ARSENIC—ENVIRONMENTAL IMPACT, HEALTH EFFECTS, AND TREATMENT METHODS

1. Introduction

Arsenic, a cancer causing substance, is present in a variety of forms in soil, water, air, and food. As a naturally occurring element in the earth's crust, arsenic enters into aquifers and wells through natural activities, and to the water cycle as a result of anthropogenic activities. The four arsenic species commonly reported are arsenite [As(III)], arsenate [As(V)], monomethyl arsenic acid (MMA), and dimethyl arsenic acid (DMA). It is generally known that As(III) is more toxic than As(V) and inorganic arsenicals are more toxic than organic derivatives. In oxygen-rich environments, where aerobic conditions persist, arsenate [As(V)] is prevalent and exists as a monovalent ($H_2AsO_4^-$) or divalent ($HAsO_4^-$) anion, whereas, arsenite [As(III)] exists as an uncharged molecule (H_3AsO_3) and anionic ($H_2AsO_4^-$) species in moderately reducing environment where anoxic conditions persist (1). Despite the fact that inorganic forms are predominant in natural waters, presence of MMA and DMA has also been reported (2), and their existence is due to microbial metabolism of inorganic arsenic.

Extensive arsenic contamination of surface and subsurface waters has been reported in many parts of the world (3–10), thereby threatening the health of a number of people in the affected areas. Due to human health concerns, arsenic standard for drinking water has been lowered in many countries. Such an action might impose a considerable burden on water utilities in respect of compliance and cost, in their effort to adopt an effective technology to remove arsenic from drinking water. A better understanding of the occurrence of arsenic species in subsurface waters and their behavior in water treatment processes can assist the water utility managers to select an appropriate technology that could help to solve the problems for arsenic removal from drinking water. Furthermore, it will provide a basis for evaluating the treatment costs, and aid the researchers and epidemiologists to estimate the risk of arsenic intake by humans. This article provides the details about the occurrence of arsenic, health effects due to arsenic exposure, and available treatment technologies for arsenic removal, so that a better understanding of problems and possible solutions can be obtained.

2. Occurrence of Arsenic in the Environment

Arsenic is mainly transported to the environment by water. Arsenic contamination of subsurface waters is believed to be geological, and high arsenic concentrations in groundwater may result from dissolution of, or desorption from iron oxide, and oxidation of arsenic pyrites (8). In addition, the occurrence of arsenic in groundwater depends on factors such as redox conditions, ion exchange, precipitation, grain size, organic content, biological activity, and characteristics of the aquifer (11). The severity of arsenic pollution of groundwater is reported in Bangladesh, where most of the people rely on wells as a source of drinking water. Until recently, occurrence of arsenic in Bangladesh was believed to be due to pyrite oxidation; however, recent studies showed that the causative mechanism of arsenic release to groundwater was reductive dissolution of arsenic-rich Fe oxyhydroxide and the reduction was driven by microbial degradation of organic matter, which was present in concentrations as high as 6% C (12).

2.1. Natural Sources. The natural weathering processes contribute ~40,000 tons of arsenic to the global environment annually, while twice this amount is being released by human activities (13). The primary natural sources are weathering of rocks, geothermal, and volcanic activity; rocks are the major reservoirs for arsenic, and soils and oceans are the remaining natural sources of arsenic. Arsenic ranks twentieth in crystal abundance, and is the major constituent of at least 245 minerals (14). These minerals are mostly ores containing sulfide, along with copper, nickel, lead, cobalt, or other minerals. The most common arsenic containing minerals are arsenic pyrites (FeAsS), realgar (AsS), lollingite ($FeAs_2$, $FeAs_3$, and $FeAs_5$), and orpiment (As_2S_3). Depending on the type of rocks, arsenic concentration varies, with sedimentary rocks having a higher level of arsenic than igneous and metamorphic rocks. The average concentration of As in igneous and sedimentary rocks is 2 mg/kg, and in most rocks it ranges from 0.5 to 2.5 mg/kg (15). The mining operations of coal containing arsenic increase the potential for soil contamination with arsenic. Soils in areas close to or derived from sulfur ore deposits may contain concentrations as high as 8000-mg As/kg soil (16); however, the mean levels of As in soils are usually 5-mg As/kg soil (17). The elemental arsenic has several allotropic forms, in which only gray arsenic is stable; it is a brittle, crystalline semimetallic solid that sublimes at 615°C (1 atm) without melting. Elemental arsenic tarnishes in air and burns with a bluish flame while heating; it gives off an odor of garlic and dense white fumes of AS_2O_3 (18).

2.2. Anthropogenic Sources. Anthropogenic activities such as mining and smelting activities, and the use of pesticides and fossil fuels have resulted in a dramatic effect on natural environmental arsenic levels. In addition, arsenic and arsenic compounds are used in pigments and dyes, preservatives of animal hides and wood, pulp and paper production, electroplating, battery plates, dye and soaps, ceramics and in the manufacture of semiconductors, glass, and various pharmaceutical substances (19). Chromated copper arsenate (CCA), an inorganic arsenic compound that is used to treat lumber, accounts for ~90% of the arsenic used annually by industry in the United States. Arsenic is a contaminant of concern at 916 of the 1467 National Priorities List (superfund) of hazardous waste sites in the United States (20).

Up to the mid-1900s, inorganic compounds, usually as Pb, Ca, Mg, and zinc arsenate, were used extensively as pesticides in orchards (21). In coal, arsenic is mainly present at concentrations from <1 to >90 mg/kg. During combustion, arsenic compounds in coal are volatilized and may condense on the surface of the fly ash particles, thereby increasing the arsenic content in the fly ash. In the leaching experiments with fly ash, it was found that both As(III) and As(V) species leached from the fly ash (22). Out of the total arsenic added to the soils from anthropogenic activities, ~23% is contributed by coal fly ash and bottom ash, 14% by atmospheric fallout, 10% by mine tailings, 7% by smelters, 3% by agriculture, and 2% by manufacturing, urban, and forestry wastes (23).

