Sustainable Engineered Processes to Mitigate the Global Arsenic Crisis in Drinking Water: Challenges and Progress

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Abstract

Millions of people around the world are currently living under the threat of developing serious health problems owing to ingestion of dangerous concentrations of arsenic through their drinking water. In many places, treatment of arsenic-contaminated water is an urgent necessity owing to a lack of safe alternative sources. Sustainable production of arsenic-safe water from an arsenic-contaminated raw water source is currently a challenge. Despite the successful development in the laboratory of technologies for arsenic remediation, few have been successful in the field. A sustainable arsenic-remediation technology should be robust, composed of local resources, and user-friendly as well as must attach special consideration to the social, economic, cultural, traditional, and environmental aspects of the target community. One such technology is in operation on the Indian subcontinent. Wide-scale replication of this technology with adequate improvisation can solve the arsenic crisis prevalent in the developing world.

INTRODUCTION

Arsenic (As) in the drinking water of millions of people living around the world has been a focus of attention for public health scientists and engineers (1–5). Both the World Health Organization and the United States Environmental Protection Agency have set arsenic limits at 10 μg liter^{-1} (6, 7). The arsenic crisis prevailing in the Ganges delta, which extends over a large area of Bangladesh and India, is arguably one of the worst global calamities in recent times (8, 9). In this geographic area alone, more than 120 million people are exposed to arsenic concentrations greater than 50 μg liter^{-1}, the prevalent regulatory limit in these countries (10). The crisis is also slowly unfolding in Southeast Asia, where it affects countries including Cambodia, Vietnam, Laos, and Myanmar (11–13). The use of groundwater in these regions is favored by its easy availability and microbial safety as well as the absence of proper infrastructure for the treatment and distribution of surface water. Surface water is often contaminated owing to poor sanitation practices. With growing populations and agricultural demand, excessive groundwater withdrawals have resulted in the dissolution of arsenic owing to the geochemical weathering of minerals within the aquifers. Drinking arsenic-contaminated water over a long period causes severe damage to the human body and often is fatal. Although the best solution to the problem is to switch to treated surface water that has no arsenic contamination, development and maintenance of surface water–based drinking water systems are expensive, time consuming, and investment intensive. Rainwater harvesting also has high investment costs, brings its own potential water quality problems, and is of doubtful suitability in countries such as Bangladesh where rainfall is seasonal. The situation is most difficult in rural areas in developing countries where arsenic-contaminated groundwater is the only drinking water source. Despite the positive laboratory performance of many point-of-use arsenic removal technologies, most of these technologies have not demonstrated adequate effectiveness and long-term sustainability in the field (14). Sustainable production of arsenic-safe water from a contaminated raw water source is thus the current challenge. A sustainable remediation technology should be robust, composed of local resources, and easy to use and maintain; it must also attach special consideration to the social, economic, cultural, traditional, and environmental aspects of the community for which it is designed. It is critical that interventions for arsenic remediation be designed such that they eliminate arsenic toxicity without introducing future sustainability challenges. In this article we discuss the technological aspects of arsenic remediation and the progress toward mitigation of the global crisis caused by the presence of arsenic in the drinking water of people around the world.

ARSENIC CHEMISTRY: ITS OCCURRENCE AND MOBILIZATION

The natural occurrence of arsenic and its fate and mobility in aquatic and soil environments are seemingly different from the engineered processes often employed to remove arsenic from contaminated water. However, the underlying chemistry governing these two diverse phenomena is quite similar. Redox conditions, pH, and the chemistry of the accompanying materials are the three primary variables in relation to arsenic's presence and mobility in the natural environment. Pertinent redox reaction and acid dissociation constants are given in Equations 1–5 (15–17). The acid-base reactions for As^{V} (arsenate) are:

$$H_3AsO_4 \rightleftharpoons H^+ + H_2AsO_4^-, \quad pK_{a,1} = 2.2, \tag{1.}$$

$$H_2AsO_4^- \rightleftharpoons H^+ + HAsO_4^{2-}, \quad pK_{a,2} = 7.0, \quad \text{and} \tag{2.}$$

$$HAsO_4^{2-} \rightleftharpoons H^+ + AsO_4^{3-}, pK_{a,3} = 11.5. \tag{3.}$$

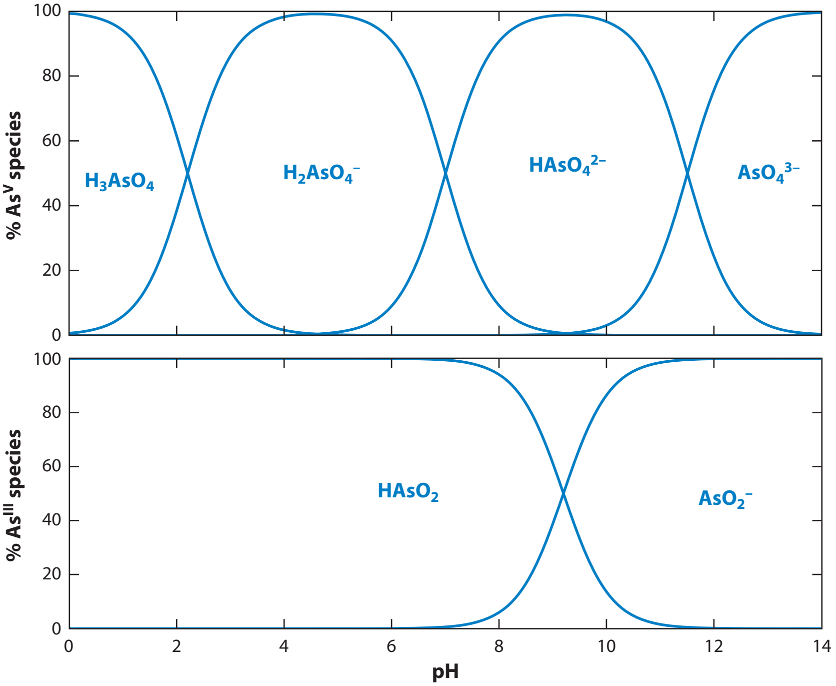

Figure 1

Distribution of As^{V} and As^{III} oxyacids and their conjugate anions as a function of pH.

The acid-base reaction for As^{III} (arsenite) is

$$HAsO_2 \rightleftharpoons H^+ + AsO_2^-, \quad pK_{a,1} = 9.2. \tag{4}$$

The redox reaction is:

$$H_3AsO_4 + 2H^+ + 2e^- \rightleftharpoons H_3AsO_3 + H_2O, \quad E_h = +0.56\,V. \tag{5}$$

Figure 1 shows the distribution of As^{V} and As^{III} species as a function of pH. At near-neutral pH, monovalent $H_2AsO_4^-$ and divalent $HAsO_4^{2-}$ are the predominant As^{V} species. An electrically neutral H_3AsO_3 (or hydrated $HAsO_2$) is the major As^{III} species under identical conditions. Combined redox-pH conditions determine the predominance of various inorganic As^{III} and As^{V} species. As^{V} is by far the most predominant species at approximately neutral pH under atmospheric conditions. As^{V} oxyanions are thus the most commonly encountered arsenic species in surface waters such as rivers and lakes. For groundwaters, prevailing redox and pH conditions favor the presence of both As^{III} and As^{V} species. Recently gathered data from groundwater wells in various parts of the world show evidence of As^{III} constituting significantly more than half of the total dissolved arsenic in many wells (18, 19).

