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Bangladesh J. Sci. Ind. Res. 49(3), 195-198, 2014

Short Communication

BANGLADESH JOURNAL  
OF SCIENTIFIC AND  
INDUSTRIAL RESEARCH

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## Arsenic leached by step-wise ions addition under aerobic and anaerobic: Speciation by Sequential Hydride Generation Flow Injection Analyzer (SHGFIA)

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### Abstract

Leaching behavior of arsenic has been investigated by step-wise ions addition of river sediment near arsenic mine; arsenic was contained in sediment 450 mg kg<sup>-1</sup>. Leachates were characterized by discriminating arsenite and arsenate under both aerobic and anaerobic. Results indicate that arsenite As(III) and arsenate As(V) were leached from the sediments by step-wise ions addition especially phosphate ion enhanced more leaching of arsenic from sediment under anaerobic mostly was As(V).

**Keywords:** Sequential Hydride Generation Flow Injection Analyzer (SHGFIA); Arsenite; Arsenate; Step-wise; Phosphate

### Introduction

In the recent year's arsenic occurrence, distributions as well as mobilization have received significant attention due to its high toxicity. It is distributed in rocks, soil, natural waters also present in trace amounts in all living matter. Despite a great number of researches, still the mechanism of geochemical occurrence of arsenic into groundwater is not clear. Many countries left their mining spoils, slag dumps and tailings near manufacturing areas which contained extremely high concentration of arsenic (Krysiak and Karczewska, 2007) from where soil is polluted later leaching of arsenic into groundwater or surface water or enter human food chain through various chemical and biological reactions.

The solubility, mobility and bioavailability of arsenic depend on the parent minerals form of oxidation state and mobilization mechanisms (Al-Abed *et al.* 2007). The mobility of arsenic in the environment depends on its interactions with metal oxides (Fe, Al, Mn) that exists as a disperse phases. The binding mechanism of arsenic on metal oxides is impacted by pH and redox potential of the environment (Masue *et al.* 2007). Retention of arsenate on ferrihydrite is usually at low pH compared to arsenite retention at higher pH (Dixit and Hering, 2003). Onset of reducing conditions in such environments can lead dissolution of iron oxy-hydroxides coating to release arsenic into groundwater.

A variety of leaching reagents have been proposed to characterize physiochemical behavior of metals from

environmental samples (Tabelin and Igarashi, 2009) and measure total arsenic. In heavy metals leaching oxidation state doesn't consider but in case of arsenic leaching oxidation state has to be considered due to its toxicity variation (Fazal *et al.* 2001).

An investigation has been carried out to have useful information of arsenic leaching from contaminated sediment by step-wise ions addition in aerobic and anaerobic. Leachates were examined as arsenite and arsenate simultaneously by SHGFIA (Toda *et al.* 2008) with perfect hydride generation.

### Materials and Methods:

#### Reagents

All reagents stock solutions were prepared from analytical grade. Each containing 100 mg L<sup>-1</sup> stock solution of As(III) and As(V) were prepared from sodium metaarsenite (Wako) and disodium hydrogenarsenate heptahydrate (Nacalai) in 0.18 M H<sub>2</sub>SO<sub>4</sub>. Arsenic trihydride (AsH<sub>3</sub>) was performed with 0.33 M NaBH<sub>4</sub> (Nacalai) which was prepared by dissolving into 10 mM NaOH. 1M phosphate buffer (pH 7) was prepared by mixing 1 M KH<sub>2</sub>PO<sub>4</sub> and 1 M Na<sub>2</sub>HPO<sub>4</sub>. AsH<sub>3</sub> absorbing solution of 15 mM KMnO<sub>4</sub> + 10 mM NaOH was prepared daily from 75 mM KMnO<sub>4</sub> stock solution. Color developing reagents 20 mM (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O/1.8 M H<sub>2</sub>SO<sub>4</sub> and 0.12 M ascorbic acid were used; these two solutions were freshly mixed at 1:1 before experiment.

