

Laboratory based approaches for arsenic remediation from contaminated water: Recent developments

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Abstract

Arsenic contamination in water has posed severe health problems around the world. In spite of the availability of some conventional techniques for arsenic removal from contaminated water, development of new laboratory based techniques along with enhancement and cost reduction of conventional techniques are essential for the benefit of common people.

This paper provides an overview of the arsenic issue in water such as modes of contamination of ground water as well as surface water by arsenic, its metabolism and health impacts, factors influencing arsenic poisoning, fundamentals of arsenic poisoning mechanism and world scenario of arsenic poisoning. It discusses and compares the conventional laboratory based techniques, like precipitation with alum, iron, Fe/Mn, lime softening, reverse osmosis, electro dialysis, ion exchanges, adsorption on activated alumina/carbon, etc., for arsenic removal from contaminated water. It also discusses the best available techniques and mentions the cost comparison among these techniques too. Recent developments in the research on the laboratory based arsenic removal techniques, like improvement of conventional techniques and advances in removal technology along with its scopes and limitations have also been reviewed.

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1. Introduction

Arsenic, the world's most hazardous chemical [1], is found to exist within the shallow zones of ground water of many countries like Argentina, Bangladesh, India, Pakistan, Mexico, Mongolia, Germany, Thailand, China, Chile, USA, Canada, Hungary, Romania, Vietnam, Nepal, Myanmar, Cambodia, etc. in various concentrations [2–19]. In some places in Bangladesh its concentration is as high as 1000 $\mu\text{g/l}$ [4]. The contaminants like iron, calcium, magnesium, bicarbonate, chloride and sulfate are found to be associated with arsenic in the ground water of these countries. Surface water is also found to be contaminated with arsenic by the anthropogenic sources to various degrees. White et al. reported that the NaCl-dominated brine of Tisakürt, Hungary, contains more than 5800 $\mu\text{g/l}$ of arsenic [20].

Considering the lethal impact of arsenic on human health, environmental authorities have taken a more stringent attitude

towards the presence of arsenic in water. World Health Organization (WHO) in 1993 and National Health and Medical Research Committee (NHMRC), Australia, in 1996 had recommended maximum contaminant level (MCL) of arsenic in drinking water as 10 and 7 $\mu\text{g/l}$ respectively [21,22]. The MCL of arsenic in drinking water has also been reduced from 50 to 10 $\mu\text{g/l}$ by European Commission in 2003 [23]. Environmental Protection Agency (EPA), USA, has decided to move forward in implementing the same MCL of arsenic that is recommended by WHO for drinking water in 1993 [24].

Japan and Canada has reduced the MCL for arsenic in drinking water to 10 and 25 $\mu\text{g/l}$, respectively. The MCL for arsenic in countries like India, Bangladesh, Taiwan, China, Vietnam, etc. is also 50 $\mu\text{g/l}$ [25].

Water is one of the most important media through which arsenic enters into the human body. As the diagnosis and medication of the arsenic related diseases are difficult the treatment of contaminated water as a preventive measure appears to be an effective alternative to combat arsenic poisoning. Arsenic may be available in water in variable oxidation states (+5, +3, 0, –3) [26,27]. From contaminated water it can be converted into

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insoluble compounds and can be co-precipitated with the hydroxides of Fe and Mn in aqueous medium under certain conditions [28–34]. Like other heavy metals it may also be adsorbed by suitable adsorbent.

Arsenic can be removed from contaminated water by physico-chemical as well as biological techniques. These techniques are classified as below:

- (I) Physico-chemical techniques
 - (a) Adsorption
 - (b) Ion exchange
 - (c) Precipitation–coagulation
 - (d) Membrane filtration
 - (e) Permeable reactive methods
- (II) Biological techniques
 - (a) Phytoremediation
 - (b) Biological treatment with living microbes/bio-filtration

The modes of contamination of water by arsenic, arsenic metabolism and its poisoning effects, severity of the arsenic poisoning around the world, and the efforts to solve this problem by conventional laboratory based technology and search for new upgraded technology are discussed below.

2. Occurrence and mobilization

Arsenic belongs to the metalloid group of elements that shows many metallic properties and co-exists in nature with other metals like Fe, Cu, Ni, Zn, etc., as sulfide or oxide ores. Arsenic cannot be destroyed it can only be converted from one form to other form. The predominant form of inorganic arsenic in aqueous oxic environments is arsenate [As(V) as H_3AsO_4 , $\text{H}_2\text{AsO}_4^{-1}$, HAsO_4^{-2} and AsO_4^{-3}], whereas, arsenite [As(III) as H_3AsO_3 and $\text{H}_2\text{AsO}_3^{-}$] is more prevalent in anoxic environments [35]. Arsenic naturally occurs in over 200 different mineral forms of which approximately 60% are arsenates, 20% sulfides and sulfosalts; the remaining 20% includes arsenides, arsenites, oxides, silicates and elemental arsenic (As) [36]. As^0 and As^{3-} are rare in aquatic environments [37,38]. Organic arsenic species available in contaminated surface and ground water are mono methyl arsenate (MMA) and dimethyl arsenate (DMA) [39–43].