The factors determining the presence of different arsenic species in the natural environment can be as diverse as: (*a*) the availability and chemical nature of primary and secondary arsenic-rich sources; (*b*) the chemical properties of the aqueous phase such as pH, redox potential, ionic strength, and organic matter content; and (*c*) the interfacial processes between the solid and fluid phases. As both As^{V} oxyanions and the As^{III} oxyacid are fairly strong ligands, they can be sorbed selectively onto surfaces of metal oxides, such as ferric oxyhydroxides, through the formation of inner-sphere complexes (20, 21). Weathering of Himalayan bedrocks, which contain mainly ferric oxyhydroxides, has released As to surface waters (22–25). This released As is strongly adsorbed by stream sediments and oxides under neutral pH and aerobic conditions. Subsequently, the sorbed arsenic is codeposited with organic matter in alluvial settings. Reduction of ferric oxyhydroxide (FeOOH) by organic matter is often postulated to be responsible for the release of As into groundwater (1, 26–31). In oxidizing aquifers, pH-dependent As desorption from and dissolution of mineral phases may control arsenic mobilization (32).

TREATMENT TECHNOLOGIES: UNDERLYING PRINCIPLES

Removal of dissolved arsenic from natural groundwater and surface water essentially constitutes the removal of both As^{V} oxyanions and the neutral As^{III} oxyacid. The list of existing and emerging arsenic removal technologies is quite long but can be summarized as follows:

- Coagulation followed by filtration/microfiltration using ferric chloride or aluminum sulfate (alum);
- Adsorption and ion exchange using activated alumina, polymeric anion exchange, iron oxide–coated sand particles, granulated iron oxide/hydroxide, titanium dioxide, zirconium hydroxide particles, polymeric ligand exchange, hybrid ion exchangers, engineered porous supports containing nanoparticles, or sand with zero-valent iron; and
- Membrane-based processes such as reverse osmosis or nanofiltration.

The technical details of the foregoing processes and their relative advantages and disadvantages are recorded in the literature (33–59). Because arsenic removal from contaminated groundwater often involves trace concentrations (less than 500 μg liter^{-1}), precipitation is rarely a major removal mechanism. Reverse osmosis and nanofiltration are essentially nonselective physical processes for exclusion of ions across a semipermeable membrane. The chemistry of arsenic removal by these membrane processes is virtually the same as that of any other dissolved species or electrolyte that can be found in the literature. Membrane-based processes are seldom economically viable for trace contaminant removal except in places where the simultaneous reduction of total dissolved solids is warranted. Although the equipment configurations and operational protocols for the other above-mentioned arsenic removal processes are often quite different, the underlying chemistry essentially rests on the following two types of interactions. First, As^{V} oxyanions (e.g., $H_2AsO_4^-$ and $HAsO_4^{2-}$) possess negative charges and therefore can undergo coulombic or ion-exchange (IX) interactions. In this instance, conventional anion exchange processes are seemingly quite suitable for removal of As^{V} oxyanions. Second, the As^{V} and As^{III} species are fairly strong ligands or Lewis bases, i.e., they are capable of donating lone pairs of electrons. Thus, they can participate in Lewis acid-base (LAB) interactions and often exhibit high sorption affinity toward solid surfaces with Lewis acid characteristics. IX and LAB interactions are discussed below in the context of existing arsenic removal processes.

Ion Exchange or Coulombic Interaction

Over a broad range of pH, As^{V} exists as oxyanions. At above-neutral pH, As^{V} exists as a divalent anion and can be removed by an anion exchanger in chloride form as shown below:

$$\overline{2(R^+)Cl^-} + HAsO_4^{2-}{}_{(aq)} \rightleftharpoons \overline{(R^+)_2HAsO_4^{2-}} + 2Cl^-{}_{(aq)}. \qquad 6.$$

The overbar denotes the exchanger phase, and R^+ represents an anion exchanger with a fixed positive charge. In natural groundwater, however, other innocuous anions (i.e., chloride, bicarbonate, and sulfate) are simultaneously present in concentrations several orders of magnitude greater than the target arsenates. The arsenic removal efficiencies of typical IX processes are greatly impaired in the presence of high concentrations of competing ions. The selectivity sequence for various competing anions toward polymeric anion exchangers, based strictly on Coulombic interactions, is as follows:

$$SO_4^{2-} > HAsO_4^{2-} > H_2AsO_4^{-} > Cl^{-} > HCO_3^{-}. \qquad 7.$$

Greater sulfate affinity toward the polymeric anion exchanger causes (*a*) reduction in As^V uptake and (*b*) chromatographic elution of arsenic, which lead to a situation in which arsenic bleeds out in the treated effluent at concentrations much higher than that in the influent stream. For contaminated waters with relatively high sulfate content, therefore, IX is not a viable process. Also, unlike As^V, the As^{III} oxyacid is nonionized and therefore is not amenable to removal solely by anion exchange processes unless it is oxidized to As^V by chlorine, sodium hypochlorite, or solid-phase oxidizing agents, e.g., $MnO_{2(s)}$ or green sand (45, 49, 60).

Lewis Acid-Base Interaction

Both $H_2AsO_4^-$ and $HAsO_2$ are monodentate ligands with one donor atom per molecule. $HAsO_4^{2-}$ is a bidentate ligand with two donor oxygen atoms. Compared with As^V and As^{III} species, sulfate and chloride are poor ligands and form only outer-sphere complexes. Thus, the LAB interaction may be used as an underlying sorption mechanism to separate both dissolved As^V and As^{III} species from relatively high background concentrations of sulfate, chloride, or bicarbonate.

Several hydrous inorganic oxides (both naturally occurring and processed) and tailored polymeric sorbents contain Lewis acid functional groups and hence are effective for arsenic removal through LAB interaction. Among the inorganic materials used in engineered processes, Ti^{IV}, Zr^{IV}, Al^{III}, and Fe^{III} oxides are the most common because they are relatively inexpensive and environmentally benign. The Lewis acid properties of the surface functional groups of these inorganic metal oxides are pH dependent (61, 62) and are as follows:

$$\overline{\equiv MOH_2^+} \rightleftharpoons \overline{\equiv MOH} + H^+ \qquad 8.$$

$$\overline{\equiv MOH} \rightleftharpoons \overline{\equiv MO^-} + H^+ \qquad 9.$$

where $\equiv MOH$ represents electrically neutral surface functional groups of hydrated oxide of metal M. In the presence of noncomplexing electrolytes (e.g., sodium perchlorate or sodium nitrate), the pH corresponding to the point of zero charge (PZC) represents conditions with no residual surface charges, i.e., negative surface charges essentially equal the positive surface charges. At pH less than the PZC, hydrated metal oxides possess fixed positive charges and thus can act as anion exchangers. The pH_{PZC} values for hydrated aluminum oxide and hydrated ferric oxide (HFO) are approximately 7.8 and 8.3, respectively (36, 61–63). As^V oxyanions (e.g., $H_2AsO_4^-$) thus can be sorbed onto such sites through an exchange reaction (say with chloride) as in Equation 10:

$$\overline{\equiv MOH_2^+Cl^-} + H_2AsO_4^- \rightleftharpoons \overline{\equiv MOH_2^+(H_2AsO_4^-)} + Cl^-. \qquad 10.$$

Cl^- and $H_2AsO_4^-$ are electrically identical, as they each have one negative charge. Hydrated aluminum oxides or HFOs highly prefer $H_2AsO_4^-$ over Cl^- owing to the formation of inner-sphere complexes through LAB interaction between arsenate (Lewis base) and the terminal Fe or Al atom in the solid oxide. Thermodynamically, the overall free energy change for the reaction in Equation 10 includes contributions from both IX and LAB interactions, i.e.,

$$\Delta G^0_{\text{overall}} = \Delta G^0_{\text{IX}} + \Delta G^0_{\text{LAB}}, \qquad 11.$$

