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Arsenic Removal from Groundwater and Its Safe Containment in a Rural Environment: Validation of a Sustainable Approach

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Of all the naturally occurring groundwater contaminants, arsenic is by far the most toxic. Any large-scale treatment strategy to remove arsenic from groundwater must take into consideration safe containment of the arsenic removed with no adverse ecological impact. Currently, 175 well-head community-based arsenic removal units are in operation in remote villages of the Indian subcontinent. Approximately 150,000 villagers collect arsenic-safe potable water everyday from these units. The continued safe operation of these units has amply demonstrated that use of regenerable arsenic-selective adsorbents is quite viable in remote locations. Upon exhaustion, the adsorbents are regenerated in a central facility by a few trained villagers and reused. The process of regeneration reduces the volume of disposable arsenic-laden solids by nearly 2 orders of magnitude. Finally, the arsenic-laden solids are contained on well-aerated coarse-sand filters with minimum arsenic leaching. This disposal technique is scientifically more appropriate than dumping arsenic-loaded adsorbents in the reducing environment of landfills as currently practiced in developed countries including the United States.

Introduction

Arsenic in Groundwater: Treatment Philosophy for Remote Villages. Natural geochemical weathering of subsurface soil has caused an unacceptable level of dissolved arsenic in groundwater in many regions of the Indian subcontinent (*1–4*). Rainfall in this geographical area is quite high but the surface water is not fit for drinking due to poor sanitation practices in the region with the potential for an outbreak of waterborne diseases. To mitigate this problem, thousands of well-head units attached to manual hand pumps were sunk during the last four decades to provide safe potable water to millions of villagers in the region. The presence of unacceptably high levels of arsenic does not alter the taste, color, or odor of water. Now in many places in this geographical area, arsenic concentration in groundwater exceeds well over 100 μg/L. An estimated 100 million people in Bangladesh and in the eastern part of India are currently affected by widespread arsenic poisoning caused by drinking water drawn from the underground (*5, 6*). Recently, natural arsenic contamination of groundwater has also been reported in Vietnam and Cambodia (*7–9*).

During the last ten years, Bengal Engineering and Science University (BESU) in Howrah, India in association with Lehigh University in Pennsylvania have installed 175 community-based well-head arsenic removal units (ARUs) in remote villages bordering Bangladesh and the State of West Bengal, India (*10, 11*). During the first two years of the project beginning in 1997, both point of use (PoU) household units and community-based well-head arsenic removal systems were installed. Note that while each PoU serves only one family in a village, nearly two hundred families collect potable water from each community-based ARU. Also, of all the naturally occurring groundwater contaminants, arsenic is by far the most toxic, and its removal, therefore, must address the consequent disposal and/or containment issues. It was recognized that coordinating collection and safe disposal of arsenic-laden sludge from individual households poses a level of complexity and enforcement effort that are difficult to sustain in remote villages. Subsequently, we pursued installation of only community-based well-head ARUs.

Role of Dissolved Iron. A fixed-bed sorption process is effective in removing trace concentrations of arsenic because it is forgiving toward fluctuations in the influent quality and can be started or stopped momentarily without any operational complexity (*12, 13*). However, in all arsenic-contaminated groundwater, dissolved iron or Fe(II) is also significantly present and often at concentrations greater than 2.0 mg/L. Similar observations have also been made for arsenic-containing groundwater in Vietnam, Cambodia, and Mexico (*7, 8, 14*). Oxidation of dissolved Fe(II) to insoluble Fe(III) hydroxide at near-neutral pH is a thermodynamically favorable process due to its relatively high negative free energy of reaction at the standard state (*15*):

$$4Fe^{2+}(aq) + O_2(g) + 10H_2O \Rightarrow 4Fe(OH)_3(s) + 8H^+ \quad (1)$$

$\Delta G^0_R = -18$ kJ/mol.

Freshly precipitated hydrated Fe(III) oxide (HFO) particle surfaces are considered to be a diprotic acid with two dissociation constants:

$$\equiv FeOH_2^+ \leftrightarrow H^+ + \equiv FeOH \quad (2)$$

$$\equiv FeOH \leftrightarrow H^+ + \equiv FeO^- \quad (3)$$

where shaded lines represent the solid phase. At circumneutral pH, $FeOH_2^+$ and FeOH are the predominant HFO species and they can selectively bind both arsenites or As(III) and arsenates or As(V) through formation of bidentate and/or monodentate inner-sphere complexes where Fe(III), a transition metal, serves as electron-pair acceptor or Lewis acid (*16–18*):