3. Arsenic Exposure and Health Effects

3.1. Arsenic Exposure. All humans are exposed to low levels of arsenic through drinking water, air, food, and beverages. Consumption of food and water are the major sources of arsenic exposure for the majority of the affected people. At present a large population worldwide has been exposed significantly to high arsenic levels in drinking water. In addition, workers involved in the operations of mining and smelting of metals, pesticide production and application, production of pharmaceutical substances, and glass manufacturing have a high level of occupational exposure to arsenic (24). The use of arsenic-containing compounds such as potassium arsenite (Fowler's solution) in medical treatment for treating various illnesses caused skin and internal cancers. Though Fowler's solution is not in use at present, some arsenicals are still prescribed as medicine in Asian countries (25).

The arsenic compounds that are known to be present in food and water, and that affect the health of human individuals upon ingestion are shown in Table 1. The food products that come from the marine environment have a high level of arsenic concentration than other food products; AsB, a nontoxic arsenic species

Table 1. **Arsenicals Present in Water and Food**

arsenic compound	Chemical formula
arsenious acid [As(III)]	H_3AsO_3
arsenic acid [As(V)]	H_3AsO_4
monomethylarsonic acid (MMA)	$H_2(CH_3)AsO_3$
dimethylarsinic acid (DMA)	$H(CH_3)_2AsO_2$
trimethylarsine oxide (TMAO)	$(CH_3)_3\ AsO$
tetramethylarsonium ion	$(CH_3)_4As^+$
arsenobetaine (AsB)	$(CH_3)_3As^+$ CH_2COOH

Table 2. **Arsenic Levels in Food and Marine Species**

Food and marine species	Total As	Inorganic As	Reference
meat: beef and pork	0.15 mg/kg		28
lobsters	4.7–26 mg/kg		18
prawns	5.5–20.8 mg/kg		18
crabs	3.5–8.6 mg/kg		18
canned tuna	1100 ng/g		29
marine fish	0.19–65 mg/kg		30
shellfish	0.2–125.9 mg/kg		30
freshwater fish	0.007–1.46 mg/kg		30
fats and oils	19 ng/g		32
potatoes	2.3 μg[a]		28
rice	NR[b]	74 ng/g	32
flour	NR[b]	11 ng/g	32
spinach	NR[b]	6.1 ng/g	32
peas	NR[b]	4.5 ng/g	32
carrots	NR[b]	3.9 ng/g	32
onions	NR[b]	3.3 ng/g	32

[a] As daily dietary intake.

[b] NR = not reported.

mainly present in seafoods such as fish and shrimp, is readily excreted in the urine (26). The studies by Schoof and co-workers (27) showed that unpolished rice had a higher inorganic arsenic concentration (74 μg/kg) than corn and flour. Among the four kinds of fruits and vegetables tested, spinach and grapes had the highest inorganic As concentration. The arsenic concentration present in the food products and marine species is shown in Table 2. The Food and Drug Administration's (FDA) total diet study showed that the average adult's total arsenic intake in the United States was ~53 μg/day (31), whereas the average daily dietary ingestion of total arsenic by Canadians was estimated to be 38.1 μg (32). The characterization studies by the United States Environmental Protection Agency (USEPA) showed that ~20 percent of the daily intake of dietary arsenic was in the inorganic form (31). Upon ingestion of inorganic arsenicals, it is methylated in the human body and the metabolites of ingested arsenic are eliminated by the kidney and excreted in urine within 1–3 days. DMA is the predominant metabolite excreted in urine and faeces of animals and humans exposed to inorganic arsenic (33).

3.2. Arsenic Toxicity and Health Effects. Arsenic is considered as a notorious poison because of its toxicity. The carcinogenic effect of arsenic compounds was first noted in the eighteenth century, when patients treated with arsenicals were found to have an unusual number of skin tumors (34). The toxicity of arsenic depends on its speciation. The toxicity of arsenite is 25–60 times higher than that of arsenate (35), and the toxicity decreases in the order of arsine > inorganic As(III) > organic As(III) > inorganic As(V) > organic As(V) > arsonium compounds and elemental arsenic. Recent studies (35, 36) showed that arsenite was more prevalent in groundwater than arsenate. Ingestion of inorganic arsenic can result in both cancer (skin, lung, and urinary bladder) and non-cancer effects (26). Acute and chronic toxicity due to the drinking of arsenic contaminated water has been well documented through population-based studies that showed the capacity of arsenite [As(III)] and arsenate [As(V)] to adversely affect numerous organs in the human body (3,10,37).

3.3. Cancer Effects.

The people living in Asian, South American, and Mexican countries with exposure to high level of arsenic concentration in drinking water are reported to have increased risks of skin, bladder, and lung cancer. The association of arsenic in drinking water and skin cancer was first reported in Taiwanese people (3). The Taiwanese study population was large, numbering 40,421 inhabitants in 37 villages. The results of the studies showed that prevalence of skin cancer was noted among the people; high incidence of skin cancer was observed among the elderly people (age >60 years). Based on the Taiwanese data, the USEPA estimated the lifetime risk of developing skin cancer as 1 or 2 per 1000 people for each microgram of inorganic arsenic per liter of drinking water (28). Recently, National Research Council (NRC) has stated that the total cancer risk due to the consumption of drinking water with 50-μg/L arsenic will be 1 in 100 (26).

