Hybrid Method for Arsenic Removal from Groundwater

MD SHAFIQUZZAMAN, IORI MISHIMA, and JUN NAKAJIMA

Department of Environmental Systems Engineering, Ritsumeikan University
1–1–1 Nojihigashi, Kusatsu, Shiga 525–8577, Japan

Abstract

Hybrid methods for arsenic removal from synthetic groundwater were investigated in this study. Batch study showed that As(III) removal was first-order at high Fe(0) shavings concentration and approached zero-order at low concentration. It was suggested that As(III) was removed by surface precipitation and adsorption processes. A single Fe(0) shavings column experiment was conducted for As(III) removal and the experimental data were evaluated by the Thomas and Yan adsorption models. As(III) removal capacity of Fe(0) shavings estimated by the Thomas model (11.3 mg/g) and Yan models (10.8 mg/g) were closed to the values calculated from the experimental data (10.3 mg/g). Two types of hybrid column filtration methods (Hybrid 1 and Hybrid 2) were conducted to evaluate the processes with regard to the applicability and remedial performance of As(III). Hybrid 1 was bacterial column (BC) filtration followed by Fe(0) shavings column filtration (MC), while Hybrid 2 was MC followed by BC. Results showed that As(III) was removed to less than 10 µg/l in Hybrid 1 but the effluent Fe concentration was higher (> 0.5 mg/l). By contrast, both As and Fe were removed to less than 10 µg/l and 0.3 mg/l, respectively in Hybrid 2. The MC columns data of Hybrid 1 and Hybrid 2 were examined by the Thomas and Yan models. As(III) removal capacity was increased in Hybrid 2 MC due to the presence of Fe(II) in the synthetic groundwater. Accordingly, it was suggested that the hybrid methods would be effective processes to remove As(III) from highly contaminated groundwater.

Key words: arsenic (As) removal; hybrid method; biological iron oxidation; Fe(0) shavings; groundwater

INTRODUCTION

Arsenic (As) poisoning of groundwater has caused a devastating health crisis in all over the world, especially in Bangladesh and West Bengal (India). Over 70 millions people in Bangladesh and other regions of the Indian subcontinent are routinely exposed to arsenic poisoning through drinking water. Recently EPA as well as WHO revised the maximum concentration limit for arsenic in drinking water from 50 down to 10 µg/l. As a result of this revision, new limit of arsenic concentration has exceeded in many areas in the world. Ingestion of inorganic arsenic can result in both cancer (skin, lung and urinary bladder) and non-cancer effects. Arsenic present in the groundwater is mainly in inorganic forms, namely arsenate (As(V)) and arsenite (As(III)). As(V) is the predominant species under atmospheric or more oxidizing environment in the pH range of 6–9. It exists predominantly as oxyanions, namely, H2AsO4– or HAsO42–. As(III) is thermodynamically stable and exists predominantly as H3AsO3 or HAsO2 under mildly reducing conditions. As(III) is the most common species in anaerobic groundwater and is generally removed less efficiently than the oxidized As(V) and is more toxic than As(V). Arsenic
release from subsurface minerals and sediments are the main cause of groundwater arsenic contamination. Different techniques have been developed and tried out for the removal of As from groundwater. They are the co-precipitation (e.g. with iron or aluminum salts), ion exchange, adsorption by activated carbon, and membrane processes. Among them, adsorption and subsequent co-precipitation of As with Fe(III) salts is the simplest and convincing arsenic removal technique.

Moreover, arsenic removal by Fe(II) and Fe(0) has received special attention due to their higher As removal efficiency. Mechanism of As removal by Fe(II) is the oxidation of Fe(II) to Fe(III) and co-precipitation of As with the Fe(III). Recent studies showed that, As(III) is partially oxidized to As(V) during the physical-chemical Fe(II) oxidation, which results the higher As removal efficiency than the direct addition of Fe(III). Arsenic removal by Fe(0) also has been studied widely. In aerobic water slow and continuous release of Fe(II) from Fe(0) and subsequent oxidation to Fe(III) could effectively remove arsenic.

