Monitoring of Arsenite Sorption to Biogenic Iron Oxide in a Flow-Through Column by X-Ray Absorption Spectroscopy*

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We have conducted a pilot study of a biological filtration (BF) system for low-cost arsenic (As) removal from groundwater containing both ferrous iron (Fe(II)) and arsenic (As). Throughout the study, we have observed that arsenite (As(III)) as well as arsenate (As(V)) could be removed with this system. In conventional water treatment technologies, the preoxidation of As(III) to As(V) by oxidizing chemical is a mandatory step for As(III) removal. However, such a preoxidation unit has not been used in our BF pilot unit, and hence the mechanisms of As(III) removal by BF have been of interest. Using a flow-through column reactor that simulates the actual BF pond for analysis by X-ray absorption spectroscopy (XAS), we could observe the adsorption of As(III) in water onto iron hydroxides deposited on the biological filter. The time-resolved As K-edge X-ray absorption near-edge structure (XANES) spectra were obtained when the water containing As(III) and Fe(II) was continuously fed to the reactor. An increase in the absorption intensity of the X-ray with time was clearly observed in the time-resolved spectra, indicating that the spectra represented the concentration and chemical state of As adsorbed at the solid-liquid interface of the biological filter. The XAS results also show that while the original water fed to the reactor was supposed to contain only As(III) and Fe(II), a small portion of As(III) was oxidized to As(V) in the influent line when the As(III) solution met the Fe(II) solution before flowing into the reactor. Consequently, besides As(III), As(V) probably formed by the oxidation of As(III) in the influent, was detected on the filter by XAS. The results demonstrate that, in BF, mechanisms of As(III) removal are at least partially explained by the adsorption of As(III) in the raw water to the biological filter as it is. [DOI: 10.1380/ejssnt.2015.455]

Keywords: X-ray absorption spectroscopy; Oxidation; Arsenic; Iron oxide; Solid-liquid interfaces

I. INTRODUCTION

A. Background of our research

In developing countries in Asia, the groundwater containing high concentration of As has caused serious health hazards to millions of people (ex. [1]). The area with potentially As contaminated groundwater may be more widespread than previously reported [2]. The chronic exposure to As through water and food causes not only well-known skin-lesions and skin cancer, but also more general, non-specific diseases such as hyper-tension, diabetes, etc [3, 4]. In order to prove the cause and effect relationships between such non-specific diseases and the exposure to As, a costly and time-consuming epidemiological survey is indispensable. Therefore, especially in developing countries, some of the arsenic related health problems could have been overlooked.

In South and Southeast Asian countries, potential mechanisms for the release of As into groundwater are microbially mediated reductive dissolution of ferric oxides

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As(III), concentration in the order of 150 mg/L. On the other hand, oxidation of As(III) to As(V) [15]. The initial As(III) oxidation rate was increased with the Fe(III) concentration from 0.14 and 0.97 mg/L/min in the solution containing Fe(III) ranging between 50 mg/L and 800 mg/L (As(III) concentration 150 mg/L). On the other hand, oxidation of As(III) at circumneutral pH values has been linked to the presence of dissolved, adsorbed, or structural Fe(II). Under such conditions, the oxidation of As(III) is optimal with prolonged low steady-state concentrations of Fe(II), which is continuously oxidized by dissolved oxygen [16]. The mechanisms of the oxidation at near-neutral pH was considered to be the formation of highly oxidizing Fe(IV). According to [16], 25-50% of As(III) was oxidized after a contact time of 5.3 s by passing As(III) containing synthetic groundwater to a filter containing zero-valent iron which exuded Fe(II). However, the treatment processes described above require treatment chemicals, and are not always sustainable in the developing countries affected by groundwater As contamination, because such chemicals are often not affordable there.