An additional strong evidence that drinking arsenic-contaminated water causes cancer is from Chile, where the population studied was nearly 10 times larger than that of the Taiwanese study population. In Northern Chile, nearly 7.3% of all deaths among those aged 30 years and over were due to internal cancers (bladder and lung cancer) caused by drinking arsenic contaminated water (37). In both the Taiwanese and Chilean studies, the people were exposed to a high level of arsenic (>500 μg/L) in drinking water. Increased risks of bladder and lung cancer were noted among men and women in Argentina, even though the average arsenic concentration was 170 μg/L (38).

3.4. Non-Cancerous Effects.

Non-cancerous effects have been reported in humans after exposure to drinking inorganic arsenic contaminated water. Inorganic arsenic in drinking water may affect many organs including central and peripheral nervous systems, dermal, cardiovascular, gastrointestinal, and respiratory systems. The most common ailments such as keratoses and hyperpigmentation may occur after 5–15 years of arsenic exposure equivalent to 700 μg/day for a 70 kg adult (26). Hyperpigmentation was the most common ailment (183.5/1000) among the affected people in Taiwan (3). Further, long-term exposure to high inorganic arsenic in drinking water caused black foot disease in Taiwan.

Dermatitis, a skin lesion of arseniasis is prevalent in Bangladesh; an increased prevalence of bronchitis has also been observed among the exposed populations in Bangladesh (7). A recent survey conducted by the Dhaka Community Hospital (DCH) in 80% of the total area of Bangladesh showed that people were affected with melanosis (93.5%), keratosis (68.3%), hyperkeratosis (37.6%), dipigmentation (39.1%), and cancer (0.8%) (10). Data from the population based and clinical case studies showed that there was a dose-response relationship for ingested arsenic water and several non-cancerous effects (26).

4. Arsenic Determination

In the past, measurement of total elemental concentrations was considered to be sufficient for environmental considerations. Since the element occurs in different species and the species have different properties, a determination of total concentration of an element alone may not provide adequate information about the physical/chemical forms of the element and its toxicological properties. Therefore, it is essential to determine the individual species of an element, enabling one to obtain realistic information about the toxicity and transformation of the species. The term speciation refers to the determination of different oxidation states of an element that prevail in a certain specimen or to the identification and quantification of the biologically active compounds to which the element is bound (39).

The presence of As(III) and As(V) in different proportions in water supplies may produce different toxic effects. Often it is documented in the literature that the measurement of total arsenic concentration is insufficient to assess the risks of As exposure in human populations. Several instrumental methods have been used to determine the concentration of arsenic and its species. Such methods include hydride generation atomic absorption spectrometry (GF−AAS), graphite furnace atomic absorption spectrometry (HG−AAS), inductively coupled plasma (ICP−AES), ICP−mass spectrometry (ICP−MS), and high-performance liquid chromatography (HPLC). A number of techniques are available for the speciation of arsenic; recently Edwards and co-workers (40) established an arsenic speciation protocol that can be applied to water treatment plant in situ.

Ficklin (41) used the anion exchange resin of 100−200 mesh size and a glass column in speciating arsenite and arsenate present in samples. One percent HCl was used to acidify the samples before resin treatment. Edwards and co-workers (40) used an anion exchange resin of 50−100 mesh size, and 0.05% H_2SO_4 (v/v) to acidify the samples before resin treatment; the column (polypropylene) used was twice in diameter compared to that of Ficklin (41). Thirunavukkarasu and co-workers (42) used a speciation protocol (Fig 1) similar to that of Edwards and co-workers (40) except that samples were acidified with nitric acid (trace metal grade) instead of sulfuric acid. Speciation recovery studies of samples preserved with nitric acid showed that recoveries of As(III) were in the range of 81.2−105.2%. Further, speciation studies with a natural water sample showed that the particulate and soluble arsenic contributed 11.4 and 88.8% of the total arsenic present in the natural water, respectively. The fractions of As(III) and As(V) present in the soluble arsenic were 47.3 and 52.7%, respectively (42).

5. Treatment Technologies for Arsenic Removal

Various treatment methods have been reported in the literature to remove arsenic effectively from the drinking water. Such treatment methods include coagulation/filtration (43−50), adsorption on activated alumina (51−57), adsorption on activated carbon (52), adsorption on ion-exchange resin (41,57,58), adsorption on hydrous ferric oxides (59−62), adsorption on various iron oxides (42,63−67), and adsorption/filtration by manganese greensand (68, 69). After careful review, the USEPA suggested ion-exchange, activated alumina, reverse osmosis, modified coagulation/filtration, and modified lime softening as the best available technologies (BAT) based on arsenate removal; however, it put forth the importance on iron-based coagulation assisted microfiltration, iron oxide-coated sand (IOCS), manganese greensand filtration, and granular ferric hydroxide (GFH)

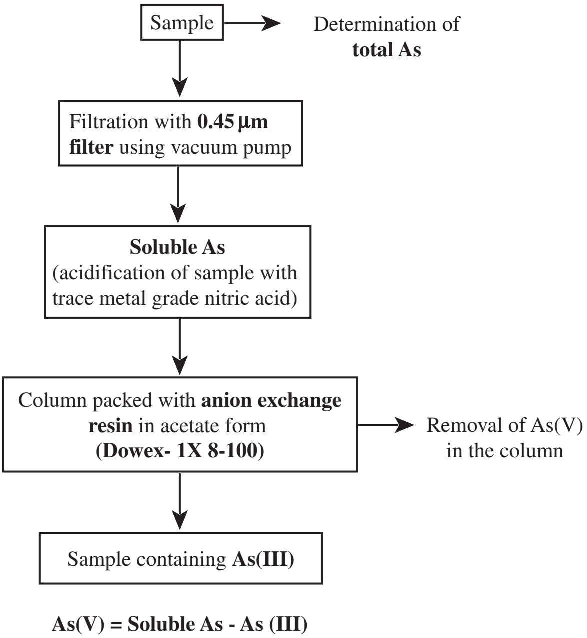

Fig. 1. Arsenic speciation protocol (42).

for arsenic removal, for which rigorous testing is necessary to validate the technologies (31,70). The removal efficiencies of the BATs are shown in Table 3.