Fe(II) can be oxidized by both physico-chemical and biological processes but the dominant process depends on the physical and chemical characteristics of the raw water and on the process conditions. The biological Fe(II) oxidation is caused by the presence of several iron oxidizing microorganisms in water such as Gallionella sp. and Leptothrix ochracea. In our previous study, As removal from synthetic groundwater containing high As and Fe (500 µg/l As(III) and 5 mg/l Fe(II)) was investigated during biological Fe(II) oxidation. Batch studies were conducted to clarify the arsenic removal mechanism during the biological Fe(II) oxidation. It was shown that, like the physicochemical Fe(II) oxidation, As(III) was also partially oxidized to As(V) during the biological Fe(II) oxidation process. Arsenic removal was also investigated by a biological sand column. In this biological column, As was reduced to less than 50 µg/l (Bangladesh standard limit in drinking water).

Therefore, other processes would be required to get the residual arsenic below the WHO standard limit (10 µg/l). Moreover, additional treatment process would be also required if groundwater contains a low concentration of Fe or a high concentration of As. Therefore, the hybrid processes i.e. the combination of biological and Fe(0) shavings column filtration could be an ideal option to remove As from the highly contaminated groundwater. To our knowledge, no such hybrid method for As removal has yet been studied.

The purposes of this study are to investigate the hybrid methods for As removal from groundwater and to evaluate the processes with regard to the applicability and remedial performance of arsenic. Accordingly, batch and column experiments were conducted with synthetic groundwater considering the highly As and Fe contaminated Bangladesh groundwater. Batch experiments were conducted to determine the kinetics of As(III) removal with Fe(0) shavings. The two sand columns included a bacterial layer and a Fe(0) shavings layer were tested either by individual or continuous filtration. The columns data were evaluated using the Thomas and Yan adsorption models and model constants and As(III) removal capacity by Fe(0) shavings were determined.

**EXPERIMENTAL SECTION**

**Synthetic groundwater** The synthetic groundwater was prepared by dissolution of specific chemicals in de-ionized water and used for all experiments. The chemical composition of this synthetic groundwater reflected the main characteristics of Bangladesh groundwater. Each liter of synthetic water consisted, commonly, of NH₄Cl 10 mg, MgSO₄•7H₂O 500 mg, NaCl 1.2 mg, KH₂PO₄ 5 mg, CaCl₂•2H₂O 400 mg, MnSO₄•5H₂O 2 mg and NaHCO₃ 50 mg. As(III) and Fe(II) or Fe(0) were added in different batch and column experiments.

**Iron bacterial sludge** The bacterial samples were collected from the sediment of the Ogure river, a small river in Gifu Prefecture, Japan. Microscopic view of bacterial samples showed (photograph not shown) that the sediment mainly contained the Leptothrix ochracea iron oxidizing species. The collected sediment was cultured on a
sand bed with a continuous tap water flow. Twenty five mg of FeSO₄•7H₂O diluted with 1 liter of de-ionized water was fed on to the biological bed daily as the sole source of ferrous iron for bacterial growth. The cultured sludge was used for biological column experiments.

**Metal iron (Fe(0))** Fe(0) shavings was collected from the mechanical workshop of Ritsumeikan University. After collection, the Fe(0) shavings was washed with acetone to remove the oil and grease. The oil free Fe(0) shavings were finally screened to 1 mm size.

**As(III) and Fe(II) stock solution** As(III) stock solution was prepared by dissolving the arsenic oxide (As₂O₃) in de-ionized water with 5 ml/l of HCl. Fe(II) stock solution was prepared by dissolving FeSO₄•7H₂O in de-ionized water just before starting each experiment to avoid any Fe(II) oxidation before the experiments.

