

## Chapter-5

# **Technological Options and Arsenic Removal Technologies**

Technological options to combat arsenic menace, in groundwater, to ensure supply of arsenic free water, in the affected areas, can be one of the followings or a combination of all:

- i) In-situ remediation of arsenic from aquifer system,
- ii) Ex-situ remediation of arsenic from tapped groundwater by arsenic removal technologies,
- iii) Use of surface water source as an alternative to the contaminated groundwater source,
- iv) Tapping alternate safe aquifers for supply of arsenic free groundwater.

In-situ remediation of arsenic from aquifer system or decontamination of aquifer is the best technological option. However, in-situ remediation of arsenic contaminated aquifer would not only be an exercise of throwing stone in the dark but would also be very expensive and a difficult task because of the size of the plan and the absence of complete understanding of the physico-chemical and geochemical processes and behavior of aquifer system,.

Ex-situ remediation of arsenic from tapped groundwater, by suitable removal technologies, seems to be a short-term option to provide potable arsenic free groundwater for domestic use only. But this would prove expensive and unsustainable for supply of irrigation water. Nevertheless, ex-situ technologies can only remove the arsenic from tapped groundwater but not from the aquifer system. Most of the existing efforts are relied on ex-situ remediation of arsenic, which have various degrees of success and failure as well. The advantage of this approach is that it can be located on site.

Although the use of surface water sources, as an alternative to the supply of treated contaminated groundwater, seems to be a logical proposition, it would require availability and supply of surface water flow and organized water supply system for ensuring supply of both drinking and irrigation water. To meet requirement of potable water in arsenic affected areas, this approach can prove to be a potential alternative in areas having thick populace. Based on this approach, Government of West Bengal has developed some schemes to supply drinking water to some of the arsenic affected areas.

Tapping alternate safe aquifers, for supply of arsenic free groundwater, could also prove to be a logical proposition. This has also been explored in many areas on a local scale. However, this approach would require extensive studies and analyses for mapping of groundwater availability, freshwater reserves and to examine mobilization of arsenic in the aquifer, both on spatial and temporal scale, due to forcing perturbation.

Out of the above options, arsenic removal technologies and ex-situ treatment technique are being practiced widely both in India and Bangladesh, to provide potable water to the people in the arsenic affected areas after treatment of contaminated groundwater. Their large scale use in West Bengal, based on different operating principles, with various degrees of success and failure, has been reported. The subsequent sections give details of scientific and technical know how about arsenic removal technologies from water and their effectiveness.

## **5.1 Scientific Standing of Arsenic Treatment Technologies**

A variety of treatment technologies, based on oxidation, co-precipitation, adsorption, ion-exchange and membrane process, have been developed and are available for removal of arsenic from contaminated water. However, question, regarding the efficiency and applicability/appropriateness of the technologies, remains, particularly because of low influent arsenic concentration and differences in source water composition. Some of these methods are quite simple, but the disadvantage, associated with them, is that they produce large amounts of toxic sludge. This needs further treatment before disposal into the environment, besides the sustainability of these methods in terms of economic viability and social acceptability.

Many of these technologies can be reduced in scale and conveniently applied at household and community level, for the removal of arsenic from groundwater. During the last few years, many small scale arsenic removal technologies have been developed, field tested and used in various countries including India. Various technologies available for removal of arsenic from contaminated water are based mainly on five principles:

- i) **Oxidation and filtration**
- ii) **Co-precipitation:** Oxidation of As (III) to As (V) by adding suitable oxidizing agent followed by coagulation, sedimentation and filtration (co-precipitation).
- iii) **Adsorption:** Activated Alumina, Iron filings (zero valent iron) and hydrated iron oxide.
- iv) **Ion exchange** through suitable action and anion exchange resins.
- v) **Membrane technology:** Reverse osmosis, nanofiltration and electrodialysis.

Arsenic is normally present in groundwater in As (III) and As (V) states in different proportions. Most treatment methods are effective in removing arsenic in pentavalent state and, hence, include an oxidation step as pretreatment to convert As (III) to As (V). Following oxidizing agents are used for conversion of As (III) to As (V):

- Oxygen (process is very slow),
- Powdered active carbon and dissolved oxygen (catalytic oxidation),
- UV irradiation,
- Chemicals (free chlorine, hypochlorite, bleaching powder, ozone, permanganate, hydrogen peroxide etc.), and
- Sunlight.



Although, As (III) can be oxidized to As (V) by various methods like oxygen, catalytic oxidation, UV irradiation, chemicals (free chlorine, hypochlorite, bleaching powder, ozone, permanganate, hydrogen peroxide, etc.) and sun light, air oxidation of arsenic is very slow and can take weeks for oxidation (Pierce and Moore, 1982). Chlorine dioxide and monochloramine are ineffective in oxidizing As (III) to As (V). Ultraviolet (UV) light, by itself, is also ineffective. However, if the water is spiked with sulfite, UV photo-oxidation shows promise for As (III) conversion (Ghurye and Clifford, 2001). Based on these considerations, only chlorine, permanganate and ozone are effective oxidizing agents for oxidizing As (III) to As (V), over wide range of working condition.

## 5.2 Conventional Technologies

The arsenic removal devices developed by different agencies, and applied to treat for removing arsenic from arsenic contaminated groundwater with some degree of success are given in **Table 5.1** and shown in **Figure 5.1**.

**Table 5.1:** Arsenic removal devices applied for removal of arsenic from contaminated groundwater

Name of the device	Operation principle	Filter media	Price	System	Performance
RPM/ Alcan AAFS -50 media by RPM Marketing Pvt. Ltd., Kolkata	Adsorption	Activated Alumina + AAFS-50.	Rs.44,300 + Rs.20,000 per charge.	The purification system consists of two containers; one to remove mud and suspended particles and other one consists of AAFS-50 media to remove arsenic and heavy metal	•Although design and model is user friendly but has mixed feelings on performance. Media replacement had showed lesser efficiency than the original.
Bucket of Resins (BOR) of Water Systems International USA by Harmonite Impex (Pvt.) Ltd., Kolkata.	Ion Exchange	Bucket of Resins	Rs.92,300 + Rs.39,000 per charge	The unit 'BOR' is a rectangular container of 40 inches long, 26 inches wide, and 40 inches height attached to a tube well hand pump. The container consists of 3 cylinders to process various phases of oxidation and absorption. The system has provision of backwashing depending on content of arsenic and iron.	Field performance of the system was below satisfactory level and inconsistent.
Granular Ferric Hydroxide (GFH) of Pal Trockner (P) Ltd., Kolkata – a German Technology	Adsorption	Granular Ferric Hydroxide (GFH)	Rs. 74,100 + Rs.25,000 per charge	The system is based on GFH and user friendly. It does not require complicated dosing of chemicals and claimed to be non-toxic and non-hazardous.	Satisfactory performance, and less cost on operation and maintenance.
Arsenic Removal Plant by Oxide India (Catalysts) Pvt. Ltd, Durgapur	Adsorption	Activated Alumina, AS-37	Rs. 47,300 + Rs.14,400 per charge	The system is made of Stainless Steel, AISI-304. It has a back wash system and removal process is based on adsorption with special grade of Activated Alumina. It also removes heavy metal, Fluoride, Nitrate, Grease and Oils.	Satisfactory performance in all 50 installed places. Company guarantees 2 years O & M, training including performance.
ADHIACON : AFDWS 2000 – Arsenic Removal Plant	Catalytic precipitation/ Electron Exchange	AFDWS - 2000	Rs. 75,000	The unit is fitted with lifted head of hand pump. It has basically three chambers - primary, secondary and Micro-filtration chambers. The water is pumped through 3 way valve to primary chamber where raw water	Field performance of the system was below satisfactory level.

