

Review

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# Perspectives of low cost arsenic remediation of drinking water in Pakistan and other countries

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ABSTRACT

Arsenic concentrations above acceptable standards for drinking water have been detected in many countries and this should therefore is a global issue. The presence of arsenic in subsurface aquifers and drinking water systems is a potentially serious human health hazard. The current population growth in Pakistan and other developing countries will have direct bearing on the water sector for meeting the domestic, industrial and agricultural needs. Pakistan is about to exhaust its available water resources and is on the verge of becoming a water deficit country. Water pollution is a serious menace in Pakistan, as almost 70% of its surface waters as well as its groundwater reserves have contaminated by biological, organic and inorganic pollutants. In some areas of Pakistan, a number of shallow aquifers and tube wells are contaminated with arsenic at levels which are above the recommended USEPA arsenic level of 10 ppb ( $10 \mu g L^{-1}$ ). Adverse health effects including human mortality from drinking water are well documented and can be attributed to arsenic contamination. The present paper reviews appropriate and low cost methods for the elimination of arsenic from drinking waters. It is recommended that a combination of low cost chemical treatment like ion exchange, filtration and adsorption along with bioremediation may be useful option for arsenic removal from drinking water.

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#### 1. Introduction

The detection of arsenic in ground waters from many countries throughout the globe has threatened the use of groundwater as major source of drinking water [1-5]. Many factors such as anthro-

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pogenic activities, biological action, and geochemical reactions help to mobilize arsenic into ground waters. Most environmental arsenic problems are the result of mobilization under natural conditions. However, mining activities, combustion of fossil fuels, use of arsenic pesticides, herbicides, and crop desiccants and use of arsenic additives to livestock feed create additional impacts [5]. Because of lethality to human health various countries have reduced the maximum contaminant level (MCL) of arsenic from 50 to  $10 \,\mu g \, L^{-1}$  in drinking water [6–8]. The concentration of arsenic in most rocks ranges from 0.5 to 2.5 mg kg<sup>-1</sup>, though higher concentrations are found in finer grained argillaceous sediments and phosphorites [9,10].

Arsenic exists in the -3, 0, +3 and +5 oxidation states [3]. Environmental forms include arsenious acids, arsenic acids, arsenites, arsenates, methylarsenic acid, dimethylarsinic acid, arsine, etc. Arsenic(III) is a hard acid and preferentially complexes with oxides and nitrogen. Conversely, arsenic(V) behaves like a soft acid, forming complexes with sulfides [11]. Inorganic forms of arsenic most often exist in water supplies [11]. Arsenic is uniquely sensitive to mobilization (pH 6.5–8.5) and under both oxidizing and reducing conditions among heavy metalloids [3]. Two forms are common in natural waters: arsenite (AsO<sub>3</sub><sup>3-</sup>) and arsenate (AsO<sub>4</sub><sup>3-</sup>), referred to as arsenic(III) and arsenic(V). Pentavalent (+5) or arsenate species are AsO<sub>4</sub><sup>3-</sup>, HASO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>AsO<sup>4-</sup> while trivalent (+3) arsenites include As(OH)<sub>3</sub>, As(OH)<sup>4-</sup>, AsO<sub>2</sub>OH<sup>2-</sup> and AsO<sub>3</sub><sup>3-</sup>. Pentavalent species predominate and are stable in oxygen rich aerobic environments. Trivalent arsenites predominate in moderately reducing anaerobic environments such as groundwater [12].

Pakistan's current population of 141 million is expected to grow to about 221 million by the year 2025. This increase in population will have direct influence on the water sector to meet the demands of domestic use, industry and agriculture. The per capita water availability has dropped from 5600 m<sup>3</sup> in 1953 to about 1000 m<sup>3</sup> in 2006. Pakistan has now essentially exhausted its available water resources and is on the verge of becoming a water deficit country [13].

In some areas of the Pakistan, the presence of arsenic in subsurface aquifers and drinking water systems is a potentially serious human health hazard. A majority of shallow subsurface aquifers and tube wells are contaminated with arsenic at levels which are of magnitude above the recommended arsenic level of 10 ppb. Serious adverse health effects, including human mortality, from arsenic contamination of drinking water are well documented [14]. In some areas of the world, the presence of As in subsurface aquifers and drinking water systems is a potentially serious human health hazard [6]. Exposure to As at work, mining and industrial emissions may also be significant [15]. Although arsenic exists in both organic and inorganic forms, the inorganic forms are more prevalent in water and are considered more toxic [3].

Human exposure to arsenic can take place through ingestion, inhalation or skin adsorption; however, ingestion is the predominant form of arsenic intake. Various effects of As caused by short term and long-term exposure have been described elsewhere [14,16,17]. It was only recently that strong adverse effects on health were found associated with long-term exposure to very low arsenic concentrations. Drinking water is now recognized as the major source of human intake of arsenic in its most toxic (inorganic) forms [18]. The presence of arsenic, even at high concentrations, is not accompanied by any change in taste, odors and/or visible appearance of water. The presence of arsenic in drinking water is therefore difficult to detect without complex analytical techniques and hence may present a significant hazard to community health.

Removal of arsenic from drinking water should be a worldwide priority. Arsenic concentration above acceptable standards for drinking waters has been demonstrated in many countries and thus is a global issue. Arsenic has been reported in groundwater in: Bangladesh, Cambodia, China (including provinces of Taiwan and Inner Mongolia), India, Iran, Japan, Myanmar, Nepal, Pakistan, Thailand, Vietnam, Alaska, Argentina, Chile, Dominica, El Salvador, Honduras, Mexico, Nicaragua, Peru, United States of America, Austria, Croatia, Finland, France, Germany, Greece, Hungary, Italy, Romania, Russia, Serbia, United Kingdom, Ghana, South Africa, Zimbabwe Australia and New Zealand [19–36]. Exposure to high levels of acute arsenic poisoning is relatively less common; however, long-term exposure to even low concentrations of arsenic in drinking water also presents a considerable health hazard. Numerous references review the effect of long-term exposure to arsenic on people's health [14,37]. Removal of arsenic from drinking water using low cost, simple and appropriate methods is highly desirable.

#### 2. Arsenic analysis and remediation technologies

Arsenic retention and mobility in surface water and groundwater are of great concern because of their toxic effects in the environment. Current remediation technologies are expensive. Thus, any lowering of the standard will put increased economic pressure on rural communities with high levels of arsenic in their drinking water [38]. Several treatment technologies have been adopted to remove arsenic from drinking water under both laboratory and field conditions. The major mode of removing arsenic from water is by physico-chemical treatment. Technologies for removing arsenic from drinking water include:

- Pre-oxidation of arsenic(III) to arsenic(V)
- Adsorption methods
- Membrane methods
- Point-of-use methods
   Coagulation/precipitation/adsorption/filtration
   Oxidation/coagulation/precipitation/filtration
   Oxidation/filtration/adsorption
   Adsorption/filtration
- Biological arsenic removal

#### 2.1. Pre-oxidation of arsenic(III) to arsenic(V)

A significant problem encountered in the removal of arsenic from groundwater aquifers and municipal water systems is that arsenic exists as both arsenic(III) and arsenic(V) compounds in water. Arsenic(III) compounds are primarily non-ionic whereas arsenic(V) compounds are ionic at normal drinking water pH [39]. Arsenic(III) compounds or arsenites are therefore not always readily removed from drinking water by methods that are very effective for removal of arsenic(V) compounds or arsenates. It is sometimes necessary to pre-oxidize any arsenites present to arsenates in order to effectively remove arsenic from drinking water to safe levels. For this purpose different oxidants are used.