**Batch experimental methods** Batch experiments using Fe(0) shavings were conducted in 1000 ml glass beaker. Each beaker was loaded with different amount of Fe(0) shavings and filled with synthetic groundwater containing 500 µg/l of As(III). Batch beaker was mixed on a jar test apparatus (30 rpm) at room temperature for the time periods up to 144 h. The solutions were covered by aluminum paper during continuous mixing. Experiments were carried out by the addition of 20, 50 and 100 mg of Fe(0) shavings. A neutral pH value (7.5 ± 0.5) of water was set for all series of experiments because natural groundwater in Bangladesh was neutral pH. After different duration of mixing time, 100 ml of water withdrawn from the beakers was immediately filtered through 5C filter paper (Advantec) and kept for the analysis of dissolved As and Fe. Each batch was run triplicate to ensure the accuracy.

**Column experimental methods** The column experiments were based on the gravitational flow fixed bed technique. Schematic diagrams of column units are shown in Fig.1. Fixed bed column runs were carried out using plexiglass column which was filled with the sand bed media. Considering the field application, column experiments were conducted with synthetic groundwater containing initial 5 mg/l of Fe(II) and 500 µg/l of As(III), which is the average concentration of Bangladesh groundwater. All column studies were focused on the removal of As(III) because the most common species in anaerobic groundwater is As(III) and it is generally removed less efficiently than the oxidized As(V). A single column containing Fe(0) shavings (MC) was run separately to investigate the As(III) removal efficiency. Two series of hybrid column experiments were conducted. “Hybrid 1” was bacterial column (BC) filtration followed by MC filtration. “Hybrid 2” was MC filtration followed by BC filtration.

Twenty ml of iron bacterial sludge (mixed liquor volatile suspended solid (MLVSS) of the sludge was 475 mg/l) from the cultured bed was seeded on the top of the BC at the beginning of each column operation. A 1 cm thick Fe(0) shavings layer (15 g) was buried at a depth of 5 cm from the top of the MC and the bed volume was equal to 12.5 ml. For BC, the thickness of active biologically oxidized iron sludge increased to 1-2 cm. Therefore, the bed volume was considered to be 12.5 ml. Two types of raw water were prepared. Water 1 was synthetic groundwater with As(III) and Water 2 was de-ionized water with Fe(II) (FeSO₄•7H₂O). The pH value of Water 2 was kept below 6 in order
to avoid the physicochemical oxidation of Fe(II) before entering the column. The raw water solutions (Water 1 and Water 2) were separately and continuously pumped to hybrid columns at flow rates of 2.16 and 1.44 l/d, respectively. The final flow rate was 3.6 l/d which corresponds to linear velocities of 286 m/d. The concentration of As(III) and Fe(II) of raw water after entering the column was 500 µg/l and 5 mg/l, respectively. As for the single column (MC) run, only Water 1 was spiked at the volumetric flow rate of 3.6 l/d. Flow rates were measured periodically throughout the experiments to ensure consistency. All the columns were sampled 3 times a week. Effluent water was sampled at the bottom of each column. pH, ORP and DO were measured immediately, and the samples were kept in the refrigerator at 4 ℃ until analysis of the total As and Fe.

**Analytical method** Arsenic was analyzed by using polarized Zeeman GFAAS equipped with graphite tube atomizer and programmable auto sampler (Hitachi Z2700). Argon gas was used to sheath the atomizer and purge internally. Arsenic hollow cathode lamp was used at a wavelength of 193.7 nm. Standard addition method was applied for analyzing and samples were prepared with 0.5 % of nitric acid prior to analysis. Concentration of Fe was determined using inductively coupled plasma (ICP) spectrometry (Seiko SPS 4000). The redox potential (ORP), dissolved oxygen (DO) and pH were measured by ORP, DO and pH meter, respectively.

**Evaluation of column data** The MC columns data were evaluated using various empirical models. The following mathematical models were used: The Thomas model and the Yan model.