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				first passes through a coarse stainless steel strainer and then comes in contact with filter media in which catalytic precipitation takes place. The purified water from the primary chamber goes to secondary chamber for downward filtration. From secondary chambers water passes through micro-filtration chamber and then purified water goes through three way valve at the outlet.	
Handpump Attached Arsenic Removal Plant by AIHH&PH, Kolkata	Oxidation + Coagulation + Flocculation/ Precipitation and filtration	Chlorinating agent (BP) + Ferric Alum	Rs. 35,000 + periodic chemical reagents	The system is comprised of a non-mechanical clari-flocculator and up-flow gravel filter and it has three chambers. Bleaching powder and alum are the two chemicals used for removal of arsenic. In the first chamber bleaching powder solution is added in appropriate dosage with pumped water where they are thoroughly mixed in presence of baffles. The chemical mixed water is thereafter passed through second chamber for precipitation of the flocs. The clean water is collected in the launder chamber. From launder water is taken to the filter (third) chamber, from where water is allowed to flow in upward direction through graded gravel media. The arsenic safe filtered water is finally collected through a tap provided in the filtered chamber.	Periodic daily dosing of chemical reagents are necessary. The system requires constant vigilance and close monitoring and chemical dosing.
IONOCHEM, Kolkata	Ion exchange	Ferric Hydroxide	Rs. 39,000	The system is comprised of one Iron Removal Filter and one Arsenic Filter and the system is fitted with Hand Pump The principal media is bonded compound of $Fe(OH)_3$ and $\beta FeOOH$ . When Hand Pump is operated, the pressurized raw water is passed initially through iron removal filter filled with catalytic filtering media and reacts with sodium arsenates and $Fe(OH)_2$ . Due to chemisorption AS is bonded with the material and Arsenic is removed.	Regular backwashing of iron filter is essential, which caused problem of operation and maintenance. Otherwise, the performance remained satisfactory.
Apyron Arsenic Treatment Units by Apyron Technologies (P) Ltd. Representing of Apyron Technologies Inc., USA	Adsorption	Aqua Bind (Activated Alumina + )	Rs. 80,000 + Rs. 15,000 per charge	The system is comprised of an assembly of Handpump with its outlet connected to the filtering media. When the Hand Pump is operated, the raw water passes through the filter media where arsenic is removed and finally treated water is collected through an outlet pipe from the filter media. The filter media is comprised of manganese oxide and activated alumina. Manganese oxide converts $As^{3+}$ to $As^{5+}$ , which is adsorbed on the alumina media. The unit also removes iron.	Showed satisfactory performance, treating arsenic levels as high as 3500 ppb to a safe level of less than 50 ppb. After use, filter media can be disposed safely as ordinary sanitary waste.
Public Health Engineering Department, Govt. of West Bengal	Adsorption	Red Hematite ( $Fe_2O_3$ ) lumps + quartz + sand activated alumina	Rs. 27,000	Removal of arsenic is accomplished in 4 chambers. Groundwater is abstracted by Hand Pump and spray into droplets over a bed containing packed hematite lumps ( $Fe_2O_3$ ) before sending to first chamber for sedimentation. Sediment free water is conveyed through chambers placed in series containing red hematite lumps.	Reported as one of the finest performing devices and capable to remove arsenic from very high level of contamination. However, the weakness is its inability to produce



				quartz and dual media (Sand-Activated Alumina), respectively.	sufficient quantity of filtered water. Towards O & M, it had poor performance.
Simple Arsenic and Iron Removal System by School of Fundamental Research (SFR), Kolkata	Adsorption	Aluminum Silicate + Ferric Hydroxide	Rs. 8000 + Rs.1200 per charge	The system is fitted to Hand Pump, which connected through the check valve with a vertical PVC cylinder filled with silicate matrix with additional oxidizing element for removal of iron before water enters into As-removal system.	Performance of the system is yet to be established through field testing.

Despite having numerous arsenic removal devices, which have been developed, based on different working principles, very few plants could show satisfactory performance at the field level, both in terms of arsenic removal efficiency and in sustainable running. The major setbacks, with most of the devices, remain with the operation, maintenance, replacement and removal of used filters. The systems in O & M have been linked to the responsibility of suppliers, and they have shown satisfactory performance. Out of the above arsenic removal technologies, only a few could prove satisfactory performance at the field level like Granular Ferric Hydroxide (GFH) of Pal Trockner (P) Ltd., Kolkata - a German Technology, Arsenic Removal Plant by Oxide India (Catalysts) Pvt. Ltd, Durgapur, and Apyron Arsenic Treatment Units by Apyron Technologies (P) Ltd. representing Apyron Technologies. It is to be mentioned that the efficiency, effectiveness and sustainability of arsenic removal technologies depend on: (i) how simple the devise is in use, and operation & maintenance? (ii) What is its removal efficiency? (iii) How much is the outflow rate and cost? (iv) How eco-friendly the device is? and (v) what mechanism in operation and maintenance is devised ?

In addition to the above devices, a number of other devices can be seen to be developed and applied in other countries. However, all the technologies are primarily based on five principles of arsenic removal: oxidation, co-precipitation, adsorption, ion-exchange and membrane process. Scientific details of these five operating principles and their different applications are explained here.

### 5.2.1 Oxidation and Filtration

Oxidation and filtration normally refer to the processes that are designed to remove naturally occurring iron and manganese from water. These processes involve the oxidation of the soluble forms of iron and manganese to their insoluble forms and then removal by filtration. If arsenic is present in the water, it is removed via two primary mechanisms: adsorption and co-precipitation. First, soluble iron and As (III) are oxidized. The As (V) then adsorbs onto the iron hydroxide precipitation that are ultimately filtered from solution.

The arsenic removal efficiency is strongly dependent on the initial iron concentration and the ratio of iron to arsenic. In general, the Fe: As mass ratio should be at least 20:1. These conditions customarily result in an arsenic removal efficiency of 80-95%. In some cases, it may

be appropriate to add ferric coagulant, in the beginning of the iron removal process, to optimize arsenic removal.

The effectiveness of arsenic co-precipitation, with iron, is relatively independent of source water pH, in the range 5.5 to 8.5. However, high levels of organic matter, orthophosphates and silicates, weaken arsenic removal efficiency by competing for sorption sites on iron hydroxide precipitates (Fields et al., 2000a, b).

**In-situ Oxidation:** In-situ oxidation of arsenic and iron in the aquifer was tried under DPHE-Danida Arsenic Mitigation Pilot Project in Bangladesh. The aerated tube well water was stored in a tank and released back into the aquifers, through the tube well, by opening a valve in a pipe connecting the water tank to the tube well pipe under the pump head. The dissolved oxygen content in water oxidizes arsenite to less mobile arsenate and also the ferrous iron in the aquifer to ferric iron causing a reduction in arsenic content of tube well water. Experimental results showed that arsenic in the tube well water following in-situ oxidation has been reduced to about half due to underground precipitation and adsorption on ferric iron.

**Solar Oxidation:** SORAS is a simple method of solar oxidation of arsenic in transparent bottles to reduce arsenic content from drinking water. The Department of Sanitary Engineering of AIHH&PH, Kolkata has studied the efficacy of arsenic removal by solar oxidation and precipitation and achieved 85 to 95% arsenic removal. The method is only applicable if the iron content in the groundwater exists beyond permissible level so as to adsorb the arsenate from water. Wegelin et al. (2000) have also used solar oxidation to reduce arsenic content of drinking water. Ultraviolet radiation can be used to catalyze the process of oxidation of arsenite in the presence of other oxidants like oxygen (Young, 1996). Experiments in Bangladesh have shown that the process on average could reduce arsenic content of water to about one-third.

**Passive Sedimentation:** Passive sedimentation also received considerable attention because of rural people's habit of drinking stored water from pitchers. Oxidation of water, during collection and subsequent storage in houses, may cause a reduction in arsenic concentration in stored water (Bashi Pani). Experiments, conducted in Bangladesh, showed zero to high reduction in arsenic content by passive sedimentation. Arsenic reduction, by plain sedimentation, appears to be dependent on water quality particularly the presence of precipitating iron in water. Ahmed et al. (2000) have shown that more than 50% reduction in arsenic content is possible by sedimentation of tube well water containing 380-480 mg/L of alkalinity as  $\text{CaCO}_3$  and 8-12 mg/L of iron. But this cannot be relied upon to reduce arsenic to desired level. Most studies showed a reduction of zero to 25% of the initial concentration of arsenic in groundwater. In rapid assessment of technologies, passive sedimentation has failed to reduce arsenic to the desired level (BAMWSP, DFID, Water Aid, 2001).



### **5.2.2 Co-precipitation**

Co-precipitation has been the most frequently used method to treat arsenic contaminated water in numerous pilot- and full-scale applications. This technology can typically reduce arsenic concentrations to less than 50 µg/L and in some cases below 10 µg/L. In order to remove arsenic by co-precipitation, coagulant is to be added. Water treatment with coagulants, such as alum [Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.18H<sub>2</sub>O], ferric chloride [FeCl<sub>3</sub>] and ferric sulfate [Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.7H<sub>2</sub>O], are effective in removing arsenic from water. Ferric salts have been found to be more effective in removing arsenic than alum on a weight basis and effect over a wider range of pH. In both cases, pentavalent arsenic can be more effectively removed than trivalent arsenic. The following steps are involved in the co-precipitation process for removal of arsenic:

- Addition of bleaching powder / hypochlorite,
- Addition of alum / ferric sulphate,
- Rapid mixing of chemical followed by slow mixing,
- Sedimentation, and
- Filtration.

In the coagulation-flocculation process, aluminum sulfate or ferric chloride or ferric sulfate is added and dissolved in water by stirring for few minutes. Aluminum or ferric hydroxide micro-flocs are formed rapidly. The water is, then, gently stirred for few minutes for agglomeration of micro-flocs into larger easily settable flocs. During this flocculation process, all kinds of micro-particles and negatively charged ions are attached to the flocs by electrostatic attachment. Arsenic is also adsorbed onto coagulated flocs. As trivalent arsenic occurs in non-ionized form, it is not subject to significant removal. Oxidation of As (III) to As (V) is, thus, required as a pretreatment for efficient removal. This can be achieved by addition of bleaching powder (chlorine) or potassium permanganate. The following three chemical precipitation processes are normally used:

- i) Enhanced Lime Softening,
- ii) Conventional Gravity Coagulation/Filtration, and
- iii) Coagulation Assisted Micro-filtration.