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### Analysis of arsenic with SHGFIA

Fig. 1 SHGFIA is shown. Reagents solutions are driven by using a 10 mL syringe pump (Versa pump 6 48K, 54021 Kloeht, USA) equipped with a 12-port selected valves (V6 rotary valve, 24105, Kloeht). Determination of arsenite was as follows: water sample (2 mL), 0.05 M ethylenediamine tetraacetate disodium salts (EDTA2Na, Dojindo) (0.5 mL) and phosphate buffer (1 mL) were transferred into hydride generator from bottom. Then, gradually 0.33 M  $\text{NaBH}_4$  was introduced into hydride generator through glass frit air inlet from bottom for 7 min.  $\text{AsH}_3$  was then collected and pre-concentrated into 100  $\mu\text{L}$  scrubber which contained absorbing solution (15 mM  $\text{KMnO}_4$  + 10 mM  $\text{NaOH}$ ). The scrubber composed of polypropylene porous membrane tube (0.5 mm i. d.  $\times$  0.9 mm o. d.  $\times$  500 mm, inner volume  $\sim$ 100  $\mu\text{L}$ , Accurel PP, Membrana Wuppertal, Germany). In absorbing solution arsenic collects as arsenate allow to be mixed with color developing reagent of molybdenum blue. Absorbance of reaction product was measured at 870 nm with an UV-VIS spectrophotometer (UV-1570, JASCO, Japan) equipped with a flow through cell to give a response signal for arsenite. Total arsenic was measured in same way but  $\text{AsH}_3$  was generated with 9 M  $\text{HCl}$  (Nacalai) for 4 min instead of phosphate buffer for 7 min. Arsenate was determined by subtraction of arsenite concentration from the total arsenic. In every 17 min generation of  $\text{AsH}_3$  from arsenite and total

arsenic were repeated by the syringe pump and measurement of collected arsenic was performed with continuous flow system. In Fig. 2 shows responses for standard solutions of arsenic.

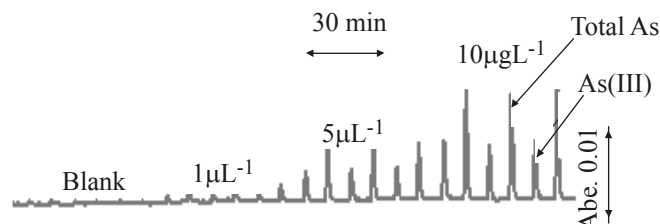


Fig. 2. Response signals of the SHGFIA system for standard solutions of 0, 1, 5 and 10  $\mu\text{g L}^{-1}$  As(III) + As(V)

### Sample collection

River sediment was collected from 300 m downstream of an old arsenic mine. The color of sediment was yellowish brown to grey, coarse in size with  $3.6 \text{ m}^2 \text{ g}^{-1}$  specific surface. Total arsenic content in sediment was determined with SHGFIA after acid digestion followed by the standard method.

### Leaching test

Prior to leaching test, sediment was washed with water on an 80-mesh sieve to remove fine particles. After air dried