The selection of an appropriate treatment process for a specific water supply system will depend on many factors such as concentration of arsenic, source water composition of other constituents, pH, and cost effectiveness. Though coagulation/filtration is a simple method, the disadvantages are the production of large amounts of sludge-containing arsenic (hazardous in nature) that will pose serious problems for safe disposal. In recent years, there has been an overwhelming research effort to develop an innovative technology to achieve a low level of arsenic in drinking water supplies. Iron salts are generally added as coagulants in conventional treatment processes. At a particular pH, the iron forms precipitates, referred to as Fe oxides, which are good adsorbents for As removal.

Table 3. **The Removal Efficiencies of the Best Available Technologies (USEPA 2000)**

Treatment technology	Maximum percent removal[a]
ion exchange	95
activated alumina	90
reverse osmosis	>95
modified coagulation/filtration	95
modified lime softening	80
electrodialysis reversal	85

[a] Percent removals based on As(V) removal.

Since adsorption processes are most effective, and iron compounds are widely available, it is obvious that iron-based material should be investigated in detail for arsenic removal from drinking water. Fixed-bed treatment systems, such as adsorption and ion-exchange, are getting increasingly popular for arsenic removal in small-scale treatment systems because of their simplicity, ease of operation and handling, regeneration capacity and sludge-free operation.

5.1. Arsenic Removal by the Coagulation/Filtration Process. Coagulation/filtration processes are mainly used in large-scale water utilities. It is a simple treatment process, in which chemicals are added to form precipitate or flocs that are removed by a subsequent sedimentation or filtration process. Based on the type and initial concentration of the contaminant, either precipitation or coprecipitation or both play an important role in the removal during coagulation (71). Alum and iron(III) salts are mainly used as coagulants in drinking water treatment for arsenic removal, and numerous studies have been conducted to evaluate the performance of these coagulants, especially for arsenic removal. In a coagulation process, arsenic removal is dependent on adsorption and coprecipitation of arsenic onto metal hydroxides (48).

In both the laboratory and field coagulation experiments, ferric chloride produced the best arsenic removal compared to ferrous and aluminum sulfate (43). In laboratory experiments, arsenic removal (82%) obtained with ferric chloride was nearly 2.5 times higher than the removal achieved with aluminum sulfate. Based on experimental results, Gulledge and O'Connor (44) reported that As(V) adsorption on ferric hydroxide exceeded the adsorption on aluminium hydroxide, and an increased coagulant dosage resulted in an increase in arsenic removal. In the pH range of 5–7, $>90\%$ removal of As(V) was achieved with a 30-mg/L dose of ferric sulfate. The results of these studies showed that ferric chloride coagulation achieved better removal in the pH range studied than alum coagulation. Similarly, the results of the studies by Sorg and Logston (45) showed that ferric sulfate achieved a better arsenic removal than alum in the pH range of 5–8.

Arsenate removal from groundwater by iron and alum coagulation/filtration treatment showed that iron coagulation was more effective than alum, and the removals achieved using iron coagulants were not pH dependent between 5.5 and 8.5 (46). In these studies, nearly 100% removal was achieved with iron coagulants (30 mg/L) in the entire pH range, when the raw-water initial arsenate concentration was 300 μg/L. Cheng and co-workers (47) concluded that for the source waters tested, enhanced coagulation was effective for arsenic removal and less ferric chloride than alum, on a mass basis, was needed to achieve the same removal. Also, in the studies with ferric chloride, pH between 5.5 and 7.0 had no significant effect on arsenate removal.

Edwards (48) reported that As(III) removal by coagulation was primarily controlled by the coagulant dose and was relatively unaffected by the solution pH. It was also found that ferric coagulants were effective in the removal of As(V) at $\mathrm{pH} < 7.5$, and iron was more effective than alum in removing both As(V) and As(III) at $\mathrm{pH} > 7.5$. The data compiled by Edwards (48) showed that >90 percent arsenate removal was achieved in the coagulation studies, when ferric chloride was used at >20 mg/L or alum at >40 mg/L. Scott and co-workers (49) reported that arsenic removal of 81–96% was achieved when source water was treated with 3–10 mg/L of ferric chloride, and concluded that ferric chloride was more effective than alum in removing arsenic.

In the coagulation experiments with ferric chloride over the pH range of 4.0–9.0, Hering and co-workers (50) observed that pH had no significant effect on arsenate removal, and nearly 100% arsenate removal was achieved in the entire pH range studied. However, they observed that pH did have an effect on arsenite removal in the studies. They also demonstrated that using ferric chloride as a coagulant at pH 7.0, both arsenite and arsenate removals were independent of the initial concentration.

5.2. Arsenic Removal by Activated Alumina. Activated alumina (AA) treatment is a physical/chemical process by which ions in the drinking water are removed by the oxidized AA surface. Activated alumina treatment is considered to be an adsorption process, even though the reactions involved in the process involve actually an exchange of ions. Several studies have demonstrated that AA is an effective treatment for the removal of arsenic from drinking water. However, factors such as pH, competing ions, arsenic oxidation state, and empty bed contact time (EBCT) have significant effects on the removal of arsenic using AA (57).

The highest arsenic removal was achieved at a pH closer to 6 (53), and arsenic removal decreased as the pH increased beyond 6 (56). In contrast, the results of the studies by Vagliasindi and co-workers (58) showed that arsenate adsorption onto AA was relatively insensitive to pH in the range of 5.5–8.5. The studies conducted by Frank and Clifford (54) observed that the bed volumes achieved for up to an effluent arsenate level of 50 μg/L were high compared to the bed volumes achieved for arsenite removal, which indicated arsenate adsorption was faster than arsenite adsorption.