The Thomas model is expressed in the following form:

\[
\frac{C_{\text{eff}}}{C_0} = 1 - \frac{1}{1 + \frac{Q^2t}{k_{\text{As}}q_{\text{As}}m} (k_{\text{As}}C_0)^t} \quad (1)
\]

The Yan model is expressed in the following form:

\[
\frac{C_{\text{eff}}}{C_0} = \frac{1}{1 + \frac{Q^2t}{k_{\text{As}}q_{\text{As}}m}} \quad (2)
\]

Where \(C_{\text{eff}}\) = effluent As concentration (µg/l); \(C_0\) = influent As concentration (µg/l); \(k_{\text{As}}\) = kinetics rate constant (l/d/µg); \(q_{\text{As}}\) = As(III) removal capacity (mg/g); \(Q\) = volumetric flow rate (l/d); \(m\) = mass of adsorbent (g); and \(t\) = time (d).

The coefficient of determination, \(R^2\) as given in Eq. (3), accounts square of the ordinary correlation coefficient for the models where \(n\) is the number of data corresponding with experimental and predicted values.

\[
R^2 = 1 - \frac{\sum_{i=1}^{n} (q_{\text{pred}} - \bar{q}_{\text{pred}})^2 (q_{\exp} - \bar{q}_{\exp})^2}{\sum_{i=1}^{n} (q_{\exp} - \bar{q}_{\exp})^2} \quad (3)
\]

A spreadsheet was used to calculate the analytical solution and simulate the models fitting curve from the column experiment pilot data. The kinetics rate constant, \(k_{\text{As}}\) and As(III) removal capacity, \(q_{\text{As}}\) were obtained by models calibration. A statistical comparison (paired t-test) between the model results and experimental data was performed in order to determine the fitness of the model calibration.

**RESULTS AND DISCUSSION**

**Batch study of As(III) removal with Fe(0) shavings** Figure 2 shows the removal of As during 144 h mixing of 20, 50 and 100 mg/l Fe(0) shavings in 500 µg/l As(III) solutions. As(III) concentrations decreased gradually from the beginning for initial 100 mg/l and from 24 h for initial 50 and 20 mg/l of Fe(0) shavings. It was found that the removal of As(III) increased significantly when initial Fe(0) shavings concentrations was higher (100 mg/l). However, no significant difference of As(III) removal was observed when the Fe(0) shavings doses were 50 and 20 mg/l. As(III) were reduced to 130 ± 43 , 95 ± 26 and 19 ± 3 µg/l after 144 h when the initial Fe(0) shavings concentrations were 20, 50 and 100 mg/l, respectively.

A combined zero and first order kinetic
model (Eq. (4)) of arsenic removal by Fe(0) in batch tests has recently been proposed:

$$\frac{d[As]}{dt} = -\frac{k_0[As]}{k_0/k_1 + [As]}$$  (4) 

Where $[As]$ is the As(V) solution concentration ($\mu$g/l), $t$ is the time (h), $k_0$ is the zero order rate constant ($\mu$g/l/h) and $k_1$ is the first order rate constant (/h). This form of kinetics expression indicates that arsenic removal follows first order kinetics when $[As]$ is sufficiently small and that zero order kinetics are followed when $[As]$ is significantly greater than $k_0 / k_1$. Farrell et al.\textsuperscript{30} described this mixed order kinetics model by comparing the competition between arsenic species and other dissolved solutes for reactive sites. At low concentration of As species or higher available reactive sites, the ratio of dissolved As species to available iron hydroxides is sufficiently low that there is no competition for reactive sites. This situation results the first order removal kinetics. By contrast, at high As species concentration or small available reactive sites, the ratio of As species to available reactive sites increases, leading to competition for reactive sites. With increasing competition, the rate of As removal becomes limited by the generation rate of new sites for As adsorption. Under this situation, removal kinetics should become zero order with respect to high concentration of As species or in the limit of low reactive sites.