$$\equiv \begin{matrix} FeOH_2^+ \\ FeOH_2^+ \\ FeOH_2^+ \end{matrix} \xrightarrow{HAsO_4^{2-} \text{ or } H_2AsO_4^-} \equiv \begin{matrix} FeOH_2^+ \\ FeOH_2^+ \leftarrow HAsO_4^{2-} \\ FeOH_2^+ \leftarrow H_2AsO_4^- \end{matrix} \quad (4)$$

$$\equiv FeOH \xrightarrow{HAsO_2} \equiv FeOH \leftarrow HAsO_2 \quad (5)$$

Commonly occurring anions present at relatively high concentrations, namely, chloride, sulfate and bicarbonate,

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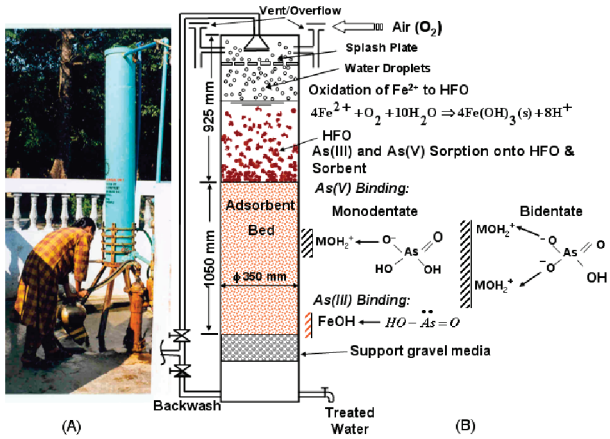


FIGURE 1. (A) Photograph demonstrating easy-to-operate community based arsenic removal unit and (B) salient reactions at different sections of the unit.

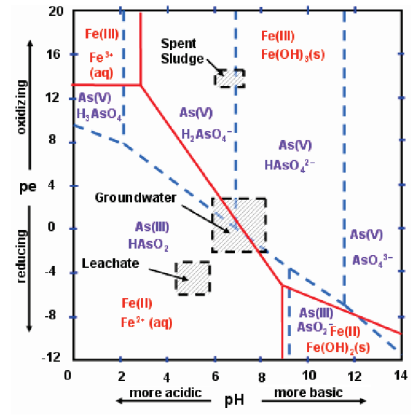


FIGURE 2. Superimposed predominance or pe-pH diagram of major As(III)/As(V) and Fe(II)/Fe(III) species.

are weak ligands and exhibit poor sorption affinity to HFO particles (*16*). However, dissolved silica and phosphate compete against arsenic sorption. Phosphate concentration in the groundwater in the region rarely exceeds 1.2 mg/L as P while silica concentration varies between 20 and 35 mg/L as SiO_2.

The top part of the gravity-flow well-head column is deliberately designed with a large void space and a vent open to the atmosphere. As the hand-pump is operated manually, the groundwater entering the column first forms small droplets (i.e., larger surface area per unit volume) aided by a splash plate. The droplets subsequently get oxygenated, thus bringing the reaction 1 to near completion. The top chamber is followed by a regenerable sorbent material, spherical activated alumina and/or arsenic-selective hybrid anion exchanger (HAIX). Figure 1A shows the photograph of an existing well-head arsenic removal unit in use demonstrating how a village woman can unilaterally operate the handpump to collect arsenic-safe water. Figure 1B depicts salient process steps at different sections of the well-head column.

Containment of Arsenic-Laden Residuals: Role of Redox Condition. In a community-based well-head arsenic removal system, arsenic-laden wastes evolve from two separate locations. First, ferric hydroxide precipitates or HFO particulates that are formed due to reaction 1 gradually increase the pressure drop or head loss in the column, thus reducing the flow rate. Once every day, it is imperative to backwash the well-head column and arsenic-loaded HFO particles are collected on the top of a coarse sand filter located in the same premise. Second, the adsorbents used are regenerated periodically in the central regeneration facility and following treatment the spent regenerants produce arsenic-laden solids. Chemically, these two wastes are similar; both are rich in iron and arsenic. Local environmental laws/regulations with regard to the safe disposal of arsenic-containing sludge in remote villages in the developing nations either do not exist or they are not enforceable. Thus, containing the arsenic removed from the groundwater with no adverse ecological impact and human health endangerment is as important as its removal to provide safe drinking water. Currently, in the developed western nations, arsenic-laden sludge or adsorbents are routinely disposed of in landfills. However, several recent investigations have revealed that leaching of arsenic is stimulated or enhanced in a landfill or a hazardous waste site environment (*19, 20*). Both pH and redox conditions uniquely determine speciation of arsenic and iron that in turn control arsenic leachability. Figure 2 shows the composite predominance or pe-pH diagram for various arsenic and iron species using equilibrium relationships available in the literature (*21, 22*). The figure highlights (shaded rectangles) the three separate predominance zones of interest: neutralized HFO-laden sludge, groundwater, and landfill leachate. Note that Fe(III) and As(V) predominate in the aerated HFO-laden sludge where Fe(III) is also insoluble. In contrast, reduced Fe(II) and As(III) are practically the sole species in the more reducing landfill environment. Relatively high solubility of Fe(II) and low sorption affinity of As(III) would always render the iron-laden sludge more susceptible to rapid leaching under the oxygen-starved environment of the landfill or underground waste site. In an aerated (i.e., oxidizing) environment arsenic and iron leaching are minimized.

