Mathematical model predicting arsenic bioleaching in groundwater treatment

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ABSTRACT

In the Southeast Asia region, arsenic contamination of groundwater has been reported in several countries and a large number of arsenic treatment units were installed in many regions. Microbial activity can greatly affect the mobilization of arsenic under anaerobic conditions when coupled with the oxidation of organic matter. In this study, a mathematical model was developed to predict the bioleaching of arsenic in response to organic matter contamination in the treatment unit. Calibration of the model was performed using the data of batch experiments, and finally the results obtained from the laboratory experiments were used to verify the developed model. The microbial decomposition of organic matter led to an anaerobic condition within the accumulated sludge in the sand filter and hence caused the bioleaching of arsenic. Under the inoperative condition of the treatment unit for 5, 10, and 15 days along with organic matter contamination of 15 mg/L as biochemical oxygen demand, the concentrations of bioleached arsenic were found to be 59, 184, and 275 μg/L, respectively. This study revealed the bioleaching potential of arsenic due to organic matter inclusion in the treatment process, which might contribute in designing safe options for drinking water.

Key words | arsenic removal, bioleaching, groundwater, mathematical model, organic matter

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INTRODUCTION

Arsenic contamination of groundwater in several parts of the world has become a high-profile problem in recent years due to the use of tubewells for water supply, causing serious arsenic poisoning to large numbers of people. With newer-affected sites discovered during the last decade, a significant change has been observed in the global scenario of arsenic contamination, especially in the Southeast Asia region (Mukherjee *et al.* 2006). Microbial activity can greatly affect the mobilization of arsenic under anaerobic conditions by either an indirect or a direct mechanism (Zobrist *et al.* 2000). The former is the reductive dissolution of iron hydroxide minerals, leading to the release of associated arsenic into solution and the latter is the direct reduction of As(V) associated with a solid phase to the less adsorptive As(III). Dissimilatory arsenate-reducing bacterium (DARB), which achieve growth by the respiratory

reduction of As(V) to As(III), are able to mobilize arsenic via reduction of As(V) contained in minerals or contaminated sediments. Ormland & Stolz (2003) reported that the reaction is energetically favorable when coupled with the oxidation of organic matter because the As(V)/As(III) oxidation/reduction potential is +135 mV. Bioleaching of arsenic is an oxidation–reduction process, where organic matter is oxidized to supply the required electrons and ferric iron or As(V) is reduced by acting as an electron acceptor (Figure 1).

This process is incorporated within a sequential terminal electron acceptor reaction framework, including aerobic, ferric iron reducing, and As(V) reducing processes (Lim *et al.* 2007). According to another study, the reduction of arsenate plays a relatively minor role in the solubilization of arsenic sorbed to iron hydroxides and
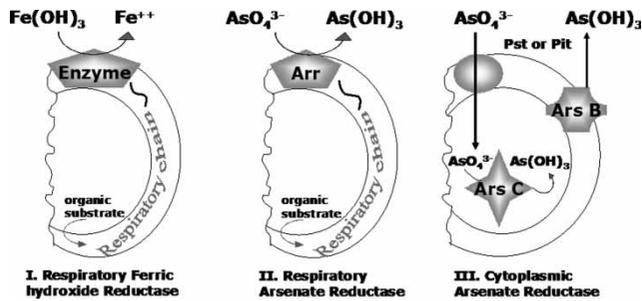
Figure 1 | Bacterial reductase of Fe(III) and As(V).