Analysis of the concentration data from this work was therefore conducted to determine both zero- and first-order rate constants for systems in which input arsenic was only present as As(III). It might be expected that similar mechanism would control As(III) and As(V) removal, but that over all rates might be different for these species.\textsuperscript{16,17} In our study, at high initial Fe(0) shavings concentrations (100 mg/l), a coefficient of determination and removal rate constant was $0.995 \pm 0.002$ and $0.0229 \pm 0.0006$ /h for first order arsenic removal kinetics and at low Fe(0) shavings concentrations (50 and 20 mg/l), the values were $0.954 \pm 0.035$, $0.941 \pm 0.016$ and $2.75 \pm 0.195$, $2.58 \pm 0.44$ $\mu$g/l/h, respectively for zero order arsenic removal kinetics (Table 1). The results of the batch study follow both first and zero order reactions, which are consistent with the study of Farrell et al.\textsuperscript{30}.

The mechanism of As(III) removal by Fe(0) also has been explained in many other studies. Previous studies have shown that in aerobic environment, surface precipitation and adsorption appears to be the predominant mechanisms for arsenic removal.\textsuperscript{17} The authors attributed this to the effect of iron (oxyhydro) oxides synthesized from Fe(II), which was formed form the corrosion of Fe(0). Oxidation of As(III) to As(V) in Fe(0)

### Table 1 As(III) removal rate constants estimated from the batch study

<table>
<thead>
<tr>
<th>As(III) ($\mu$g/l)</th>
<th>Fe(0) shavings (mg/l)</th>
<th>Zero-order rate Constant ($\mu$g /l/h)</th>
<th>$R^2$</th>
<th>First-order rate Constant (1 / h)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>100</td>
<td>0.0229 $\pm$ 0.0006</td>
<td>0.995 $\pm$ 0.002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>50</td>
<td>2.75 $\pm$ 0.19</td>
<td>0.954 $\pm$ 0.035</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>20</td>
<td>2.58 $\pm$ 0.44</td>
<td>0.941 $\pm$ 0.016</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
solution also has been reported in several works\textsuperscript{13, 14, 17, 20, 31). In our experiment, As(III) could be removed by oxidation and precipitation process because of the favorable aerobic condition (DO 9.0 ± 1.0 mg/l and pH 7.5 ± 0.5)\textsuperscript{32). This might be attributed to oxidation of As(III) to As(V) and adsorption of As(V) to iron and its corrosion products because of the interaction between arsenic and iron (oxyhydro) oxides\textsuperscript{31).}

**Single column (MC) study of As(III) removal by Fe(0) shavings** Removal efficiency of As(III) from the synthetic groundwater was investigated in a single column packed with Fe(0) shavings. The column was continuously run at 3.6 l/d for a total of 120 days. The effluent As concentration values versus the number of bed volumes treated by Fe(0) shavings in the fixed bed column is shown in Fig. 3. The effluent As(III) was found to be high at the beginning of the column operation. Channeling might have occurred at the beginning of the column operation reflected by higher As(III) levels during the initial period of column operation. High Fe was found to be released at the beginning of the column operation (up to 10,000 bed volume) while afterwards there was a negligible quantity of Fe released. The Fe(0) shavings were able to achieve effluent As(III) of approximately 150 µg/l or below ($C_{\text{eff}} / C_0 \leq 0.3$) for up to 20,000 bed volume and gradually approached to 60% of $C_{\text{eff}} / C_0$ after 35,000 bed volume of continuous flow. However, the effluent As(III) concentration never met the WHO standard limit (10 µg/l) nor Bangladesh standard limit (50 µg/l). Low empty bed contact time (5 min) could be the reason that the effluent arsenic levels were higher than the standard limit. pH, ORP and DO values in the influent and effluent were not significantly changed during the process. The pH, DO and ORP of the influent water were 7.0 ± 0.1, 8.6 ± 0.5 mg/l and 177 ± 42 mV, respectively, while those values at the effluent were 6.9 ± 0.1, 7.8 ± 0.9 mg/l and 169 ± 54 mV, respectively.