Objectives of the Study. Different treatment strategies are currently in place for arsenic removal from contaminated groundwater (*14, 23–28*). The general goal of this paper is to emphasize sustainable approaches to contain arsenic-laden sludge in remote villages while providing arsenic-safe potable water through well-head treatment units. Specifically, the subject study presents field data to confirm the following: first, a regenerable adsorbent can produce arsenic-safe potable water for a prolonged period of time in a community-based treatment system through active participation of villagers; second, the central regeneration facility streamlines the disposal problems associated with arsenic-laden sludge in comparison with single-cycle nonregenerable adsorbent media; and third, through appropriate control of redox environment, the containment of arsenic-laden sludge can be managed without adverse environmental impact even in a rural environment.

Materials and Methods

Activated alumina (AA) with nearly spherical physical configuration was procured from an indigenous chemical company (Oxide India Ltd., Durgapur, West Bengal) after carrying out laboratory tests to confirm its amenability to regeneration and reuse. In addition, hybrid anion exchanger (HAIX) or ArsenX with specific affinity toward dissolved As(V) and As(III) species was also used in several locations for its regenerability over multiple cycles (*29, 30*). Each well-head unit contains 100 L of AA or HAIX and the average sizes of the adsorbent particles vary between 600 and 900 μm.

In the central regeneration facility aerated coarse-sand filters as shown in Figure 3 are used to contain arsenic-laden solids from the treated spent regenerant to avoid anoxic conditions. Indigenously available brick, cement, PVC pipes, gravels, and coarse sands were the primary materials needed for the construction. Existing sand filters can safely store arsenic residues for 20 more years. Every well-head unit is

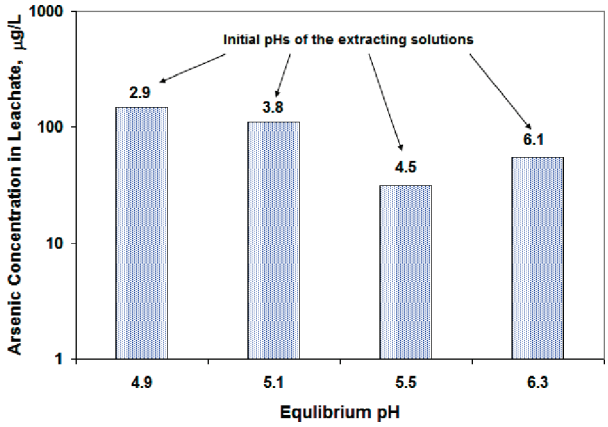


FIGURE 7. Arsenic concentrations in the leachate during extended-TCLP test for a spent regenerant sludge collected from the coarse sand filter.

groundwater. Filtered samples were obtained after vacuum filtration through a 0.45 μm membrane. Although activated alumina does not possess As(III) removal capacity, note that As(III) was removed significantly i.e., from 90 to 35 μg/L. The postulated mechanism of As(III) removal in an activated alumina column has been discussed previously (*10, 11*). The difference in arsenic level between filtered and unfiltered treated water is very marginal. Similar observations were also made for many other operating well-head units suggesting that arsenic in the treated water is present only in the dissolved state.

Regeneration and Fate of Arsenic in the Spent Regenerant. An easy-to-operate stainless steel batch reactor is used for the regeneration in the central facility. The individual regeneration steps have been streamlined and they are delineated in Table 1, presented earlier. Dissolved arsenic in the spent caustic regenerant varies from 30 to 100 mg/L and arsenic is present solely as arsenate or As(V). However, after mixing of waste regenerants, addition of Fe(III) chloride and subsequent adjustment of pH between 6.5 and 7.0, residual dissolved arsenic concentration promptly drops to less than 200 μg/L. The entire amount of arsenic is essentially transferred into the solid phase along with ferric hydroxide precipitate.