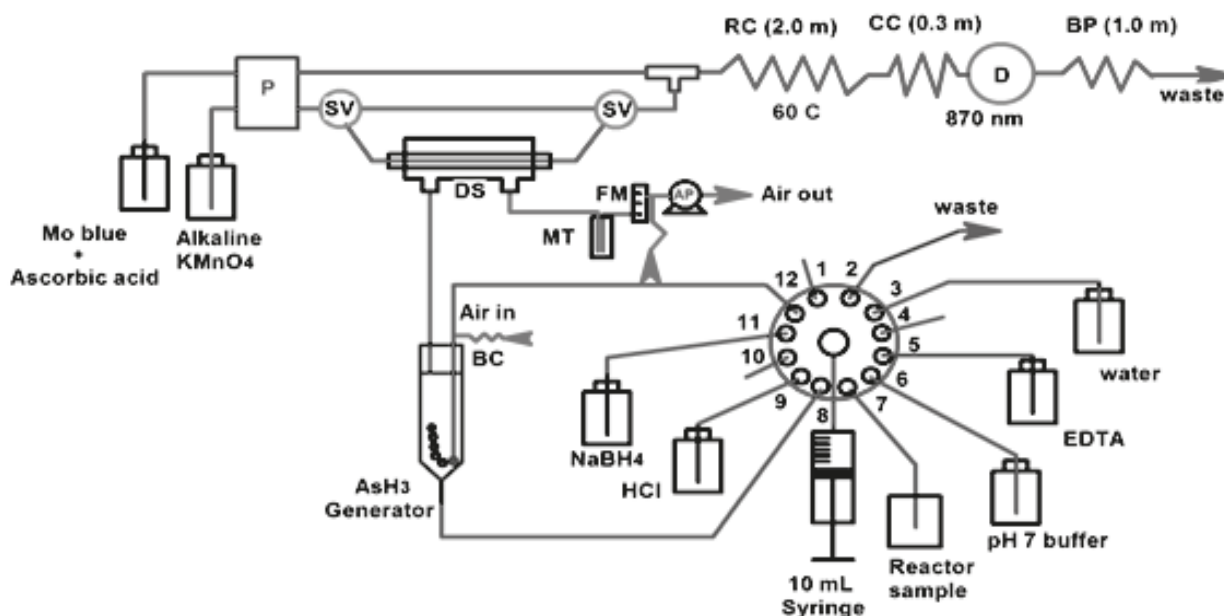


Fig. 1. Flow diagram for SHGFIA. SV: three-way solenoid valves, DS: miniature diffusion scrubber, RC: reaction coil, CC: cooling coil, D: absorbance detector, BP: back pressure coil, MT: mist trap, FM: air flow meter, mAP: miniature air pump.

sediment was dried at 135°C in oven for 3 h to remove adsorbed water by introducing air or N<sub>2</sub> gas at 500 mL min<sup>-1</sup> to make it aerobic or anaerobic. Thus, the treated 100 g sediment was added into 800 mL deionized water (DIW). Air or nitrogen was purged to water at 20 mL min<sup>-1</sup> since 3 h before to add sediment into water to make aerobic or anaerobic. Step-wise synthetic groundwater compositions (calcium 100 mg L<sup>-1</sup>, bicarbonate 100 mg L<sup>-1</sup>, silicate 20 mg L<sup>-1</sup>, nitrate 2 mg L<sup>-1</sup>, and phosphate 3 mg L<sup>-1</sup>) were added and arsenite as well as arsenate were monitored. Additional amount of phosphate was added into two steps (7 mg L<sup>-1</sup> and 20 mg L<sup>-1</sup>) and arsenite and arsenate were monitored by SHGFIA. pH of deionized water (DIW) was 6.7; finally it was above 9 and pH was monitored with ion meter (F-53, Horiba, Japan). The experiment was conducted for 5 h in aerobic and anaerobic.

## Results and Discussion:

### *Arsenic leached by the stepwise ions addition*

Before washing arsenic was in sediment 476 mg kg<sup>-1</sup> and after washing it was 450 mg kg<sup>-1</sup>. It seems that huge amount arsenic

increased. At 2.55 h in aerobic, arsenic was leached as 2.7 µg L<sup>-1</sup> As(III) and 12.9 µg L<sup>-1</sup> As(V) while in anaerobic arsenic was leached as 2.6 µg L<sup>-1</sup> As(III) and 16.6 µg L<sup>-1</sup> As(V).

After adding of (calcium 100 mg L<sup>-1</sup> + bicarbonate 100 mg L<sup>-1</sup>) as well as (20 mg L<sup>-1</sup> silicate + 2 mg L<sup>-1</sup> nitrate + 3 mg L<sup>-1</sup>) pH was above 9. By the addition of additional phosphate 7 mg L<sup>-1</sup> and 20 mg L<sup>-1</sup> pH was constant in both cases but leaching of As(V) was very steep and leaching of As(III) also increased. In case of anaerobic, leaching amount of arsenic was more than aerobic. At higher pH desorption of arsenic is increased because suspension pH decreases positive surface charge on metals oxides resulting increasing pH aid desorption of As oxyanions (Patrick *et al.* 1991). Arsenic was leached at 5 h, under aerobic 5.1 µg L<sup>-1</sup> As(III) and 44.2 µg L<sup>-1</sup> As(V) but at same time under anaerobic, arsenic was leached as 9.5 µg L<sup>-1</sup> As(III) and 61.9 µg L<sup>-1</sup> As(V). Evidently, anaerobic condition enhances to leach more arsenic than under aerobic not only leached as As(V) but also As(III); phosphate ion accelerates to leach arsenic mostly As(V) from the sediment.