arsenic release from contaminated soils and sediments proceeds considerably faster under conditions favoring dissimilatory reduction of ferric iron leading to the dissolution of sorbing phases (Langner & Inskeep 2000). Ormland & Stolz (2003) concluded that DARB isolated to date are physiologically diverse and capable of using arsenate as electron acceptors for growth and most of them are strict anaerobes. Because organic matter is not only potentially reactive toward arsenic but also ubiquitous in natural waters, typically found at concentrations between 1 and 50 mg/L as total organic carbon (TOC), its potential influence on arsenic mobility is great (Redman et al. 2002). Apart from DARB, arsenate reduction can also be achieved by various bacteria possessing cytoplasmic arsenate reductase (ArsC) that is a part of an arsenic resistance system. The capacity for arsenic release was severely limited by the availability of electrone donor (i.e. organic carbon) in the sediments (Islam et al. 2004). Hassan et al. (2009) found that the settled sludge in arsenic treatment unit became anaerobic inside due to organic matter contamination and caused the bioleaching of arsenic. A number of studies identified that the shallow groundwater of Bengal Delta Plain is frequently combined with high concentrations of nitrogen and phosphorus (Bhattacharya & Mukherjee 2001). This contamination was presumed to be highly biodegradable wastewaters from pit latrines as well as greywaters. Thus, the biological importance of organic matter interactions for the arsenic mobility is immense to warrant its consideration in designing safe remediation strategies in the context of groundwater treatment. Hence, organic matters present in groundwater and also from unsanitary operation and maintenance of the treatment unit would

significantly contribute to the release of arsenic with the effluent water (Figure 2). Microbial decomposition of organic matters may lead to anaerobic conditions within the accumulated sludge in the filter bed and hence the anaerobic bacteria can greatly affect the mobilization of arsenic from the associated solid phase. This study presents the development of mathematical models simulating the biological effects of organic matter contamination in arsenic removal practice and to further the prediction of how the environmental conditions, such as the concentration of organic matter and operational modes of the treatment unit, affect the arsenic removal performance.

METHODS

Model concept

In the developed model, As(V) was considered to be the dominant species present in the sorption process with iron hydroxide solid phase in the treatment operation. The influx of organic matter promoted the microbial processes resulting in the depletion of oxygen and a lowering of the redox potential. Under reducing conditions, microbial activity would respire Fe(III) and As(V), with its conversion to Fe(II) and As(III), respectively (Ormland & Stolz 2003) leading to the release of associated arsenic into solution.
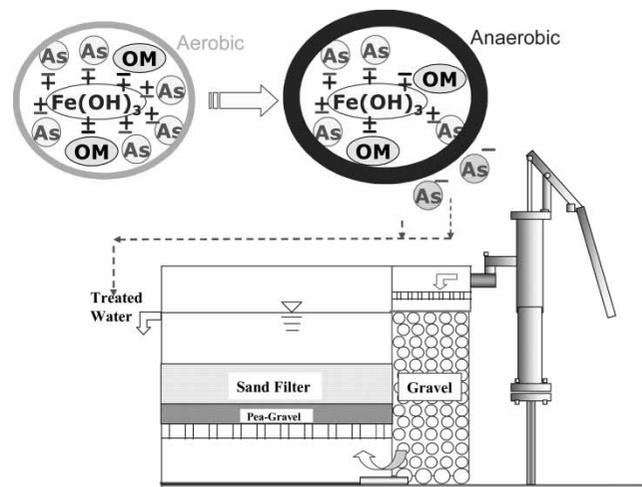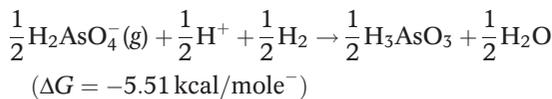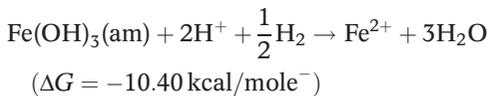

Figure 2 | Bioleaching of arsenic from the accumulated sludge in groundwater treatment.