#### **5.2.2.1 Enhanced Lime Softening**

Lime softening is a chemical-physical treatment process used to remove calcium and magnesium from solution. The addition of lime increases the pH of solution, thereby, causes a shift in the carbonate equilibrium and the formation of calcium carbonate and magnesium hydroxide precipitates. These precipitates are amenable to removal by clarification and filtration.

Lime softening solely, for arsenic removal, is uneconomical and is generally considered cost-prohibitive. However, for water systems that use lime softening to reduce hardness, the

process can be enhanced for arsenic removal. To remove As (V), additional lime is added to increase the pH value above 10.5 units. In this range, magnesium hydroxide precipitates and As (V) is removed by co-precipitation with it. As (V) removal by co-precipitation, with calcium carbonate (i.e., below a pH of 10.5), is poor (less than 10%).

The amount of waste residual, produced by lime softening, is dependent on the hardness removed. While the total volume of waste, produced from lime softening, is typically higher than that produced by coagulation/filtration and co-precipitation processes, the arsenic concentration, in the sludge, is generally lower because more solids are produced. Prior to disposal, this waste residual will require thickening and dewatering, most likely via mechanical devices. Previous studies have indicated that typical lime sludge should not exceed toxicity characteristics limits, enabling it to be disposed in a municipal solid waste landfill (Fields et al., 2000a, b).

### ***5.2.2.2 Conventional Gravity Coagulation/Filtration***

Coagulation is the process of destabilizing the surface charges of colloidal and suspended matter to allow agglomeration of particles. This process results in the formation of large, dense floc, which is amenable to removal by clarification or filtration. The most widely used coagulants for water treatment are aluminum and ferric salts, which hydrolyze to form aluminum and iron hydroxide particles, respectively.

Conventional gravity coagulation/filtration processes use gravity to push water through a vertical bed of granular media, that retains the floc and are typically used within surface water treatment plants. They are less commonly used for treatment of groundwater supplies as these sources usually contain much lower concentrations of suspended solids, organic carbon and pathogenic microorganisms. Installation and operation of a conventional gravity coagulation/filtration process, solely for arsenic removal, is uneconomical.

Coagulation/filtration processes can be optimized to remove dissolved inorganic As (V) from water. The mechanism involves adsorption of As (V) to an aluminum or ferric hydroxide precipitate. The As (V) becomes entrapped as the particle continues to agglomerate. As (III) is not effectively removed because of its overall neutral charge under natural pH conditions. Therefore, pre-oxidation is recommended. The efficiency and economics of the system are contingent upon several factors, including the type and dosage of coagulant, mixing intensity and pH. In general, however, optimized coagulation-filtration systems are capable of achieving over 90% removal of As (V) and producing water with less than 5 µg/L of As (V). Influent As (V) levels do not appear to impact the effectiveness of this treatment process.

Iron-based coagulants, including ferric sulfate and ferric chloride, are more effective for removing As (V) than that of aluminum-based. This is because iron hydroxides are more stable than aluminum hydroxides, in the pH range 5.5 to 8.5. A fraction of the aluminum, which remains as a soluble complex, is incapable of adsorbing As (V) and this can pass through the filtration



stage. The optimal pH ranges for coagulation, with aluminum and ferric salts, are 5 to 7 and 5 to 8, respectively. At pH values above 7, the removal performance of aluminum-based coagulants drops markedly. Feed water pH should be adjusted to the appropriate range, prior to coagulant addition. Post-filtration pH adjustment may be necessary to optimize corrosion control and comply with other regulatory requirements.

Several batch studies have demonstrated that As (V) removal is positively related to coagulant dosage. However, specific dose requirements, needed to meet As (V) removal objectives, were contingent upon the source water quality and pH. Effective coagulant dosage ranges were 5-25 mg/L of ferric chloride and as much as 40 mg/L of alum.

### **5.2.2.3 Coagulation Assisted Micro-filtration**

Coagulation-assisted micro-filtration uses the same coagulation process described above. However, instead of the granular media filtration step, the water is forced through a semi-permeable membrane by a pressure differential. The membrane retains the As (V) laden floc formed in the coagulation step.

The use of pre-engineered coagulation assisted microfiltration package plants is a realistic possibility for new installations, where water quality precludes the use of sorption treatment. The membrane must be periodically backwashed to dislodge solids and restore hydraulic capacity. Backwash water is typically a high-volume, low solids (less than 1.0%) waste stream. The specific amount of solids will depend on several factors, including coagulant type, dosage, filter run length and ambient solids concentration.

The co-precipitation technique for removal of arsenic has been applied in the following systems:

- Central Arsenic Removal Plant (ARP) attached with tube wells for piped water supply,
- Arsenic Removal Plant (ARP) attached with Hand Pump, and
- Domestic Arsenic Removal Units using Earthen Pots, Plastic Buckets, Bucket Treatment Units, Modified BTUs, Stevens Institute Technology, Fill and Draw Units, Naturally Occurring Iron, Chemical Packages, etc.

### **5.2.3 Adsorption**

Adsorption technology has been widely used to treat groundwater and drinking water containing arsenic. The technology can reduce arsenic concentrations to less than 50 µg/L in general and in some cases even below 10 µg/L. Its effectiveness is sensitive to a variety of untreated water contaminants and characteristics. It is used less frequently than precipitation/co-precipitation technologies, and is most commonly used to treat groundwater and drinking water.

In adsorption technology, solutes (contaminants) concentrate at the surface of a sorbent, thereby, reducing their concentration in the bulk liquid phase. The adsorption media is usually packed into a column. Contaminants are adsorbed, as the contaminated water is passed through the column. When adsorption sites get filled, the column must be regenerated or disposed of and replaced with new media.

Several adsorbents are available for removal of arsenic from water, viz., activated alumina, activated carbon, iron and manganese coated sand, kaolinite clay, hydrated ferric oxide, activated bauxite, titanium oxide, silicon oxide and many natural and synthetic ones. The efficiency of sorptive media depends on the use of oxidizing agent as aids to sorption of arsenic. Saturation of media, by different contaminants and components of water, takes place at different times of operation, depending on the specific sorption affinity of the medium to the given component.

Adsorption is probably the most prospective technology for removal of arsenic. It largely depends on capital cost, operation and maintenance cost, operational procedure and user-friendliness. The following media are commonly used for removal of arsenic through adsorption technique:

- i) Activated alumina (AA),
- ii) Activated Carbon (AC),
- iii) Iron Based Sorbents (Granular Ferric Hydroxide, Iron Coated Sand, etc.),
- iv) Indigenous Filters, and
- v) Cartridge Filters.

#### **5.2.3.1 Activated Alumina (AA)**

Activated Alumina (AA),  $Al_2O_3$ , is a porous, granular material having good sorption properties. The media, aluminum trioxide, is prepared through the dehydration of aluminum hydroxide at high temperatures. AA grains have a typical diameter of 0.3 to 0.6 mm and a high surface area for sorption. Activated alumina is commonly used to remove arsenic from drinking water and ground water (EPA, 2000a, b). The reported adsorption capacity of AA ranges from 0.003 to 0.112 grams of arsenic per gram of AA. It is available in different mesh sizes and its particle size affects contaminant removal efficiency. Up to 23,400 bed volumes of wastewater can be treated before AA requires regeneration or disposal and replacement with new media.

When water passes through a packed column of activated alumina, the impurities including arsenic present in water are adsorbed on the surfaces of activated alumina grains. The selectivity of AA towards As (III) is poor, owing to the overall neutral molecular charge at pH levels below 9.2. Therefore, pre-oxidation of As (III) to As (V) is critical. Several different studies have established the optimum pH range as 5.5-6.0, and demonstrated greater than 98% arsenic removal under these conditions. AA column runs operated under acidic pH conditions are 5 to 20 times longer than under natural pH conditions (6.0-9.0).



Several constituents can interfere with the adsorption process, either by competing for adsorption sites or clogging the media with particulate matter. The presence of suspended solids in the feed water could gradually clog the media and, therefore, pre-filtration is recommended for sources where the turbidity exceeds 0.3 NTU.

Activated Alumina media can either be regenerated on-site or disposed of and replaced with fresh media. Regeneration of saturated alumina is carried out by exposing the medium to 4% caustic soda, NaOH, either in batch or by flow, through the column, resulting in high arsenic contaminated caustic waste water. On-site regeneration of AA media produces 37 to 47 bed volumes of caustic soda waste (EPA, 2000a, b) generally. The residual caustic soda is, then, washed out and the medium is neutralized with 2% solution of sulfuric acid rinse. During the process, about 5-10% alumina is lost and the capacity of the regenerated medium is reduced by 30-40%. The activated alumina needs replacement after 3-4 regeneration. Like coagulation process, pre-chlorination improves the column capacity dramatically.

Activated Alumina is a low cost chemical (Rs. 100/- to Rs. 110/- per kg.) and it can be regenerated by washing with acid and alkali. It has a useful life expectancy and after which fresh activated alumina will replace the exhausted alumina. Bengal Engineering College, Shibpur, has developed both hand pump attached model and domestic model. A good number of hand pumps attached arsenic removal plants, with activated alumina as adsorbent, have been installed in West Bengal through various initiatives.

