Arsenic removal from arsenic-contaminated water by biological arsenite oxidation and chemical ferrous iron oxidation using a down-flow hanging sponge reactor

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ABSTRACT

The down-flow hanging sponge (DHS) reactor was used for continuous As removal treatment of As-contaminated water. The treatment scheme was: (1) As(III) in contaminated water is oxidized by arsenite-oxidizing bacteria fixed in the sponges in the reactor; (2) Fe(II) naturally existing in the water is oxidized by dissolved oxygen; (3) Fe(III) is precipitated as iron hydroxide and As(V) is co-precipitated with the iron hydroxide; and finally (4) the co-precipitates are fixed in the sponges. This system could remove As from As-contaminated water on a small scale and at low cost. The results showed that, after using the DHS reactor, As and Fe concentrations in the treated water were lower than water quality standards for drinking water when Fe(II) concentration in the influent was lower than 10 mg/L and the Fe/As ratio was higher than 6.67–8.42, with dependence on the Fe concentration. Additionally, even if Fe concentration is higher than 10 mg/L, the treatment system is still applicable if the pH of the influent is higher than 7 or the retention time is longer than 2 h.

Key words | arsenite, arsenite-oxidizing bacteria, bioreactor, iron co-precipitation

INTRODUCTION

Arsenic is known to cause liver, kidney, bladder, and skin cancers in long-term human exposure (Ng et al. 2005). Arsenic-contaminated groundwater is used for drinking water in Bangladesh, India and elsewhere (Kinniburgh & Smedley 2001; Murphy & Guo 2003; Ahamed et al. 2006; Ning et al. 2007), which poses a serious health risk to people living there. Indeed, over 45 million people are potentially exposed to As from As-contaminated groundwater (Nordstrom 2002). To reduce the health risk, As removal technologies have been developed for providing As-free safe water.

The uncharged species arsenite (H3AsO3: As(III)) is dominantly present in groundwater, under reducing conditions at pH less than about 9.2 (Smedley & Kinniburgh 2002). Because the removal efficiency of arsenite is low, generally arsenite is oxidized to arsenate (HAsO4^2-: As(V)) for high removal efficiency, which is the first step of the As removal process. The As(III) oxidizing process usually employs oxidizing reagents such as chlorine or ozone (USEPA 2003). On the other hand, biological As(III) oxidation was investigated by using As(III) oxidizing bacteria such as the genus Pseudomonas, the genus Xanthomonas, and the genus Achromobacter (Turner 1954), Rhizobium sp., Microbacterium sp., and Pseudomonas sp. (Paul et al. 2014), and Bacillus sp. (Pattanapipitpaisal et al. 2015). Biological As(III) oxidation

has a possibility of reducing the cost for As removal from
As-contaminated groundwater. Autotrophic-type As(III)
oxidizing bacteria oxidize As(III) in the following reaction
(Santini et al. 2000):

$$2H_3AsO_3 + O_2 \rightarrow HAsO_2^- + H_2AsO_4^- + 3H^+$$

Some bioreactors using As(III) oxidizing bacteria were
developed for As(III) oxidation: a stirred tank reactor
(Wang & Suttigarn 2007; Dastidar & Wang 2010), a fixed
bed reactor (Michon et al. 2010), and a down-flow hanging
sponge (DHS) reactor (Segawa et al. 2013).