Arsenic-laden solids in the central regeneration facility are kept at the top of a well-aerated sand filter as shown in Figure 3. To validate low arsenic leachability, an extended TCLP test (*34*) was performed for a sludge sample collected from the top of the well-aerated coarse sand filter; Figure 7 shows the results. While the sludge had approximately 32 mg As/g of dry solids, the arsenic concentration in the leachate was consistently less than 200 μg/L in the pH range of 4.3−6.3.

Discussion

Sustainability Issues: Developed vis-à-vis Developing Nations. Two consecutive cycles with the ARU in Sangrampur village (Figure 4) demonstrated the overall effectiveness of the system for a period of five years. Currently 175 well-head arsenic removal units are in use in villages bordering eastern India and Bangladesh; no other viable source of potable water currently exists for these villagers. Nearly 150,000 villagers currently drink arsenic-safe water from these units that are run and maintained by a villagers' committee in every location. The three most salient features of the arsenic removal process are as follows: first, the adsorbent media chosen are robust and regenerable; second, a central regeneration facility is adequately equipped to collect and regenerate exhausted media; and third, arsenic removed is contained as solids on aerated sand filters with a minimum

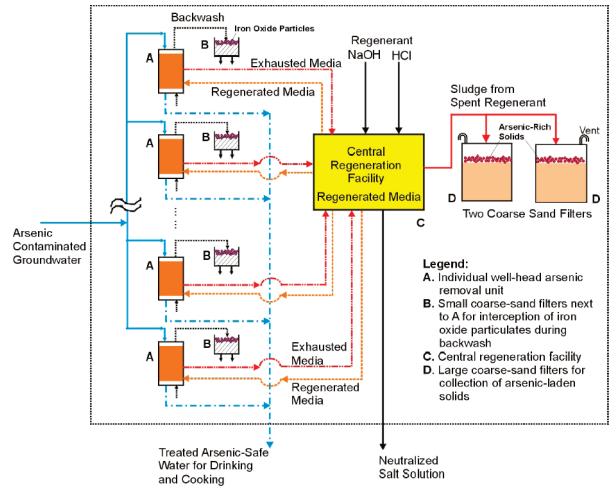
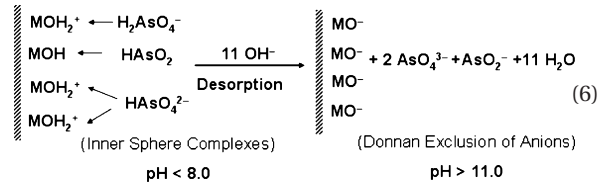


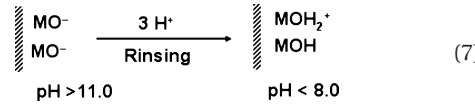
FIGURE 8. Global arsenic treatment protocol with a central regeneration facility and safe arsenic containment.

potential for arsenic leaching. A global scheme for the overall process of arsenic removal including the management of treatment residuals is presented in Figure 8.

The primary reactions during regeneration of exhausted adsorbents with 2% NaOH and rinsing with dilute acid are presented below where M represents Al(III) or Fe(III) in AA or HAIX, respectively:



(6)



(7)

At high alkaline pH, the surface hydroxyl groups get deprotonated and negatively charged, thus causing desorption of negatively charged arsenic species very efficiently. Subsequent rinsing with dilute acid allows formation of protonated surface functional groups with high arsenic sorption affinity. The regeneration step allows reuse of the adsorbent media and reduces the volume of arsenic-laden sludge by over an order of magnitude. In contrast, nonregenerable adsorbent media are used universally for arsenic removal in the developed western world. After one-cycle application, such high-volume adsorbent media are routinely disposed of in landfills and hazardous waste sites. Hundreds of such single-application-throw-away adsorption units imported from a western country are currently lying abandoned in remote villages after their arsenic removal capacities have been exhausted (see Supporting Information Figure S1).

It is worth noting that the chronic toxicity caused by the presence of low concentration of arsenic (well below 1 mg/L) in ingested water is not influenced by the relative distribution of As(III) and As(V). At such low concentration, As(V) gets instantaneously converted to As(III) upon ingestion (*35*). That is why various international governing bodies, namely the World Health Organization (WHO), the United States Environmental Protection Agency (USEPA), and the European Union (EU), specify only total arsenic for the maximum contaminant level (MCL) in drinking water. Results presented in Figure 6 demonstrate that the community-based