The technologies and market for alumina-based adsorptive media are continuously expanding. There are several emerging proprietary media, commonly referred to as modified AA, which contain alumina in a mixture with other substances such as iron and sulfur. In some instances, these media have greater overall adsorptive capacities, enhanced selectivity towards arsenic, and/or greater overall operational flexibility than conventional AA, thus, making them more cost-effective. Some of the activated alumina based sorptive media include:

- BUET Activated Alumina,
- Alcan Enhanced Activated Alumina,
- Arsenic Removal Units (ARUs) of Project Earth Industries Inc., USA, and
- Apyron Arsenic Treatment Unit.

The BUET and Alcan activated alumina have been extensively tested in field condition in different parts of Bangladesh and found very effective in arsenic removal (BAMWSP, DFID, Water Aid, 2001). The Arsenic Removal Units (ARUs) of Project Earth Industries Inc., USA uses hybrid aluminums and composite metal oxides as adsorption media. They are able to treat 200-500 Bed Volume (BV) of water containing 550 mg/L of arsenic and 14 mg/L of iron (Ahmed et al., 2000). The Apyron Technologies Inc. (ATI) also uses inorganic granular metal oxide based media that can selectively remove As (III) and As (V) from water. The Aqua-Bind™ arsenic media, used by ATI, consists of non-hazardous aluminum oxide and manganese oxide for cost-effective removal of arsenic. The proponents have claimed that the units, installed in India and Bangladesh, are consistently reducing arsenic to less than 10µg/L.

### **5.2.3.2 Activated Carbon (AC)**

Activated carbon is an organic sorbent, commonly used to remove organic and metal contaminants from water and waste water. Activated carbon media are normally regenerated using thermal techniques to desorb and volatilize contaminants. However, regeneration of activated carbon media, used for the removal of arsenic from water, might not be feasible. The arsenic might not volatilize at the temperatures, used in activated carbon regeneration. In addition, off-gas, containing arsenic from the regeneration process, may be difficult or expensive to manage. The reported adsorption capacity of activated carbon is 0.020 grams of As (V) per gram of activated carbon. As (III) is not effectively removed by activated carbon. Activated carbon, impregnated with metals such as copper and ferrous iron, has a higher reported adsorption capacity for arsenic. The reported adsorption capacity for As (III) is 0.048 grams per gram of copper impregnated carbon and for As(V) is 0.2 grams per gram of ferrous iron-impregnated carbon.

### **5.2.3.3 Iron Based Sorbents (IBS)**

Adsorption on IBS is an emerging treatment technique for arsenic removal. Examples of IBS products, currently available in the market, include granular ferric hydroxide, iron coated sand, modified iron, iron/sulfur, and iron oxide. The sorption process has been described as chemisorption (Selvin et al., 2000), which is generally considered to be irreversible. It can be applied in fixed bed pressure columns, similar to those for AA.

The studies, conducted with IBS media, have revealed that the affinity of this media for arsenic is strong under natural pH conditions, relative to AA. This feature allows IBS to treat much higher bed volumes, without the need for pH adjustment. However, similar to AA, optimal IBS performance is obtained at lower pH values. Phosphate has been shown to compete aggressively with As (V) for adsorption sites. Each 0.5 mg/L increase in phosphate above 0.2 mg/L will reduce adsorption capacity by roughly 30%. The exhausted IBS media can be disposed in a municipal solid waste landfill (MacPhee et al., 2001).

**Granular Ferric Hydroxide:** Ferric hydroxide is an excellent adsorbent for removal of arsenic. A few manufacturers have already installed a considerable number of hand pumps attached arsenic removal plants, in West Bengal. M/S Pal Trockner (P) Ltd, India and Sidko Limited, Bangladesh, have installed several Granular Ferric Hydroxide based arsenic removal units, in India and Bangladesh. The Technical University, Berlin, Germany, has also developed Granular Ferric Hydroxide (AdsorpAs®) based adsorbent for arsenic removal. The unit requires iron removal as pre-treatment to avoid clogging of filter bed. The proponents of the unit claim to have very high arsenic removal capacity and produces non-toxic spent granular ferric hydroxide. As iron content in ground water is generally high, all hand pump attached arsenic removal plants working under adsorption principles require regular backwashing/cleaning for removal of arrested iron particles. Such backwashing needs to be done in alternate days for optimal operation of ARP.



**Iron Coated Sand:** BUET has constructed and tested iron coated sand based small scale units, for the removal of arsenic from ground water. Iron coated sand has been prepared following a procedure similar to that adopted by Joshi and Choudhuri (1996). The iron content of the iron coated sand has been found to be 25 mg/g of sand. Raw water having 300 µg/L of arsenic, when filtered through iron coated sand, becomes essentially arsenic-free. It has been found that 350 bed volumes could be treated, satisfying the Bangladesh drinking water standard of 50 µg/L. The saturated medium is regenerated by passing 0.2N sodium hydroxide through the column or soaking the sand in 0.2N sodium hydroxide, followed by washing with distilled water. No significant change in bed volume, in arsenic removal, has been found after 5 regeneration cycles. It is interesting to note that iron coated sand is equally effective in removing both As (III) and As (V). Iron coated brick dust has also been developed in Bangladesh for arsenic removal from drinking water.

**Read-F Arsenic Removal Unit:** Read-F is an adsorbent produced and promoted by M/s Shin Nihon Salt Co. Ltd., Japan (2000), for arsenic removal in Bangladesh. Read-F displays high selectivity for arsenic ions under a broad range of conditions and effectively adsorbs both arsenite and arsenate without any pretreatment. The Read-F is Ethylene-vinyl alcohol copolymer (EVOH)-borne hydrous cerium oxide in which hydrous cerium oxide ( $CeO_2 \cdot n H_2O$ ) is the adsorbent. The material contains no organic solvent or other volatile substance and is not classified as hazardous one. Laboratory test at BUET, and field testing of the materials at four sites, under the supervision of BAMWSP, has showed that the adsorbent is highly efficient in removing arsenic from ground water.

#### **5.2.3.4 Indigenous Filters**

There are several filters available that use indigenous material as arsenic adsorbent. Red soil, rich in oxidized iron, clay minerals, iron ore, iron scrap or fillings and processed cellulose materials, is known to have capacity for arsenic adsorption. Some of the filters manufactured using these materials include:

- Sono 3-Kolshi Filter,
- Granet Home-made Filter,
- Chari Filter,
- Adarsha Filter,
- Shafi Filter, and
- Bijoypur Clay/Processed Cellulose filters.

The Sono 3-Kolshi filter uses zero valent iron fillings and coarse sand in the top Kolshi, wood coke and fine sand in the middle Kolshi while the bottom Kolshi is the collector of the filtered water (Khan et al., 2000). Nikolaidis and Lackovic (1998) showed that 97 % arsenic can be removed by adsorption, on a mixture of zero valent iron fillings and sand. The Sono 3-Kolshi unit has been found to be very effective in removing arsenic, but the media has over growth of microorganism (BAMWSP, DFID and Water Aid, 2000). If ground water contains excessive iron, the one-time use unit becomes quickly clogged.

The Garnet home-made filter contains relatively inert materials like brick chips and sand, as filtering media. No chemical is added to the system. Air oxidation and adsorption on iron-rich brick chips and flocs of naturally present iron in ground water can be the reason for arsenic removal from ground water. The unit has produced inadequate quantity of water and has not shown reliable results in different areas of Bangladesh, under different operating conditions. The Chari filter also uses brick chips and inert aggregates, in different Charis as filter media. The effectiveness of this filter in arsenic removal is not known.

The Shafi and Adarshs filters use clay material as filter media in the form of candle. The Shafi filter has been reported to have good arsenic removal capacity but has suffered from clogging of filter media. The Adarsha filter has participated in the rapid assessment program but has failed to meet the technical criterion of reducing arsenic to acceptable level (BAMWSP, DFID and Water Aid, 2000). Bijoypur clay and treated cellulose have also been found to adsorb arsenic from water (Khair, 2000).

#### **5.2.3.5 Cartridge Filters**

Filter units with cartridges, filled with sorptive media or ion-exchange resins, are readily available in the market. These units remove arsenic like any other dissolved ions present in water, but are not suitable for water, having high impurities and iron content. Presence of ions, having higher affinity than arsenic, can quickly saturate the media requiring regeneration or replacement. Two household filters, tested at BUET laboratories, include:

- Chiyoda Arsenic Removal Unit, Japan, and
- Coolmart Water Purifier, Korea.

The Chiyoda Arsenic Removal Unit can treat 800 BV, meeting the WHO guideline value of 10  $\mu\text{g/L}$  and 1300 BV, meeting the Bangladesh Standard of 50  $\mu\text{g/L}$ , when the feed water arsenic concentration is 300  $\mu\text{g/L}$ . The Coolmart Water Purifier can treat only 20 L of water with an effluent arsenic content of 25  $\mu\text{g/L}$  (Ahmed et al., 2000). The initial and operation costs of these units are high and beyond the reach of the rural people.