Some processes to follow As(III) oxidation have been
suggested: ion exchange, coagulation, and adsorption
(USEPA 2003). In particular, adsorption by iron-based sor-
bents is known to be highly effective, such as granular
ferric oxide (Sazakli et al. 2015), and zero-valent iron (Tkac-
zynska 2015). Moreover, Wan et al. (2010) developed a fixed-
bed reactor combining two types of sand layers; one con-
tained As(III)-oxidizing bacteria *Thiomonas arsenivorans*
for biological As(III) oxidation, and the other contained
zero-valent iron for As(V) coagulation. The authors devel-
oped a low-cost biological As(III) oxidizing treatment
method using a DHS reactor, in which As(III)-oxidizing
bacteria fixed with hung cylindrical sponge carriers oxidi-
dized As(III) to As(V) as shown in Figure 1 (Segawa et al.
2013). As(III) in the solution supplied from the
upper part of the reactor was oxidized to As(V) through
the reactor. The reactor can provide sufficient oxygen to
the As(III)-oxidizing bacteria and so does not need any
aeration system. One of the general processes to follow oxida-
tion is co-precipitation of As(V) with Fe(III) hydroxide
(USEPA 2003; Tokoro et al. 2010). A certain amount of Fe
is naturally present in groundwater; therefore, As removal
from the groundwater can be accomplished without
adding an Fe reagent if Fe is contained sufficiently for As
removal in the groundwater. One concern is that Fe is pre-
sent as Fe(II) in groundwater. Fe(II) must be oxidized to
Fe(III) in order to produce Fe(III) hydroxide precipitates.
Fe(II) is oxidized by dissolved oxygen, but Fe(II) oxidation
behavior depends on pH. Moreover, in many areas Fe con-
centrations in groundwater are higher than 0.3 mg/L,
which is the drinking water quality for Fe in the WHO
guideline (WHO 2011). To supply water suitable for
drinking, Fe concentration in the treated water must be
lower than 0.3 mg/L after the As removal treatment.

In this study, the As removal system combined with
biological As(III) oxidation and Fe(III) hydroxide–As(V)
co-precipitation processes was evaluated using the DHS
reactor. First, As(III) in As-contaminated water was oxidized
to As(V) by As(III)-oxidizing bacteria. Simultaneously with
this step, Fe(II) in the water was oxidized to Fe(III) by dis-
solved oxygen. Then, the Fe(III) precipitated as Fe(III)
hydroxide and As(V) co-precipitated with the Fe(III) hydrox-
ide. These treatment processes were performed within the
DHS reactor, thus allowing As removal at low cost and
small scale. To remove As sufficiently by a coagulation-
sedimentation method, a USEPA study reported that the
Fe/As mass ratio should be 20 (USEPA 2003) while the
The authors found the ratio should be 40 (Segawa et al. 2014). The authors also found that when As(III) concentration in the influent was 0.5 mg/L and the Fe/As ratio was 10 or 50, the As concentration in the effluent was decreased to around 0.01 mg/L, but Fe concentration in the effluent was higher than the Fe concentration suggested by the WHO guideline for drinking water. Therefore, it was necessary to optimize the Fe/As ratio to meet the suitable value. The effect of Fe/As ratio in the influent on As removal and the effect of pH on Fe(II) oxidation by dissolved oxygen were investigated for the removal system.

MATERIALS AND METHODS

As(III)-oxidizing bacteria group

The As(III)-oxidizing bacteria group used in this study was obtained by enrichment culture from activated sludge collected from an oxidizing tank at the Akiu hot spring wastewater treatment plant, Sendai, Japan (Segawa et al. 2013). The As(III)-oxidizing bacteria group was subcultured with the culture solution suggested by Weeger et al. (1999) except that the present study did not include sodium lactate as an organic carbon source (Table 1). The As(III)-oxidizing bacteria grew in the culture medium without organic carbon source, which suggested that the bacteria were autotrophic (Andrianisa et al. 2008; Ito et al. 2012) and the type of electron donor was arsenite. As(III) concentration in the culture solution was 100 mg-As/L. The effects of temperature, pH, and dissolved oxygen on As(III)-oxidizing capacity have been reported by the authors (Segawa et al. 2014). The pH of the culture solution was adjusted to 7.0 ± 0.1.

DHS reactor

Figure 2 shows a schematic drawing of the DHS reactor. The DHS reactor consisted of 25 polyurethane cylindrical sponge carriers (Figure 1) connected by strings. The diameter, height and porosity of the cylindrical sponge carrier were 4 cm, 4 cm and about 0.98, respectively. The DHS reactor was set up in a temperature-controlled room (25 °C). The enrichment culture solution containing the As(III)-oxidizing bacteria group was circulated through the DHS reactor for about 1 week to fix the bacteria group by the sponge carriers. Then, the DHS reactor was used to carry out a continuous As removal treatment experiment.