The use of dissolved oxygen (DO) supplied from ambient air, i.e., aeration, may be a more sustainable way for peroxidation of As(III) in underfunded water treatment plants in affected areas. In practice, however, oxidation of As(III) by aeration alone is too slow and unstable to be used in actual water treatment processes. The reported oxidation rate values for As(III) varied widely, e.g., As(III), concentration in the order of μg/L in some soil pore water could be oxidized in 5 hrs, whereas As(III) of the similar concentration in certain soil extracts was not oxidized for 3 weeks [17]. According to these studies, the time scales needed to convert As(III) to As(V) by DO are orders of hours or weeks, which are too long for an economical water treatment.

B. The biological filtration for removal of As in groundwater and the purpose of the present research

We have developed a biological filtration (BF hereafter) system, a low-cost method to remove As from the groundwater containing both ferrous iron (Fe(II)) and As, by utilizing indigenous iron-oxidizing bacteria (IRB) in the water [18]. Since most of the As contaminated groundwater in South and Southeast Asia contains Fe(II), the BF technology is widely applicable there. “IRB” is the name for various bacterial species that biologically oxidize dissolved Fe and/or Mn, and deposit them as oxides. They are widespread in soils, sediments and natural water bodies [19]. The BF system consists of an aeration unit and a sand filter with backwashing system (Fig. 1). The sand filter is inoculated with indigenous IRB through continuous feeding of the groundwater to be treated. Usually 2 weeks of feeding the water is enough for the start-up of the system. With the percolation of the feed water through the filter on which IRB proliferate, dissolved Fe(II) and/or Mn first undergo biological oxidation and oxygenation actions by IRB, then precipitate on the surfaces of IRB as biogenic iron oxides (BIO hereafter), and finally are filtered out. When As is present in the feed water, As...
is adsorbed onto BIO continuously formed on the filter, and removed from the water. The system is backwashed periodically to maintain the filtration as well as to eliminate the precipitated BIO and the adsorbed As. The backwash interval is decided based on the head loss (i.e., the decrease in the permeability) in the filter bed [20]. In water treatment plants, backwash of rapid sand filter is conducted when head loss becomes higher than filter bed heights, e.g., 1.5–2.5 m. Empirically, the increase in the head loss is approximately directly proportional to the amount of impurities collected in the filter bed as suspended solid. In our study, impurities are iron and manganese oxides containing some As. Higher concentrations of Fe and Mn in the raw water lead to more frequent backwash. We could increase the linear velocity (LV) of BF to as high as 600 m/day maintaining the removal efficiency of As and Fe [18]. The operating cost of BF is only the power (electricity) for groundwater pump, aeration pump, feed water pump and backwashing pump. For BF, treatment chemicals are not required and the removal of As is better when the same filter media are used without exchange. After pilot tests in Japan and Vietnam [18, 21], we installed the BF system as an actual potable water treatment plant in a rural village in Hà Nam Province, Vietnam (in operation since April, 2012).

In our pilot study of the BF system in Vietnam, As(III) was determined on-site by anodic stripping voltammetry analysis, and more than 90% of As in raw water was shown to be present as As(III). The raw water in the study site contained 0.058 ± 0.008 mg/L and 0.169 ± 0.03 mg/L of As during Run1 and Run 2, as well as 8.8 ± 2.9 mg/L Fe, 0.12 ± 0.11 mg/L Mn, and 2.0 ± 1.0 mg/L NH₄-N (described as average ± one standard deviation of the concentration values). Removal of As(III) was expected to be more difficult compared to that of As(V) as discussed in the previous section, and there was no peroxidation system for As(III) in the BF unit. However, the average removal of As was higher than 80% in our case [21]. The reason why As(III) could be removed with the BF system without peroxidation was the matter of debate. We first suspected the microbial oxidation of As(III) during the aeration or the percolation of As(III)-containing water through the BF reactor, because microbial oxidation of As(III) is known to occur in the natural environment [22, 23]. The half-lives derived from As(III) oxidation kinetics are 0.6 min [24] and 3 hr [25] in thermal water, 3 min in the water treatment system that involves bacteria and Mn oxides [26], and 0.2 to 0.5 days in continuously aerated bacterial suspension isolated from soil [27].