#### **5.2.4 Ion Exchange**

Ion exchange is a physical-chemical process in which ions are swapped between a solution phase and solid resin phase. The solid resin is typically an elastic three-dimensional hydrocarbon network, containing a large number of ionizable groups electrostatically bound to the resin. These groups are exchanged for ions of similar charge in solution that have a stronger exchange affinity (i.e., selectivity) for the resin. In drinking water treatment, this technology is commonly used for softening and nitrate removal. This technology can reduce arsenic concentrations to less than 50  $\mu\text{g/L}$  in general and in some cases to below 10  $\mu\text{g/L}$ . Its effectiveness is sensitive to a variety of untreated water contaminants and characteristics. It is used less frequently than precipitation/co precipitation. And it is most commonly used to treat ground water and drinking water.



Arsenic removal is accomplished by continuously passing water, under pressure through one or more columns, packed with exchange resin. As (V) can be removed by the use of strong-base anion exchange resin, in either chloride or hydroxide form. These resins are insensitive to pH in the range 6.5 to 9.0 (EPA, 2000a, b).

Different categories of synthetic resins can be used for arsenic removal. The process is similar to that of adsorption; just the medium is a synthetic resin of more well defined ion exchange capacity. Few manufacturers have developed synthetic resins suitable for arsenic removal. However, the resins need to be replenished after use and renewal interval is dependent on the quantity of arsenic in water. The hand pump attached arsenic removal plants working with ion exchange principle need meticulous attention for operation as well as for regular backwashing.

The arsenic removal capacity is dependent on sulfate and nitrate contents of raw water as sulfate and nitrate are exchanged before arsenic. The ion exchange process is less dependent on pH of water. The efficiency of ion exchange process is radically improved by pre-oxidation of As (III) to As (V) but the excess of oxidant often needs to be removed before the ion exchange in order to avoid the damage of sensitive resins. Development of ion specific resin for exclusive removal of arsenic can make the process very attractive.

The exchange affinity of various ions is a function of the net surface charge. Therefore, the efficiency of the ion exchange process for As (V) removal depends strongly on the solution pH and the concentration of other anions, most notably sulfates and nitrates. High levels of total dissolved solids (TDS) can adversely affect the performance of an Ion Exchange system. In general, the Ion Exchange process is not an economically viable treatment technology if source water contains over 500 mg/L of TDS (Wang et al., 2000) or over 50 mg/L of sulfate. The presence of suspended solids in the feed water could gradually plug the media, thereby increasing head loss and necessitating more frequent backwashing. Therefore, pre-filtration is recommended if the source water turbidity exceeds 0.3 NTU.

Tetrahedron ion exchange resin filter tested under rapid assessment program in Bangladesh (BAMWSP, DFID and Water Aid, 2000) showed promising results in arsenic removal. The system needs pre-oxidation of arsenite by sodium hypochloride. The residual chlorine helps to minimize bacterial growth in the media. The saturated resin requires regeneration by re-circulating sodium chloride (NaCl) solution. The liquid wastes, rich in salt and arsenic, produced during regeneration require special treatment. Some other ion exchange resins have also been tried in Bangladesh but sufficient field test results are not available on the performance of those resins.

### **5.2.5 Membrane Technology**

Membrane technology can remove a wide range of contaminants from water. This technology typically can reduce arsenic concentrations to less than 50 µg/L and in some cases to below 10 µg/L. However, its effectiveness is sensitive to a variety of untreated water

contaminants and characteristics. It also produces a larger volume of residuals and tends to be more expensive than other arsenic treatment technologies. Therefore, it is used less frequently than precipitation/co precipitation, adsorption and ion exchange.

Membrane techniques are capable of removing all kinds of dissolved solids including arsenic from water. They can address numerous water quality problems while maintaining simplicity and ease of operation. In this process, water is allowed to pass through special filter media which physically retain the impurities present in water. The water, for treatment by membrane techniques, should be free from suspended solids and the arsenic in water shall be in pentavalent form. Most membranes, however, can not withstand oxidizing agent.

There are four types of membrane processes: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). All the four processes are pressure-driven and are categorized by the size of the particles that can pass through the membranes or by the molecular weight cut off (i.e., pore size) of the membrane (EPA, 2000a, b). The force required to drive fluid across the membrane depends on the pore size; NF and RO require a relatively high pressure (50 to 150 psi), while MF and UF require lower pressure (5 to 100 psi). The low pressure processes primarily remove contaminants through physical sieving and the high pressure processes through chemical diffusion across the permeable membrane (EPA, 2000a, b).

Because arsenic species dissolved in water tend to have relatively low molecular weights, only NF and RO membrane processes are likely to effectively treat dissolved arsenic (EPA, 2000a, b). MF has been used with precipitation/co precipitation to remove solids containing arsenic. MF generates two treatment residuals from the influent waste stream: a treated effluent (permeate) and a rejected waste stream of concentrated contaminants (reject).

RO is a high pressure process that primarily removes smaller ions typically associated with total dissolved solids. The molecular weight cut off for RO membranes ranges from 1 to 20,000, which is a significantly lower cut off than that for NF membranes. The molecular weight cut off for NF membranes ranges from approximately 150 to 20,000. NF is a high pressure process that primarily removes larger divalent ions associated with hardness (for example, calcium [Ca], and magnesium [Mg] but not monovalent salts (for example, sodium [Na] and chlorine [Cl]). NF is slightly less efficient than RO in removing dissolved arsenic from water (EPA, 2000a,b).

Reverse Osmosis (RO) units can be used as stand-alone arsenic treatment under most water quality conditions. Most RO membranes are made of cellulose acetate or polyamide composites cast into a thin film. The semi-permeable (non-porous) membrane is then constructed into a cartridge called an RO module, typically either hollow-fiber or spiral-wound. It is a pressure-driven membrane separation process capable of removing dissolved solutes from water by means of particle size, dielectric characteristics and hydrophilicity/hydrophobicity. Reverse osmosis is capable of achieving over 97% removal of As (V) and 92% removal of As (III) in a



single pass (NSF, 2001a; NSF 2001b). As an added benefit, RO also effectively removes several other constituents from water including organic carbon, salts, dissolved minerals and color. The treatment process is relatively insensitive to pH. In order to drive water across the membrane surface against natural osmotic pressure, feed water must be sufficiently pressurized with a booster pump. For drinking water treatment, typical operating pressures are between 100 and 350 psi. Water recovery is typically 60-80%, depending on the desired purity of the treated water.

Most RO modules are designed for cross-flow filtration, which allows water to permeate the membrane while the retentate flow sweeps rejected salts away from the membrane surface. In many cases, pre-filtration (commonly through sand or granular activated carbon) is worthwhile. This minimizes the loading of salt precipitates and suspended solids on the membrane surface, thereby extending run length, improving system hydraulics and reducing O&M requirements.

Some membranes, particularly those composed of polyamides, are sensitive to chlorine. In such cases, feed water should be dechlorinated. Another potential concern associated with RO treatment is the removal of alkalinity from water, which in turn could affect corrosion control within the distribution system. If feasible, this problem can usually be avoided by conducting side-stream treatment for arsenic removal. Residual can be discharged either to a treatment plant or on-site sewerage system.

**MRT-1000 and Reid System Ltd.:** M/s Jago Corporation Limited promoted a household reverse osmosis water dispenser MRT-1000 manufactured by B & T Science Co. Limited, Taiwan. This system was tested at BUET and showed As (III) removal efficiency more than 80%. A wider spectrum reverse osmosis system developed by M/s Reid System Limited was also promoted in Bangladesh. Experimental results showed that the system could effectively reduce arsenic content along with other impurities in water. However, the capital and operational costs of the reverse osmosis system are relatively high.

**Reverse Osmosis and Low-pressure Nanofiltration:** Oh et al. (2000) applied reverse osmosis and nanofiltration membrane processes for the treatment of arsenic contaminated water applying low pressure by bicycle pump. A nanofiltration membrane process coupled with a bicycle pump could be operated under condition of low recovery and low pressure range from 0.2 to 0.7 MPa. Arsenite was found to have lower rejection than arsenate in ionized forms and hence water containing higher arsenite requires pre-oxidation for reduction of total arsenic acceptable level. In tube well water in Bangladesh the average ratio of arsenite to total arsenic was found to be 0.25. However, the reverse osmosis process coupled with a bicycle pump system operating at 4 Mpa can be used for arsenic removal because of its high arsenite rejection. The study concluded that low-pressure nanofiltration with pre-oxidation or reverse osmosis with a bicycle pump device could be used for the treatment of arsenic contaminated ground water in rural areas (Oh et al., 2000; Rahman and Rahaman, 2000).

### **5.3 Innovative Technologies**

Innovative technologies, such as permeable reactive barriers, phytoremediation, biological treatment and electrokinetic treatment, are also being used to treat arsenic-contaminated water, waste water and soil. However, only a few applications of these technologies at full scale are available in the literature and additional treatment data are needed to determine their applicability and effectiveness in field condition. These technologies may be developed at full scale to treat arsenic contaminated aquifers. A brief description of these technologies is given below.