The sources of arsenic contamination in ground water are:

- (A) *Natural*: Through dissolution of arsenic compounds adsorbed onto the pyrite ores in to the water by geothermal, geo hydrological and bio geo chemical factors [44].
- (B) *Anthropogenic*:
 - (i) From processing of varieties of ores like Cu, Au, Ni, Pb, and Zn [45].
 - (ii) From ingredients of many insecticides and herbicides [46].
 - (iii) From cotton and wool processing [42].
 - (iv) From arsenic based wood preservative [44].
 - (v) From feed additives in various metal alloys and in mining [37,44].
 - (vi) From seepages from hazardous waste site [44].

- (vii) From areas near cemeteries where burials were conducted from about 1880 to 1910 when arsenic was used as an embalming fluid [44].
- (viii) From power generation by the burning of arsenic contaminated coal [32].
- (ix) From semiconductor and glass manufacturing units [45].

It has been found that when river water, which is a primary source of drinking water, is polluted by industrial or mining effluent or by geothermal waste the arsenic concentration increases [3]. The highest reported arsenic concentration so far is 850,000 $\mu\text{g/l}$ from an acid seep in the Richmond mine at Iron Mountain, California [47].

It has been reported that groundwater from shallow tube wells (12–33 m) contain considerably high amount of arsenic where as, the water from deep tube wells (200–300 m) contain low amount of arsenic (<50 $\mu\text{g/l}$) [48]. The arsenic concentration in ground water depends on various factors like presence of thick clay barriers surrounding the aquifer, depth of tube well, etc. It is a proven fact that the presence of elevated concentrations of phosphate or silicate may enhance the sub-surface mobility of As(V) in soils contaminated with arsenate [49,50]. Different adsorptive affinities of both arsenate and arsenite to various common mineral surfaces (i.e., ferrihydrite, alumina, etc.) are considered to affect this arsenic mobilization in the aqueous phase [34,51].

The sub surface mobilization of arsenic is caused by the combination of chemical, physical and microbial factors [52]. The following theories have been proposed to explain this mobilization.

- (i) Oxidation of As containing pyrites [2,53].
- (ii) Release of As(V) from reduction of iron oxides by autochthonous organic matter (e.g., peat) [35].
- (iii) Reduction of iron oxides by allochthonous organic matter (from dissolved organics in recharging waters) [54].
- (iv) Exchange of adsorbed As(V) with fertilizer phosphates [55].
- (v) Reduction of oxy hydroxides by microbial oxidation of sedimentary carbon [56].

Mobilization may also occur by displacement of arsenic by carbonate [57]. Arsenic mobility appears to be related to recent inflow of carbon through either organic carbon-driven reduction or displacement by carbonate. However, the apparent relation of arsenic mobility to inflow of organic carbon raises concerns about the appropriate depth of new drinking water wells and their position relative to irrigation. Large-scale ground water withdrawal for irrigation during the summer months causes lowering of water table, provides oxidants (e.g., oxygen, nitrate) and enhances oxidation that would further stimulate As(III) oxidation. This would cause a build-up of microbial biomass (and its associated organic matter) and the creation of anoxic conditions. This microbial biomass along with other organic matters received from sources such as decomposed buried peat deposits or seasonal recharge (4–6 months in a year) from agricultural surface waters, would in turn promote the dissimilatory reduction of As(V) adsorbed on the minerals like ferrihydrite by

disassimilatory arsenate reducing prokaryotes (DARPs). Consequently, arsenic finds its way to ground water and affects the drinking water tube wells of that region [35,58]. The release of arsenic is 10–13 times more in the reduction process as compared to that under oxidation process [58,59]. However, recently it has been shown that the primary mechanism for the arsenic release from solid phases is the competition between arsenic and organic anions for sorption sites and red-ox reactions probably play minor role [60].

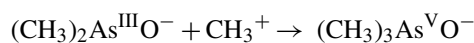
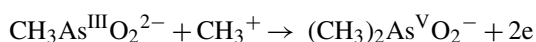
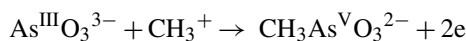
3. Arsenic metabolism

All living organisms have system for detoxification of arsenic. The common schemes for arsenic metabolism are as follows [61]:

- Uptake of As(V) as arsenate and As(III) as arsenite by phosphate transporters.
- Reduction of As(V) to As(III) by arsenate reductases.
- Extrusion or sequestration of As(III).