Continuous As removal experiment

The continuous As removal experiment was carried out with the DHS reactor. Pumps supplied simultaneously separate flows of As(III) solution and Fe(II) solution from the upper part of the reactor (Figure 2). The inflow volume ratio of As(III) solution to Fe(II) solution was 1:1. The retention

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As$_2$O$_3$</td>
<td>0.132</td>
</tr>
<tr>
<td>MgSO$_4$·7H$_2$O</td>
<td>2</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>0.2</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>1</td>
</tr>
<tr>
<td>K$_2$HPO$_4$</td>
<td>0.001</td>
</tr>
<tr>
<td>CaCl$_2$·2H$_2$O</td>
<td>0.06</td>
</tr>
<tr>
<td>FeSO$_4$·7H$_2$O</td>
<td>0.0033</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 1 | Composition of As(III) stock solution

Figure 2 | Schematic drawing of the DHS reactor.
time was set to 2 h. The As(III) solution was prepared by diluting As(III) stock solution as shown in Table 1. The initial As(III) concentration was 0.5 or 1 mg/L. The Fe(II) solution was prepared by dissolving FeSO₄·7H₂O. The continuous As removal experiment was done as a function of the Fe/As ratio of the influent. The pH of the Fe(II) solution was about 4. The pH of the influent, which was a mixture of the As(III) and Fe(II) solutions, was adjusted to 6.6–7 by controlling the pH of the As(III) solution.

In this study, the continuous As removal experiment was performed as a function of several Fe/As ratios. During the experiment, influent containing As(III) flowed from the upper part of the reactor, and then the influent and effluent were periodically collected. During the reactor operation, As(III) and Fe(II) concentrations in the influent were changed. The experiment was carried out two times (Run-1, Run-2). Table 2 shows As(III) concentration, Fe(II) concentration and Fe/As ratio in each run. One run was done continuously for 60–150 days. After one run was finished, the used sponge carriers were exchanged for brand new ones because Fe precipitates could potentially block pores in the sponge carriers.

The collected influent and effluent samples were filtered through a 0.2 μm pore-size membrane filter (Advantec, polyethersulfon). As(III), As(V), Fe(II), and Fe(III) concentrations in these filtrates were determined. As(III) and As(V) concentrations in these filtrates were determined according to the analytical method described by Sakai & Inoue (1998): 0.2 mM phosphate buffer solution and 0.2 mM EDTA-2Na (pH 6.0) were used as a mobile phase, and the filtrates plus mobile phase were passed through a GelPack GL-ICA column (Hitachi Chemical) connected to a high performance liquid chromatograph (Shimadzu, SLC-10Avp system), and introduced to an inductively coupled plasma mass spectrometer (ICP-MS, Thermo, iCAP Qc). Fe(II) and Fe(III) concentrations in these filtrates were determined by the 1,10-phenanthroline method (Japan Society for Analytical Chemistry 1996). Removal rates of As and Fe from the influent with the DHS reactor were calculated as follows:

\[
\text{Removal rate } \% = \left( \frac{C_{\text{inf}} - C_{\text{eff}}}{C_{\text{inf}}} \right) \times 100
\]

where \(C_{\text{inf}}\) and \(C_{\text{eff}}\) are As or Fe concentrations in the influent and effluent, respectively.

After each operation was finished, two types of sampling procedure were used. One sampled solutions at given sponges to obtain the vertical distributions of degrees of oxidation of As(III) and Fe(II) as well as the degree of As removal. For this, each sample was filtered through a 0.2 μm pore-size membrane filter and then As(III), As(V) and Fe(II) concentrations in the filtrates were measured as described above. The other procedure sampled the sponges themselves to determine the amount of remaining As and Fe in each sponge. For this each sponge sample was immersed in 3 M HNO₃ and squeezed to elute As and Fe into the HNO₃ solution. This process was repeated three times to completely elute As and Fe from the sponge. The eluant was decomposed on a hot plate at 110 °C and then As and Fe concentrations in the decomposition solution were determined with the ICP-MS and ICP-atomic emission spectrometer (Shimadzu, ICPE-9000).