We have conducted a batch sorption experiment of BIO in As(III) spiked water (pH 7, contact time 0.5 hr at ambient temperature) and determined the relative abundance of the adsorbed As(III) in the BIO sample by XANES spectroscopy [28, 29]. Based on the results, we concluded that As(III) was adsorbed onto BIO as As(III), that is, sorbed before it was oxidized by biological and/or chemical processes. But our observation was made for BIO samples which were in contact with As(III) for 0.5 hr under static condition. In the actual BF system, the water containing As is constantly percolating through the filter, and the contact time of As with BIO deposited on a 1cm segment of the filter media is only 1.3 sec when linear velocity is 600 m/day (a flow rate typically used in our pilot study). To clarify the mechanisms of As(III) removal by BF, it was desirable to observe the relative abundance of As(III) on BIO when the water containing As(III) is continuously fed to the filter media. Mitsunobu et al. [30] reported that by using quick scan X-ray absorption fine structure (QXAFS) technique, XAS could be applied to a column reactor where As(III) solution was continuously flowing through MnO₂ beads (a strong oxidizer of As(III)). By applying this technique, they obtained time-resolved As K-edge XANES spectra, showing the absorption edge of As being shifted to higher energy with time as As(III) was oxidized to As(V) at the solid-water interface [30]. The application of QXAFS technique to a column reactor suitable for our purpose was expected to produce the time-resolved As K-edge XANES spectra for As adsorbed on BIO, and enable us to determine whether As(III) is adsorbed as it is.

We therefore developed a flow-through column reactor that simulates the actual BF pond, and obtained the XANES spectra when the water containing As(III) and Fe(II) was continuously fed to the column. The focus of the research was to observe the abundance of As(III) and As(V) on BIO formed on the filter media, and clarify the processes relevant to the removal of As(III) in the BF system.

II. EXPERIMENTAL

A. Materials

All chemicals used were purchased from Wako Chemical Industries, and were of Japanese Industrial Standard special grade unless otherwise stated. The As(III) and Fe(II) spike solutions were prepared from NaAsO₂ and FeSO₄·7H₂O. A 1,000 mg/L As standard solution for atomic absorption spectrometry was used as a standard As(III) material for XAS measurement. Pellets made by mixing boron nitride and NaAsO₂ or Na₂H₂AsO₄·7H₂O, and As(V) solution obtained by dissolving Na₂H₂AsO₄·7H₂O in Milli-Q water (As(V) concentration 1,000 mg/L) were also used as standard materials.

The quartz sand (called filter-F hereafter) acclimated at the drinking water plant treating groundwater by BF at Suita city, Osaka, Japan was used as a filter media for our column experiment. The biological oxidation of Fe(II) and formation of BIO was readily achieved by the acclimated filter. The Filter-F was collected one day before the flow-through column experiment was conducted.

B. Flow through column for X-ray absorption spectroscopy

We designed and used a column reactor made of aluminum, equipped with a 25 μm thick polyimide film as window for the X-ray beam (Fig. 2). During the experiment, BIO is generated and gradually clogs the filter media, thereby creating hydraulic pressure inside the cavity of the column. To avoid water-leaking during the column experiment, the column and the window have to withstand the build-up of the pressure. In our case, the
FIG. 2. The home-made pressure-resistant flow-through column.

copolyimide film glued to a ring-shaped film-holder by adhesives was sandwiched in between the part of the column that holds biological filter media (filter-holder) and a piece of metal board with a 30 mm diameter of opening for the window, and was carefully screwed together using M5 bolts and nuts. The use of an O-ring on the filter holder was important to prevent the leakage of water. The biological filter media (filter-F) in the filter-holder faced the polyimide film window.

A peristaltic pump (Masterflex model L/S) with two pump heads was used to feed water via two streams connected to a T-shaped tubing connector at the column inlet. One stream, called stream 1 hereafter, supplied the groundwater containing IRB (treated water from a BF plant in Nara Prefecture, Japan) or synthetic river water (dilute salt solution with pH 7.5). Water in stream 1 was always spiked with 8 mg/L of As(III). The other stream, stream 2 hereafter, was Milli-Q water spiked with 80 mg/L of Fe(II). Water from the two streams met at the T-connector and entered the column reactor. The flow rate was 15 mL/min for each of the streams (total 30 mL/min), equivalent to LV 216 m/day. The LV value was within the range of LV used in our BF pilot study (between 150 and 600 m/day).