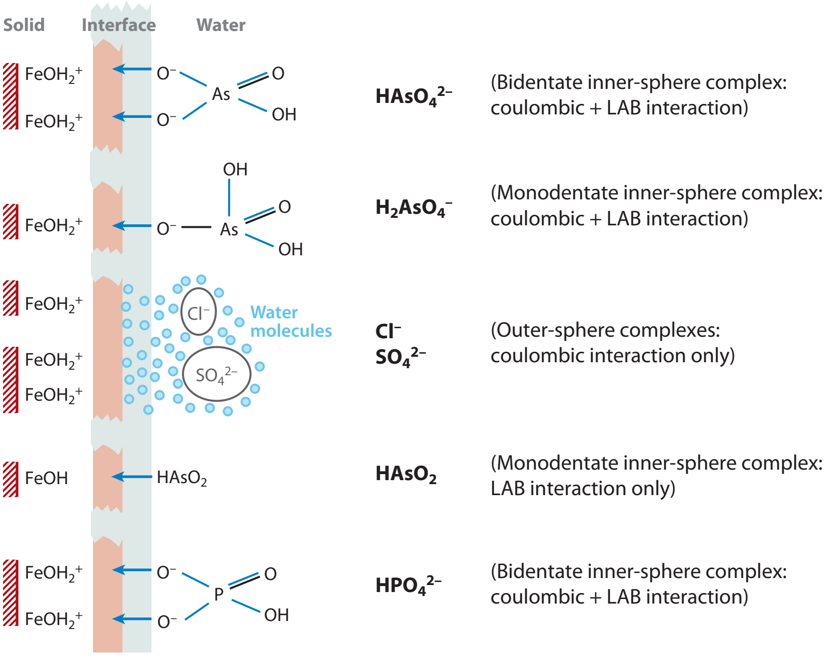

Figure 2

The binding mechanisms of various solutes onto hydrated ferric oxide particle surfaces through the formation of inner- and outer-sphere complexes. Abbreviation: LAB, Lewis acid-base.

or

$$-RT \ \ln K_{\text{overall}} = -RT \ \ln K_{\text{IX}} - RT \ \ln K_{\text{LAB}}, \qquad 12.$$

or

$$K_{\text{overall}} = K_{\text{IX}} K_{\text{LAB}}, \qquad 13.$$

where ΔG^0 denotes the free energy changes in the standard state, R is the universal gas constant, T is the temperature in Kelvin, and K is the equilibrium constant. For $H_2AsO_4^-$ and Cl^- exchange, K_{LAB} is significantly greater than unity, and consequently, $H_2AsO_4^-$ uptake is significantly preferred over that of Cl^-. The sorption of monodentate nonionized arsenite (i.e., $HAsO_2$) takes place solely through LAB interactions. **Figure 2** depicts the sorption of several solutes onto HFO surfaces through formation of inner-sphere and outer-sphere complexes.

As^V compounds exist as anions, and they are best removed by hydrated metal oxides in protonated forms, i.e., $\equiv MOH_2^+$, owing to the concurrent presence of both IX and LAB interactions. On the contrary, the IX interaction is altogether absent for As^{III} sorption. Among $\equiv MOH_2^+$, $\equiv MOH$, and $\equiv MO^-$, $HAsO_2$ is most favorably sorbed onto nonionized surface functional groups, i.e., $\equiv MOH$, which for HFO predominate at approximately pH $\approx$ 8.0. Therefore, $HAsO_2$ sorption on HFO is most favored at slightly greater than neutral pH. For the same reason, aluminum oxides exhibit a similar property. However, As^{III} removal by aluminum oxides is always lower than that by iron oxides. Compared with As^V oxyanions, in which oxygen is the primary donor atom, $HAsO_2$ is a softer Lewis base (64). Electronic configurations of Al^{3+} and Fe^{3+} suggest that Al^{3+} is a hard cation with an electronic configuration similar to that of inert argon, whereas Fe^{3+} is a transition metal cation with an incomplete 3d orbital. Therefore, Fe^{III} is a relatively soft Lewis acid compared with Al^{III}. The formation of an inner-sphere complex (i.e., LAB interaction) is thus favored between $HAsO_2$ and relatively soft Fe^{III} Lewis acids but not with harder Al^{III} oxides. From a strictly engineering viewpoint, this observation clearly suggests that alum coagulant– or alumina-based technologies alone are not appropriate choices if arsenic occurs, wholly or partly, in the +III oxidation state in contaminated source water.

Owing to their weak acid-base properties, hydrated metal oxides have high affinities toward hydroxyl ions (OH^-). Thus, ligand sorption is greatly reduced at alkaline pH, which essentially causes desorption of the ligands from negatively charged functional groups of hydrated metal oxides owing to Donnan co-ion exclusion effects. In engineered processes, this phenomenon forms the basis of the regeneration step that allows reuse of hydrated metal oxides for multiple cycles.

ARSENIC REMOVAL: CHOICE OF APPROPRIATE MITIGATION STRATEGY

A successful remediation technology must take into account the geological differences in groundwater compositions, especially in terms of concentration and species of arsenic and other competing species such as phosphate, dissolved silica, and natural organic matter. A sustainable mitigation strategy should also take into consideration the economic resources of the target population, availability of infrastructure for water treatment, and options for the safe disposal of treatment residuals.

Although coagulation using ferric chloride followed by microfiltration (C/MF) removes As^{III} and As^{V} equally well, it is rarely the technology of choice in view of the trace concentrations of arsenic to be removed and relative costs of dosing of ferric chloride followed by filtration. Furthermore, unless combined with other downstream processes, C/MF alone may not remove arsenic to less than 10 $\mu g\ liter^{-1}$, the safe limit set by the World Health Organization (7). Also, a significant amount of sludge containing high concentrations of arsenic is produced in this process, which requires proper disposal to avoid any leaching of arsenic back to the environment. For groundwater with higher alkalinity, C/MF treatment processes need an enhanced acid dosage for the same degree of arsenic removal.

IX processes to remove arsenic tend to be expensive because the arsenic removal capacity of the common anion exchangers is severely reduced owing to competition from commonly occurring ions such as chloride, sulfate, and bicarbonate. Therefore, IX is rarely chosen for arsenic remediation from water with high total dissolved solids. Activated alumina–based processes are effective for selective adsorption of arsenate ions from a background of other commonly occurring anions. However, unless supported by another arsenic removal technology, activated alumina–based adsorption units have limited utility in locations where As^{III} constitutes a significant proportion of the total arsenic present in the contaminated water.

The presence of dissolved silica, phosphate, or natural organic matter alters the arsenic removal efficiencies of selective arsenic removal processes (65, 66), but not to the same degree, and hence, these compounds influence the relative economic viability of removal processes. The presence of iron in the raw water also has effects on the choice of appropriate technology. For example, in the Red River delta of Vietnam, the iron content of the raw water is high, but competing species are absent. Oxidation of iron in contact with the atmosphere produces fine precipitates of ferric hydroxide that are excellent adsorbents for As^{III} as well as As^{V}. The high iron content in the raw water makes conventional low-cost sand filters a good option in Vietnam and in other affected regions with high concentrations of dissolved iron. However, in Bangladesh the raw water contains less iron and a significantly higher concentration of competing phosphate ions (67). Thus, to bring the arsenic concentration down to the acceptable limit, a selective adsorption process is needed in addition to simple oxidation of raw water followed by sand filtration. In fact, selective adsorption in a fixed-bed configuration is considered the best possible technology to remove trace concentrations of arsenic from groundwater used for drinking purposes, provided that it is cost effective. A fixed-bed adsorption process is operationally simple, requires virtually no start-up time, and is forgiving toward fluctuations in feed composition.

