the soil surface. Munksgaard and Lottermoser [6] investigated the immobilization of metals (Pb, Zn, Cu, and Cd) and metalloids (As and Sb) in soil; they found that fertilizer was the most effective amendment for stabilization of Cd (potassium orthophosphate) and Pb (superphosphate and triple superphosphate). Phosphate did not stabilize As, Cu, Mn, Sb and Zn, and these metals were released with the fertilizers [6]. Owing to the use of phosphate fertilizer in agricultural activities, released arsenic ions are sorbed to aquifer minerals by competitive ion exchange with phosphate ions that migrate into aquifers [7].

Increasing industrialization has led to the increased disposal of mine tailings [8] metallurgical slags [9], and municipal sewage sludge [10]. In many countries, mine spoils, slag dumps, and tailings contain extremely high concentrations of arsenic [11]. Soil is polluted through possible mobilization, and subsequently arsenic is leached into ground- or surface water and enters into the human food chain by various chemical and biological reactions. The form of arsenic present in the soil depends on the type and amount of sorbing compound. Soil pH and redox potential is related closely to adsorption of the arsenate fraction but varies with soil type under the same pH conditions [12]. Arsenate binds more strongly with metal oxides as compared with arsenite [13] and the retention of arsenate on ferrihydrite usually occurs at low pH compared with arsenite retention at high pH [14].

Many researchers have investigated the potential release of arsenic from various environmental samples [15,16] in the presence of various ions and measured total arsenic concentrations. In most cases, the sequential extraction procedure, after extraction of water soluble/non-specifically adsorbed arsenic by $\text{MgCl}_2/(\text{NH}_4)_2\text{SO}_4$ [17] and $\text{NH}_4\text{H}_2\text{PO}_4$, is used to extract specifically-sorbed arsenic from mineral surfaces [18]. Finally, only total arsenic was measured without distinguishing between As(III) and As(V).

We investigated the kinetic behavior of arsenic leaching from contaminated sediments. Leached arsenic was monitored as arsenite and arsenate by flow injection-hydride generation-atomic fluorescence spectrometry (FI-HG-AFS) as reported in the previous paper [19]. Arsine was generated at a selective pH 5.6 and pH 0 for As(III) and total As [As(III) + As(V)], respectively. The leaching process was monitored with high time resolution and high sensitivity.

2. Experimental

2.1. Samples and reagents

Sediment samples were collected from water exiting an old mine that formed a river stream. Sediments were collected from three places: samples A to C were taken 0.1, 0.5 and 3.5 km downstream from the mine, respectively. The sediment color was

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yellowish brown to grey with specific surface areas of 4.3, 3.8 and 5.19 m²/g for samples A, B and C, respectively.

Characterization of arsenic in sediments was performed by sequential extraction with water for water soluble arsenic (Ws-As), NH₄F for aluminum arsenate (Al-As), NaOH for iron arsenate (Fe-As), dithionite citrate bicarbonate for hydrated iron oxide (reductant-As), and H₂SO₄ for calcium arsenate (Ca-As). The remaining As was residual (Residue-As). See [1] for details of the fractions.

Reagents used in this work were 3 M HCl, 1 M phosphate buffer (pH 5.6) and 3% (w/v) NaBH₄ in 0.1 M NaOH as described in the previous paper [19].

2.2. Leaching tests

Before starting the leaching tests, the sediment samples were washed with water on an 80-mesh sieve to remove fine particles. Then, the sediment was dried at 135°C for 3 h to remove adsorbed water. The treated sediment sample (100 g) was added to 800 mL water. Phosphate was added to be 0, 0.05, 0.11 and 0.16 mM Na₂HPO₄·12H₂O solutions. Air was purged through the solution at 20 mL/min for 3 h before the addition of sediment to make the solution aerobic. Every 2 min, As(III) and As(V) were measured by FI-HG-AFS for 3 h (Fig. 1). Subsequently, As(III) and As(V) were measured every 24 h until the concentrations were constant. The solution pH was monitored with an ion meter (F-53, Horiba, Japan) and maintained neutral.