Table 1 summarizes the comparison of various methods used for oxidation of arsenites to arsenates, prior to precipitation/coagulation for arsenic removal from water [40].

#### 2.2. Precipitation and coagulation methods

Precipitation and coagulation methods for arsenic removal from water depend upon the co-precipitation of both water in soluble arsenates and inorganic oxides of other metals. The water insoluble inorganic oxides are produced by the hydrolysis in the arseniccontaminated water of added coagulants such as alum (aluminum sulfate), ferric chloride or ferric sulfate pettine. The coagulant must be uniformly mixed into the arsenic-contaminated water in order to obtain the maximum arsenic removal efficiency. If alum is the coagulant, the pH of the contaminated water must be very close

#### Table 1

Comparison of methods for oxidation of arsenites to arsenates, prior to precipitation/coagulation for arsenic removal from water.

| Oxidation method              | Advantages                                                                                   | Disadvantages                                                                                              |
|-------------------------------|----------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------|
| Oxygen (from air)             | Oxidation agent is readily available and is not hazardous                                    | Oxidation is slow and additional equipment to speed it up increases system capital and operating costs     |
| Ozone                         | Oxidation agent is generated at point-of-use which<br>reduces exposure to ozone              | Ozone is a known health hazard and the oxidation system<br>has high operating and maintenance costs        |
| Hydrogen peroxide             | The oxidation agent is a safe solution that can be manually<br>or automatically metered      | The oxidation reaction may be too slow for practical use<br>and oxidant solution can lose oxidation power  |
| Liquid chlorine               | The oxidation reaction is very fast and completely removes<br>any potential disease carriers | The oxidant is difficult to store or transport safely and system parts can be degraded by corrosion        |
| Hypochlorite                  | The oxidation reaction is relatively fast and removes any<br>potential disease carriers      | The system parts can be degraded by corrosion and oxidant solution can lose oxidation power with time      |
| Permanganate                  | The oxidation agent is a safe solution that can be manually<br>or automatically metered      | The oxidation reaction results in a solid manganese compound that may interfere with system operation      |
| Iron(III) or Mn(IV) compounds | The system design allows oxidation and filtration steps to<br>be combined in one unit        | Iron(III) compounds can hydrolyze to form gelatinous solids which may plug up the oxidation/filtration bed |
| Fenton's reagent              | The oxidation rate is faster than hydrogen peroxide and<br>oxidant solution more stable      | Operator error in mixing the iron(II) compound with the hydrogen peroxide can degrade the results          |

Source: [40].

#### Table 2

Precipitation/coagulation for arsenic removal from water.

| Method              | Advantages                                                                              | Disadvantages                                                                                                                         |
|---------------------|-----------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------|
| Co-precipitation    | No monitoring of a break through is required, with relatively low cost simple chemicals | Serious short and long-term problems with toxic sludge, multiple<br>chemicals requirement, operation requires training and discipline |
| Alum coagulation    | Durable powder chemicals normally available                                             | Efficient pre-oxidation is compulsory                                                                                                 |
| Iron coagulation    | More efficient than alum on weight basis                                                | Medium removal of As(III)                                                                                                             |
| Lime softening      | Most common chemicals                                                                   | Re-adjustment of pH is required                                                                                                       |
| Sorption techniques | No daily sludge problem                                                                 | Requires monitoring of break through or filter use. Requires periodical regeneration or medium shift                                  |
| Activated alumina   | Relatively well known and commercially available                                        | Re-adjustment of pH is required                                                                                                       |

to neutral pH whereas ferric salts are useful coagulants over a wider pH range [41]. The usual range of coagulant addition to the contaminated water is between 5 and  $50 \text{ mg L}^{-1}$ . The amount of coagulant used can be significantly reduced by the addition of polymers or colloidal clays during the mixing of the coagulant with the arsenic-contaminated water [42]. Many aquifers where arsenic contamination is present also contain phosphates or silicates in the water. The presence of phosphates or silicates in the contaminated water reduces the efficiency of arsenic removal. This also must be taken into consideration when precipitation and coagulation is the chosen arsenic removal method [43]. Table 2 summarizes the advantages and disadvantages of precipitation/coagulation methods for arsenic removal from water.

#### 2.3. Low cost adsorbents

Low cost adsorbents can be successfully applied to the high efficiency removal of arsenic from groundwater. Adsorption involves the use of granular adsorptive media for the selective removal of arsenic from water with or without pH adjustment and with or without spent media regeneration. Adsorptive media that have been most widely used are activated alumina, ion exchange resin, elemental iron or iron compounds, organic polymers, chars, coal, red mud, blast furnace slag (BFS), kaolin clay and silica sand, etc. Sometimes a combination of the media mentioned above is used together to maximize the adsorption of arsenic compounds. Adsorption media may also be used in combination with oxidants such as manganese compounds to pre-oxidize any arsenites present to arsenates which are more efficiently adsorbed from the contaminated water. Pre-filtration of the contaminated water may also be required in order to remove particulate matter that can deactivate the adsorption media and/or physically plug the adsorption bed. The effectiveness of adsorption for arsenic treatment is more likely than precipitation processes to be affected by characteristics and contaminants other than arsenic. Small capacity systems

using these technologies tend to have lower operating and maintenance costs and require less operator expertise. Adsorption and ion exchange therefore tend to be used more often when arsenic is the only contaminant to be treated, for relatively smaller systems, and as an auxiliary process for treating effluent from larger systems. Table 3 summarizes the advantages and disadvantages of each of the above mentioned adsorption media for the removal of arsenic from contaminated water.

#### 2.3.1. Agricultural by-products

Agricultural wastes are by-products, currently unused or underused for animal feed. Agricultural waste/by-products such as rice husks were used for arsenic removal from water. Maximum adsorption occurred at 0.01 mol L<sup>-1</sup> of HNO<sub>3</sub>, HCl, H<sub>2</sub>SO<sub>4</sub> or HClO<sub>4</sub> using 1.0 g of adsorbent for  $5.97 \times 10^{-3}$  mol L<sup>-1</sup> of arsenic for 5 min. The Freundlich isotherm was followed over concentration range from  $8.69 \times 10^{-5}$  to  $1.73 \times 10^{-3}$  mol L<sup>-1</sup> arsenic (l/n = 0.83 and K = 4.43 mmol g<sup>-1</sup>). The uptake of arsenic increased with increasing temperature [44].

Untreated rice husk was utilized for aqueous arsenic remediation [45]. Complete removal (using rice husk columns) of both As(III) and As(V) was achieved using initial As concentration,  $100 \text{ gL}^{-1}$ ; rice husk amount, 6g; average particle size, 780 and 510 m; flowrate, 6.7 and 1.7 mLmin<sup>-1</sup>; with pH of 6.5 and 6.0, respectively. Desorption (71–96%) was also achieved with 1 M of KOH.