Model for arsenic bioleaching

The bioleaching of arsenic occurs through an oxidation–reduction process, where organic matter is oxidized to supply the required electrons and ferric iron (Fe(III)) or arsenate (As(V)) is reduced by acting as an electron acceptor. The above processes are listed in the order in which they are expected to occur depending on the achievement of Gibbs free energy (ΔG) in the biochemical reactions. Using H_2, produced from the carbon source, as the ultimate electron donor and O_2, Fe(III), and As(V) as electron acceptors, the stoichiometry of different degradation processes can be described by the following set of biochemical reactions (Newman *et al.* 1998):

$$\frac{1}{4}O_2(g) + \frac{1}{2}H_2 \rightarrow \frac{1}{2}H_2O \quad (\Delta G = -23.55\,\text{kcal/mole}^-)$$

$$Fe(OH)_3(am) + 2H^+ + \frac{1}{2}H_2 \rightarrow Fe^{2+} + 3H_2O$$
$$(\Delta G = -10.40\,\text{kcal/mole}^-)$$

$$\frac{1}{2}H_2AsO_4^-(g) + \frac{1}{2}H^+ + \frac{1}{2}H_2 \rightarrow \frac{1}{2}H_3AsO_3 + \frac{1}{2}H_2O$$
$$(\Delta G = -5.51\,\text{kcal/mole}^-)$$

Several field studies have shown that first-order biodegradation kinetics can be used to approximate the organic matter degradation processes via various pathways (Lu *et al.* 1999). The kinetic model for biochemical system can be written as follows:

$$r_{\text{ED},O_2} = k_{\text{ED},O_2}.[\text{ED}].\left(\frac{[O_2]}{K_{\text{EA},O_2} + [O_2]}\right)$$

$$r_{\text{ED,Fe(III)}} = k_{\text{ED,Fe(III)}}.[\text{ED}].\left(\frac{[\text{Fe(III)}]}{K_{\text{EA,Fe(III)}} + [\text{Fe(III)}]}\right).k_{i,O_2}$$

$$r_{\text{ED,As(V)}} = k_{\text{ED,As(V)}}.[\text{ED}].\left(\frac{[\text{As(V)}]}{K_{\text{EA,As(V)}} + [\text{As(V)}]}\right).k_{i,O_2/\text{Fe(III)}}$$

where r_{ED,O_2} represents the electron donor (ED) (i.e. organic matter) degradation rate using oxygen as the electron acceptor (EA), $[O_2]$ is the oxygen concentration

(mg/L), k_{ED,O_2} is the first-order degradation rate constant (day^{-1}) for the ED using oxygen as the EA, K_{EA,O_2} is the half-velocity constant for oxygen (mg/L), and k_{i,O_2} is the oxygen inhibition constant; similar nomenclature is used in subsequent reactions. In the developed model of this study, instead of oxygen inhibition constant (k_{i,O_2}), a switching function was used for the aerobic/anaerobic reactions. However, the inhibition constant for $k_{i,O_2/\text{Fe(III)}}$ was adjusted to 0.7 for Fe(III) $\neq 0$ and 1.0 for Fe(III) $= 0$. The differential equations for the EDs can be written as follows:

$$\frac{d[O_2]}{dt} = -r_{\text{ED},O_2}.Y_{O_2/\text{ED}}; \quad \frac{d[\text{Fe(III)}]}{dt} = -r_{\text{ED,Fe(III)}}.Y_{\text{Fe(III)}/\text{ED}};$$
$$\frac{d[\text{As(V)}]}{dt} = -r_{\text{ED,As(V)}}.Y_{\text{As(V)}/\text{ED}}$$

$$Y_{O_2/\text{Org}} = \frac{\Delta DO}{\Delta TOC}; \quad Y_{\text{Fe(III)}/\text{Org}} = \frac{\Delta \text{Fe(III)}}{\Delta TOC}; \quad Y_{\text{As(V)}/\text{Org}} = \frac{\Delta \text{As(V)}}{\Delta TOC}$$

where Y is the yield coefficient (mg/mg). Square brackets represent the concentrations of each species (mg/L). The above kinetic reactions are in general a framework for the bioleaching model of arsenic and iron where a number of EAs exist. In this study, laboratory experiments were primarily designed to study the bioleaching of arsenic under the conditions where oxygen, Fe(III) and As(V) were available as EAs. The first-order rate constants for the biodegradation of organic matter and half-velocity constants for the substrate utilization rate were determined through laboratory batch experiments and are summarized in Table 1.