### Table 2 | As(III) and Fe(II) concentrations in the influent for each experiment

<table>
<thead>
<tr>
<th>As(III) (mg/L)</th>
<th>Fe(II) (mg/L)</th>
<th>Fe/As ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run-1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>0.5</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Run-2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>1</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

**Effect of pH on Fe(II) oxidation by dissolved oxygen**

About 100 mL of FeSO₄ solution (Fe concentration: 10 mg/L) was put in a beaker. The pH of the solution was adjusted from 4 to 10 with NaOH or HCl solutions. The solution was agitated using a magnetic stirrer, and an aliquot of the solution was taken periodically. Fe(II) concentrations in the samples were determined by the 1,10-phenanthroline method. This experiment was performed in the temperature-controlled room (25 °C).
RESULTS AND DISCUSSION

Continuous As removal by the DHS reactor

Figure 3 shows the result of the continuous As removal experiment for Run-1. There was no Fe(II) feed for 15 days after the experiment was started. In this period As(III) in the influent was mostly oxidized to As(V). It was suggested that As(III) in the influent was oxidized by the As(III)-oxidizing bacteria group fixed in the sponge carriers because chemical As(III) oxidation by dissolved oxygen in solution was very slow (Segawa et al. 2014). The Fe/As ratio was then set to 4 from day 16 to 74 of operation. The operation was almost stable from day 23 to 74; the average sum of Fe(II) and Fe(III) concentrations (Fe(II + III)) in the effluent was 0.07 ± 0.2 mg/L (average removal rate: 96.4%), which meant that Fe(II) was oxidized to Fe(III) by dissolved oxygen, then Fe(III) hydroxide adhered to the sponge carriers. According to these results, it was indicated that the chemical form of As in the effluent was As(V) and then As(V) was removed from the solution due to co-precipitation with Fe(III) hydroxide. The Fe/As ratio was set to 10 from day 75 to 97 of operation. The average sum of As(III) and As(V) concentrations (As(III + V)) in the effluent was 0.013 ± 0.29 mg/L (average removal rate: 97.3%), which is close to the WHO guideline value for drinking water (0.01 mg/L). The result showed stable and sufficient As removal was achieved due to the increase of Fe concentration in the influent. However, the average concentration of Fe(II + III) in the effluent was 0.81 ± 0.75 mg/L (average removal rate: 87.2%), which was higher than the WHO guideline value for drinking water (0.3 mg/L). From day 98 of operation, the Fe/As ratio was set to 5, and the average effluent concentrations of As(III + V) and Fe(II + III) were 0.23 ± 0.15 mg/L (average removal rate: 73.7%) and 0.54 ± 0.88 mg/L (average removal rate: 89.6%), respectively. Both these concentrations exceeded the WHO guideline values. One reason for this could be unstable concentrations in the influent during the operation.

Figure 4 shows the results of the continuous As removal experiment for Run-2. As in Run-1, almost all of the As(III) in the influent without Fe was oxidized to As(V) through the reactor in the effluent by day 10 of operation, which...
confirmed that As(III) was oxidized to As(V) by the As(III)-oxidizing bacteria group. From day 10 to 30, the Fe/As ratio was set to 5, and Fe was sufficiently removed, i.e., the average Fe(II + III) concentration in the effluent was 0.09 ± 0.14 mg/L (average removal rate: 98.3%). The As(III + V) concentration in the effluent was not stable, but ranged from <0.01 to 0.67 mg/L. The Fe/As ratio of 5 was too low for stable As removal treatment.

The Fe/As ratio was set to 10 from day 30 to 44 of operation. During this period As was constantly removed and the average As(III + V) concentration was 0.08 ± 0.06 mg/L (average removal rate: 92.8%). The result showed that enhancement of Fe supply in the influent led to stable As removal. In addition, the average effluent Fe(II + III) concentration was 0.08 ± 0.11 mg/L (average removal rate: 94.4%), which was lower than the WHO guideline value.

After day 44 of operation, the Fe/As ratio was set to 20, and the average As concentration in the effluent (0.03 ± 0.04 mg/L) reached around the WHO guideline value; however, the average effluent Fe(II + III) concentration (4.56 ± 2.35 mg/L) considerably exceeded the WHO guideline value. Fe in the effluent was Fe(II), which meant Fe(II) oxidation by dissolved oxygen could not be performed sufficiently when the Fe(II) load was higher than 10 mg/(L·h).