C. X-ray absorption spectroscopy data collection

XAS was applied to obtain the K-edge spectra of the As adsorbed to the BIO formed on the biological filter during continuous feeding of the solution containing Fe(II) and As(III). A Si(111) double crystal monochromator was used to vary the energy of the incident X-ray. The X-ray energy was calibrated using pellets of NaAsO2 (As(III) reference) and Na2HAsO4·7H2O (As(V) reference). All the measurements were conducted at BL14b2 beam line of the synchrotron X-ray facility SPring8 (Synchrotron Radiation Research Institute, Hyogo, Japan).

The technique used for the flow through column observation was QXAFS in fluorescence mode using a 19 element - germanium semiconductor detector. The scan was repeated until a spectrum of the desired quality was obtained. Approximately 5 minutes of data accumulation was necessary in our case to obtain a spectrum of moderate quality.

The flow through column experiment was conducted at the ambient temperature inside the beamline hutch. To prevent a short circuit flow between the inlet and the outlet of the column, we arranged the vertical locations of the pump, column and feed water bottles so that the filter media in the column were always submerged in the influent water.

We obtained XANES spectra for 1,000 mg/L As(III) and As(V) standard solutions, the feed water in stream 1 (containing only As(III)), the influent water (mixture of stream 1 and stream 2 solutions), and BIO deposited on the filter media in the column reactor during the column experiment. The standard As solution and water from stream 1 was measured in the empty column with the polyimide film window. The spectrum of the influent water was obtained by aiming the X-ray beam at the water pooled over the filter media in the column.

III. RESULTS AND DISCUSSION

In Fig. 3, As K-edge spectra (all normalized) of the influent water are compared with those of the standard As(III) and As(V) solutions, and also with the water containing 4 mg/L of As(III). The 4 mg/L As(III) solution was used because 8 mg/L of As in stream 1 solution was mixed with the stream 2 solution before entering the column, and since the flow rate of the two streams are the same, As concentration in the influent was diluted by a factor of 2. The spectra of influent water were noisy because they were obtained for the continuously flowing, potentially inhomogeneous solution pooled over the filter media. By comparing these spectra with the spectra of As standard solutions (two curves in the bottom of Fig. 3) and 4 mg/L As(III) in groundwater (third curve from the bottom), we can see that influent water appears to contain some As(V). We also analyzed the stream 1 wa-
ter (groundwater containing IRB or synthetic river water spiked with As(III)) for the presence of As(V) by XAS after standing it at room temperatures for 12 hrs, but no As(V) was found (figures not shown). It was therefore confirmed that As(V) was formed only after it was mixed with stream 2 solution (Fe solution containing Fe(II) as well as some Fe(III) formed through auto-oxidation of Fe(II) by DO).

We conducted a linear combination fitting using a free software Athena by Chicago University, and obtained a rough estimate of the amount of As(V) in total As in the influent to the column. The values were 13% for Fe+As(III) in sterile water (the top curve in Fig. 3), and between 19 and 24% for Fe+As(III) in groundwater (2nd, 3rd and 4th curve from the top in Fig. 3). These estimates are subject to large error and should be treated as the rough references. But the results do indicate that between 10 and 20% of As(III) was oxidized to As(V) before entering the filter media.

The reason that As(III) was oxidized in the influent water in our experiment remains unknown at present. A literature states that the oxidation of As(III) by iron, e.g., Fe(III), has not been observed [31]. It is also possible that some substances leached from the filter media diffused back into the influent water and caused the oxidation of As(III), but considering the short hydraulic retention time of water in our experiment, it is not a likely explanation for the behavior of As in the influent. We are planning to investigate the reason in the future research.