Choice of Adsorbent

For the fixed-bed process to be viable and economically competitive, the sorbent must exhibit high selectivity toward the target contaminant, amenability to efficient regeneration, and durability. Amorphous and crystalline HFO precipitates show strong affinity toward both As^{III} and As^{V} oxyanions through ligand exchange in the coordination spheres of structural Fe atoms. Understandably, minerals such as ferrihydrites, hematites, and goethites, whose surfaces contain HFO functional groups, possess the requisite attributes to be effective as arsenic-selective sorbents. A significant proportion of the arsenic removal technologies, if not all, use sorption onto innocuous hydrated metal oxides; the metals are iron, aluminum, titanium, and zirconium (37, 47, 49, 52, 55).

HFO particles are a popular adsorbent for arsenic. The sizes of freshly precipitated amorphous particles are in the range of 20 to 100 nm. Although this small size provides a high specific surface area, it is nearly impossible to use these nanoscale particles in the field owing to excessive pressure drops and the poor mechanical strength of the particles. Granulated ferric oxide (GFO) and granulated ferric hydroxide (GFH) particles have been developed and used in fixed-bed columns for selective removal of arsenic from contaminated water (38). However, their mechanical properties are weaker as compared with the polymeric and other inorganic sorbents normally used in fixed beds. Another drawback is that both GFO and GFH are not regenerable and produce voluminous contaminated waste after the conclusion of one cycle of operation. Disposal of water treatment residuals, which are essentially arsenic-laden solids, accounts for a significant portion of the operating expenses in developed countries where separate disposal sites for hazardous wastes are maintained. In places where such facilities do not exist or are poorly enforced, the risk of further contamination of the environment through the mismanagement of the arsenic-rich waste is high.

Hybrid Nanosorbents

To overcome the problems associated with the isolated use of nanosorbents, the adsorbent nanoparticles must be dispersed irreversibly within a host material that provides enough mechanical strength and chemical stability for their use in fixed beds. Naturally occurring as well as synthetic materials (polymeric or inorganic), such as alginate, zeolites, activated carbon, chitosan, cellulose, polymeric sorbents, and polymeric cation exchangers, have been used as hosts to contain the nanosorbents (37, 43, 68–74). All these support materials improved the permeability and durability of the adsorbent in fixed-bed columns. However, the chemical and physical nature of the host material influences the properties and adsorption capabilities of the hybrid nanosorbent. Morphological features of the host materials, such as pore size and pore distribution, influence the size and nature of the nanoparticles dispersed within the pores. In addition, for host materials with charged surface functional groups, the nature and charge density of these groups influence the process and extent of dispersion of nanoparticles within the matrix.

Compared with other host materials with fixed neutral or negatively charged functional groups, a polymeric anion exchanger with positively charged fixed functional groups is an excellent

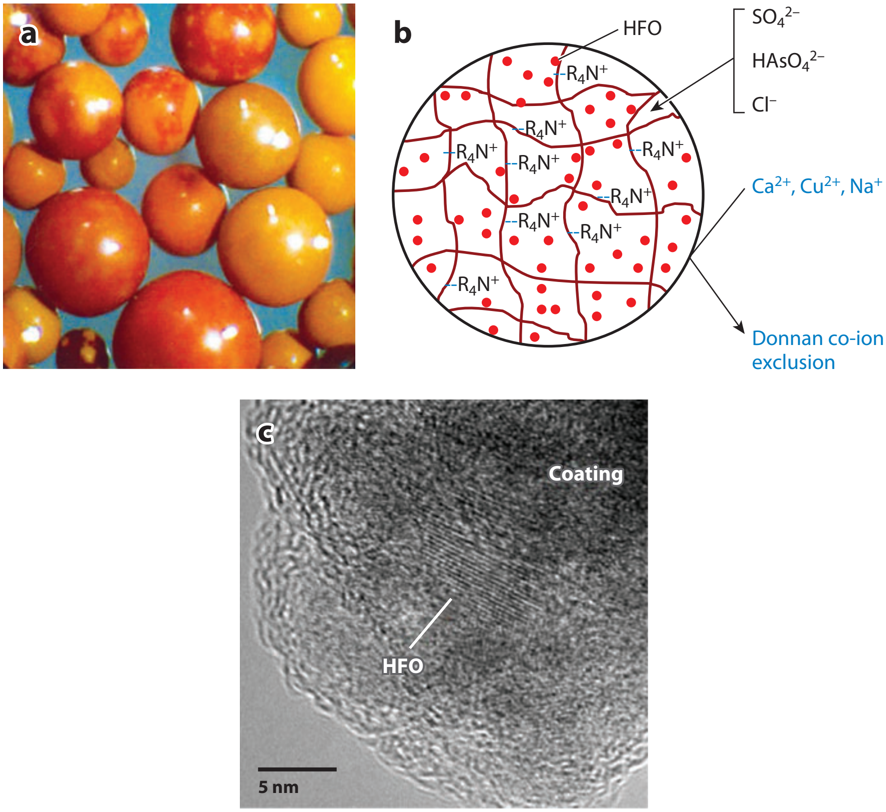

Figure 3

(*a*) Enlarged photograph of hybrid anion exchange resin (HAIX) beads (average diameter 300–600 μm). (*b*) The effect of the Donnan membrane principle on enhanced arsenic sorption by HAIX. (*c*) Transmission electron micrograph of the interior of a HAIX bead showing hydrated ferric oxide (HFO) nanoparticles. Abbreviation: R_4N^+, quaternary ammonium functional group.

substrate because it allows enhanced permeation of anions within the polymer phase owing to its high concentration of fixed positive charges. The hybrid anion exchange resin (HAIX) beads shown in **Figure 3*a*** are prepared by carefully dispersing HFO nanoparticles within anion exchange resins. The enhanced attraction of arsenic and other ligands towards anion exchange resins, as illustrated in **Figure 3*b***, is the reason for choosing them as appropriate substrate materials. The transmission electron micrograph in **Figure 3*c*** confirms the presence of HFO as nanosized particles within the HAIX beads. In the same way that anion exchangers exclude cations, cation exchangers prevent anions from entering the resin phase. A high concentration of nondiffusing fixed charges (R^+ or R^-) in the polymer phase acts as either a highly permeable or an impermeable interface for arsenate, thus influencing its sorption onto the HFO particles embedded in the polymer phase. For HAIXs, the fixed positively charged functional groups many-fold increase the adsorption capability of the HFO-based adsorbents owing to a phenomenon known as the Donnan membrane principle. Judicious design of the hybrid polymeric sorbent with an appropriate functional group thus offers a synergy leading to an enhanced sorption capacity of the metal oxide nanoparticles that is not otherwise achievable (75, 76). In fact, HAIXs have outcompeted granulated ferric hydroxide adsorbents during some field trials (77).

Owing to its chemical stability and durable physical structure, the hybrid polymeric sorbent is amenable to regeneration. Regeneration and subsequent containment of the treatment residuals make the removal process cost effective as well as environmentally sustainable. Because HAIXs can be reused over many cycles, regeneration of the hybrid resin decreases the cost of the treated water. Additionally, the arsenic removed can be concentrated in a small volume of spent regenerant that subsequently can be transformed into a small mass of solids (78, 79).

Regeneration of exhausted resins used for arsenic removal was successfully accomplished in a laboratory column using a solution containing 2 wt% NaCl and 2 wt% NaOH. Nearly 95% of the adsorbed arsenic came out of the HAIX phase within 15 bed volumes (76). Regeneration and reuse of the adsorbent are particularly helpful in attaining economy of operation, which is necessary for the success of a technology when the cost of labor and chemicals is not significant.