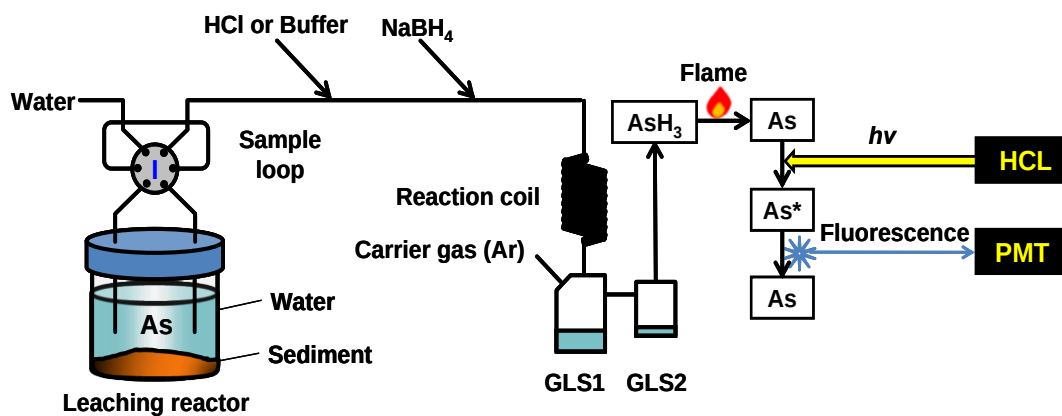


Fig. 1 Flow diagram of FI-HG-AFS for arsenic leaching monitoring. GLS: gas-liquid separator; I: injector; HCL: hollow cathode lamp; PMT: photomultiplier tube.

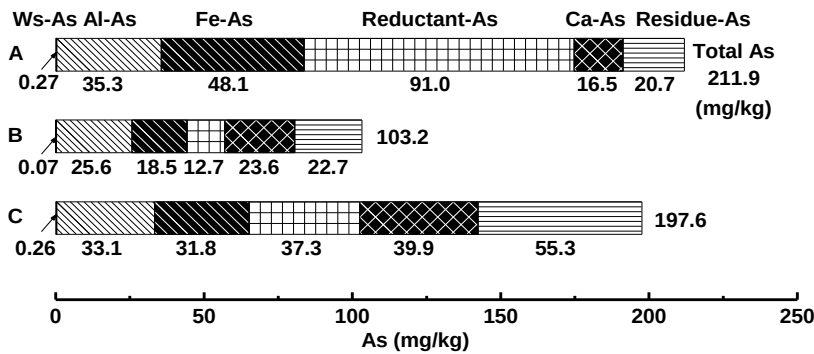


Fig. 2 Fractional analysis of arsenic for contaminated sediments A, B and C.

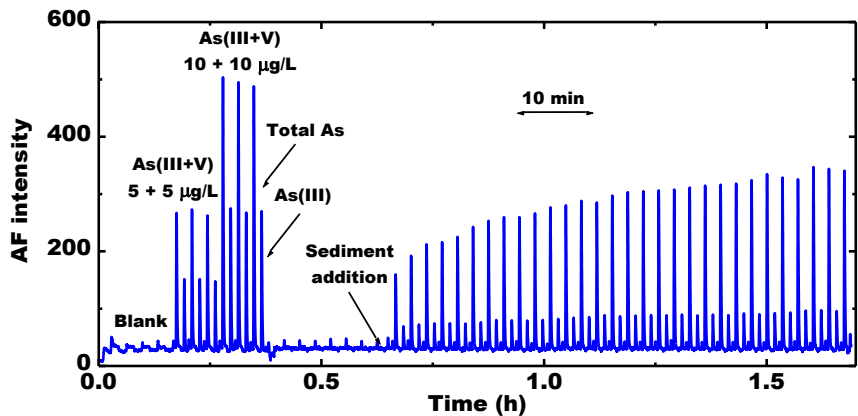


Fig. 3 Atomic fluorescence responses obtained for standard solutions of 0, 5 and 10 µg/L As(III)+As(V) (left) and leached arsenic monitoring from sediment sample C (right).

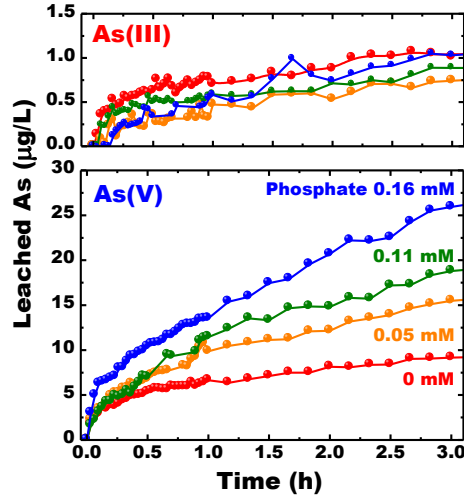


Fig. 4 Effect of phosphate on leaching of As(III) (top) and As(V) (bottom) from sediment sample A.