#### 2.3.2. Industrial wastes/by-products

*2.3.2.1. Chars, and coals.* Lignite, peat chars [46–49] bone-char [50] and biochar [51,52] use in wastewater treatment has received increasing attention [46,47]. Being good substitutes for activated carbons, they are plentiful, inexpensive and locally available.

Arsenic(V) removal from aqueous solution by mixture of synthetic hydroxylapatite and baryte or bone-char was carried out [50] in the concentration range of  $4-100 \text{ mg L}^{-1}$ . Although the

### Table 3

Advantages and disadvantages of different methods for adsorption of arsenic from contaminated groundwater.

| Adsorption medium      | Advantages                                                                                                                       | Disadvantages                                                                                                                                              |
|------------------------|----------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Activated alumina      | Very efficient removal and the adsorbent can be regenerated <i>in situ</i> to extend the useful life                             | Adsorption efficiency is highest only at low pH and arsenites must<br>be pre-oxidized to arsenates before adsorption                                       |
| Ion exchange resin     | Removal efficiency independent of water pH and the adsorbent can be also be regenerated <i>in situ</i> to extend the useful life | Sulfates, nitrates or dissolved solids reduce adsorption efficiency<br>and must monitor removal efficiency to prevent adsorbent<br>saturation with arsenic |
| Iron or iron compounds | Higher removal efficiency at lower cost than some of the other<br>adsorbents and also oxidizes arsenites to arsenates            | Adsorption efficiency is highest only at low pH and the adsorbent<br>is not regenerable in order to extend life                                            |
| Organic polymer        | Removal efficiency optimized by composition of adsorbent and is replenishable <i>in situ</i>                                     | Adsorbent cost is higher than others and other water contaminants<br>such as dissolved solids reduce efficiency                                            |
| Kaolin clay            | Low cost adsorbent available worldwide and can be <i>in situ</i> regenerated to extend life                                      | Adsorption efficiency lower than most other adsorbents and other water contaminants can deactivate it                                                      |
| Silica sand            | Low cost adsorbent available worldwide and can be <i>in situ</i> regenerated to extend life                                      | Adsorption efficiency lower than most other adsorbents and other water contaminants can deactivate it                                                      |

Source: [140].

hydroxylapatite and baryte mixture had a little influence on arsenic concentrations, bone-char was very effective sorbing agent for As(V) in the pH range of 2–5.

Biochar by-products from fast wood/bark pyrolysis, were investigated as adsorbents for the removal of the As<sup>3+</sup>, Cd<sup>2+</sup>, and Pb<sup>2+</sup> from water [51]. Oak bark, pine bark, oak wood, and pine wood chars were obtained from fast pyrolysis at 400 and 450 °C in an augerfed reactor and characterized. Sorption studies were performed at different temperatures, pHs and solid to liquid ratios in the batch mode. Maximum adsorption occurred over a pH range of 3-4 for arsenic and 4-5 for lead and cadmium. The equilibrium data were modeled with the help of Langmuir and Freundlich equations. Overall, the data were well fitted with both the models, with a slight advantage for Langmuir model. As(III) removal followed the order: pine wood char  $(1.20 g g^{-1})$  < oak wood char  $(5.85 g g^{-1})$  < oak bark char  $(12.1 \text{ g g}^{-1})$  < pine bark char  $(12.15 \text{ g g}^{-1})$ . This study showed that by-product chars from bio-oil production might be used as abundant inexpensive adsorbents for arsenic remediation at a value above their pure fuel value.

2.3.2.2. Red mud. Red mud is a waste material generated during the production of alumina when bauxite ore is subjected to caustic leaching. A typical Bayer process plant generates 1 and 2 ton of red mud per ton of alumina produced [52]. Red mud has been explored as an alternate adsorbent for arsenic [53,54]. An alkaline aqueous medium (pH 9.5) favored As(III) removal, whereas the acidic pH range (1.1-3.2) was effective for As(V) removal [53]. The capacities were 4.31 mol  $g^{-1}$  at the pH of 9.5 for As(III) and 5.07 mol  $g^{-1}$  at the pH of 3.2 for As(V). Heat and acid treatments on red mud increased its adsorptive capacity [54]. Arsenic adsorption on acid and heat treated red mud was also pH-dependent, with an optimum range of 5.8-7.5 for As(III) and 1.8-3.5 for As(V) [54]. Adsorption followed a first-order rate expression and fitted the Langmuir isotherm well. Isotherms were used to obtain the thermodynamic parameters. The As(III) adsorption was exothermic, whereas As(V) adsorption was endothermic [53,54]. As(V) removal by using liquid phase of red mud (LPRM) was also reported [55]. Authors suggested that it was advantageous to use a waste material of red mud liquid phase in the treatment of arsenical wastewater.

Seawater-neutralized red muds (Bauxsol) [56], Bauxsol activated by acid treatment, and by combined acid and heat treatment, and Bauxsol with added ferric sulfate or aluminum sulfate [57], activated Bauxsol (AB), and chemically modified and activated Bauxsol (AB)-coated sand [58,59] were all applied to arsenic removal. Seawater-neutralized red mud (not activated) was prepared by suspending the red mud in the seawater solution and stirring until equilibrium pH was achieved [56]. Adsorption increased with decreasing pH (i.e., ligand-like adsorption), higher adsorbent dosages, and lower initial arsenate concentrations. Arsenate

adsorption decreased in the presence of HCO<sup>3-</sup>, while Cl<sup>-</sup> had little effect and Ca<sup>2+</sup> increased arsenic adsorption.

Water quality assessment after treatment with Bauxsol indicated that none of the trace elements tested were released from the adsorbent. The sorption capacity of this Bauxsol was  $14.43 \text{ mol g}^{-1}$ . The acid treatment alone, as well as in combination with heat treatment, increased arsenic removal efficiency [57,58]. Combined acid/heat treatment provided best removal [57]. Addition of ferric sulfate or aluminum sulfate suppressed arsenic removal. The activated Bauxsol (AB) produced using combined acid and heat treatment removed roughly 100% of the arsenate (at pH 4.5) with or without the presence of competing anions (i.e., phosphate, bicarbonate, and sulfate) at an initial arsenate concentration of  $\leq 2 \text{ mg L}^{-1}$ . Combined acid and heat treatments were performed by refluxing Bauxsol in HCl, adding ammonia for complete precipitation, filtering, washing with distilled water (DIW), and calcining at 500 °C for 2 h [58]. The optimal pH for As(V) and As(III) adsorption were 4.5 and 8.5, respectively. The adsorption data fitted the linear form of the Langmuir isotherm. The FITEQL and PHREEQC models were used to predict As(V) adsorption at various pH values (based on diffuse double layer models). The kinetics followed a pseudo first-order rate expression. Chemically modified Bauxsol and activated Bauxsol (AB)-coated sand were also investigated to remove As(V) from water [59]. Bauxsol-coated sand (BCS) and AB-coated sand (ABCS) were prepared by mixing Bauxsol or AB with wet sand and drying. The adsorption capacities of 3.32 and 1.64 mg  $g^{-1}$  at pH 4.5 and 7.1, respectively, for BCS; and of 2.14 mg  $g^{-1}$  for ABCS at pH 7.1 were reported.