Both arsenate and arsenite are taken up by phosphate transporters. Phosphate transporters available in prokaryotes are different from that of human. Some examples of phosphate transporters are given in Table 1.

As(V) is reduced to As(III) by glutathione in higher eukaryotes. The reduced arsenic moiety then accepts a methyl group from *S*-adenosylmethionine and produces monomethylarsonic acid (MMA) or dimethylarsonic acid (DMA) [62]. Similarly fungi produce trimethylarsine [63], whereas bacteria may produce MMA and DMA [64]. Scheme for the stepwise conversion of arsenite into mono-, di-, and tri-methylated products has recently been suggested as follows [65]:



Some diverse microbes such as anaerobic methanogenic Archaea [66] and aerobic Eubacteria [67] can also form methylated arsines. Arsenic may also be converted to arsenobetaine and arsenic-containing sugars, benign compounds that are found in high abundance in some marine animals and algae as well as terrestrial plants and animals [68]. In *Escherichia coli* and yeast, arsenic(V) reductase enzymes ArsC and Acr2P mediate the reduction of As(V) to As(III) in cytoplasm, respectively. A cysteine residue near the N-terminal of ArsC binds the As(V), which is then reduced with electrons donated by the reduced glutathione. In both the cases glutathione and glutaredoxin serves as the reducing potential. Although the reduction of As(V) to As(III) in mammal was believed previously to take place in the cell by a non-enzymatic chemical reduction via intracellular GSH, this appears to be now unlikely. Recently, it has been found that human liver arsenate reductase; a protein identical to purine nucleoside phosphorylase reduces arsenate to arsenite during arsenolysis in presence of dihydro lipoic acid [69].

As(III) can be excreted via an As(III)-specific transporter ArsB. This ArsB transporter is produced from *arsB* gene, which may be available in chromosome as well as plasmids of prokaryotes. In *E. coli* the As(III) is expelled from the cytoplasm through an adenosine 5'-triphosphate (ATP)-dependent arsenite transporter formed by ArsAB [70] whereas in of *S. aureus* As(III) may be expelled from the cell via an ATP-independent ArsB produced from plasmid gene *arsB*. Although this process has been studied in detail in *E. coli* and *S. aureus*, it is found in many other bacteria and occurs in strict anaerobes like *Clostridium* [71] and *Desulfovibrio* [72]. In yeast, Acr3P a plasma membrane arsenite reflux protein and YcfP, a member of multi drug resistance associated protein; transport As(GS)₃ into vacuole. In mammals MrP plays a major role for the extrusion of arsenic from cells. For example, MrP2 extrudes As(III) into bile. The role of the proteins/enzymes on arsenic metabolism/detoxification is summarized in Table 1.

Table 1
Proteins/enzymes responsible for arsenic metabolism in different living organisms

Metabolic action	Living species	Responsible proteins	Reference
As(V) uptake	<i>E. coli</i>	Pit and Pst Pit predominant	Rozenberg et al. [73] Willesky et al. [74]
	Mammal	Not yet demonstrated	
As(III) uptake	Yeast	GlpF	Sanders et al. [75]
	<i>S. cerevisiae</i>	Fps1	Wysocki et al. [76]
	Mammal	AQP9 (suggested)	Liu et al. [77]
Reduction of As(V) to As(III)	<i>E. coli</i>	Ars C enzyme	Martin et al. [78]
	Yeast	Acr 2P enzyme	Mukhopadhyay et al. [79]
	Mammal	Non enzymatic reduction via intracellular GSH	Scott et al. [80]
		Human liver arsenate reductase	Radabough et al. [81] Radabough et al. [82]
Extrusion or sequestration of As(III)	<i>E. coli</i>	Ars B alone or with ArsAB ATPase	Dey et al. [83]
	Yeast	Acr3P	Ghosh et al. [84]; Wysocki et al. [85]
	Mammal	YcfP	Ghosh et al. [86]
		MrP2	Kala et al. [87]

4. Arsenic poisoning

The toxicity scale of arsenic decreases in the following order: arsine > inorganic arsenic(III) > organic arsenic(III) > inorganic arsenic(V) > organic arsenic(V) > arsonium compounds and elemental arsenic. The carcinogenic and mutagenic effects of arsenic have been established. Its teratogenic effect has also been reported recently. Poisoning effect of arsenic on human health, fundamentals of the poisoning mechanism, effect of dose and nutritional factors on the poisoning is discussed in subsequent sections below.