3. Results and discussion

3.1. Fractional analysis of arsenic from sediments

The fractional extraction procedure was used to determine the operationally defined arsenic binding phases. The efficiency of the extraction procedure was assessed by the separation and dissolution of one particular geochemical phase depending on the extractant affinity and specificity. In Fig. 2, the fractional data of arsenic from the sediment samples are shown.

Water soluble arsenic (Ws-As) in sediments A and C was 0.27 and 0.26 mg/kg, and 0.07 mg/kg in sample B. The total arsenic contained in the sediments was 211.9, 103.2 and 197.6 mg/kg for samples A, B and C, respectively. Most of the arsenic was extractable from the sediments with most of the arsenic in sediment A being extracted by the extractants and the residual part being less than the arsenic in sediments B and C.

3.2. Arsenic monitoring with FI-HG-AFS

The behavior of arsenic leaching from the sediment samples was examined by FI-HG-AFS. A typical response chart is shown in Fig. 3. Before commencing, responses were obtained for standard solutions containing 0, 5 + 5 and 10 + 10 μg/L of As(III) + As(V). The sampling line was inserted into the aqueous phase of the leach reactor to obtain signals without sediment. When the prepared sediment was added into the reactor, the response increased as shown in Fig. 3. As described in the previous paper [19], the signal for total As and As(III) was recorded alternately. Changes in arsenic concentration were relatively high and were impossible to monitor by conventional batchwise analysis.

3.3. Arsenic leached in the presence of phosphate

The amount of arsenic leached from the sediment gradually increased with time as well as with the amount of phosphate concentration in suspension. The amount of arsenic leached from the sediment was dependent on phosphate concentration as shown in Fig. 4. The amount of arsenic leached increased until equilibrium was reached. After 2 h, the leached As(III) concentration was almost 1 μg/L and not dependent on phosphate concentration. On the other hand, the arsenate concentration increased with respect to phosphate concentration, probably because arsenate is a phosphate analog and both are in

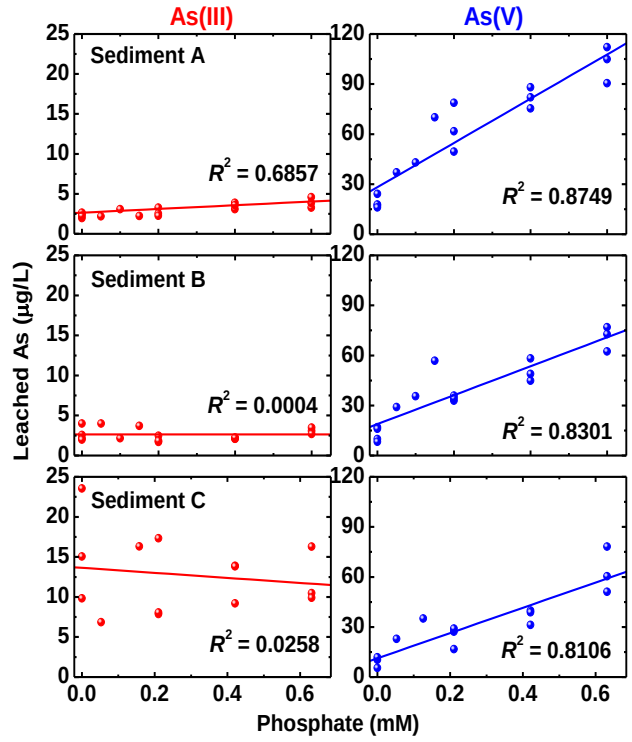


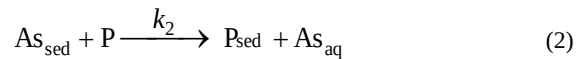
Fig. 5 Leached arsenite (left) and arsenate (right) from sediments A, B and C with different phosphate concentrations after 24 h.

the VA group of elements. They have similar electron configurations and form triprotic acids with similar dissociation constants. Moreover, phosphate has a higher charge density than arsenate and is replaced from the sediment surface.

The extracted As(III) and As(V) at 24 h are shown in Fig. 5. It is obvious that there was a correlation between the phosphate concentrations and leached amount of As(V). The R^2 values for A, B and C were 0.8749, 0.8301 and 0.8106, respectively, whereas the correlations were poorer for As(III). Sample A contained a higher amount of arsenic and the leached amount of arsenic was higher than samples B and C. This result implies that more arsenic is contained in the extractable arsenic fraction in the sediment.