Similarly, in both the laboratory and pilot plant studies (57), the bed volumes achieved for arsenate removals were higher than for arsenite removal, and this was mainly due to the oxidization of As(III) to As(V). In the pilot plant studies on arsenic removal using AA (56), the results showed that arsenic run length was directly proportional to EBCT, and high bed volumes were achieved at high EBCTs. Further, it was observed that at a pH of 7.5 the arsenic removal capacity of AA to 10-μg/L arsenic varied between 0.19- and 0.35-g As/kg AA at different EBCTs. The presence of sulfate and chloride had a significant effect on arsenic removal using AA (53), whereas the results of the studies by Vagliasindi and co-workers (58) showed that presence of sulfate had little effect on arsenate adsorption and the presence of chloride had no effect on arsenate adsorption.

5.3. Arsenic Removal by Ion-Exchange. Although ion exchange is an efficient treatment system for arsenic removal from drinking water, its application is limited to small and medium scale point-of-entry (POE) systems because of its high treatment cost as compared to other treatment technologies (72). Ion-exchange is an ion selective process, which removes As(V) significantly but does not remove As(III). It is an effective process for arsenic removal, if the source water contains <500-mg/L total dissolved solids and <150-mg/L sulfate; preoxidation of As(III) to As(V) is necessary (57).

The factors that affect the efficiency of the ion-exchange process include competing ions such as sulfate and total dissolved solids, EBCT and regenerant strength (57). In the ion exchange studies for arsenic removal, Vagliasindi and Benjamin (73) found that high bed volumes were achieved at high EBCTs for different source waters tested. The results of the column studies showed that the column continued to run for longer time until arsenate breakthrough occurred. However, they reported that the treatment efficiency was affected by the source water composition, and the presence of sulfate drastically reduced the adsorption capacity of the resin. In the batch studies using an ion exchange resin, Vagliasindi and co-workers (58) reported that arsenate adsorbed strongly onto the resin, when the source water had the lowest total organic carbon and sulfate among the different source waters tested.

5.4. The Role of Iron Oxides in Arsenic Removal. Iron oxides, oxyhydroxides, and hydroxides (all are called iron oxides) consist of Fe in association with O and/or OH. They differ in composition, in the nature of Fe, and in crystal structure. The basic structural unit of all Fe oxides is an octahedran, in which each Fe atom is surrounded either by six O or by both O and OH ions. The O and OH ions form layers that are either approximately hexagonally close-packed (hcp), or cubic close-packed (ccp). The hcp forms are termed as α-phases, and ccp forms are termed as γ-phases. The α-phases are more stable than γ-phases (74).

There are 16 iron oxides, and these iron oxides play an important role in a variety of industrial applications, including pigments for the paint industry, catalyst for industrial synthesis, and raw material for iron and steel industry (74). The application of iron oxide has been extended to remove metals from water and wastewater (63,75). Arsenic removal with iron oxides had been investigated (59–69,42). It is generally assumed that arsenate [As(V)] has a stronger affinity than arsenite [As(III)] on iron oxide surfaces. However, recent studies by Raven and co-workers (65) showed that at high initial As concentration, arsenite adsorption on ferrihydrite was higher than arsenate adsorption throughout the pH range of 3.0–11.0. They used a suspension containing a known amount of ferrihydrite to study the removal of As(III) and As(V) in synthetic water. Pierce and Moore (59) reported that adsorption of As(III) onto amorphous ferric hydroxide increased with pH up to a maximum pH of 7.0. Pierce and Moore (60) found that the rate of adsorption of As(V) onto amorphous ferric hydroxide was much faster than that of As(III) in the initial phase (1h) of contact with the adsorbent. They also recommended that for maximum arsenic removal, pH 7.0 was optimum for As(III) and pH 4.0 was optimum for As(V).

In the studies using hydrous ferric hydroxide (HFO) for arsenic removal, Hsia and co-workers (61) observed that the amount of As(V) adsorbed onto the iron oxide surface increased as the equilibrium concentration of arsenate in the solution increased. They also reported that at high initial As(V) concentration, nearly 100% of arsenate was adsorbed over the pH range of 4.0–9.0. In similar batch studies with HFO, Wilkie and Hering (62) found that As(V) was adsorbed stronger than As(III), and the adsorption of As(III) over the pH range of 4.0–9.0 was not strongly dependent on pH. They reported that adsorption of As(III) onto HFO increased as the pH increased up to a maximum at pH 7.0, whereas complete As(V) removal was observed over the pH range examined in the studies with the solution, which had an initial arsenic [As(III) or As(V)] concentration of 1.33 μM and a background electrolyte of 0.01 M $NaNO_3$. In a separate study, the initial arsenic concentration was varied from 0.033 to

1.33 μM and they reported that As(III) adsorption was high (maximum removal of 96%) at a low initial As(III) concentration, and one of the reasons was attributed to the partial oxidation of As(III) on HFO surface.

In the column studies using IOCS, Joshi and Chaudhury (64) reported that the bed volumes achieved at the value of 10 μg/L for arsenic in drinking water were in the range of 163–184 and 149–165 per cycle for As(III) and As(V), respectively. They added that 94–99% of arsenic was recovered at the end of each cycle during regeneration, and virtually no iron was detected in the effluent. The rate of influent feed maintained in the tests performed by Joshi and Chaudhury (64) was low, and insufficient while scaling up to pilot or small water facilities. Thus, the performance of IOCS will be different and have an impact on the arsenic removal efficiency at normal filtration rates that are being maintained in water facilities.