The simulated As concentration curves of the column for As(III) removal was found to be fitted with both Thomas and Yan adsorption models. Simulated As concentration curves predicted by the Thomas and Yan models for As(III) removal are also shown in Fig. 3. The adsorption capacity of Fe(0) shavings for As(III) estimated by the Thomas and Yan models are provided in Table 2. The total amount the As(III) removal was calculated by integrating the upper area of experimental As concentration curve (Fig. 3). The total amount of As(III) removal through column was determined to be 154 mg As. The arsenic removal capacity of Fe(0) shavings can be determined by dividing the

![Graph showing effluent As and Fe concentrations of the single column MC and the models fitting curve. Influent As(III)= 500 µg/l, mass of Fe(0) shavings= 15g, bed volume= 12.5 m³ and empty bed contact time = 5 min.]

**Table 2** As(III) removal capacity of Fe(0) shavings, kinetic constants and coefficient of determination estimated by the Thomas and Yan models.

| Column         | Thomas model | | Yan model | | 
|----------------|--------------|-----------------|-----------------| 
|                | $k_{At}$ (l/d/µg) | $q_{At}$ (mg/g) | $R^2$ | $k_{Ay}$ (l/d/µg) | $q_{Ay}$ (mg/g) | $R^2$ |
| Single column MC | 0.000008 | 11.3 | 0.839 | 0.01 | 10.8 | 0.820 |
| Hybrid 1 MC     | 0.000006 | 11.0 | 0.637 | 0.089 | 10.5 | 0.668 |
| Hybrid 2 MC     | 0.000045 | 19.0 | 0.773 | 0.011 | 19.5 | 0.820 |
amount of As removal by the mass of Fe(0) shavings. Accordingly, the arsenic removal capacity was determined to be 10.3 mg/g and this value was close to the values predicted by the Thomas and Yan model (11.3 and 10.8 mg/g, respectively). The $R^2$ values of linear regression were 0.839 for the Thomas model and 0.820 for the Yan model. The results were significant at the 95% confidence level based on $t$-testing.

**Hybrid 1 filtration method for As(III) removal** Hybrid 1 columns were run continuously for 107 days. The results of As(III) and Fe(II) removal in the BC are presented in Fig. 4a. The effluent arsenic concentrations was found to be about 50 µg/l ($C_{\text{eff}} / C_0 = 0.1$) and remained constant from the beginning to the end of column operation (30,000 bed volume). Fe was removed by biological oxidation of Fe(II) and found to be always less than 0.5 mg/l at the effluent water. The pH of influent water was maintained at 7.1 ± 0.1 and steady at 6.6 ± 0.2 at effluent water. The DO values of influent and effluent were 8.1 ± 0.5 and 7.9 ± 0.8 mg/l, respectively. The ORP value of influent water was about −95 ± 32 mV and increased to about 120 ± 47 mV at the outlet of the BC.

The constant arsenic concentration at the effluent water from the beginning to end of column operation suggested that the accumulated iron hydroxides did not have any effect of As(III) removal. Therefore, the removal of As(III) in the column was occurred mainly due to the simultaneous oxidation of As(III) and Fe(II) and their subsequent adsorption. This mechanism was explained in our previous study [27].