#### **5.3.1 Permeable Reactive Barriers (PRBs)**

PRBs are walls containing reactive media that are installed across the path of a contaminated groundwater plume to intercept the plume. The barrier allows water to pass through while the media remove the contaminants by precipitation, degradation, adsorption or ion exchange. PRBs are used to treat groundwater in-situ. This technology tends to have lower operation and maintenance costs than ex-situ (pump and treat) technologies, and typically requires a treatment time of many years.

PRBs are applicable to the treatment of both organic and inorganic contaminants. The former usually are broken down into carbon dioxide and water, while the latter are converted to species that are less toxic or less mobile. The most frequent application of PRBs is the in-situ treatment of groundwater contaminated with chlorinated solvents. A number of different treatment media have been used, the most common being zero valent iron (ZVI). Other media include hydrated lime, slag from steel making processes that use a basic oxygen furnace, calcium oxides, chelators (ligands selected for their specificity for a given metal), iron oxides, sorbents, substitution agents (e.g., ion exchange resins) and microbes (EPA, 1998; Smyth et al., 2000).

PRBs are being used to treat arsenic in groundwater at full scale at only few sites. Although many materials for the reactive portion of the barrier have been tested at bench scale, only zero valent iron and limestone have been used at full scale. The installation techniques for PRBs are established for depths less than 30 feet, and require innovative installation techniques for deeper installations. The following chemicals and reactive media are used in PRBs to treat arsenic:

- Zero valent iron (ZVI),
- Limestone,
- Basic oxygen furnace slag,
- Surfactant modified zeolite, and
- Ion exchange resin.

As groundwater reacts with ZVI, pH increases Eh decreases and the concentration of dissolved hydrogen increases. These basic chemical changes promote a variety of processes



that impact contaminant concentrations. Increases in pH favor the precipitation of carbonates of calcium and iron as well as insoluble metal hydroxides. Decreases in Eh drive reduction of metals and metalloids with multiple oxidation states. Finally, an increase in the partial pressure of hydrogen in subsurface systems supports the activity of various chemotrophic organisms that use hydrogen as an energy source, especially sulfate-reducing bacteria and iron-reducing bacteria.

Arsenate ions bind tightly to the iron filings, causing the ZVI to be oxidized to ferrous iron, aerobically or anaerobically in the presence of water. The process results in a positively charged iron surface that sorbs the arsenate species by electrostatic interactions (Su and Puls, 2001). In systems where dissolved sulfate is reduced to sulfide by sulfate-reducing bacteria, arsenic may be removed by precipitation of insoluble arsenic sulfide ( $As_2S_3$ ) or co-precipitated with iron sulfides ( $FeS$ ).

PRBs can be constructed by excavating a trench of the appropriate width and backfilling it with a reactive medium. Commercial PRBs are built in two basic configurations: the funnel-and-gate and the continuous wall. The funnel-and-gate uses impermeable walls, for example, sheet pilings or slurry walls, as a "funnel" to direct the contaminant plume to a "gate(s)" containing the reactive media, while the continuous wall transects the flow path of the plume with reactive media (EPA, 1998).

PRBs are a passive treatment technology, designed to function for a long time with little or no energy input. They produce less waste than active remediation, as the contaminants are immobilized or altered in the subsurface. PRBs can treat ground water with multiple contaminants and can be effective over a range of concentrations. PRBs require no above ground equipment, except monitoring devices, allowing return of the property to economic use during remediation. PRBs are best applied to shallow, unconfined aquifer systems in unconsolidated deposits, as long as the reactive material is more conductive than the aquifer (EPA, 2001a,b ).

The technology relies on the natural movement of ground water; therefore, aquifers with low hydraulic conductivity can require relatively long periods of time to be remediated. In addition, PRBs do not remediate the entire plume, but only the portion of the plume that has passed through the PRB. Because cleanup of ground water contaminated with arsenic has been conducted at only few sites, the long-term effectiveness of PRBs for arsenic treatment has not been demonstrated fully (EPA, 2001a,b).

### **5.3.2 Phytoremediation**

Phytoremediation is an in-situ technology applicable to contaminated soil and ground water. It is designed to use plants to degrade, extract, contain or immobilize contaminants in soil, sediment or ground water (Zhang et al., 2001). Typically, trees with deep roots are applied to ground water and other plants are used for shallow soil contamination. This technology tends to have low capital, operating and maintenance costs relative to other arsenic treatment technologies because it relies on the activity and growth of plants.

The mechanisms of phytoremediation include phytoextraction (also known as phytoaccumulation, the uptake of contaminants by plant roots and the translocation/accumulation of contaminants into plant shoots and leaves), enhanced rhizosphere biodegradation (takes place in soil or ground water immediately surrounding plant roots), phytodegradation (metabolism of contaminants within plant tissues), and phytostabilization (production of chemical compounds by plants to immobilize contaminants at the interface of roots and soil). Most applications of phytoremediation for arsenic removal include phytoextraction and phytostabilization.

Experimental research into identifying appropriate plant species for phytoremediation is ongoing. It is generally applicable only to shallow soil or relatively shallow ground water that can be reached by plant roots. In addition, the phytoremediating plants may accumulate high levels of arsenic during the phytoremediation process, and may require additional treatment prior to disposal.

The selection of the phytoremediating species depends upon the species' ability to treat the contaminants and the depth of contamination. Plants with shallow roots (e.g. grasses) are appropriate only for contamination near the surface, typically in shallow soil. Plants with deeper roots, (e.g. trees) may be capable of remediating deeper contaminants in soil or ground water plumes.

Examples of vegetation, used in phytoremediation, include sunflower, Indian mustard, corn, and grasses (such as ryegrass and prairie grasses) (EPA, 2001b). Some plant species, known as hyperaccumulators, absorb and concentrate contaminants within the plant at levels greater than the concentration in the surrounding soil or ground water. The ratio of contaminant concentration in the plant to that in the surrounding soil or ground water is known as the bioconcentration factor. A hyperaccumulating fern (*Pteris vittata*) has been used in the remediation of arsenic-contaminated soil, waste and water. The fern can tolerate as much as 1,500 ppm of arsenic in soil, and can have a bioconcentration factor up to 265. The arsenic concentration in the plant can be as high as 2% (dry weight) (Ma et al., 2001; Zhang et al., 2001).

### **5.3.3 Biological Treatment**

Although biological treatments have usually been applied to the degradation of organic contaminants, some innovative techniques have applied biological remediation to the treatment of arsenic. This technology involves biological activity or micro-organisms that promote precipitation/co precipitation of arsenic from water and leaching of arsenic in soil. Biological precipitation/co precipitation processes for water create ambient conditions intended to cause arsenic to precipitate/co precipitate or act directly on arsenic species to transform them into species that are more amenable to precipitation/co precipitation. The microbes may be suspended in the water or attached to a submerged solid substrate.



An adequate nutrient supply should be available to the microbes to enhance and stimulate growth. If the initial solution is nutrient deficient, nutrient addition may be necessary. Iron or hydrogen sulfide may also be added. For biologically enhanced iron precipitation, iron must be present in the water to be treated. The optimal iron level depends primarily on the arsenic concentration.

Biological treatment for arsenic is used primarily to treat water above-ground in processes that use microorganisms to enhance precipitation/co precipitation. This technology may require pretreatment or addition of nutrients and other treatment agents to encourage the growth of key microorganisms. The leachate from bioleaching requires additional treatment for arsenic prior to disposal.

Another process uses anaerobic sulfate-reducing bacteria and other direct arsenic-reducing bacteria to precipitate arsenic from solution as insoluble arsenic sulfide complexes. The water containing arsenic is typically pumped through a packed-bed column reactor, where precipitates accumulate until the column becomes saturated. The arsenic is then stripped and the column is biologically regenerated. Hydrogen sulfide has also been used in suspended reactors to biologically precipitate arsenic out of solution. These reactors require conventional solid/liquid separation techniques for removing precipitates. Removal of arsenic from soil biologically via "accelerated bioleaching" has also been tested on a bench scale. The microbes in this system produce nitric, sulfuric and organic acids which are intended to mobilize and remove arsenic from ores and sediments. This biological activity also produces surfactants, which can enhance metal leaching.

#### **5.3.4 Electrokinetic Treatment**

Electrokinetic treatment is an emerging remediation technology designed to remove heavy metal contaminants from soil and ground water. It is an in-situ treatment technology and therefore does not require excavation of contaminated soil or pumping of contaminated ground water. Fine-grained soils are more amenable to electrokinetic treatment due to their large surface area, which provides numerous sites for reactions necessary for electrokinetic processes (Acar and Gale, 1995; Evanko and Dzomback, 1997). However, its effectiveness may be limited by a variety of contaminants and soil and water characteristics. In addition, its treatment depth is limited by the depth to which the electrodes can be placed. The technology has limited number of applications for arsenic.

Electrokinetic remediation is based on the theory that a low density current will mobilize contaminants in the form of charged species. A current passed between electrodes is intended to cause water, ions and particulates to move through the soil, waste and water (Will, 1995). Contaminants arriving at the electrodes can be removed by means of electroplating or electrodeposition, precipitation or coprecipitation, adsorption, complexing with ion exchange resins, or by pumping of water (or other fluid) near the electrode.