The complete mass balance equations for the bioleaching of arsenic in the sand filter reactor can be represented

Table 1 | Kinetic constants for the biodegradation of organic matters

Terminal electron acceptor in organic biodegradation	First-order rate constant, k_{ED} (day^{-1})	Half-velocity constant, K_{EA} (mg/L)	Yield coefficient, Y (mg/mg)
Oxygen	0.23	7.0	1.01
Fe(III)	0.10	7.0	0.29
As(V)	0.07	7.0	0.08

as follows:

$$d[Org]/dt = -Degradation$$

$$d[DO]/dt = -Deoxygenation(Org\,degradation) + Re$$
$$- oxygenation + Diffusion$$

$$d[Fe(III)]/dt = -Reduction\,to\,Fe(II) + Re$$
$$- oxidation\,to\,Fe(III)$$

$$d[Fe(II)]/dt = +Reduction\,of\,Fe(III) - Re$$
$$- oxidation\,to\,Fe(III)$$

$$d\left[As(V)_{liquid}\right]/dt = +Release(Fe(III)\,reduction)$$
$$- Adsorption\,(re - oxidation\,to\,Fe\,(III))$$

$$d[As(V)_{solid}]/dt = -Reduction\,to\,As(III) + Adsorption\,(re$$
$$- oxidation\,to\,Fe(III))$$

$$d[As(III)]/dt = +Reduction\,of\,As(V)$$

Preparation of artificial contaminated groundwater

Several studies reported that the concentrations of arsenic, iron and organic matters in the shallow groundwater of Bengal Delta Plain were typically found in the range of 2–900 µg/L, 0.4–15.7 mg/L and 1–15 mg/L, respectively (Karim 2000; BGS & DPHE 2001; Bhattacharya & Mukherjee 2001). In this study, the contaminated groundwater was prepared artificially using arsenic (H_3AsO_4 standard solution, Merck) and iron ($FeSO_4. 7H_2O$) in Milli-Q water to concentrations of 500 µg/L and 5 mg/L, respectively which would correspond to a real groundwater situation of mass arsenic poisoning in the Bengal Delta Plain. The pH was then adjusted to 7 by using sodium hydroxide (NaOH) reagent. Mostly, in groundwater, the organic matter contamination is contributed by humic and fulvic acids originated through chemical and microbial decomposition of terrestrial and aquatic animals as well as plants. The humic and fulvic substances are not easily biodegradable

and thus arsenic reducing bacteria could hardly use them in the aquatic environment. However, several studies identified that the organic matter contamination in groundwater of the shallow reducing aquifer was frequently combined with high concentrations of nitrogen and phosphorus (Bhattacharya & Mukherjee 2001; Stollenwerk *et al.* 2007). The source of this contamination was suspected to be the wastewater from pit latrines as well as the greywater, which were highly biodegradable. Thus, in the laboratory study, the simulated wastewater organic matter stock solution was prepared using tryptone (T), yeast extract (Y) and glucose (G) in pure water, following *Standard Methods* (American Water Works Association 2005) for plate count (G:Y:T ≡ 1:2.5:5 wt/wt) excluding agar, which would give a preferable environment for the growth of bacteria. Laboratory reagent grade chemicals from Becton Dickinson (BD), USA, were used in the above preparation. Laboratory analysis for total arsenic and iron concentrations in sample water was carried out by inductively coupled plasma mass spectrometry (ICP-MS, HP 4500, Yokogawa). The analytical detection limits for arsenic and iron were 0.3 and 0.1 µg/L, respectively. Dissolved oxygen (DO) concentrations were determined using electrode (Unisense, Denmark).