It was suggested that the surface of Bauxsol and activated Bauxsol particles at pH 4.5 primarily covered by positively charged surface groups, which adsorb the negatively charged arsenate anions by electrostatic attraction. When ferric sulfate or aluminum sulfate is added both coagulation and adsorption take place. It was suggested clear that ligands (arsenate anions, e.g.,  $H_2AsO^{4-}$ ) are adsorbed on iron hydroxide flocs as Fe complexes. A similar mechanism was given for aluminum sulfate by Mohan et al. [51].

Recently Brunori et al. [60] also utilized red mud for treating contaminated waters and soils with particular attention to the Italian regulatory system. Experiments studied the metal trapping ability of treated red mud and the subsequent release of these trapped metals at low pH conditions. The treated red mud exhibited a high metal trapping capacity and metal release at low pH was generally low. The removal capability of treated red mud was increased using more mud in contact with the solution. After 48 h, only 35% of As (corresponding to an absolute value of  $230 \text{ g L}^{-1}$ ) was removed with  $2 \text{ g L}^{-1}$ , but the percentage significantly increased up to 70% (corresponding to an absolute value of  $400 \text{ g L}^{-1}$ ) with  $10 \text{ g L}^{-1}$ .

Modified calcined bauxite was also used for As(III) and As(V) remediation from ground water [61–64] in batch and column

modes. The optimum pH was ~7.0 for both As(III) and As(V). Adsorption was unaffected by temperature variations [61]. No appreciable ionic effects except from  $SO_4^{2-}$  and EDTA were observed from the background ions including  $Ca^{2+}$ ,  $Fe^{3+}$ ,  $Cl^-$ ,  $NO_3^-$ ,  $PO_4^{3-}$  and  $F^-$ . Sorption capacities were calculated using Langmuir model.

2.3.2.2.1. Blast furnace slag. Steel plants generate a large volume of granular blast furnace slag. It is being used as filler or in the production of slag cement. Recently, it was converted into an effective and economical scavenger and utilized for the remediation of aqueous arsenic [65,66].

Zhang and Itoh [65] synthesized an adsorbent for aqueous arsenic removal by loading iron(III) oxide onto melted municipal solid waste incinerator slag. The simultaneous generation of amorphous hydrous ferric oxide sol and a silica sol in situ eventually led to the formation of Fe-Si surface complexes which tightly bonded the iron oxide to the slag. For comparison, amorphous hydrous ferric oxide was also prepared. Loading of iron oxide on the slag increased the surface area of iron(III) oxi deloaded melted slag (IOLMS) by 68% compared to FeOOH, which could be attributed to the porous structure formed in IOLMS during the synthesis process. This adsorbent effectively removed both arsenate and arsenite, exhibiting removal capacities for As(V) and As(III) 2.5 and 3 times of those of amorphous hydrous ferric oxide, respectively. About 15 g of IOLMS is sufficient to remove 200 mg As(V) from 1 L of aqueous solution to meet the metal ion concentrations allowed by regulations for industrial wastewater discharge. In contrast 65 g of IOLMS was necessary to remove As(III) from 1 L solution to meet the permissible limit. Arsenic removal by IOLMS occurred by (1) affinity adsorption, (2) reaction with iron oxides and (3) reaction with calcium and other metallic elements initially contained in the slag. Affinity adsorption dependent on the surface area of IOLMS while chemical reactions depended on the existing forms of the arsenic species. The dominant arsenic species in aqueous solution correlated closely with the solution pH. In the pH range of 2–7, As(V) may be removed through the following reaction since  $H_2AsO^{4-}$  predominates:

 $FeOOH + 3H_2AsO_4^- + 3H_2 = Fe(H_2AsO_4)_3 + 2H_2O_3$ 

On the other hand, calcium and other metallic elements in the slag are also supposed to be effective for As(III) and As(V) removal.

Lower pH (2–7) was found more effective for As(V) removal than As(III) since As(III) was generally available as neutral molecules at pH < 9, and trace amounts of metallic elements could be leached out at pH > 9. The removal of As(III) at pH ~ 10 could be explained by the above Ca2+ coagulation route, i.e., anionic H<sub>2</sub>AsO<sup>3–</sup> predominates at pH ~ 10. Thus, Ca(H<sub>2</sub>AsO<sub>3</sub>)<sub>2</sub>·nH<sub>2</sub>O could form from Ca<sup>2+</sup> in the leachate, and if the solution pH increases only small amounts of Ca<sup>2+</sup> could be leached, while neutral H<sub>3</sub>AsO<sub>3</sub> could not react with Ca<sup>2+</sup> at pH < 9.

Zhang and Itoh [67] also used photocatalytic oxidation of arsenite and removal using slag iron oxide– $TiO_2$  adsorbent. The oxidation of arsenite was rapid, but the adsorption of the generated arsenate was slow. A concentration of 100 mg L<sup>-1</sup> arsenite was oxidized to arsenate within 3 h in the presence of adsorbent and under UV-light, but the reaction rate was approximately 1/3rd of the photocatalyzed reaction. The optimum application pH for the adsorbent for oxidation and adsorption was ~3.0.

Elemental iron, iron oxides, Ca–Fe oxides and calcium hydroxides from typical steel manufacturing processes were tested as adsorbents for treating mine-tailing leachate with high As concentrations [66]. These by-products were placed *in situ* as permeable reactive barriers to control arsenic release. Evaporation cooler dust (ECD), oxygen gas sludge (OGS), basic oxygen furnace slag (BOFS) and, to a lesser degree, electrostatic precipitator dust (EPD) effectively removed both As(V) and As(III). ECD, OGS and BOFS reduced As concentrations to <0.5 from 25 mg  $L^{-1}$  As(V) or As(III) solution in 72 h. Each exhibited higher As removal capacities than zero-valent iron. High Ca concentrations and alkaline conditions (pH ca. 12) provided by the dissolution of Ca hydroxides may promote the formation of stable, sparingly soluble Ca-As compounds. At an initial pH of 4, As reduction was enhanced by adsorption onto iron oxides. The elution rate of As adsorbed onto OGS and ECD decreased with treatment time. Thus, increasing the residence time within the permeable barrier would enhance As immobilization. ECD was found to be the most efficient barrier material to increase pH and to remove both As and dissolved metals in real tailing leachate. Authors did not attempt to determine the monolayer sorption capacities of various adsorbents. Kanel et al. [68] used blast furnace slag for aqueous As(III) remediation. The maximum As(III) adsorption capacity by BFS was 1.40 mg As(III) g<sup>-1</sup> of BFS at 1 mg L<sup>-1</sup> As(III) initial concentration. Oxidation of As(III) to As(V) and its adsorption/precipitation onto BFS was the dominating mechanism.