Benjamin and co-workers (63) studied the removal of arsenite in the column studies by using IOCS as an adsorbent. The influent had an initial As(III) concentration of 75 μg/L and an EBCT of 5 min was maintained in the column studies. They reported that the column removed 100% arsenite up to 650 bed volumes treated, which indicated extreme binding capacity of arsenite onto IOCS. In kinetic studies using IOCS prepared in a high temperature coating process, the results showed that 85–90% of arsenic was removed in the initial phase (1 h) of contact, and >95% removal was obtained for both As(III) and As(V) in the pH range of 5.0–7.6 after 6 h of contact (67). It was also reported that the bed volumes achieved up to 5 μg/L of As(III) in the effluent were 1380 in the column studies (Fig 2), and the column continued to remove As(III) to a value <5 μg/L for a period of 50 h, where the influent had an arsenite [As(III)] concentration of 300 μg/L. Driehaus and co-workers (66) reported that the results obtained

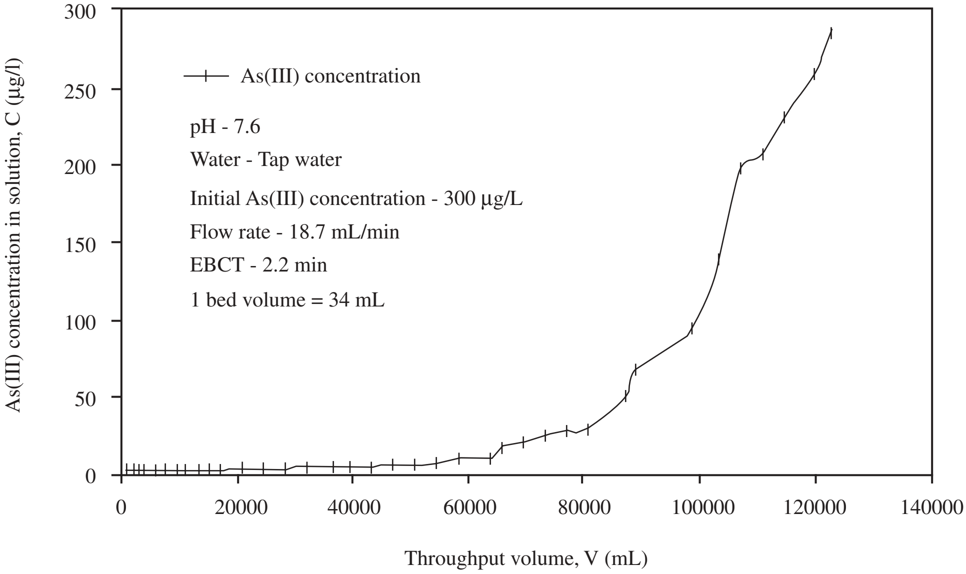

Fig. 2. Arsenite concentration remaining in solution in the column studies (1 bed volume = 34 mL) (67).

from the fixed adsorber tests with GFH for arsenic removal were encouraging, and nearly 30000 bed volumes were treated with the effluent As concentration at 10 μg/L.

Recent studies (42,63–67) showed that iron-based materials are effective in reducing arsenic to a low level in drinking water, which indicated that filtration systems containing iron-based materials offer an excellent choice among the treatment systems available for arsenic removal in small water facilities. Though the use of GFH to remove arsenic from drinking water was proven to be successful at pilot-scale facilities in Germany (66), the detailed cost economics has to be worked out while extending the applicability of GFH to small water facilities. On the other hand, IOCS filtration systems that are tested at the laboratory-scale level (42,63,64,67) may offer the best choice in respect of arsenic removal efficiency and cost economics, for which testing is necessary at the pilot-scale level. In addition, conducting experiments at various initial arsenic concentrations [both As(III) and As(V)] using IOCS is necessary to study the effect of initial arsenic concentration on the adsorptive capacity of IOCS, and arsenic adsorption behavior. Further research and evaluation is required to develop cost-effective treatment technologies for arsenic removal, especially for rural communities in developing countries. Research is also needed to develop and integrate environmentally acceptable disposal of treatment system residuals into the overall treatment philosophy.

6. Legislation and Economic Aspects

The World Health Organization (WHO) standard for arsenic has been lowered from 50 to 10 μg/L. The German drinking water standard had been lowered to 10 μg/L, and the Commission of European Community is aiming at a standard of 2–20 μg/L (Driehaus and co-workers 1998). The existing arsenic standard for drinking water in Canada and Australia is 25 and 7 μg/L, respectively. Recently, USEPA adopted a new arsenic standard for drinking water at 10 μg/L after an additional review by the National Academy of Sciences (76). Since the majority of the affected people worldwide live in small communities, it is essential to develop an appropriate treatment technology that would solve the problems for small communities. Simplicity and cost are the two major factors that should influence the selection of a treatment system for arsenic removal in small communities dependent on groundwater for their drinking water supply. Though several technologies were proven to be successful in the removal of arsenic from drinking water at laboratory and pilot-scale studies, the practical applicability of such systems to small communities has not been fully tested and exploited.

Although coagulation-assisted microfiltration, ion exchange systems may be suitable for large communities, systems based on adsorption/filtration process are appropriate and advantageous to small communities, especially in developing countries such as Bangladesh, because of simplicity, ease of construction, cost-effectiveness, and operation and maintenance. Currently, simple household purification systems such as bucket filtration systems containing sand and iron fillings are used in most of the arsenic affected areas in Bangladesh as short-term measures; however, permanent measures are necessary.