EXAMPLE OF A SUSTAINABLE ENGINEERED PROCESS IN USE ON THE INDIAN SUBCONTINENT

Arsenic Removal Unit

In an effort to mitigate the arsenic crisis, more than 200 community-scale arsenic removal units have been installed since 1997 in the villages of West Bengal, an Indian state neighboring Bangladesh (79). Each of these units serves an average of 150 families residing in one or two villages. The arsenic removal units are installed at the top of the well and are attached to the hand pump. The units are designed in such a way that even after their installation, there is no change in the traditional method of water collection by the users (**Figure 4*a*,*c***). This particular attribute prompted instant acceptance of the treatment unit by the villagers. The schematic diagram in **Figure 4*b*** shows the details of reactions taking place within these simple-to-operate treatment units. The units do not require any electricity, chemical addition, or pH adjustment for their daily operation. Scale of operation is important for making arsenic removal units environmentally and economically sustainable. Household treatment units are initially easier to install than the community-based system, but the latter provides a more sustainable solution with potential for further economic growth.

The community-scale arsenic removal unit essentially consists of a stainless steel column filled with approximately 100 liters of adsorbent. The raw water inlet is located at the top of the column. The inlet has a spray head and splash plates so that small water droplets are formed at the entry point. Also, the top part of the column contains a large void space and vent connections that allow air to readily dissolve into the water droplets. The dissolved air helps oxidize the ferrous iron in the raw water to form fine precipitates of HFO according to the following reaction:

$$4\mathrm{Fe}^{2+}{}_{(\mathrm{aq})} + \mathrm{O}_{2(\mathrm{g})} + 10\mathrm{H}_2\mathrm{O} \rightarrow 4\mathrm{Fe(OH)}_{3(\mathrm{s})} + 8\mathrm{H}^+ \quad \Delta G^0_{\mathrm{R}} = -18\ \mathrm{kJ\ mol}^{-1}. \qquad 14.$$

Oxidation of dissolved $\mathrm{Fe}^{\mathrm{II}}$ to insoluble $\mathrm{Fe}^{\mathrm{III}}$ hydroxide at near-neutral pH is a thermodynamically favorable process owing to its relatively high negative free energy of reaction (ΔG^0_{R}) at the standard state (17). Hydrogen ions generated in the above reaction react with alkalinity present in the groundwater so that there is no appreciable change in the resultant pH. Freshly precipitated HFO particle surfaces at circumneutral pH selectively adsorb a significant portion of influent arsenic, which contains both $\mathrm{As}^{\mathrm{III}}$ and As^{V} species. The remaining arsenic in the water is removed by a bed of adsorbent media contained within the rest of the unit. The adsorbent bed, which is packed with particles in the 500- to 900-μm size range, also helps to trap and retain arsenic-laden HFO particles (78). The design of the unit thus helps to exploit the presence of dissolved iron for arsenic removal through the oxidation and subsequent precipitation of HFO particles. In most of the raw

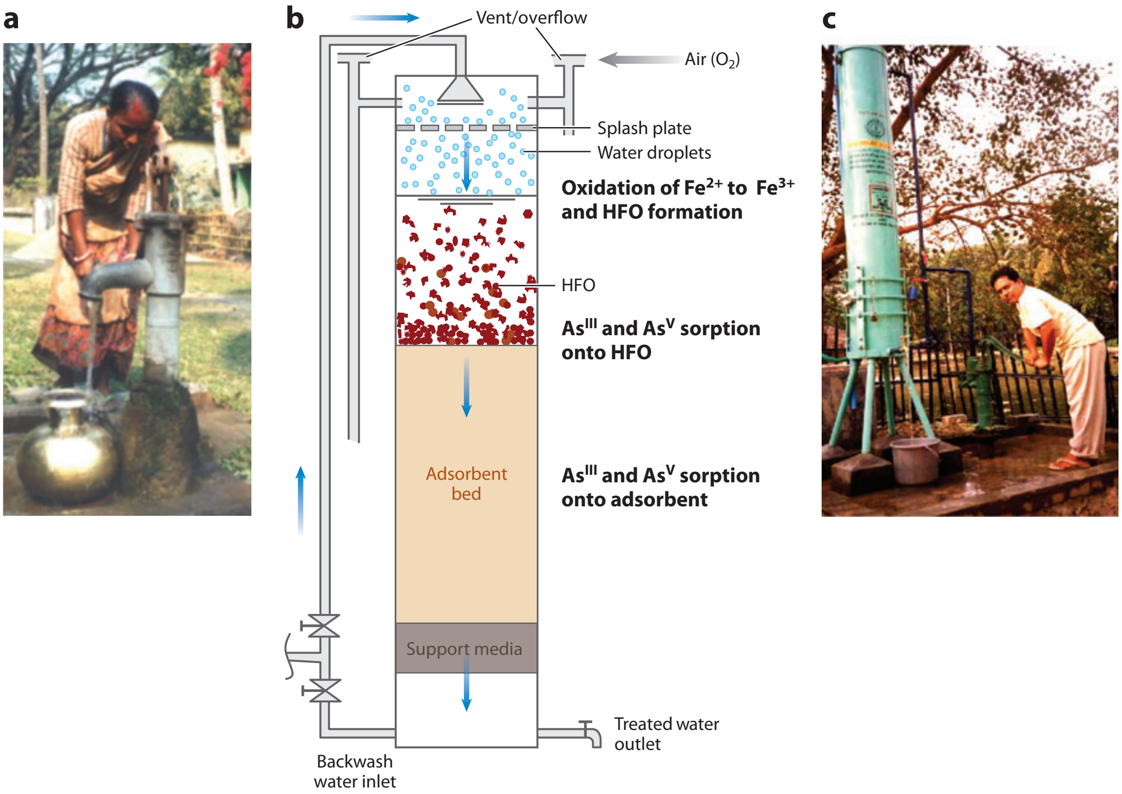

Figure 4

(*a*) Photograph of the conventional water collection method in remote villages in India. (*b*) Schematic of the arsenic removal unit. Blue arrows indicate water flow. (*c*) Photograph of the treatment unit attached to an arsenic-contaminated well. Abbreviations: HAIX, hybrid anion exchange resin; HFO, hydrated ferric oxide.

water samples, iron is present in concentrations ranging from 2–10 mg liter^{-1}, most of which is removed by the unit. As a polishing step, adsorption of arsenic takes place within the media bed of the unit. Activated alumina, which is a locally available low-cost adsorbent with high affinity for As^{V} species, has been used in most of the units. More recent installations use HAIX (82).

The water flow rate through the arsenic removal units is 10–12 liter min^{-1}. The flow rate diminishes over time owing to the precipitation of HFO particles within the bed. Backwashing of the column every other day to drive out the HFO particles is necessary to maintain a sufficient flow rate. The arsenic-laden HFO particles contained in the waste backwash are trapped on top of a coarse sand filter in the same location. The treatment units are robust and are fabricated locally with indigenous materials. These units consistently produce arsenic-safe water in a reliable manner. Details of the equipment design are available elsewhere (78, 79).