2.3.2.2.2. Fly ash. Coal combustion produces a huge amount of by-product fly ash, whose disposal requires large quantities of land and water. Currently, its applications are limited to civil engineering uses including cement and brick production and roadbeds. Bottom ash can also serve as an adsorbent [69,70]. Resource recovery from coal fly ash is one of the most important issues in waste management worldwide. Since the major chemical compounds contained in fly ash are aluminosilicate, intensive efforts have been recently made to utilize this material as an adsorbent. Fly ash obtained from coal power stations was examined for As(V) removal from water and to restrict As(V) migration in the solid wastes or the soil [71]. Kinetic and equilibrium experiments were performed to evaluate the As(V) removal efficiency by lignite-based fly ash. Removal at pH 4 was significantly higher than that at pH 7 or 10. Maple wood ash without any chemical treatment was also utilized to remediate As(III) and As(V) from contaminated aqueous streams in low concentrations [72]. Static tests removed ≤80% arsenic while the arsenic concentration was reduced from 500 to <5 ppb in dynamic column experiments.

2.3.2.2.3. *Miscellaneous*. Drinking water treatment residuals (WTRs) were also evaluated for As(V) and As(III) removal [73]. The Al-WTR effectively removed As(V) and As(III) while Fe-WTR removed more As(III) than As(V) in the pH range of 6.0–6.5.

Singh et al. [74] employed hematite and feldspar to As(V) removal from aqueous systems at different pHs, temperatures, and adsorbent particle size. Uptake followed first-order kinetics and fitted the Langmuir isotherm. The maximum removal was 100% with hematite (pH 4.2) and 97% with feldspar (pH 6.2) at an arsenic concentration of 13.35 mol L<sup>-1</sup>. Arsenate adsorption was favored electrostatically up to the pHzpc (7.1 for hematite and 8.5 for feldspar) of the adsorbents. Beyond this point, specific adsorption played an important role. The decrease in the extent of adsorption below pH 4.2 in case of hematite and below pH 6.2 in case of feldspar attributed to the dissolution of the adsorbents and a consequent decrease in the number of adsorption sites.

A low cost ferruginous manganese ore (FMO) removed both As(III) and As(V) from groundwater without any pretreatment in the pH range of 2–8 [75]. The major mineral phases present in the FMO were pyrolusite ( $-MnO_2$ ) and goethite [-FeO(OH)]. The FeO(OH) can directly adsorb arsenite and arsenate anions. Pyrolusite ( $-MnO_2$ ), the major mineral phase of the FMO behaved in a manner similar to hydrous manganese oxide, MnO(OH), because of the presence of chemically bound moisture. As(III) adsorbed more strongly than As(V). Once adsorbed, arsenic did not desorb in the pH range of 2–8. Bivalent cations, Ni<sup>2+</sup>, Co<sup>2+</sup>, Mg<sup>2+</sup>, enhanced the adsorption capability of the FMO. The cost of the FMO was ~50–56 US\$ per metric ton. This was much cheaper than the commercially available carbons. Recently, pisolite, a waste material from Brazilian manganese ore mines, was used for arsenic removal [76]. Both piso-

lite and activated pisolite were tested in batch and column modes. Maximum loadings of 1.5 and  $3.5 \text{ mg g}^{-1}$  were obtained for Pisolite and activated pisolite at pH 6.5.

Arsenite sorption on galena (PbS) and sphalerite (ZnS) was *Sand*. A variety of treated and coated sands were employed for arsenic remediation [77–81]. Sand coated with iron oxide had more pores and a high specific surface area [82]. Manganese greensand (MGS), iron oxide-coated sand (IOCS-1 and IOCS-2) and an ion exchange (Fe<sup>3+</sup> form) resin columns were used for dimethylarsinate removal from tap water [83].

Batch studies of IOCS-2 demonstrated an organic arsenic adsorption capacity of  $8 g g^{-1}$  IOCS-2. Higher bed volumes (585 BV) and high arsenic removal capacity (5.7 g cm<sup>-3</sup>) were achieved by this resin versus the other adsorbents. Poor performance was observed with MGS and IOCS-1. Recently, Nguyen et al. [80] synthesized iron coated sponge (IOCSp) for As(III) and As(V) removal. Each gram of IOCSp adsorbed about 160 g of arsenic within 9 h. Iron oxide-coated sand was also investigated by Joshi and Chaudhuri [84]. A home unit was designed for the arsenic removal from water. Lo and et al. [82], also reported the adsorption of heavy metal ions including arsenic on iron coated sand.

2.3.2.2.4. Clay minerals. Clay minerals are hydrous aluminum silicates, sometimes with minor amounts of iron, magnesium and other cations [85]. Clays have structures similar to the micas and therefore form flat hexagonal sheets. Typical clay minerals are kaolinite, illite and montmorillionite [85]. Clay minerals and oxides are widespread and abundant in aquatic and terrestrial environments. Finally divided clay minerals and oxides exhibit large surface areas. Clay minerals and oxides adsorb the cationic, anionic, and neutral metal species. They can also take part in the cation- and anion-exchange processes. Their sorption capacities, cation- and anion-exchange properties and binding energies vary widely. Many studies exist on arsenate and arsenite removal from water using oxides and clay minerals [74,75,86–93].

Arsenic remediation by clay-rich limestone from the Soyatal formation in Zimapán, Mexico was studied and compared with other rocks from the region [88]. The experimentally contaminated water  $(0.6 \text{ mg L}^{-1} \text{ As})$  was reacted with various rocks from the Zimapán region. All rocks decreased the aqueous arsenic concentration below detection limits (<0.030 mgL<sup>-1</sup>) in any contaminated waters that were reacted with the Soyatal formation. A rock:water weight ratio of 1:10 reduced the aqueous arsenic concentration in native water from 0.5 to <0.030 mgL<sup>-1</sup>. The calcareous shale of the Soyatal formation contains kaolinite and illite. Both minerals adsorbed arsenic. Adsorption of arsenate on kaolinite, montmorillonite and illite [94] and arsenite [86,87] on kaolinite, illite, montmorillonite, and amorphous aluminum hydroxide (am-Al(OH)<sub>3</sub>) were investigated as a function of pH and competing anions. The As(V) concentration ( $6.7 \times 10^{-7}$  M), the amount of suspended clay  $(2.5 \text{ g L}^{-1})$  and the ionic strength (0.1 M NaCl) were held constant [94].

#### 2.4. Membrane methods

Membrane methods have been applied primarily to purify brackish water or seawater for use as drinking water. Membrane processes can remove arsenic through filtration, electric repulsion, and adsorption of arsenic-bearing compounds. The viability of microfiltration and ultrafiltration as a technique for arsenic removal was highly dependent on the size distribution of arsenic-bearing particles in the source water [95]. Nano-filtration membranes were capable of removing significant portions of the dissolved arsenic compounds in natural waters. Reverse Osmosis (RO) was a technology proven through several bench- and pilot-scale studies, and was very effective in removing dissolved constituents. Since arsenic in groundwater was typically 80–90% dissolved, RO was a suitable technology for arsenic removal in groundwater [96–98].

Membrane filtration was effective in removing both As(III) and As(V) species. However, efficiency in removing As(V) was higher than for As(III). The effectiveness of membrane filtration for arsenic removal is sensitive to a variety of untreated water contaminants and characteristics [99]. It also produced a larger volume of residuals and tended to be more expensive than other arsenic treatment technologies. Therefore, its use is less frequent than precipitation/co-precipitation, adsorption and ion exchange.