BIBLIOGRAPHY

1. J. F. Ferguson and J. Gavis, *Water Res.*, **6**, 1259 (1972).
2. R. S. Braman and C. C. Foreback, *Science*, **182**, 1247 (1973).
3. W. P. Tseng, H. M. Chu, S. W. How, J. M. Fong, C. S. Lin, and S. Yeh, *J. Nat. Cancer Inst.*, **40**, 453 (1968).
4. M. E. Cebrian, A. Albores, M. Aguilar, and E. Blakely, *Human Toxicol.*, **2**, 121 (1983).
5. A. Chatterjee, D. Das, B. K. Mandal, T. Roy Chowdhry, G. Samanta, and D. Chakraborti, *Analyst*, **120**, 643 (1995).
6. S. Niu, S. Cao, and E. Shen, in C. O. Abernathy, R. L. Calderon, and W. R. Chappell, eds., *Arsenic exposure and health effects*, Chapmann and Hall, London, pp. 78–83, 1997.
7. R. K. Dhar, B. K. Biswas, G. Samanta, B. K. Mandal, D. Chakraborti, S. Roy, A. Jaffer, A. Islam, G. Ara, S. Kabir, A. W. Khan, S. A. Ahmed, and S. A. Hadi, *Curr. Sci.*, **73**, 48 (1997).
8. A. H. Welch, D. R. Helsel, M. J. Focazio, and S. A. Watkins, in W. R. Chappell, C. O. Abernathy, and R. L. Calderon, eds., *Arsenic exposure and health effects*, Elsevier Science, Elmsford, N. Y., pp. 9–17 1999.
9. I. Koch, J. Feldman, L. Wang, P. Andrewes, K. J. Reimer, and W. R. Cullen, *The Sci. Total Environ.*, **236**, 101 (1999).
10. M. M. Karim, *Wat. Res.*, **34**, 304 (2000).
11. F. N. Robertson, *Environ. Geochem. Health*, **11**, 171 (1989).
12. R. T. Nickson, J. M. McArthur, P. Ravenscroft, W. G. Burgess, and K. M. Ahmed, *Appl. Geochem.*, **15** 403 (2000).
13. C. R. Paige, W. J. Snodgrass, R. V. Nicholson, and J. M. Scharer, *Water Environ. Res.*, **68**, 981 (1996).
14. E. A. Woolson, in B. A. Fowler, ed., *Biological and environmental effects of arsenic*, Elsevier Science, Elmsford, N. Y., pp. 51 1983.
15. A. Kabata-Pendias, and H. Pendias, *Trace elements in soils and plants*, CRC press, Boca Raton, Fl., pp. 315, 1984.
16. I. Thornton, and M. Farago, in C. O. Abernathy, R. L. Calderon, and W. R. Chappell, eds., *Arsenic exposure and health effects*, Chapmann and Hall, London, pp. 1–16, 1997.
17. ATSDR, Agency for Toxic Substances and Disease Registry, Toxicological profile for arsenic, U.S. Public Health Service, Atlanta, Ga, 1997.
18. K. A. Francesconi, and J. S. Edmonds, in J. O. Nriagu, ed., *Arsenic in the Environment, Part 1: Cycling and Charecterization*, John Wiley & Sons, Inc., New York, pp. 189–219, 1994.
19. J. M. Azcue and J. O. Nriagu, in J. O. Nriagu, ed., *Arsenic in the Environment, Part 1: Cycling and Charecterization*, John Wiley & Sons, Inc., New York, pp. 1–15, 1994.
20. ATSDR, Agency for Toxic Substances and Disease Registry, Toxicological profile for arsenic, U.S. Public Health Service, Atlanta, Ga., 1998.
21. D. Chisholm, *Can. J. Plant. Sci.*, **52**, 584 (1972).
22. V. T. Breslin and I. W. Duedall, *Mar. Chem.*, **13**, 341 (1983).
23. D. K. Bhumbla and R. F. Keefer, in J. O. Nriagu, ed., *Arsenic in the Environment, Part 1: Cycling and Charecterization*, John Wiley & Sons, Inc., New York, pp. 51–82 1994.