The chemicals used in electrokinetic process for arsenic removal include sulfuric acid, phosphoric acid and oxalic acid. In situ electrokinetic treatment of arsenic uses the natural conductivity of the soil (created by pore water and dissolved salts) to affect movement of water, ions and particulates through the soil (Will, 1995). Water and/or chemical solutions can also be added to enhance the recovery of metals by electrokinetics. Positively charged metal or metalloid cations, such as As (V) and As (III) migrate to the negatively-charged electrode (cathode), while metal or metalloid anions migrate to the positively charged electrode (anode) (Evanko and Dzomback, 1997). Extraction may occur at the electrodes or in an external fluid cycling/extraction system. Alternately, the metals can be stabilized in situ by injecting stabilizing agents that react with and immobilize the contaminants. Arsenic has been removed from soils treated by electrokinetics using an external fluid cycling/extraction system.

This technology can also be applied ex-situ to groundwater by passing the water between electrodes. The current causes arsenic to migrate toward the electrodes, and also alters the pH and oxidation-reduction potential of the water, causing arsenic to precipitate/co precipitate. The solids are then removed from the water using clarification and filtration (Pensaert, 1998).

A pilot-scale test of electrokinetic remediation of arsenic in ground water was conducted in Belgium in 1997. This ex situ application involved pumping groundwater contaminated with zinc, arsenic and cadmium and treating it in an electrokinetic remediation system with a capacity of 6,600 gpm. The treatment system precipitated the contaminants and the precipitated solids were removed using clarification and filtration. The electrokinetic treatment system did not use additives or chemicals. The treatment reduced arsenic concentrations in groundwater from 0.6 mg/L to 0.013 mg/L. The reported costs of the treatment were \$0.004 per gallon for total cost, and \$0.002 per gallon for O&M (Pensaert, 1998).

## **5.4 Waste Disposal / Sludge Management**

Waste disposal is an important consideration in the treatment selection process. Arsenic removal technologies produce several different types of waste, including sludges, brine streams, backwash slurries and spent media. These wastes have the potential for being classified as hazardous and can pose disposal problems.

The arsenic-rich sludge should be disposed in a controlled manner. According to the study conducted by AIH&PH, arsenic rich sludge may be disposed by the following method:

- Disposal in on-site sanitation pits,
- Mixing with concrete in a controlled ratio,
- Mixing with clay for burning for brick manufacturing.



The adsorbed media rich in arsenic can also be mixed with concrete as an additional aggregate but in a controlled proportion. Liquid wastes must have lower concentrations than the toxicity characteristic in order for the waste to be classified as non-hazardous. The arsenic toxicity characteristic is 5.0 mg/L. Those liquid wastes that contain more than 5.0 mg/L of arsenic would, therefore, be classified as a hazardous waste. Many of the arsenic removal technologies also remove other constituents and therefore the liquid waste must also be analyzed for other substances that may be present in concentrations above their respective toxicity characteristics. Because of the cost implications, on-site treatment or off-site disposal of hazardous waste is likely to be infeasible for small water systems. Indirect discharge through sewer to treatment plants may be viable option for waste disposal. There are five realistic methods for the disposal of arsenic wastes.

#### **5.4.1 Landfill Disposal**

Historically, municipal solid waste landfills have been commonly used for the disposal of Non-hazardous solid wastes emanating from treatment processes. However, the hazard potential of arsenic may limit the feasibility of this alternative.

Dewatered sludge and spent media can be disposed in a municipal solid waste landfill if the waste passes both the Paint Filter Liquids Test (PFLT) and the TCLP. The PFLT is used to verify that there is no free liquid residual associated with the waste. However, if the TCLP extract contains arsenic or any other contaminant (e.g., chromium) above the TC, the waste residuals must be disposed in a designated hazardous waste landfill. As such, the costs of disposal are relatively high. As with municipal solid waste landfill disposal, waste sludges must not contain free liquid residuals.

#### **5.4.2 Direct Discharge to Surface Waters**

Direct discharge refers to the disposal of liquid wastes to nearby surface waters, which act to dilute and disperse the waste by-products. The primary advantage of direct discharge is to reduce capital and operations and maintenance costs due to the elimination of residuals treatment. The feasibility of this disposal method is subject to provisions of the guidelines for waste disposal. The allowable discharge is a function of the ability of the receiving water to assimilate the arsenic without exceeding water quality criteria established under the Govt. regulations. Different water quality criteria exist depending on the classification of the receiving water. For specific criteria, conditions and limits, the appropriate agency should be contacted, because the conditions and limits can vary according to the receiving water's particular characteristics.

#### **5.4.3 Indirect Discharge**

The discharge of liquid wastes to a treatment plant is a potential disposal alternative. In this case, the wastes can be discharged to sewer systems. The arsenic limit is usually on the

order of 50 to 10 µg/L. The TBLs are computed for each POTW to take into account the background levels of contaminants in the municipal wastewater. The background level will change because of the drinking water treatment process, which may lead to revised TBLs. The revised TBL can be used to determine if the liquid waste stream could be discharged to the POTW.

#### **5.4.4 Land Application**

Land application of concentrated sludge may be allowed under certain conditions depending on the state law and regulations. As per USEPA guidelines, sewage sludge (also called "biosolids") containing <41 mg As/kg biosolids can be land-applied with no restrictions. Biosolids with arsenic concentrations between 41 and 75 mg/kg can be land-applied, but must track arsenic accumulation. The lifetime arsenic accumulation limit is 41 kg As/hectare of land.

#### **5.4.5 On-site Sewerage**

Liquid wastes from Reverse Osmosis POU devices can suitably be disposed in on-site sewerage or septic system. Arsenic is concentrated in the RO retentate during normal process operation. However, eventually this retentate is combined with other domestic wastewater in the septic tank. Because the amount of water consumed is small relative to the total flow entering the dwelling, the concentration of arsenic in the blended wastewater is nearly identical to that in the influent stream.

### **5.5 Alternative Options**

West Bengal-India and Bangladesh are lands of rivers. The average annual rainfall in these two areas is 2000 mm. West Bengal has about 7,000 m<sup>3</sup> and Bangladesh has 11,000 m<sup>3</sup> of available surface water per capita. Besides this, West Bengal has about 4000 km<sup>2</sup> of wetland and vast river basin is flooded almost every year, but due to the negligence most of these water goes as waste. Therefore, there is an urgent need for a proper watershed management so that the vast surface and rain water resource could be used to combat with the situation. A proper watershed management approach with active participation from the people can also prove to be a possible alternative to resolve problem of freshwater availability arising out of arsenic groundwater contamination.

### **5.6 Performance Audit, Evaluation and People's Participation**

As per the performance audit of arsenic alleviation programme (PHED, 2005), the Govt. of West Bengal took up measures to combat arsenic poisoning in potable ground water since 1992-93. However, the schemes for arsenic alleviation were not executed in a mission mode as warranted by the situation and there was inadequate monitoring. Despite 13 years of effort and expenditure of Rs. Rs.832.46 crores on arsenic alleviation measures, only 43% of the



at risk population was supplied with arsenic free drinking water as of March 2005 against the capacity created to cover 56%. As of June 2005, no comprehensive mapping of arsenic affected areas was done. Screening of results of 1.20 lakh out of 1.31 lakh tube wells in the eight affected districts revealed that 27% (0.32 lakh) of them were yielding water with arsenic concentration even above 50 µg/L. In spite of execution of the short term, long term and medium term programmes at a cost of Rs 721.24 crore to combat arsenic poisoning, 21.47 lakh people continued to remain exposed to arsenic contamination due to non-adherence to the stipulated performance standards. Out of 2396 Arsenic Removal Units (ARUs) and 77 PWSS installed with Arsenic Removal Plants (ARPs), 135 ARUs and 32 PWSS were yielding water contaminated beyond 50µg/L while 989 ARUs remained non-functional due to use of defective adsorption media, non regeneration and non replacement of adsorption media affecting 7.89 lakh people. Arsenic rich sludges generated in ARUs were also not disposed scientifically leaving substantial risks of environmental hazards (PHED, 2005).

Arsenic removal plants (ARPs) could be one possible option to provide arsenic-free drinking water to the affected people. However, these technologies need evaluation in respect of effectiveness in arsenic removal and community acceptance. The ARPs are mainly based on adsorption, co-precipitation, ion exchange and membrane techniques. Installation of ARPs in West Bengal, India, started at the end of 1998. The West Bengal government and other organizations have already invested about 3 million dollars in installing ARPs purchased from both national and international manufacturers (1900 ARPs were set up at an average price of US\$1500 for each ARP) in mainly 5 out of 9 arsenic affected districts of West Bengal.

School of Environmental Studies of Jadavpur University had initiated investigations on the efficiency of arsenic removal plants (ARPs) in West Bengal in late 1998. They have evaluated the efficiency of 577 ARPs in the districts of North 24 Parganas, Murshidabad and Nadia of West Bengal and submitted their evaluation reports to the Government of West-Bengal, manufacturers of ARPs and other concerned NGOs for their information and follow-up action (SOES, 2000, 2001, 2003a,b, 2004).