Capital and operating costs of reverse osmosis systems could also be high relative to alternate methods especially for smallscale applications. Membrane systems were therefore best suited for large-scale applications where multiple contaminants must be removed from the water [98]. Table 4 summarizes the advantages and disadvantages of membrane techniques for removal of arsenic from groundwater.

#### 2.5. Ion exchange method

Small-scale systems and point-of-entry (POE) systems (treating water as it enters the home or building) often use ion exchange (IX) for arsenic removal because of ease of handling and sludge-free operation. However, treatment costs are relatively high than for conventional treatment in large-scale systems.

Ion exchange does not remove As(III) because it occurs predominantly as neutral complexes (H<sub>3</sub>AsO<sub>3</sub>) in water with a pH value of less than 9.0 [17]. The predominant species of As(V), H<sub>2</sub>AsO<sub>4</sub> and HAsO<sub>4</sub><sup>2-</sup> are negatively charged, and thus are removable by IX. If As(III) is present, it is necessary to oxidize As(III) to As(V) before removal by IX [100].

#### 2.6. Point-of-use methods

Experience with point-of-use methods in Bangladesh, India and elsewhere have indicated their success in small communities, individual households or small groups of households seeking arsenic removal from their drinking water. Table 5 summarizes the technical approaches used in selected point-of-use methods for arsenic removal. Various point-of-use methods include following:

- 1. Coagulation/precipitation/adsorption/filtration
- 2. Oxidation/coagulation/precipitation/filtration
- 3. Adsorption only
- 4. Oxidation/filtration/adsorption
- 5. Adsorption/filtration

The application of the individual methods varies from point to point depending upon the economic cost and given contaminated water source. Given the wide variation in arsenic concentrations in different locations as well as differences in water quality before treatment and that desired after treatment.

Some of these arsenic removal systems are under pilot-scale field trials to determine the technical advantages/disadvantages of the method and also determine the actual installed and operating costs under field conditions. Table 5 summarizes the technical approaches used in selected point-of-use methods while Table 6 summarizes other common methods employed for arsenic removal from water.

#### 2.7. Biomaterials for arsenic removal

Significant research has been conducted on biomaterials for their metal sorption capacity [101,102]. A promising approach is sorption technology, where biomaterials are used to remove heavy metals from aqueous solution. Sorption is the cheapest available

#### Table 4

Membrane techniques for removal of arsenic from groundwater.

| Method           | Advantage                                                                                   | Disadvantage                                                                                                                                                                                       |
|------------------|---------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Reverse osmosis  | Well defined performance<br>High removal efficiency                                         | High running costs<br>High investment costs                                                                                                                                                        |
| Electro-dialysis | No solid waste<br>Low space requirement<br>Capable of removal of other contaminants, if any | High tech operation and maintenance<br>Toxic wastewater<br>Re-adjustment water quality is required<br>Membrane does not withstand oxidizing agents<br>Membrane does not withstand oxidizing agents |

#### Table 5

Point-of-use methods, applied for arsenic removal from groundwater.

| Removal method         | Summary of known operating principles                                                                                             |
|------------------------|-----------------------------------------------------------------------------------------------------------------------------------|
| Double bucket (BUET)   | Coagulation/co-precipitation/adsorption (Bucket 1) followed by sand filtration (Bucket 2)                                         |
| DPHE or Danida         | Oxidation/coagulation/co-precipitation (stirred tank) followed by sand filtration (second smaller tank)                           |
| AIIPH in India         | Mixing/oxidation (Tank 1) followed by flocculation (Tank 2) followed by sedimentation (Tank 3) followed by filtration (Tank 4)    |
| Alcan                  | Activated alumina adsorption in a two bucket series                                                                               |
| BUET activated alumina | Oxidation/coagulation/co-precipitation/adsorption/filtration, followed by activated alumina adsorption                            |
| Sidko/Pal/Trockner     | Aeration/filtration followed by ferric hydroxide adsorption                                                                       |
| Sono-3-Kolshi          | Sand/iron/brick filter (Bucket 1) followed by sand/charcoal/brick filter (Bucket 2) followed by clean water collection (Bucket 3) |
| Sono 45-25             | Iron filings oxidation (Bucket 1) followed by sand filtration (Bucket 2)                                                          |
| Read-F                 | Copolymer/cerium oxide adsorption followed by sand filtration                                                                     |
| SAFI                   | Kaolin adsorption simultaneous with ferric oxide oxidation                                                                        |
| Tetrahedron            | Chlorination/pre-filtration (Column 1) followed by ion exchange (Column 2)                                                        |

Source: [140].

technology when the biomass is a waste material. Sorption mechanisms can be metabolism dependent (a function of the microbial cell activity) or independent [103], although the most common mechanisms are adsorption, ion exchange, complexation, and/or microprecipitation. Cell walls, consisting mainly of polysaccharides, proteins, and lipids, offer many functional groups which can bind ions, and these include carboxylate, hydroxyl, sulfate, phosphate, amide and amino groups. Metal sorption performance depends on external factors such as pH, other ions in solution which may be in competition, organic material such as complexing agents, cell metabolic products which may cause metal precipitation, and temperature [103].

Amongst various treatment options the surface modified adsorbents and biological treatment with living microbes are gaining momentum in recent years for the removal of arsenic from contaminated water [104]. Some of the bacteria having arsenic removal capability are Alcaligenes faecalis, Agrobacterium tumafecians, bacteria NT26, Bacillus indicus, Bacillus subtilis, Corynebacterium glutamicum, Desulfovibrio desulfuricans, Galleonella ferrigunea, Leptothrix ocracia, Pseudomonas putida, Pseudomonas rsenitoxidans, Ralstonia picketti, Thiomonas Ynys1, Thiobacillus ferroxidans, etc. [104–114].

Amongst these arsenic bacteria the *A. faecalis, B. subtilis*, bacteria *NT26, C. glutamicum*, etc. have been exploited recently to remove arsenic in batch reactor study [105,107,109,110]. The arsenic bacteria

may be arsenic oxidizing type, iron oxidizing type, sulfate reducing type or arsenic resistant type. Different types of bacteria have different types of gene. Although all the arsenic bacteria can survive in arsenic atmosphere, the bacteria type which reduces As(V) to As(III) and accumulate As(III) is specifically termed as arsenic resistant bacteria [110]. Arsenic resistant bacteria normally contain arsR and arsC gene in either plasmid or chromosome or in both and produce arsenic regulatory ArsR protein and arsenate reductase enzyme [106,110]. ArsR has specific active sites for accumulating As(III) [106] Recently, arsR–arsC gene cluster has been observed in *Ralstonia eutropha CH34* [106], which is also known as *R. eutropha MTCC 2487* [15]. This strain can produce ArsR protein and arsenate reductase enzyme [106]. However, the arsenic removal by this strain is not yet demonstrated [106].

*R. eutropha* has also the capability to grow autotrophically in absence of organic source [116]. The chemoautotrophic nature of *R. eutropha* increases its potential for treating arsenic containing water where organic carbon is hardly present. Efficient removal of some heavy metals like Cd, Co, Hg, Ni and Zn from contaminated water by using *R. eutropha MTCC 2487*, isolated from Zn factory wastewater, has been well documented [115].