Effluent of the BC was then entered as influent of the MC. Figure 4b shows the effluent As and Fe concentration of the MC. The level of effluent As was found to be less than 10 µg/l ($C_{\text{eff}} / C_0 < 0.3$) until the end of column operation (30,000 bed volume). However, the Fe concentration was high in the effluent of MC. It increased steadily from 0 to about 5 mg/l until 15,000 bed volumes, then decreased steadily to less than 0.5 mg/l at 30,000 bed volumes. These effects were most likely due to the continuous release of Fe(II) from Fe(0) at the beginning, followed by power reactivity of the metal iron as it was masked by iron hydroxides toward the end of the column operation. Furthermore, ferrous iron (Fe(II)) released from Hybrid 1 MC was higher than the single column MC. This was probably the effect of phosphorus (P) in the column influent water. P is known to act as a Fe(0) corrosion inhibitor [16, 17] as well as inner sphere complex-forming anion that is strongly adsorbed to Fe(0) surface or is co-precipitated to form discrete solid phase on Fe(0) surfaces [20]. Therefore, presence of P in water would reduce the Fe(II) released from Fe(0). In our study, synthetic groundwater contained 1.0 mg/l phosphorus and in the single column MC the Fe released inhibited by phosphorus. On the contrary, P was almost removed by the BC of Hybrid 1 [27] and did not effect the MC. Therefore, Fe release was higher in Hybrid 1 MC.

During 107 days of column operation, 30,000 bed volume of water for the MC was treated. The effluent As concentration was not exceeded the WHO standard limit ($C_{\text{eff}} / C_0 < 0.3$).
pH, ORP and DO values in the influent and effluent were not significantly changed during the process. The pH, DO and ORP at the influent water were equal to the effluent values of BC column, while pH, DO and ORP values at the effluent of the MC were 6.8 ± 0.2, 7.9 ± 0.8 mg/l and 150 ± 59 mV, respectively.

The quality data for As(III) removal observed in Hybrid 1 MC were attempted to fit to the Thomas and Yan kinetics model (Fig. 4b). The determination coefficient suggested that removal of As(III) in the MC column can be appropriately expressed by Thomas and Yan model. The model parameters $q_{As}$, $k_{As}$ and $R^2$ of the Thomas model were found to be 11.0 mg/g, 0.00006 l/d/µg and 0.637 (Table 2). Whereas, those values for the Yan model were found to be 10.5 mg/g, 0.089 l/d/µg and 0.668 (Table 2). The predicted values of As(III) removal capacity were consistent with the values predicted by the single column MC (11.3 and 10.8 mg/g, respectively), whereas the models constants were varied due to the different influent As(III) concentrations.

Compared to the single column MC, Hybrid 1 filtration method could treat highly arsenic contaminated (500 µg/l As(III)) groundwater to less than the WHO standard limit (<10 µg/l) and also could enhance arsenic treatment capacity by the column. Therefore, it was suggested that with the natural Fe(II) in groundwater, it was possible to enhance the As(III) removal efficiency with optimized use of Fe(0) shavings. To summarize the results of the Hybrid 1 method, the residual As concentration after the final filtration was always less than the 10 µg/l but the residual Fe concentration was higher than the WHO standard limit of Fe in drinking water. Therefore, the filtration was carried out in an opposite column filtration system (Hybrid 2).

Hybrid 2 filtration method for As(III) removal

Figure 5a shows the effluent As and Fe concentrations of the MC and the models fitting curve. Influent As(III)= 500 µg/l, Fe(II) = 5.0 mg/l, mass of Fe(0) shavings= 15g, bed volume= 12.5 m³ and empty bed contact time = 5 min. (b) Effluent As and Fe concentrations of the BC. Influent As(III)= effluent As(III) of the MC, bed volume= 12.5 m³ and empty bed contact time = 5 min.

The column data were tested to fit to the Thomas and Yan models. Figure 5a also shows the As concentration curves predicted by the Thomas and Yan models. As(III) removal capacity, kinetics constant and coefficients of determination predicted by the models are shown in Table 2. The models gave a good fit of the experimental data examined for As(III) with high determination concentration drastically increased to about average 50 µg/l ($C_{eff}/C_0=0.1$) until the end of the column operation (25,000 bed volume). On the other hand, the effluent Fe concentration was low (about 0.5 mg/l) until 2,500 bed volume and drastically increased to 4–6 mg/l and then became steady throughout the whole column operation. The influent pH, DO and ORP of the MC were 7.2 ± 0.2, 9.2 ± 0.7 mg/l and −52 ± 50 mV, respectively, whereas the slight change of pH (6.9 ± 0.2), DO (7.3 ± 0.1 mg/l) and ORP (−27 ± 37 mV) were observed at the outlet of the column.