Performance of the Units

Depending on the arsenic and iron concentrations in the raw water, the arsenic removal units produce, on average, approximately 1,000,000 liters or 10,000 bed volumes of treated water before the concentration of arsenic in the treated water exceeds the maximum contaminant level (MCL), which is currently set at 50 μg liter^{-1} in India and Bangladesh. Once this occurs, the cycle is terminated, and the exhausted adsorption media is replaced by adsorption media that has been regenerated (whereupon a new cycle begins). **Figure 5*a*** presents the arsenic breakthrough history of one such treatment unit located at Habra, West Bengal, for five cycles of operation. The unit uses activated alumina as adsorbent. A new protocol for regeneration involving desorption of arsenic from the exhausted media that uses two consecutive steps of contact with NaOH solution significantly improved the regeneration efficiency in the field. The effect of the new regeneration procedure can be observed in the improved breakthrough curve in the fifth cycle. **Figure 5*b*** shows the iron breakthrough history of the unit. Owing to their unique design, the arsenic removal units are also capable of achieving a high degree of removal of dissolved iron from the raw water. **Figure 6** provides the arsenic breakthrough history of another arsenic removal unit in India in which HAIX was used as the adsorbent. HAIX is a better adsorbent than activated alumina; the underlying mechanism of its superior performance is the Donnan membrane principle, which has been discussed in detail elsewhere (76, 83). Under identical conditions, the units using HAIX have significantly longer column runs compared with the units using activated alumina. Arsenic removal units have also been installed in Cambodia. These units are functionally similar to those installed on the Indian subcontinent and use HAIX adsorbents for arsenic removal. **Figure 7*a*** shows an arsenic removal unit recently installed in Cambodia, and **Figure 7*b*** shows its arsenic breakthrough history.

Regeneration of Exhausted Media

Economy of operation is necessary for a technology to be acceptable to the masses in the developing countries. Significant savings in terms of the cost of treated water are possible when a regenerable adsorbent is used instead of a single-use adsorbent. This design philosophy is particularly true when labor and chemicals, the two major resources required for regeneration, are relatively inexpensive in developing countries. However, the regeneration procedure must be simple and easy, so that a group of trained villagers with little or no prior technical knowledge can carry out the whole regeneration process effectively. The current cost of regeneration is one-fourth of the price of fresh activated alumina and one-sixth of that of fresh HAIX. Upon exhaustion of the adsorption column, media from the unit are replaced by fresh or already regenerated media. The exhausted media are taken to a central regeneration facility. More than 200 batches of activated alumina and HAIX have been regenerated to date in the central regeneration facility by local youths trained for the purpose. An easy-to-operate stainless steel batch reactor is used for the regeneration process. The individual regeneration steps have been streamlined and are delineated in **Table 1**, which also indicates the quality of the wastewater generated in each step.

The primary reactions during regeneration of exhausted adsorbents with 2% NaOH and rinsing with dilute acid are presented below; M represents Al^{III} or Fe^{III} in activated alumina or HAIX, respectively. During regeneration at high alkaline pH (pH > 11.0),

$$\begin{aligned}
&\overline{(\equiv MOH_2^+)_2HAsO_4^{2-}} + 5OH^- \rightarrow 2\overline{\equiv MO^-} + AsO_4^{3-} + 5H_2O\\
&\overline{(\equiv MOH)HAsO_2} + 2OH^- \rightarrow \overline{\equiv MO^-} + AsO_2^- + 2H_2O\\
&\overline{\equiv MOH_2^+(H_2AsO_4^-)} + 4OH^- \rightarrow \overline{\equiv MO^-} + AsO_4^{3-} + 4H_2O.
\end{aligned} \qquad 15.$$

During protonation of the surface functional groups using dilute acid (pH < 7.5),

$$\begin{aligned}
\overline{\equiv MO^-} + 2H^+ &\rightarrow \overline{\equiv MOH_2^+}\\
\overline{\equiv MO^-} + H^+ &\rightarrow \overline{\equiv MOH}.
\end{aligned} \qquad 16.$$

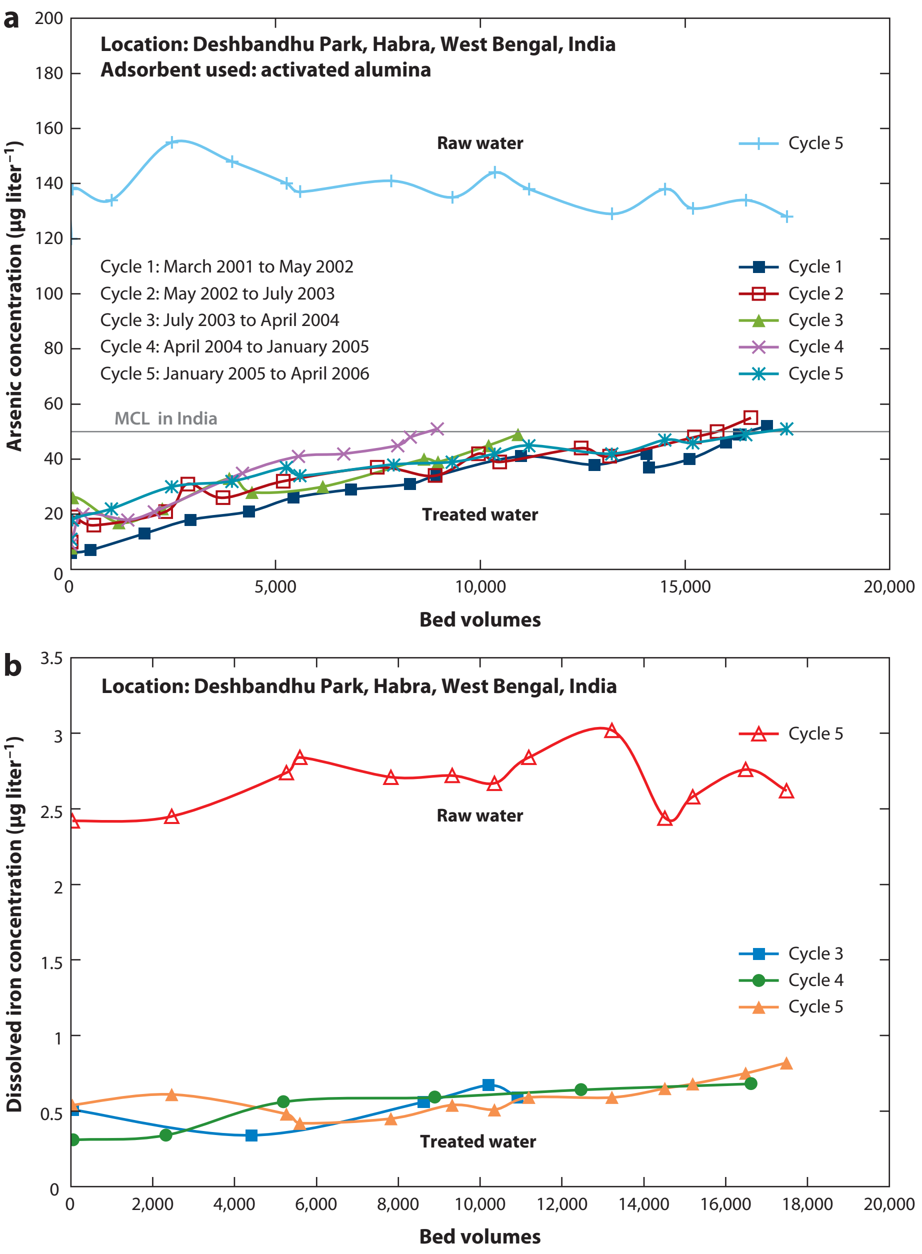

Figure 5

Breakthrough histories of (*a*) arsenic and (*b*) iron for an arsenic removal unit using activated alumina adsorbent in Habra village in West Bengal, India, over five cycles of operation. Abbreviation: MCL, maximum contaminant level.