In Fig. 4, time resolved arsenic K-edge XANES spectra for filter-F are shown. These spectra were obtained when stream 1 was the groundwater spiked with 8 mg/L of As(III) and stream 2 was the Milli-Q water spiked with 80 mg/L of Fe(II). Accordingly, the influent contained 4 mg/L of As (mostly As(III), but a small portion was oxidized to As(V)) and 40 mg/L of Fe (Fe(II) plus Fe(III) formed by auto-oxidation). Some data are skipped for the sake of clarity in this figure. A spectrum for 4 mg/L As(III) is also shown for comparison. The X-ray absorption intensity of the filter-F spectra is markedly higher than that of 4 mg/L As(III) which represents the absorption by As in the influent. It means that the spectra of filter-F are, in essence, the spectra of As adsorbed and concentrated in BIO. The increase in the X-ray absorption intensity of filter-F with time indicated that the concentration of As at the liquid-water interface was increasing as time went by. It was also notable from Fig. 4 that both As(III) and As(V) were present in filter-F.

The sorption of As(V) to most adsorbents is higher than that of As(III) [13,19]. We also observed that the sorption of As(V) to BIO was more efficient than that of As(III).

In our experiment, we conducted a batch sorption test by adding 2 g of wet BIO (approximately 0.5 g dry weight) from a drinking water plant to 500 mL of water (pH 7.5) spiked with 0.4 mg/L or 2.0 mg/L of As(III) or As(V). The plot of the time after the sorption was started versus As concentration in the liquid phase followed a pseudo-first-order sorption kinetics with reaction half-life of 25 min and 6 min for As(III) and As(V), respectively. The sorption isotherm of As (the plot of As concentration in the liquid phase versus the amount of As sorbed per unit dry weight of BIO after 96 hrs of equilibration time) was quasi-linear, and the slope of the isotherm plot was 3,600 and 21,000 [L/kg] for As(III) and As(V), respectively.

As discussed previously, a small portion of As in the influent was transformed to As(V) in our experiment. Considering the facts that both As(V) and As(III) were contained in the influent, and that As(V) is more preferentially adsorbed to BIO than As(III) according to our batch experiment, As(V) / As(III) ratio was expected to become higher in the adsorbed phase than in the influent.

Based on the discussion above, it is natural that both As(III) and As(V) were detected in filter-F by the time-resolved XANES spectra. It is more important to note that, despite the high sorptivity of As(V) to BIO compared to As(III), As(III) adsorbed onto BIO was detected in significant amount. There is a report that the ox-
treatment of As(III) was catalyzed by IRB, leading to enhanced overall arsenic removal [32]. But the results of the present work indicate that at least part of the As(III) was adsorbed to BIO as it is, implying that the oxidation of As(III) prior to its sorption may not be the principal mechanisms of As(III) removal in BF.

When groundwater containing IRB was used in stream 1, Fe(II) was rapidly oxygenated to form BIO and was deposited on the filter-F inside the column. On the other hand, the amount of BIO created within the filter media was apparently smaller when sterile synthetic river water was used in place of groundwater in stream 1. It is probably because biological oxidation of Fe(II) by the acclimated filter-F alone was less active compared to the same filter media continuously fed with groundwater (and thus continuously inoculated with IRB). And when the synthetic river water was used in stream 1, the X-ray absorption intensity of As K-edge spectra obtained for the synthetic river water was used in stream 1, it should be noted that the absorption intensity of As K-edge spectra obtained for the filter-F was less than 10% of the absorption intensity observed for the filter-F. And when groundwater was used in stream 1 (figure not shown). The results prove that for the efficient removal of Fe as well as As in actual biological filtration systems, continuous feeding of groundwater containing IRB to inoculate IRB on the filter media is important.

IV. CONCLUSIONS

By developing a flow-through column reactor that simulated the actual water treatment system and conducting XAS, we observed the adsorption of As(III) onto biologically formed iron hydroxides. The time-resolved As K-edge XANES spectra reflecting the concentration and the chemical state of adsorbed As were obtained when water containing As(III) and Fe(II) was continuously fed to the biological filter. The results indicate that the As(III) removal in biological filter can be explained by the sorption of As(III) as it is, rather than the quantitative oxidation of As(III) to As(V) prior to the sorption.

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