The column data were tested to fit to the Thomas and Yan models. Figure 5a also shows the As concentration curves predicted by the Thomas and Yan models. As(III) removal capacity, kinetics constant and coefficients of determination predicted by the models are shown in Table 2. The models gave a good fit of the experimental data examined for As(III) with high determination
coefficients of 0.773 for the Thomas model and 0.820 for the Yan model (Table 2).

It was shown that As(III) removal capacity of Hybrid 2 MC was higher than the maximum removal capacity of Fe(0) shavings (Values predicted from the single column MC). The As(III) removal capacities of the single column MC predicted by the Thomas and Yan models were 11.3 and 10.8 mg/g, respectively. By contrast, the removal capacities of Hybrid 2 MC were predicated 19.0 and 19.5 mg/g, respectively. This might be the effect of Fe(II) (5 mg/l) concentration at the influent of Hybrid 2 MC. The influent values of pH, ORP and DO of Hybrid 2 MC was corresponded to those present in competition zone between biological and physicochemical oxidation of Fe(II)\(^{24,25,33}\). Therefore, Fe(II) might be oxidized chemically in Hybrid 2 MC due to favorable oxidation condition and removed a part of As(III), resulting enhanced the As(III) removal capacity. However, further study on specific role of Fe(II) combine with Fe(0) shavings would be required to model their role for arsenic removal.

Effluent water of the MC was then filtered through the BC and the results of the effluent As and Fe are shown in Fig. 5b. The dissolved Fe released from the MC was oxidized by the iron bacteria in the BC and reduced the effluent As and Fe concentration (final filtration of Hybrid 2) less than 10 µg/l and 0.3 mg/l throughout the experiment, which met the WHO standard limit. The pH, DO and ORP values were observed 6.8 ± 0.1, 8.4 ± 0.8 mg/l and 180 ± 89 mV, respectively at the effluent of BC. Compared to Hybrid 1 method, Hybrid 2 method was found to be more effective to remove both As and Fe from synthetic groundwater.

**CONCLUSIONS**

This study confirmed that combination of the biological process and the Fe(0) filtration process was effective to treat highly As and Fe contaminated groundwater. Batch results showed that, a mixed order kinetics was able to describe for As(III) removal by Fe(0) shavings. The removal rate was first order when concentration of Fe(0) shavings high and zero order when concentrations were low. This behavior suggested that As was removed by the corrosion of Fe(0) shavings and the oxidation and precipitation processes. As(III) removal data of single MC column was evaluated by the Thomas and Yan adsorption models. The experimental data were well fitted to the models and the models constant and As(III) removal capacity were determined from the model fitting curves. The present investigation suggested that the hybrid processes could be used as effective arsenic remedial methods for remediation of groundwater contaminated with As and Fe. In Hybrid 1 filtration method, As was reduced to less than 10 µg/l but effluent Fe concentrations were high due to the corrosion products of Fe(0). On the other hand, effluent As and Fe concentration were less than 10 µg/l and 0.3 mg/l, respectively in Hybrid 2 filtration method. As(III) removal efficiency, treated amount of contaminated water and As(III) removal capacity were also increased in the hybrid columns. Accordingly, it was suggested that the hybrid methods would be effective processes to remove As(III) from highly contaminated groundwater.

**Acknowledgements:** This work was supported by Grant-in-Aid (No.18560534) for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. The authors thank to Khulna University of Engineering and Technology and ADAMS, Bangladesh for their cooperation.

**REFERENCES:**


3) Environmental Protection Agency (EPA): EPA Office of ground water and drinking water implementation guidance for the arsenic rule, *EPA Report*–816–D–02–005,


Supply, 3, 111–123 (1985)


(Submitted 2008. 4. 28)

(Accepted 2008. 7. 16)