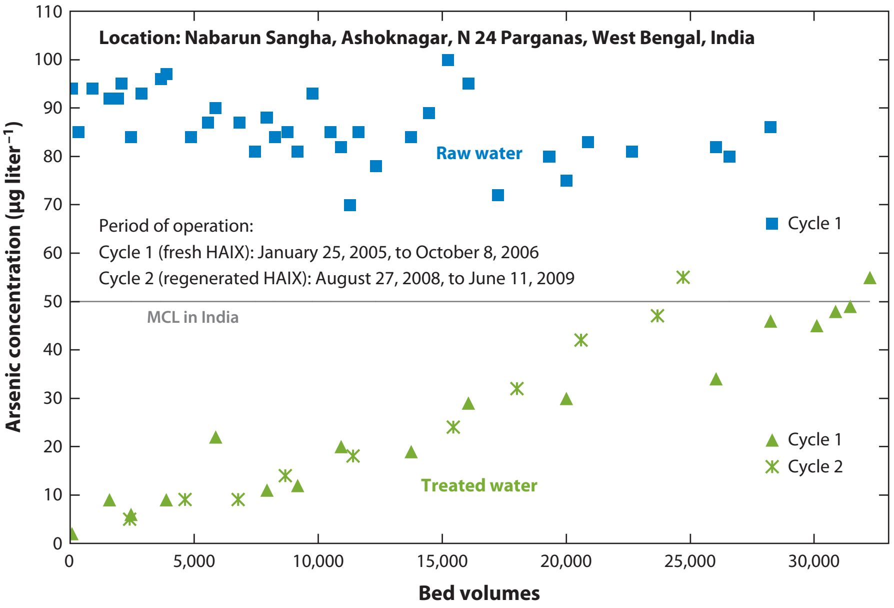

Figure 6

Arsenic breakthrough history for two cycles of an arsenic removal unit using hybrid anion exchange resin (HAIX) at Ashoknagar in West Bengal, India. Abbreviation: MCL, maximum contaminant level.

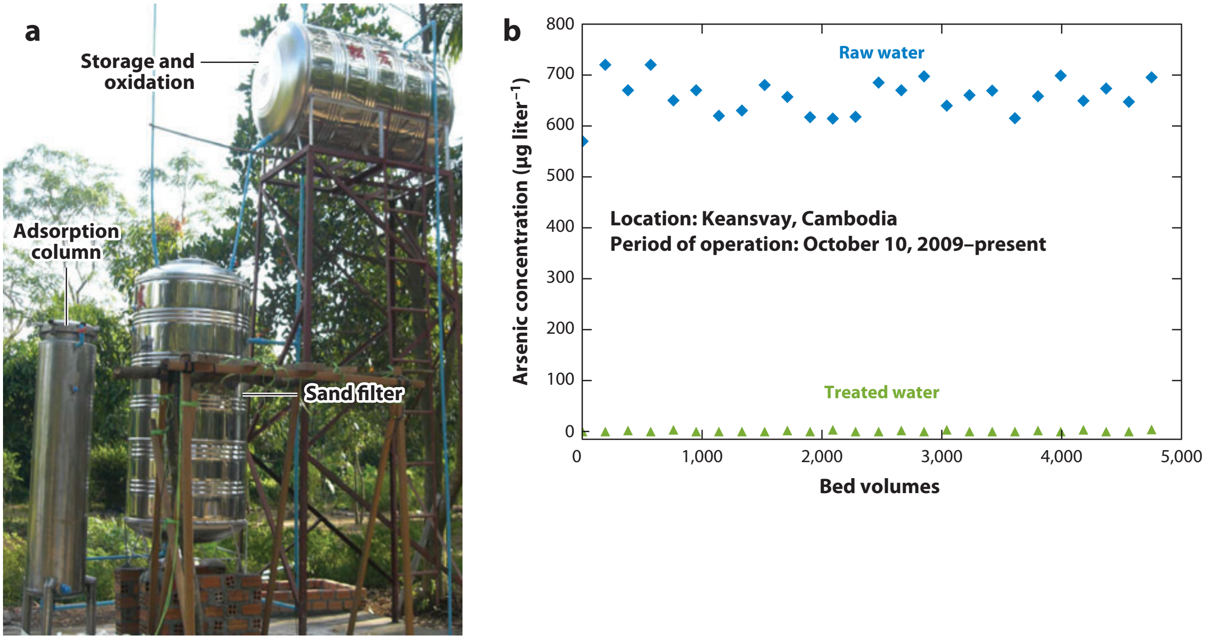

Figure 7

(*a*) An arsenic removal unit installed at Keansvay, Cambodia. (*b*) Arsenic breakthrough history of the unit.

Table 1 Steps followed and quality of wastewater generated during regeneration of a 50-kg batch of exhausted media

Steps	Solutions used/obtained	Volume (liter)	Time of contact/ agitation (min)	Approximate equilibrium pH	Arsenic (μg liter^{-1})	Total iron (mg liter^{-1})
Alkali rinse	2% sodium hydroxide	140	60	12–13	39,600	2,500
Alkali rinse	2% sodium hydroxide	140	60	12–13	11,200	245
Water rinse	Well water	100	15	12	3,700	10.5
Acid rinse	0.5 N HCl	140	15	5–6	320	2.86
Detoxification of spent regenerant	Treated spent regenerant[a]	≈520	60	6–7	120	2.8

[a] The spent regenerant and rinse solutions were collected and mixed together; $FeCl_3$ was added, and pH was adjusted. After 60 min of contact time, the arsenic in the spent regenerants coprecipitated with hydrated ferric oxide.

At high alkaline pH, the surface hydroxyl groups are deprotonated and negatively charged; as such, anionic arsenic species desorb efficiently owing to the Donnan exclusion effect (84). Subsequent rinsing with dilute acid allows the formation of protonated surface functional groups with high arsenic sorption affinity. In addition to NaOH, the regenerant for HAIX also contains NaCl at a concentration of 2% to avoid poisoning of the anion exchange sites of the hybrid adsorbent by the arsenate anions that are present at high concentrations in the spent regenerant solution.

Treatment of Spent Regenerants and Containment of Treatment Residuals

Dissolved arsenic in the spent caustic regenerant varies from 30 mg liter^{-1} to 100 mg liter^{-1}, 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 the pH to between 6.5 and 7.0, the residual dissolved arsenic concentration promptly drops to less than 150 μg liter^{-1}. All arsenic present in the spent regenerant is essentially transferred into the solid phase along with ferric hydroxide precipitate, forming a sludge of dry weight often less than 2 kg. This small volume of solid residue can be handled easily and transported to suitable disposable facilities. In contrast, use of nonregenerable adsorbent produces a treatment residual of approximately 100 kg of arsenic-rich exhausted media that poses a significant challenge for safe disposal, especially in the rural settings of the affected area. Obviously, the management of the toxic treatment residual would be more difficult if an equivalent number of household units took the place of a community unit, each one producing treatment residuals from isolated and dispersed sources. Community-scale units with regenerable adsorbent represent a sustainable approach that will prevent future crises.