The pH in the effluent ranged from 6.0 to 7.6 with an average of 6.9. The pH variation likely depended on the status of the treatment. Table 3 summarizes Fe(II + III) and As(III + V) concentrations in the effluent on average for each Fe/As ratio. Figure 5 shows the relationships between As removal ratio and Fe(II)/As(III) ratio for each As(III) concentration in the influent. The As removal ratio was high enough at an

<table>
<thead>
<tr>
<th>Fe/As ratio</th>
<th>As(III + V) (mg/L)</th>
<th>Fe(II + III) (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run-1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.12 ± 0.10</td>
<td>0.18 ± 0.4</td>
</tr>
<tr>
<td>10</td>
<td>0.01 ± 0.03</td>
<td>0.84 ± 0.8</td>
</tr>
<tr>
<td>5</td>
<td>0.21 ± 0.15</td>
<td>0.49 ± 0.8</td>
</tr>
<tr>
<td>Run-2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.17 ± 0.19</td>
<td>0.09 ± 0.1</td>
</tr>
<tr>
<td>10</td>
<td>0.06 ± 0.06</td>
<td>0.08 ± 0.1</td>
</tr>
<tr>
<td>20</td>
<td>0.03 ± 0.04</td>
<td>4.56 ± 2.3</td>
</tr>
</tbody>
</table>

Figure 4  | Experimental variation of the As(III), As(V), Fe(II) and Fe(III) concentrations in the influent and effluent for Run-2. ‘Fe/As ratio’ at the top of the figure means Fe(II)/As(III) ratio.
Fe/As ratio higher than 10, but reduced with decreasing Fe/As ratio from 10 to 5. This result suggested that sufficient As removal needed an Fe/As ratio of at least 10 for the experimental conditions in this study.

Vertical distributions of As and Fe concentrations in the sponge carriers in the DHS reactor

Figures 6 and 7 show vertical distributions of As and Fe concentrations in the DHS reactor for Run-1 (Fe/As ratio at the end of the operation: 5) and Run-2 (Fe/As ratio at the end of the operation: 20), respectively. Segawa et al. (2013) reported the dissolved oxygen (DO) concentrations in the solution of the sponges of the same DHS reactor were about 5 to 8 mg/L. This fact suggested that the DHS sponges could provide almost the maximum DO level for As and Fe oxidations since the saturated DO level in water is 8.11 mg/L at 25 °C. When the Fe/As ratio was set to 5 for Run-1, Fe(II) was immediately oxidized to Fe(III) in the upper part of the DHS reactor. As well as Fe(II), most of the As(III) was oxidized to As(V) in the upper part of the DHS reactor due to rapid As(III) oxidation by the As(III)-oxidizing bacteria group fixed in the sponge carriers. Moreover, As(V) concentration was gradually lowered downwards, which suggested that As(V) co-precipitated with Fe(III) hydroxide. However, a small amount of As(V) flowed out from the DHS reactor before sufficient As(V) co-precipitation was attained. When the Fe/As ratio was set to 20 for Run-2, As(III) oxidation and Fe(II) oxidation were completed in the upper part of the DHS reactor and Fe and As were sufficiently low in the effluent. However, Fe(II) oxidation was unstable during the operation when Fe(II) concentration was high in the influent (Fe concentration: 20 mg/L; Fe/As: 20) (Figure 4). From these results, when the Fe/As ratio was increased As could be sufficiently removed, while oxidation of Fe(II) to Fe(III) was insufficient and then the remaining Fe(II) flowed out in the effluent.
Vertical distribution of the amount of As and Fe fixed with the sponge carriers

Figure 8 shows the vertical distributions of the amount of As and Fe in the sponge carriers at the end of operation for Run-1 (Fe/As = 5). The amounts of As and Fe fixed in the sponge carriers were lowered on going downward in the reactor, which was attributed to As and Fe being mainly removed in the upper part of the DHS reactor as described in the preceding section. Moreover, for all runs, the amounts of As and Fe fixed in each sponge carrier had a positive correlation with a high correlation coefficient ($R > 0.99$). It was confirmed that As was co-precipitated with Fe.