Model for arsenic bioleaching in the laboratory reactor

The DO concentration in the liquid phase of the bioleaching reactor (Figure 3) was estimated using the Streeter–Phelps type equation. The sand filter was located under the liquid phase where the deoxygenation (biochemical oxygen demand (BOD) removal) rate was similar to that of the
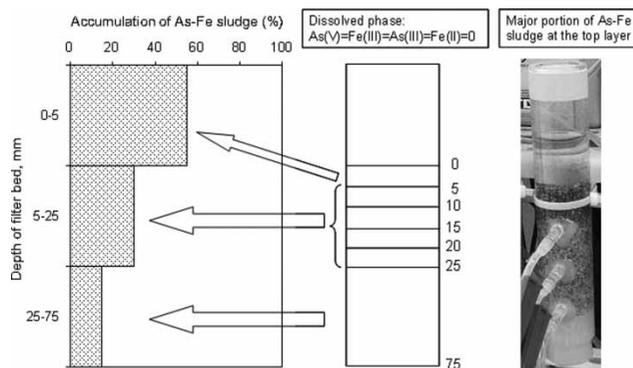

Figure 3 | Simulation of initial condition for the bioleaching of arsenic in laboratory reactor.

liquid phase but the reoxygenation rate was slow through the diffusion of oxygen. Moreover, the water saturated sand filter bed containing arsenic-iron sludge resulted in a limited diffusivity (Table 2) of oxygen.

$$D_{O_2} = \frac{k_1 L_i}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) + D_i e^{-k_2 t};\ \text{Deoxygenation,}$$

$$D_{O_2} = L_i\left(1 - e^{-k_1 t}\right) + D_i;\ O_2\ \text{Diffusion}$$

$$= D\left(\frac{C_{i+1} - C_i}{\Delta X^2} - \frac{C_i - C_{i-1}}{\Delta X^2}\right)\cdot \Delta t$$

where D_{O_2} is dissolved oxygen concentration (mg/L); k_1 is first-order reaction rate constant (day^{-1}); L_i is initial BOD (mg/L); k_2 is rate constant for atmospheric re-oxygenation (day^{-1}); D_i is initial oxygen deficit (mg/L). D is the coefficient of diffusion (cm^2/s); C_{i+1}, C_i and C_{i-1} are the concentrations of DO (mg/L) at the top, middle and bottom segments; Δt is time of diffusion (s) and ΔX is the depth of each segment (cm).

Bioleaching of arsenic from the accumulated sludge in laboratory reactor was carried out using a 75 mm depth of sand filter (Figure 3). In order to minimize the hazardous and toxic waste generation during the research activity in the laboratory, a small cross-sectional area (diameter, $\varphi = 25$ mm) reactor was taken into consideration for the development of the arsenic-iron removal unit (AIRU). A coarse grained sand (effective size, $D_{10} = 0.4$ mm; uniformity coefficient, $U_C = 1.7$) filter bed having a depth of 75 mm was used for the reactor. The filtration rate was maintained at 0.6–0.7 m/hr, which is the highest permissible filter loading rate for the slow sand filtration process (Montogomery JM Consulting Engineers Inc. 1985). There were three small outlets connected at different depths (5, 25 and 75 mm) of the sand filter bed. The outlets were arranged in such a way that the sand filter bed would always be submerged under water, which is a common practice for the arsenic and

iron removal process at the field level of Bangladesh and India (Ahmed 2001). In the course of this study, the effluent water samples were collected from these outlets for various laboratory analyses. Accumulation of arsenic-iron sludge was performed through filtering the artificially prepared contaminated groundwater for 10 bed volumes (volume of permeate/volume of filter bed) of effluent water. The selected 10 bed volumes and hence a preliminary stage of the reactor operational condition was considered in this study to observe the potential bioleaching of arsenic in response to organic matter inclusion in the treatment process. In field conditions, the bioleaching of arsenic would be even more severe due to a large amount of deposited sludge in the long-term operational condition of the treatment unit. Water samples collected from different depths of sand filter identified that 55, 30 and 15% of the total sludge were retained in 0–5, 5–25 and 25–75 mm depths of the sand filter bed (Figure 3).