Arsenic removal efficiency of bacteria improves when it is immobilized on a solid support like GAC [104]. If fresh GAC is used some amount of physico-chemical adsorption may occur along with bio-adsorption/accumulation leading to simultaneous adsorption

#### Table 6

Other common methods for removal of arsenic from water.

| Method              | Advantages                                                              | Disadvantages                                                                                                                                               |
|---------------------|-------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Lime softening      | Most common chemicals                                                   | Re-adjustment of pH is required                                                                                                                             |
| Sorption techniques | No daily sludge problem                                                 | Requires monitoring of break through or filter use. Requires periodical regeneration or medium shift                                                        |
| Activated alumina   | Relatively well known and commercially available                        | Re-adjustment of pH is required                                                                                                                             |
| Iron coated sand    | Expected to be cheap. No regeneration is required                       | Yet to be standardized. Toxic solid waste [97,98]                                                                                                           |
| Ion exchange resin  | Well defined medium and hence capacity                                  | High cost medium, high tech. operation and maintenance. Regeneration<br>creates a sludge problem [100]                                                      |
| Membrane techniques | Low space requirement. Capable of removal of other contaminants, if any | High running costs, high investment costs, high tech operation and<br>maintenance. Toxic wastewater. Re-adjustment of water quality is required<br>[96,141] |
| Reverse osmosis     |                                                                         | Membrane does not withstand oxidizing agents                                                                                                                |

bioaccumulation (SABA). Use of spent GAC minimizes the physicochemical adsorption as the arsenic adsorption capacity of spent GAC is very low. The removal efficiency of bio removal process may also be dependent on the other process parameters like agitation time, pH, etc. The initial arsenic concentration also influences the % removal.

Haque et al. [117], investigated the adsorption of arsenic on sorghum biomass (SB) for the removal of arsenic from aqueous solutions. Potentiometric titrations and FTIR analysis evidenced two potential binding sites associated with carboxyl and hydroxyl groups. Batch experiments were carried out to determine the equilibrium time for arsenic adsorption to SB. The effect of pH on arsenic adsorption to SB was investigated for a pH range of 2.0–10.0. A strong influence of pH was demonstrated with a maximum removal of arsenic at pH 5.0. Freundlich and Langmuir isotherms were applied to equilibrium data. The Freundlich model fitted the equilibrium data and provided evidence for site heterogeneity at the binding surface [117].

Micro fungi including Aspergillus niger offer low cost adsorbents for heavy metal cations removal from aqueous solutions [118]. Bai and Abraham [119], reported better sorption of Cr(VI) by chemically modified Rhizophus nigricans compared to the untreated biomass. Loukidou et al. [120] also reported enhancement of arsenate removal with chemically [polyelectrolyte (magnafloc), dodecylamine, and cetyl trimethyl ammonium bromide] modified Penicillium chrysogenum compared with the unmodified biomass. Most of these chemicals used for fungal cell surface modifications are hazardous and use of such adsorbents for water purification pose a threat to public health. Earlier experiments with A. niger in a batch mode showed that it could be used as an effective adsorbent after certain chemical modifications and iron oxide treatment significantly enhanced arsenic removal efficiency [121]. The relative advantage of this adsorbent is that it can be used for drinking water treatment. The other benefits are that waters containing both cationic and anionic heavy metals can be simultaneously treated by passing the polluted water through a column packed with A. niger and another column packed with iron oxide-coated A. niger.

Pokhrel and Viraraghavan [122] examined arsenic removal in a continuous flow system and analyzed the breakthrough behavior of a column packed with iron oxide-coated fungal biomass. Column studies were conducted, using iron oxide-coated *A. niger* biomass, to examine the removal of arsenic [As(III) and As(V)] from an aqueous solution. The Thomas and Yan models were examined to predict the breakthrough curves. The Yan model described the data better (based on the  $R^2$  values) when compared with the Thomas model. The adsorption capacity of the iron oxide-coated biomass estimated by the Thomas model [1070 Lgg<sup>-1</sup> for As(V) and 700 Lgg<sup>-1</sup> for As(III)] was comparable to the calculated value of its adsorption capacity [1080 Lgg<sup>-1</sup> for As(V) and 880 Lgg<sup>-1</sup> for As(III)] [122].

The water hyacinth (Eichhornia crassipes) is a member of the pickerelweed family (Pontederiaceae). The plants vary in size from a few centimeters to over a meter in height [123]. The glossy green, leathery leaf blades are up to 20 cm long and 5-15 cm wide and are attached to petioles that are often sponge-like and inflated. Numerous dark, branched, fibrous roots dangle in the water from the underside of the plant. The water hyacinth family is one of the most productive plant groups on earth. They are also one of the world's most troublesome aquatic plants, forming dense mats that interfere with navigation, recreation, irrigation, and power generation. These mats competitively exclude native submersed and floating-leaved plants. Water hyacinth mats deplete dissolved oxygen and the dense floating mats impede water flow and create good mosquito breeding conditions. The plant is called a "green plague". However, Haris's report [124] published by the Royal Society of Chemistry in the United Kingdom suggests that it may be a natural solution to arsenic water contamination.

Haris and co-workers [124] demonstrated that dried roots of the water hyacinth rapidly reduce arsenic concentrations in water to levels less than the maximum value (10 ppb) for drinking water recommended by the World Health Organization [124]. Water hyacinth plants from a pond in Dhaka, Bangladesh were dried in air and a fine powder was prepared from the roots. More than 93% of arsenite and 95% of arsenate was removed from a solution containing 200 g of arsenic per L within 60 min of exposure to the powder. The arsenic concentration remaining was less than the WHO drinking water guideline value of  $10 \text{ gL}^{-1}$ .

Earlier, Misbahuddin and Fariduddin [125] had noted that water hyacinths removed arsenic when placed in arsenic-contaminated water for 3–6 h. The extent of arsenic removal depended on the arsenic concentration present, the amount of water hyacinth used, the exposure time and the presence of air and sunlight. These authors reported that whole plants were more effective than fibrous roots alone.

Water hyacinths (*E. crassipes*) were used as a pollution monitor for the simultaneous accumulation of arsenic, cadmium, lead and mercury [126]. After 2 days of cultivation in tanks containing 10 ppm each of As, Cd, Pb and Hg in aqueous solution, the plants were harvested and rinsed with tap water. The leaves and stems were separated and analyzed for each of the metals. The ratio of the arsenic and mercury concentrations in the leaves to the concentrations in the stems was found to be 2:1. Cadmium and lead showed a concentration ratio of about 1:1 in the leaves versus the stems. The arsenic concentration in leaves was the lowest of all the metals at 0.3 mg g<sup>-1</sup> of dried plant material.