The effect of pH on oxidation rate of Fe(II) by dissolved oxygen

Figure 9 shows Fe(II) oxidation to Fe(III) by dissolved oxygen with time under several pH conditions when Fe(II) concentration was 10 mg/L. Most of the Fe(II) was oxidized within 10 min at pH values higher than 7. Fe(II) was not oxidized for 60 min at pH 5. At pH 6, Fe(II) was oxidized but its rate was slow; 50% of the Fe(II) was oxidized in 60 min. Therefore, Fe(II) could be sufficiently oxidized to Fe(III) in the DHS reactor with a retention time of 2 h when Fe(II) concentration was lower than 10 mg/L and pH was higher than 6. For Run-2, the pH of the influent ranged from 6.6 to 7.5 (average: 6.9). During the operation, the pH of the influent was generally lower than 7, and Fe(II) oxidation was insufficient at a retention time of 2 h. Therefore, when Fe(II) concentration in the influent was lower than 10 mg/L, Fe(II) oxidation was completed at a pH higher than 7 under the treatment conditions. Even when the pH was 6–7, it seemed that extension of the retention time could enhance Fe(II) oxidation and then reduction of Fe(II + III) concentration in the effluent.

Possibility of As removal treatment for actual As-contaminated groundwater by the DHS reactor under study conditions

In a report compiled by the British Geological Survey on As concentration in groundwater throughout Bangladesh, As concentration as well as Fe concentration and pH were measured at 271 sampling points in Nawabganj, Faridpur and Lakshmipur as special study areas (Kinniburgh & Smedley 2001). The possible use of the DHS reactor under the present study conditions was considered for 143 out of 271 sampling points in which all data for As concentration,
Fe concentration and pH are included and As concentration is greater than 0.01 mg/L. At the 143 sampling points, the As concentration was in the range 0.01–2.4 mg/L (average: 0.212 mg/L), Fe concentration ranged from 0.007–24.8 mg/L (average: 4.1 mg/L) and pH was in the range 6.4–8.9 (average: 7.1). The possibility of application to these sampling sites was evaluated for As removal from As-contaminated groundwater by the DHS reactor.

Figure 10 shows the relationship between the ratio ($R_{\text{inf}}$) of Fe concentration ($C_{\text{Fe inf}}$) to As concentration ($C_{\text{As inf}}$) in the influent and the Fe/As ratio ($R_{\text{removal}}$) removed by the reactor for all study conditions.

$$R_{\text{inf}} = \frac{C_{\text{Fe inf}}}{C_{\text{As inf}}}$$

$$R_{\text{removal}} = \frac{C_{\text{Fe removal}}}{C_{\text{As removal}}}$$

where $C_{\text{Fe removal}}$ and $C_{\text{As removal}}$ are the Fe and As concentrations removed by the reactor, calculated as follows:

$$C_{\text{As removal}} = C_{\text{As inf}} - C_{\text{As eff}}$$

$$C_{\text{Fe removal}} = C_{\text{Fe inf}} - C_{\text{Fe eff}}$$

where $C_{\text{As eff}}$ and $C_{\text{Fe eff}}$ are the As and Fe concentrations in the effluent, respectively. When $R_{\text{inf}}$ was lower than 10, the removed Fe/As ratio significantly increased with $R_{\text{inf}}$. When $R_{\text{inf}}$ was higher than 10, the removed Fe/As ratio gently increased with $R_{\text{inf}}$. $C_{\text{Fe inf}}$ at $R_{\text{inf}}$ of 20 was 20 mg/L. Fe(II) removal was unstable because of insufficient retention time for Fe(II) oxidation. It was suggested that sufficient Fe(II) oxidation in the effluent was reached when the Fe(II) concentration was lower than 10 mg/L in the influent as shown in Figures 3 and 4. Therefore, As removal using the DHS reactor at the HRT of 2 h was applicable for As-contaminated water with Fe(II) concentration lower than 10 mg/L. From the plotted findings of Figure 10, the relationship between $R_{\text{inf}}$ and $R_{\text{removal}}$ can be experimentally expressed as the following equation with a high determination coefficient ($R^2 = 0.93$):

$$\frac{C_{\text{Fe removal}}}{C_{\text{As removal}}} = 1.78 \times (R_{\text{inf}})^{0.74}$$