Following the accumulation of arsenic-iron sludge in the sand filter bed, an organic matter contamination of 15 mg/L as BOD was added in the reactor and then kept inoperative for a few days for the observation of bioleaching of arsenic. At the initial condition of the laboratory reactor, the dissolved phase As(V) = Fe(III) = As(III) = Fe(II) = 0, while the concentration of organic matter was uniform, 15 mg/L as BOD, throughout the whole depth of reactor. In the developed model, segments at 5 mm were taken into consideration for 0–25 mm depth of sand filter. However, a single segment of 25–75 mm depth was considered because of its limited accumulation of As-Fe sludge. The bioleaching of arsenic from the accumulated sludge in the filter bed of the reactor was estimated using the kinetic equations of the sequential terminal electron acceptor reaction model for the biodegradation of organic matters.

RESULTS AND DISCUSSION

In the field situation, the arsenic treatment unit is usually operated in both the 'continuous flow' and the 'intermittent flow' modes and occasionally it is kept inoperative for a few days. The microbial decomposition of organic matter would most likely happen in the inoperative condition. The bioleaching potential of arsenic from the accumulated sludge

Table 2 | Oxygen diffusion coefficients in water and water saturated soil

Oxygen diffusion coefficient, D	Unit (cm²/s)	Reference
Water D_w at 20 °C	20×10^{-6}	Fan *et al.* (1990)
Water saturated soil, D_{sw}	1×10^{-6}	Smith (1980)
For thin biofilm, D_f/D_w	≈ 1	Fan *et al.* (1990)

in the sand filter reactor was estimated using the developed model in this study (Figure 4).

In the course of the biodegradation process of organic matter, aerobic oxidation preceded the other reactions because oxygen reducers would derive more energy (i.e. higher Gibbs free energy) from the substrate than the iron and arsenic reductions. The model predicted DO concentration at different layers of the sand filter reactor, as shown in Figure 4(a). In the topmost layer of sand filter, 0–5 mm depth, aerobic conditions prevailed, always with a temporary drop of DO concentration to around 3.4 mg/L from its initial value of 7.6 mg/L. As a result, this layer of sand filter did not contribute to bioleaching of arsenic from the accumulated sludge (Figure 4(b)). However, in subsequent layers of sand filter, the depletion of DO due to
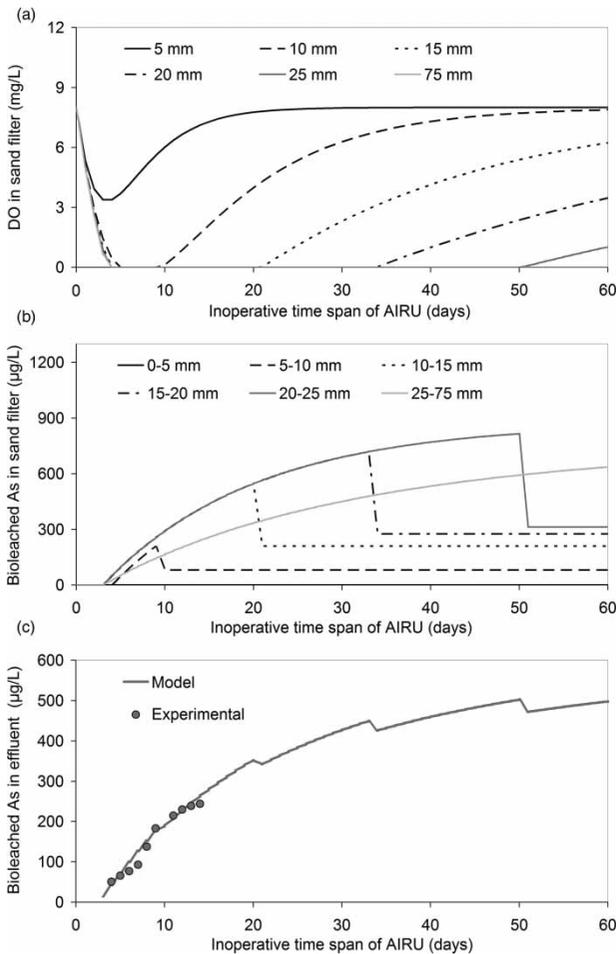
microbial action led to an anaerobic reducing environment within the accumulated sludge and hence caused the bioleaching of arsenic (Figures 4(a) and (b)). Within the sand filter, the deoxygenation (BOD removal) rate was almost uniform throughout the whole filter bed; however, atmospheric reoxygenation rate was gradually decreased at the bottom layers due to slower diffusion of oxygen. On the 10th day of observation in the 5–10 mm depth of sand filter, a sharp drop in arsenic bioleaching was observed due to returning aerobic conditions; consequently, soluble ferrous iron (Fe^{2+}) was oxidized to an insoluble ferric (Fe^{3+}) form and hence As(V) was re-adsorbed onto the iron hydroxide solid phase while As(III) remained in a liquid phase because of its weak affinity for adsorption. The overall bioleached arsenic in effluent from the sand filter reactor is shown in Figure 4(c). The experimental values for the bioleaching of arsenic were found to be comparable with the model predicted values. For an organic matter contamination of 15 mg/L as BOD in the laboratory reactor, under the inoperative time span of 5, 10, and 15 days, the concentrations of bioleached arsenic were found to be 59, 184, and 275 μg/L, respectively. In the case of drinking water quality, the bioleached arsenic was found to be far beyond the WHO (World Health Organization) guideline value of 10 μg/L.