Hossain et al. (2005) evaluated efficiency of arsenic removal plants (ARPs) in removing arsenic and iron from raw ground water covering 18 ARPs from 11 manufacturers, both from India and abroad, installed in Baruipur Block of South 24 Parganas district under a project titled 'Technology Park Project' implemented by All India Institute of Hygiene and Public Health (AIHH&PH), Govt. of India, Kolkata, in partnership with a number of NGOs under the financial support from India-Canada Environment Facility (ICEF), New Delhi. Immediately after installation of ARPs on August 29, 2001, the villagers began using filtered water for drinking and cooking even though first analysis on September 13, 2001 found that ten out of 13 ARPs failed to remove arsenic below the WHO provisional guideline value of 10 µg/L, while six plants could not even achieve the Indian standard value of 50 µg/L. The highest concentration of arsenic in filtered water was observed to be 364 µg/L. Two years study showed that none of the ARPs could maintain arsenic in filtered water below the WHO provisional guideline value and

only two could meet Indian standard value of 50 µg/L throughout where the users were able to recognize the ARPs as an asset for the community and maintained it properly. Standard statistical techniques also showed that ARPs from the same manufacturers were not equally efficient. During the study period almost all the ARPs have undergone minor or major modifications to improve the performance and after the study, 15 out of 18 ARPs were no longer in use. The study concluded ineffectiveness and poor reliability of the ARPs. It is further reported that in most cases authorities installed the ARPs abruptly without checking the ground realities. Lack of awareness and relevant information is one of the major hurdles in arsenic mitigation program. Without cost sharing it is difficult to inculcate in users' mindset a sense of 'belonging' (Hossain et al., 2005).

Hossain et al. (2006) also evaluated effectiveness of arsenic removal plants (ARPs) as a remediation approach to provide safe water based on systematic study of 577 ARPs installed in 3 districts out of 1900 total ARPs installed in five arsenic affected districts of West Bengal, India. Overall study showed that 475(82.3%) of the ARPs installed in the arsenic affected areas were not useful. The reasons for ineffectiveness and low performance included improper maintenance, sand gushing problem, lack of user friendliness and absence of community participation. A comparative study of ARPs in two different blocks Domkol in Murshidabad district and Swarupnagar in North 24 Parganas showed that 39(80%) and 38(95%) ARPs, respectively, were not useful. A micro-level study in a Gram Panchayat, Kolsur, Deganga block, North 24 Parganas showed that 14(87.5%) ARPs were not useful (Hossain et al., 2006).

There are few examples where ARPs were able to run successfully through community participation. These include two ARPs of BE College, one installed in Village Parpatna, GP Chakla, Block Deganga, District North 24 Parganas and another installed in Village Sangrampur Paschimpara, GP Sangrampur Sibhati, Block Bosirhat 1, District North 24 Parganas. Another example of successful ARP is of Pal Trockner installed near Ichhapur Ayurvedic Hospital, GP Ichapur 1, Block Gaighata, District North 24 Parganas. One ARP of Oxide India Plant in Chandranath Basu Sebasangha, in Betai of Dangapara GP, Block Tehatta, District Nadia is also running successfully with people's participation.

Based on the above observations, it is strongly recommended that awareness amongst the people and their whole hearted participation is very much essential to achieve success at field level. The technologies found effective and safe for arsenic removal from contaminated water should be promoted for wider implementation in the acute arsenic problem areas to avoid ingestion of excessive arsenic through water. The arsenic removal technologies may improve further through adaptation in rural environment through people's participation.

## **5.7 Observations, Analysis and Appraisal**

The main technological options for the remediation of arsenic are: i) decontaminate aquifers from arsenic by in-situ treatment of soil-water system, or (ii) switch over to alternative,



arsenic-free water sources; instead of opting exclusively for ex-situ arsenic removal technologies. Former case is the best option when complete understanding of the physico-chemical processes and system behavior are methodically known; while the later case could be considered as a potential alternative when sustainable surface water and groundwater flows are ensured. However, in either case, extensive feasibility studies would be necessary. Ex-situ arsenic removal technologies can be a suitable option when the dimension of the problem is small and short lived, such as the source is anthropogenic. For a large scale groundwater arsenic problem, as in different states in the Country where demand of and dependability on ground water resources both for drinking and irrigation water in such places are continuum, ex-situ treatment of tapped groundwater by arsenic removal technologies could merely be thought to be a stopgap arrangement to meet the requirement of drinking water to the people in the arsenic affected area. Requirement of agricultural irrigation water in rural areas is far more than the drinking water. Irrigation water requirement cannot be sustained by the ex-situ arsenic removal devices. Use of arsenic contaminated groundwater in agriculture has far reaching consequences in terms of contamination through food chain and environmental aspects. Further, in ex-situ treatment technologies another additional problem is arsenic sludge management. The key issues thus emanate as: whether to adopt strategy for in-situ remediation of arsenic from soil-water system, or switching over to alternate surface water-groundwater management strategies letting remediation of arsenic groundwater menace undisturbed in its existing state-of-affairs, or to adopt mixed management strategies such as; supply of drinking water through arsenic removal technologies and irrigation water through conjunctive use of surface water and fresh aquifer tapping? To ensure non-hazardous supply of drinking and irrigation water to the people in the arsenic affected areas, a suitable water management strategy on scientific footings needs to be evolved.

If it is considered that arsenic removal technologies can be one of the technological options to ensure supply of drinking water in the arsenic affected areas, the questions generally raised are: sustainability of the technologies in terms of cost, O & M, and efficiency. Most of the existing devices showed unsatisfactory results in terms of cost (total and per capita), operation and maintenance and expected sustainability. Although a remarkable technological development in arsenic removal processes has taken place during last few years, however, very few in which O & M has been taken care, could show potential field satisfaction. The technologies and its field applications, which could prove satisfactory results, can be thought for promotion with improvisation for long term sustainability. One should also realize that arsenic mitigation strategy is location specific. A method suitable for a specific area can not be generalized for the other affected regions due to i) geographical and geomorphological variations, and ii) different socio-economic and literacy conditions of people. Therefore, a considerable R & D is necessary to evolve eco-friendly, cost effective and user friendly arsenic removal technology. A comparison of different arsenic removal processes is shown in Table 5.2.

**Table 5.2:** Comparison of conventional arsenic removal technologies

Technologies	Advantages	Disadvantages
Oxidation/Precipitation: - Air Oxidation - Chemical oxidation	- Relatively simple, low-cost but slow process - Relatively simple and rapid process - Oxidizes other impurities and kills microbes	- The processes remove only a part of arsenic
Coagulation/Co-precipitation: - Alum Coagulation - Iron Coagulation	- Relatively low capital cost - Relatively simple operation - Common Chemicals available	- Produces toxic sludges - Low removal of As(III) - Pre-oxidation required
Sorption Techniques: - Activated Alumina - Iron Coated Sand - Ion Exchange Resin - Other Sorbents	- Relatively well known and commercially available - Well defined technique - Plenty possibilities and scope of development	- Produces toxic solid waste - Replacement/regeneration required - High tech operation and maintenance - Relatively high cost
Membrane Techniques: - Nanofiltration - Reverse osmosis - Electrodialysis	- Well defined and high removal efficiency - No toxic solid wastes produced - Capable of removal of other contaminants	- Very high capital and running cost - High tech operation and maintenance - Toxic wastewater produced



## **5.8 Summary**

All the technologies described in this document have their own merits and demerits and should be refined to make them suitable and sustainable for a particular situation. The modifications should be based on the pilot-scale implementation of the technologies with objectives to:

- Improve effectiveness in arsenic removal,
- Reduce the capital and operation cost of the system,
- Make the technology user friendly,
- Overcome maintenance problems, and
- Resolve sludge and arsenic concentrates management problems.

Arsenic removal technologies have to compete with other technologies in which cost appears to be a major determinant in the selection of a treatment option by the users. The rural people habituated in drinking tube well water may find arsenic removal from tube well water as a suitable option for water supply. In many arsenic affected areas, arsenic removal may be the only option in the absence of an alternative safe source of water supply. Awareness amongst the people and their whole hearted participation is very much essential to achieve success at field level. A proper watershed management approach with active participation from the people can also prove to be a possible alternative in many areas to meet requirement of water for drinking and irrigation purposes.



**RPM /ALCAN AAFS-50 MEDIA**



**BUCKET OF RESINS OF WRI**



**GRANULAR FERRIC HYDROXIDE  
- PAL TROCKNER**



**ARSENIC REMOVAL PLANT - OXIDE INDIA**



**ADHIACON-AFDWS 2000**



**HANDPUMP ATTACHED ARSENIC REMOVAL  
PLANT-AIHH & PH**

**Figure 5.1:** Arsenic Removal Devices Developed and Promoted by Different Organizations in various places in West Bengal.





**IONOCHEM- ARSENIC TREATMENT UNIT**



**APYRON ARSENIC TREATMENT UNIT**



**ARSENIC TREATMENT PLANT-PHED MODEL**



**ARSENIC AND IRON REMOVAL SYSTEM-SFR MODEL**

**Figure 5.1:** Arsenic Removal Devices Developed and Promoted by Different Organizations in various places in West Bengal.