The leaf concentration of cadmium was highest at  $0.5 \text{ mg g}^{-1}$  of dried plant material. Arsenic removal by water hyacinths (*E. crassipes*) was also reported by Low and Lee [127]. Phytofiltration, the use of plants to remove contaminants from water, is a promising technology [128,129]. Eapen and D'Souza [130] reviewed the use of genetic engineering to modify plants for metal uptake, transport and sequestration in order to enhance phytoremediation efficiency Metal chelator, metallothionein (MT) and metal transporter; phytochelatin (PC) genes have been transferred to plants for improved metal uptake and sequestration. As more genes related to metal metabolism are discovered new vistas will be opened for development of efficient transgenic plants for phytoremediation. Floating plant systems have been introduced to adsorb contaminants followed by harvesting the biomass [129]. However, these systems are not particularly efficient, especially in temperate zones [131].

The potential of using recently identified arsenichyperaccumulating ferns to remove arsenic from drinking water was investigated [132,133]. Hydroponically cultivated arsenichyperaccumulating fern species (Pteris vittata and Pteris cretica cv. Mayii) and a non-accumulating fern species (Nephrolepis exaltata) were suspended in water containing 73As-labeled arsenic with initial arsenic concentrations ranging from 20 to  $500 \text{ g L}^{-1}$  [132]. The arsenic phytofiltration efficiency was determined by monitoring the depletion of 73As-labeled arsenic. P. vittata reduced the initial arsenic concentration of  $200 \text{ g L}^{-1}$  by 98.6% to  $2.8 \text{ g L}^{-1}$ in 24 h. An initial aqueous arsenic concentration of 20 g L<sup>-1</sup> was reduced to  $7.2 \text{ g L}^{-1}$  in 6 h and to  $0.4 \text{ g L}^{-1}$  in 24 h by *P. vittata*. P. vittata and P. cretica plants of same age had similar arsenic phytofiltration efficiencies, rapidly removing arsenic from water to achieve arsenic levels below the new drinking water limit of  $10 \text{ gL}^{-1}$ . However, N. exaltata failed to achieve this arsenic concentration limit under the same experimental conditions. The significantly higher efficiency of arsenic phytofiltration by arsenic-hyperaccumulating fern species is associated with their ability to rapidly translocate absorbed arsenic from roots to shoots. The non-accumulating fern N. exaltata was unable to effect this arsenic translocation [132]. Webb et al. [134] showed that P. vittata L. accumulated As(III) predominantly in the leaves. The live plant maintained As as As(III), but after biomass sample collection, aging and drying, As(III) was gradually oxidized to As(V). At very high As concentrations (ca. 1 wt.% As versus dry biomass wt.), the As was most often coordinated by sulfur and oxygen. *P. vittata* (bake fern) extracts arsenic from soil and translocates it into its above ground biomass extremely efficiently [135]. Tu and Ma [136] also examined the effects pH, As and P, on the As hyperaccumulator *P. vittata* L. to optimize plant growth and maximize As removal from contaminated sites.

Low pH enhanced the plant's uptake of As (pH  $\leq$  5.21) and P (pH  $\leq$  6.25). The fern had a relatively high P uptake at low pH/low As or at high pH/high As. The saddle points (turning points) were pH 6.33 and As 359Mm for plant biomass and pH 5.87 and As 331Mm for P uptake based on the response surface plot. Tu et al. [137] further examined the phytoremediation of arsenic-contaminated groundwater by the fern *P. vittate* L. Alkorta et al. [138] reviewed plants which might be used to combat arsenic poisoning epidemic.

# 3. Mitigating the water arsenic problem: social and institutional aspects

#### 3.1. Awareness

Because arsenic contamination is largely a natural phenomenon, it is important that communities are engaged in taking local action and pressing for support to mitigate the effects of arsenic contamination of water supplies. Public awareness campaigns will be needed where the problem is not already familiar to communities. The mass media need accurate information and facilitation to make public problems and solutions, and to generate action rather than alarm. Radio and television especially can play an important role in public information and education. While mass media is critical to generate political will and public awareness, it tends to have less penetration and influence in rural areas. Local popular media, such as folk theatre, can make a difference especially when this is linked to group discussion and participatory groups.

Special efforts may be needed to reach women and very poor people who do not have regular access to media. Public meetings to raise awareness and plan local action may be needed, and in some areas these may need to be planned so that women and men are seated separately (with equal access to the meeting), or separate meetings may needed to be arranged for women and men.

#### 3.2. Sharing arsenic-free point sources

Due to differences in sedimentary characteristics, not every drinking water source is affected. Since only water for drinking and cooking has to come from an unaffected source, it is in principle possible to share an arsenic-free point source (usually a hand pump well). But it depends upon the number of users and willingness of the owner of the well or pump to share arsenic free water. However, sharing a source is less simple than it sounds, due to sociocultural and economic constraints. Solutions based on sharing may prove only temporary. An arsenic-free source may become contaminated, while population growth may put unsustainable pressure on unpolluted sources.

#### 3.3. Arsenic removal at household level

A second option is the removal of arsenic at household level. Communities and households need to know about the different types of equipment, available in the market, at what price, and how long each equipment can be expected to last. This information needs to be available to all people. Meetings and demonstrations should be arranged to show operation and maintenance tasks. Even if incentives/subsidies are available, the cost of equipment will be beyond most poor families, where poverty prevents people from acquiring the equipment in one go, arrangements for credit and saving through banks and/or credit and savings groups will be needed. Although banks do not easily give loans to low-income individuals, there are promising experiences with micro-credit schemes [139].

#### 3.4. Communal plant

Another option is that the people can consider is to have a treatment plant installed at community level. A community level solution has the advantage of being able to deliver arsenic free water to a large number of households. However, there are financial costs for an (part time) operator, and costs in time for a management committee and for regular meetings. A successful communal system depends on the operator, management committee and implementing agency interacting well together and functioning effectively. A communal plant is therefore best installed when there is a clear sense of community and experience with community processes and services.

#### 3.5. Institutional aspects

Informed choice implies good quality information, communication and decision-making processes. In the early stages, there is a need for experienced facilitators who know how to work with different user groups using participatory techniques in an equitable manner facilitators also need to be well-versed in the technology so that they can explain the processes and answer any questions that may arise in group discussions. Within many cultures, it is important to have male and female facilitators, and for a woman to train the women in operational skills and for a man to train the men.

#### 4. Conclusion

Arsenic in drinking water is a problem just about anywhere in the world, particularly in developing parts of Asia (Bangladesh, Pakistan and India). Arsenic contamination is largely a natural phenomenon, and no preventive measures can usually be taken, so only remediation technologies can help to minimize the effect. Arsenic can be removed from water in various ways like water purification techniques. Some of technologies are traditional treatment processes coagulation/filtration, lime softening, iron/manganese oxidation, and membrane filtration, which have been used to improve removal of arsenic from drinking water in water treatment plants. Technologies such as ion exchange, manganese greensand filtration and adsorption on activated alumina have been employed in small and domestic systems these are cheep and easily adoptable by local community after small information training. Innovative technologies, such as permeable reactive barriers, biological treatment, phytoremediation (using plants), and electrokinetic treatment, are also used to treat arsenic-contaminated water. However, many of these techniques are at the experimental stage and some have not been demonstrated at full-scale. It is recommended that a combination of low cost chemical treatment like ion exchange, filtration and adsorption along with bioremediation may be useful option for arsenic removal from drinking water.

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