The developed model also simulated the effect of organic matter concentrations on the bioleaching of arsenic under a series of inoperative time span of the sand filter reactor (Figure 5). For the organic matter concentrations of 12, 15 and 20 mg/L as BOD, under an inoperative time span of 10 days, the bioleached arsenic was found to be 125, 176 and 222 μg/L, respectively. The bioleaching

Figure 4 │ Simulation of the biodegradation of organic matter (15 mg/L as BOD) on the DO concentration and bioleaching of arsenic under the inoperative time span (days) of the laboratory scale AIRU (Arsenic-Iron Removal Unit).
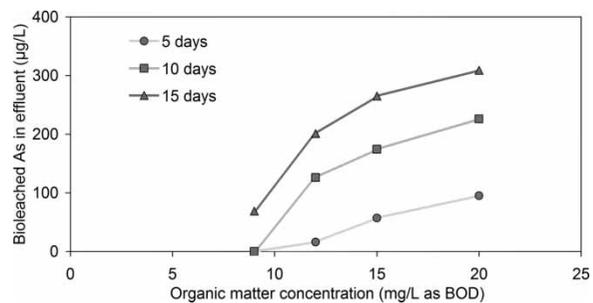

Figure 5 │ Simulation of organic matter inclusion (as BOD mg/L) in feed water on the bioleaching of arsenic from the accumulated sludge in the sand filter reactor under the inoperative time spans of 5, 10, and 15 days.

process was completely inhibited for an organic matter concentration less than 7.6 mg/L as BOD due to prevailing aerobic conditions across the whole sand filter reactor. In this simulation, the temperature was considered to be 20 °C. However, in many Southeast Asian countries having arsenic pollution in groundwater, the temperature in the summer season rises beyond 30 °C and in that case the bioleaching of arsenic would be even more serious due to the higher reaction rate. Thus, the biological significance of organic matter interactions for the mobility of arsenic is essential to affirm its reflection in designing safe remediation strategies in the context of groundwater treatment.

CONCLUSIONS

The mathematical model presented in this study was aimed at simulating the effect of organic matter in an arsenic removal process for drinking water. In the course of the biodegradation of organic matters, the release of arsenic was predicted by this model. Simulation of the arsenic bioleaching was performed using the kinetic equations of sequential terminal electron acceptor reactions for the biodegradation of organic matters. Anoxic conditions within the accumulated sludge in sand filter bed were responsible for the bioleaching of arsenic. Microbial reduction of ferric iron (Fe^{3+}) sorbing phase to ferrous (Fe^{2+}) form caused the release of associated arsenic in the aqueous phase. The bioleaching of arsenic occurred in the inoperative time span of the sand filter reactor and augmented with higher organic matter contamination but was restrained in lower contamination less than 7.6 mg/L as BOD. The experimental results were comparable with the model predicted values.

ACKNOWLEDGEMENTS

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