24. U.S. Public Health Service, Toxicological profile for arsenic, U.S. Public Health Service, Washington D.C., 1989.
25. R. E. Grissom, C. O. Abernathy, A. S. Susten, and J. M. Donohue, in W. R. Chappell, C. O. Abernathy, and R. L. Calderon, eds., *Arsenic exposure and health effects*, Elsevier Science, Elmsford, N. Y., pp. 51–60, 1999.
26. National Research Council, Arsenic in drinking water, National Academy Press, Washington, D.C., 1999.
27. R. A. Schoof and co-workers, in W. R. Chappell, C. O. Abernathy, and R. L. Calderon, eds., *Arsenic exposure and health effects*, Elsevier, New York, pp. 81–88, 1999.
28. USEPA, Special report on ingested inorganic arsenic, EPA/625/3-87/013, Washington, D.C. 1988.
29. L. J. Yost, R. A. Schoof, and R. Aucoin, *Human Ecol. Risk Assess.*, **4**, 137 (1998).
30. J. M. Donohue and C. O. Abernathy, in W. R. Chappell, C. O. Abernathy, and R. L. Calderon, eds., *Arsenic exposure and health effects*, Elsevier Science, Elmsford, New York, pp. 89–98 1999.
31. USEPA, http://www.epa.gov/safewater/arsenic.html (June 22, 2000).
32. R. W. Dabeka and co-workers, *J. AOAC Int.*, **76**, 14 (1993).
33. M. Vahter, in W. R. Chappell, C. O. Abernathy, and C. R. Cothern, eds., *Arsenic exposure and health*, Science and Technology Letters, Northwood, pp. 171–180, 1994.
34. J. Hutchinson, *Br. Med. J.*, **2**, 1280 (1887).
35. N. E. Korte and Q. Fernando, *Crit. Rev. Environ. Control*, **21**, 1 (1991).
36. D. K. Chada, in P. Bhattacharya and A. H. Welch, eds., *Proceedings of the 31st International Geological Congress, Arsenic in groundwater of sedimentary aquifers*, Rio de Janeiro, Brazil, pp. 33–35, 2000.
37. A. H. Smith, M. Goycolea, R. Haque, and M. L. Biggs, *Am. J. Epidemiol.*, **147**, 660 (1998).
38. A. Hopenhayn-Rich, M. L. Biggs, A. H. Smith, *Int. J. Epidemiol.*, **27**, 561 (1998).
39. M. Burguera and J. L. Burguera, *Talanta*, **44**, 1581 (1997).
40. M. Edwards, S. Patel, L. Mcneill, H. W. Chen, M. Frey, A. D. Eaton, R. C. Antweiler, and H. E. M. Taylor, *J. AWWA*, **90**, 103 (1998).
41. W. H. Ficklin, *Talanta*, **30**, 371 (1983).
42. O. S. Thirunavukkarasu, T. Viraraghavan, and K. S. Subramanian, *Water Qual. Res. J. Can*, **36**, 55 (2001).
43. Y. S. Shen, *J. AWWA*, **65**, 543 (1973).
44. H. J. Gulledge and T. J. O'Connor, *J. AWWA*, **65**, 548 (1973).
45. T. J. Sorg and G. S. Logsdon, *J. AWWA*, **70**, 379 (1978).
46. T. J. Sorg, *Proc. of the AWWA WQTC*, Denver, Colorado, 1993.
47. R. C. Cheng, S. Liang, H. C. Wang, and M. D. Beuhler, *J. AWWA*, **86**, 79 (1994).
48. M. Edwards, *J. AWWA*, **86**, 64 (1994).
49. N. K. Scott, F. J. Green, D. H. Do, and J. S. McLean, *J. AWWA*, **87**, 114 (1995).
50. J. G. Hering, P. Y. Chen, J. A. Wilkie, M. Elimelech, and S. Liang, *J. AWWA*, **88**, 155 (1996).
51. E. Bellack, *J. AWWA*, **63**, 454 (1971).
52. S. K. Gupta and K. Y. Chen, *J. Water Poll. Control Fedn.*, **50**, 493 (1978).
53. E. Rosenblum and D. Clifford, EPA-600/52-83-107, Cincinnati, Ohio, (1984).
54. P. Frank and D. Cifford, EPA-600-52-86/021, Cincinnati, Ohio (1986).
55. S. W. Hathway and J. F. Rubel, *J. AWWA*, **79**, 61 (1987).
56. J. Simms and F. Azizian, *Proceedings of the AWWA WQTC*, Denver, Colo, 1997.
57. D. A. Clifford, in R. D. Letterman, ed., *Water quality and treatment, AWWA*, McGraw-Hill Book Co. Inc., 5th ed., New York, 1999.
58. F. G. A. Vagliasindi, M. Henley, N. Schulz, and M. M. Benjamin, *Proceedings of the AWWA WQTC*, Denver, Colorado, pp. 1829–1853, 1996.

59. L. M. Pierce and B. C. Moore, *Environ. Sci. Technol.*, **14**, 214 (1980).
60. L. M. Pierce and B. C. Moore, *Wat Res.*, **16**, 1247 (1982).
61. T. H. Hsia, S. L. Lo, C. F. Lin, and D. Y. Lee, *Colloids Surfaces A: Physicochem. Eng. Aspects.* **85**, 1 (1994).
62. J. A. Wilkie and J. G. Hering, *Colloids Surfaces A: Physicochem. Eng. Aspects.* **107**, 97 (1996).
63. M. M. Benjamin, R. S. Sletten, R. P. Bailey, and T. Bennet, *Wat Res.*, **30**, 2609 (1996).
64. A. Joshi and M. Chaudhuri, *J. Environ. Eng.*, **122**, 769 (1996).
65. K. P. Raven, A. Jain, and R. H. Loeppert, *Environ. Sci. Technol.*, **32**, 344 (1998).
66. W. Driehaus, M. Jekel, and U. Hildebrandt, *J. Water SRT - Aqua*, **47**, 30 (1998).
67. T. Viraraghavan, O. S. Thirunavukkarasu, and K. S. Subramanian, in M. M. Sozanski, ed., *Proceedings of the Fourth International Conference on Water Supply and Water Quality*, Krakow, Poland, pp.1013 2000.
68. K. S. Subramanian, T. Viraraghavan, T. Phommavong, and S. Tanjore, *Water Qual. Res. J. Can.*, **32**, 551 (1997).
69. T. Viraraghavan, K. S. Subramanian, and J. A. Aruldoss, *Wat Sci. Tech.*, **40**, 69, (1999).
70. USEPA, Technologies and costs for removal of arsenic from drinking water, Draft report, EPA-815-R-00-012, Washington D.C., 1999.
71. L. D. Benefield and J. S Morgan, R. D. Letterman, ed., *Water quality and treatment AWWA*, McGraw-Hill Book Co., Inc., 4th ed., New York, 1990.
72. USEPA, Arsenic removal from drinking water by ion exchange and activated alumina plants, EPA/600/R-00/088, Cincinnati, Ohio, 2000.
73. F. G. A Vagliasindi and M. M. Benjamin, *Proceedings of the AWWA annual conference*, Denver, Colorodo, 1997.
74. R. M. Cornell and U. Schwertmann, *The iron oxides-structure, properties, reactions, occurrence and uses*, VCH Publishers, New York, 1996.
75. M. Edwards and M. M. Benjamin, *J. Water Poll. Control Fedn.*, **61**, 1523 (1989).
76. USEPA, http://www.epa.gov/safewater/arsenic.html (October 31, 2001).

O. S. THIRUNAVUKKARASU
T. VIRARAGHAVAN
University of Regina