3.4. Kinetic study of arsenic leaching

We assume that As leaching consists of natural leaching (Eq. 1) and phosphate (P) exchange (Eq. 2).



Eq. 3 results if both As(III) and As(V) follow these mechanisms.

$$-\frac{dC_{\text{sed}}}{dt} = \frac{dC_{\text{sol}}}{dt} \frac{W_{\text{sed}}}{V_{\text{sol}}} = (k_1 + k_2 [\text{P}]) C_{\text{sed}} \quad (3)$$

C_{sed} is the leachable As concentration in the sediment (μg/kg), C_{sol} is the leached As concentration (μg/L), W_{sed} is the sediment mass (kg) and V_{sol} is the volume of the test solution (L). Integrating Eq. 3 yields Eq. 4.

$$(k_1 + k_2[P])t = \ln \left(\frac{\frac{W_{\text{sed}}}{V_{\text{sol}}} C_{\text{sed}}}{\frac{W_{\text{sed}}}{V_{\text{sol}}} C_{\text{sed}} - C_{\text{sol}}} \right) \quad (4)$$

The logarithmic term of the leached arsenic for sample B was plotted in the top panel of Fig. 6. The rate constants, k_{obs} , were obtained from the slopes for As(III) and As(V). The bottom panel of Fig. 6 is a plot of k_{obs} against phosphate. k_1 and k_2 were obtained from the intercept and slope, respectively (see Table 1). The results indicate that the phosphate concentration affected the leaching rate of only As(V) and not As(III). Normally, the leaching rate of As(III) is faster than that of As(V) [20]. Here we found that phosphate affected the amount of arsenic leached and accelerated the leaching of As(V). The leaching rate (k_2) was highest for sediment sample B, in spite of the minimal amount of arsenic leached in the other sediment samples. This indicates that the amount of arsenic leached and the leaching rate are not necessarily related to the amount of arsenic contained in the sediment.

5. Conclusion

The developed FI-HG-AFS allows for low sample consumption, does not affect the leaching process and is highly sensitive with high time resolution, which is useful for monitoring the leaching process. The proposed method was applied to leaching investigations and to the evaluation of contaminated sediments. These results suggest that phosphate can effectively leach arsenic, especially As(V), from the

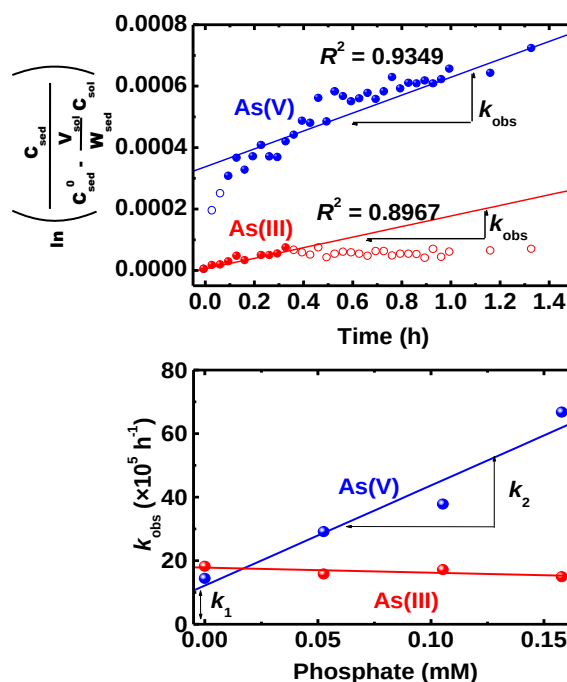


Fig. 6. Kinetic plot for arsenic leached from sediment B (top) and k_{obs} against phosphate concentration (bottom).

sediment. The concentration of leached As(V) and leaching rate depended strongly on phosphate concentration. It can be concluded that phosphate plays an important role in mobilizing arsenic from groundwater sediments.

Table 1. Kinetic constants of As leaching from sediments

Elements	As(III)		As(V)		Total As at 24 h (μg/L)	
	$k_1 (\times 10^5 \text{ h}^{-1})$	$k_1 (\times 10^5 \text{ h}^{-1})$	$k_2 (\text{h}^{-1})$		[P] = 0 mM	[P] = 42 mM
Sediment A	8.15	5.80	1.20		22.1 ± 3.5	85.4 ± 6.6
Sediment B	16.6	12.0	3.15		13.9 ± 4.6	52.8 ± 6.9
Sediment C	40.3	5.23	2.50		23.5 ± 2.6	48.9 ± 7.4

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(Received August 5, 2012)

(Accepted October 10, 2012)