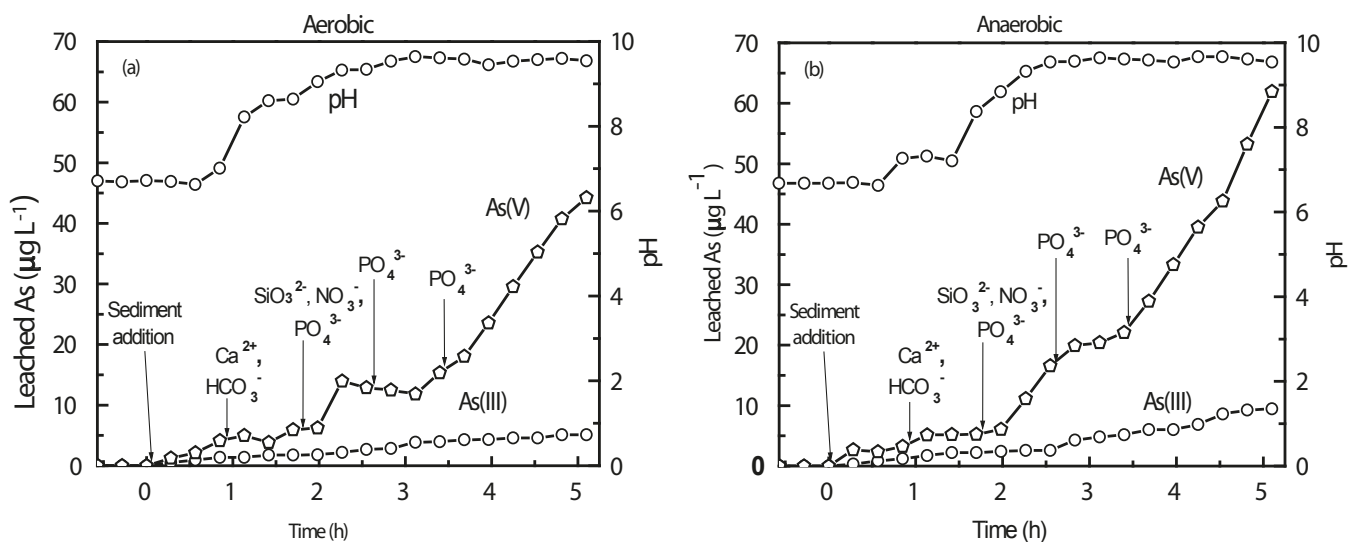


Fig. 3. Arsenic leached by the effect of step-wise ions addition under aerobic a) and arsenic leached under anaerobic b). Ions added: (calcium 100 mg L<sup>-1</sup> + bicarbonate 100 mg L<sup>-1</sup>), (silicate 20 mg L<sup>-1</sup> + nitrate 2 mg L<sup>-1</sup> + phosphate 3 mg L<sup>-1</sup>), (phosphate 7 mg L<sup>-1</sup>), and (phosphate 20 mg L<sup>-1</sup>).

in sediment and only washing with water 5.5% arsenic was leached. Fig. 3 shows arsenic leached by the effect of step-wise ions addition in aerobic and anaerobic. Initially, sediment was added into deionized water (DIW); both cases leaching amount of As(III) and As(V) was very low. Subsequently, step-wise addition of ions (calcium 100 mg L<sup>-1</sup> + bicarbonate 100 mg L<sup>-1</sup>) and (silicate 20 mg L<sup>-1</sup> + nitrate 2 mg L<sup>-1</sup> + phosphate 3 mg L<sup>-1</sup>) arsenic leaching was gradually

## Conclusions

Arsenic was leached as As(III) and As(V) but mostly As(V) by step-wise ions addition. Leaching of arsenic was very significant with increasing phosphate ion especially As(V) under anaerobic. SHGFIA is useful device for monitoring As(III) and As(V) leached from sediments; it could be use for kinetic behavior of As(III) and As(III) leaching from sediment and other environmental samples.

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*Received: 23 September 2013; Revised: 05 March 2014;  
Accepted: 03 June 2014.*