The treatment plants generate residuals that are rich in arsenic. To avoid any adverse ecological impacts and human health endangerment, safe containment of the arsenic removed from the groundwater is as important as its removal to provide safe drinking water. Conventional leaching potential determination methods, such as Toxicity Leaching Test Protocol tests (85, 86), have proven to underestimate the risk of arsenic leaching from such solid wastes. A landfill or a hazardous waste site environment stimulates or enhances arsenic leaching (87, 88). In solid waste disposal facilities, both pH and redox conditions determine the speciation of arsenic and iron, which in turn control arsenic leachability. **Figure 8** shows the composite predominance or pe-pH diagram for various arsenic and iron species; pe is the negative logarithm of electron activity and is a measure of redox equilibria, pe $= -\log(e^-)$, where e^- represents an electron. The figure highlights the two predominance zones of interest: neutralized HFO sludge open to the atmosphere and sludge inside

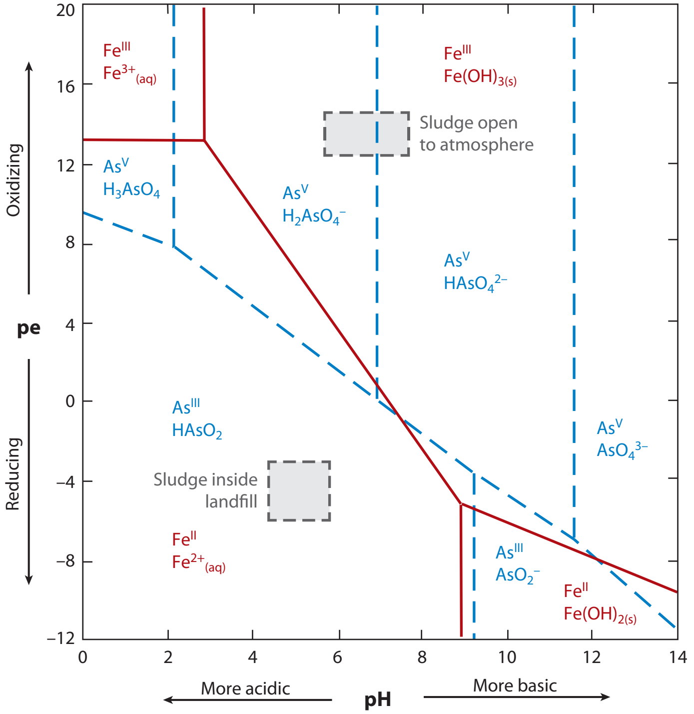

Figure 8

Composite predominance diagram for arsenic and iron species at different pe-pH conditions.

a landfill. Reduced and more soluble Fe^{II} and As^{III} are practically the sole species inside a landfill environment, where anoxic conditions prevail. In contrast, insoluble Fe^{III} and As^{V} predominate in neutralized arsenic-laden HFO sludge under aerated conditions. Thus, the arsenic-laden HFO sludge is more susceptible to rapid leaching under anoxic conditions such as those in a landfill. Conversely, the aerated conditions imposed by the atmosphere create a more stable environment that prevents any arsenic leaching.

Following the above scientific understanding, the low-volume treatment residuals from the treatment units in India are stored within a coarse sand filter chamber, the interior of which is kept well aerated using vent pipes to avoid the development of anoxic conditions (78). As the regeneration step reduces the volume of the treatment residual by more than an order of magnitude, the size of the coarse sand filter is adequate to store the contaminated treatment residuals for decades without any significant chance of leaching of arsenic. Field testing of leachate collected at the bottom of the coarse sand filter confirmed that that it does not contain a significant arsenic concentration. The leachate from the coarse sand filters at the central regeneration facility is regularly monitored for arsenic. Any accidental leaching of arsenic owing to the onset of adverse environmental conditions can therefore be contained quickly. Again, the community-based centralized system greatly simplifies the control of the residuals produced.

Socioeconomic Sustainability

Community participation has long been recognized as an effective means to help rural and urban people focus energy and mobilize resources to solve their health, environmental, and economic

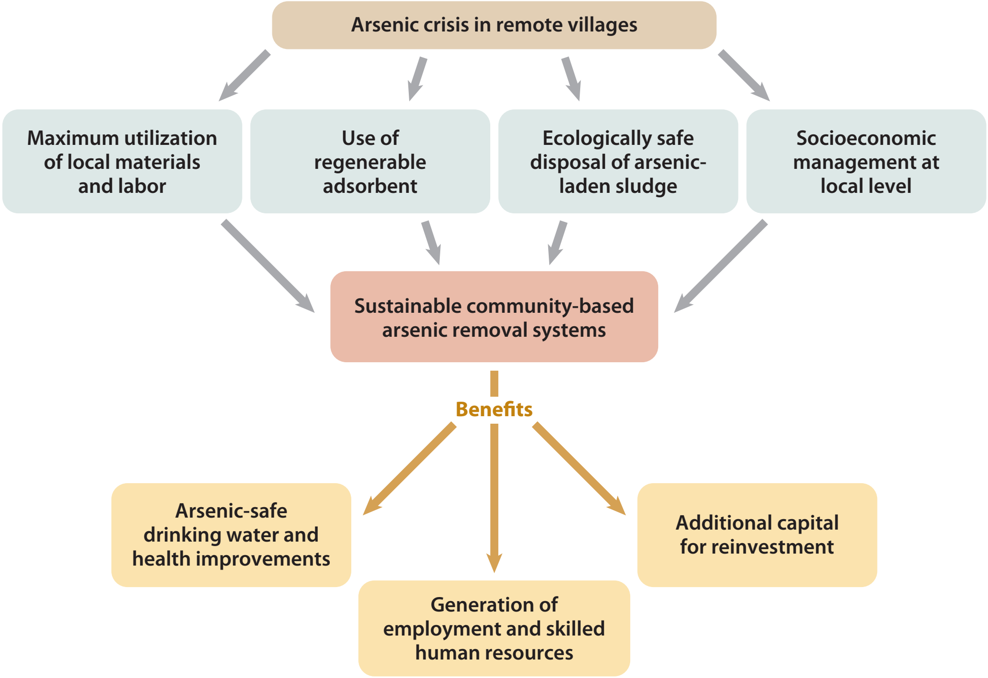

Figure 9

Relationship between the input conditions for design of a community-based arsenic removal system and the benefits obtained thereof.

problems. Community participation was ensured at every stage of the installation and operation of each of the 200 treatment units. In each location, the villagers formed a water committee to manage the treatment unit. Caretakers appointed by the villagers' committee conduct regular maintenance on the unit. Expenditures related to unit maintenance, monthly water testing, and regeneration are covered through the collection of a monthly water tariff from users. In most places, a tariff of INR 15 (equivalent to US$0.30) per family per month covers the expenses related to the unit. The users are regularly updated about the water quality, funds generated, and issues related to the management of the unit. **Figure 9** summarizes the interrelationships among the input conditions for an arsenic-affected community, the development and installation of technology, and the benefits accrued through the community-based project. The entire system, which involves the arsenic-affected community, equipment manufacturers, upkeep and maintenance personnel, and social entrepreneurs, has evolved as a viable business model in which everyone associated earns a benefit, either financial or health related. Establishment of such an enterprise ensures long-term socioeconomic sustainability for the arsenic removal systems.

CONCLUSION

Many arsenic removal technologies currently exist. As diverse as they may appear in their physical configurations, IX and/or LAB interaction are the primary arsenic removal mechanisms in each case. A sustainable engineered process for arsenic removal should have the following attributes: (*a*) effective and user-friendly; (*b*) cost-effective in terms of both capital investments and operating costs; (*c*) manufactured with locally available materials, parts, and regenerable adsorbents; (*d*) can be understood, controlled, and maintained by villagers without a high level of specific training;

(*e*) flexible and adaptable to different places and changing circumstances; and (*f*) does not pose future sustainability challenges due to leaching of arsenic from treatment residues. The arsenic removal units in India successfully incorporate all the above characteristics. The simplicity of the technology also offers opportunities for local people to be involved in the modification and innovation process. It also attracts spontaneous and active participation of end users in every aspect of the operation and upkeep of the unit. Reported natural geochemical arsenic contamination of groundwater in Vietnam, Argentina, and Mexico is similar to that on the Indian subcontinent (11, 89). Similar community-based treatment strategies with active participation of villagers may go a long way toward mitigating the arsenic crisis in these countries.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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