With the assumption that the Fe concentration in the effluent was 0.07 mg/L, the lowest concentration achieved by the reactor, $C_{\text{Fe removal}}$ can be calculated as follows:

$$C_{\text{As removal}} = C_{\text{As inf}} - C_{\text{As eff}} - 0.07$$

From the substitution of Equation (7) into Equation (6), $C_{\text{As eff}}$ can be calculated as follows:

$$C_{\text{As eff}} = C_{\text{As inf}} - \frac{C_{\text{Fe inf}} - 0.07}{1.78 \times (R_{\text{inf}})^{0.74}}$$

Sufficient removal of Fe was obtained when $C_{\text{Fe inf}}$ ranged from 0.07 to 10 mg/L under the present study conditions using the DHS reactor. When the desired $C_{\text{As eff}}$ is lower than 0.01 mg/L at $C_{\text{Fe inf}}$ lower than 10 mg/L, $C_{\text{As inf}}$ and its $R_{\text{inf}}$ can be calculated by Equation (8). The minimum value of $R_{\text{inf}}$ which can achieve sufficient As and Fe removal from As-contaminated water depends on $C_{\text{Fe inf}}$. For example, when $C_{\text{Fe inf}}$ are 2 mg/L and 10 mg/L, $R_{\text{inf}}$ which can achieve sufficient As and Fe removal can be higher than 8.26 and 8.42, respectively, as calculated by Equation (8). Figure 11 shows the maximum $C_{\text{As inf}}$ value and the $R_{\text{inf}}$ with $C_{\text{Fe inf}}$ for sufficient As and Fe removal. The resulting $C_{\text{As inf}}$ was 0.0011 mg/L (Fe/As ratio: 6.67) for 0.007 mg/L of $C_{\text{Fe inf}}$, and $C_{\text{As inf}}$ was lower than
1.188 mg/L (Fe/As ratio: 8.42) for 10 mg/L of $C_{\text{Fe}}^{\text{inf}}$. It was found that $R_{\text{min}}$ ranged from 6.67 to 8.42 depending on $C_{\text{Fe}}^{\text{inf}}$.

Figure 12 indicates the combination range of Fe and As concentrations in groundwater in the 143 sampling points. The DHS reactor had the possibility of removing As and Fe significantly from groundwater in those combinations of As and Fe concentrations that are plotted in the filled triangle part of Figure 12. The circle plots in the figure show significant removal of As and Fe from As-contaminated water by the reactor. Thus, the DHS reactor was applicable for As and Fe removal from groundwater for 80.4% of the sampling points (115 sampling points out of 143). On the other hand, there were nine sampling points with Fe concentration higher than 10 mg/L. In two of these sampling points the pH was higher than 7, which meant that As and Fe removal treatment was possible even if the Fe concentration was higher than 10 mg/L because Fe(II) was rapidly oxidized when the pH was higher than 7. At the remaining seven points the pH ranged from 6.38 to 6.96. Such groundwater could be treated if the retention time of the reactor was extended.

**CONCLUSIONS**

This study investigated three processes that were carried out simultaneously for As removal from As(III) solution by the DHS reactor: As(III) oxidation to As(V) by an As(III)-oxidizing bacteria group; Fe(II) oxidation to Fe(III) by dissolved oxygen; and co-precipitation of produced Fe(III) hydroxide with As(V). It was found that when the Fe/As ratio was higher than 20 in the influent, the As concentration in the effluent was close to 0.01 mg/L. On the other hand, when Fe(II) was higher than 10 mg/L in the influent, Fe(II) oxidation could not be completed with a retention time of 2 h, and $>0.3$ mg/L of Fe remained in the effluent. For that case it was suggested that As and excess Fe could be removed for drinking water use if the pH in the influent was adjusted to higher than 7 or the retention time was extended. It was concluded that As removal treatment by the DHS reactor has a good possibility for application to As removal from As-contaminated groundwater at low cost in various areas around the world.

**REFERENCES**