4.1. Effects on human health

Health effects of arsenic on human are classified as acute and sub acute which are typically reversible and chronic effects. Acute and sub acute poisoning results from ingestion of large quantities of arsenic with lower exposure time whereas, chronic poisoning occurs due to consumption of arsenic contaminated water for a long time period. Nonspecific gastrointestinal effects such as diarrhoea and cramping; hematological effects including anaemia and leukaemia; and peripheral neuropathy might occur after weeks or month of exposure to high doses of arsenic (0.04 mg/kg/day or higher) [88]. Consumption of large arsenic at a time may also cause stomach pain, nausea, vomiting or diarrhoea, which may lead to shock, coma, and even death. It has also been reported by many researchers [89–93] that chronic arsenic poisoning causes hypertension, peripheral vascular diseases, cardiac vascular diseases, respiratory diseases, diabetes mellitus, malignancies including cancer of the lungs, bladder, kidney, liver, uterus and skin. The skin is quite sensitive to arsenic and skin lesion (hyperkeratosis and dyspigmentation) has been observed even at the exposure levels in the range of 5–10 µg/l arsenic in drinking water [89].

As per 2001 update of drinking water by NRC [88], diffuse or spotted hyper pigmentation may be seen after 6 months to 3 years by chronic ingestion of high doses of arsenic (0.04 mg/kg/day or higher) or 5–15 years of ingestion of low doses of the order of 0.01 mg/kg/day or higher. Palmer-plantar hyperkeratosis is usually evident within years of the initial appearance of arsenical hyper pigmentation. Perturbed porphyrin metabolisms are irreversible non-cirrhotic portal hypertension, which have been seen following chronic exposure to 0.01–0.02 mg/kg/day or higher. A risk of mortality from hypertension and cardiovascular disease has also been associated with chronic exposure to arsenic. An association has been reported between chronic ingestion of arsenic in drinking water and an increased risk of diabetes mellitus. Some evidence also suggests that the ingestion of arsenic can have effects on the immune and respiratory systems. Teratogenic effects have been seen following parental arsenic exposure in a number of mammalian species, but little evidence suggests that those effects follow oral or inhalation exposure. There are inadequate data to draw conclusions on the effects of arsenic on fertility and pregnancy outcomes. Young children, the elderly, unborn babies, and people with long-term illness are at great risk of arsenic poisoning.

Table 2
Arsenic level in tap water and cancer risk

Arsenic level in tap water (in parts per billion, or ppb)	Approximate total cancer risk (assuming 2 l consumed/day)
0.5	1 in 10000
1	1 in 5000
3	1 in 1667
4	1 in 1250
5	1 in 1000
10	1 in 500
20	1 in 250
25	1 in 200
50	1 in 100

Table 2 shows the lifetime risks of cancer from arsenic in tap water, based on the National Academy of Sciences' 1999 (USA) risk estimates [94].

4.2. Fundamentals of poisoning mechanism

The mode of poisoning depends on the chemical form of arsenic [35]. Arsenate is a molecular analog of phosphate and inhibits oxidative phosphorylation thereby short-circuiting life's main energy-generation system. Arsenite is even more broadly toxic because it binds to sulfhydryl groups impairing the function of many proteins [62]. It also affects respiration by binding to the vicinal thiols in pyruvate dehydrogenase and 2-oxoglutarate dehydrogenase [95]. The mechanisms, by which arsenic induces cancer however, remain poorly understood although multiple pathways such as inhibition of DNA repair, DNA methylation, gene amplification and co-carcinogenesis with other environmental toxicants have been proposed. Recently, it has been reported that arsenic induces both small and large mutations in the PZ189 shuttle vector system in cultured mammalian cells [90] as well as intra chromosomal recombination in the hprt gene of CHO cells [91] due to the generation of free radical on arsenic exposure.

4.3. Dose–response relationship

It is proved that arsenic poisoning occurs by consumption of drinking water that naturally contains high amount of inorganic arsenic [93]. Tondel et al. by their study in Bangladesh have correlated the prevalence of malignancies with arsenic intake [96]. By prospective study in large endemic areas of chronic arsenic poisoning, many researchers have reported contradictory results regarding the dose–response relationship between arsenic concentration in drinking water and skin lesions. Many of them have reported a clear dose–response relationship between the arsenic level in drinking water and rate of skin lesions [97–99]. While others have reported that the non-malignant skin lesions induced by arsenic occurs more in male subjects than female [100], although some reports describe no difference between genders [99]. Some researchers by their US based epidemiological studies of cancer risk from exposure to arsenic have shown negative report on dose-response relationship between arsenic

Table 3
Dose–response relationship of arsenic poisoning

Reference	Location/country	Dose		Effects		Blinding factors	Remarks
		Concentration ($\mu\text{g/l}$)	Frequency	Health impact	Prevalence		
Tondel et al. [96]	Bangladesh	150 1000	–	Skin lesion	18.6 (M) 37.0 (M)	Not reported	
Majumder et al. [97]	India	50–100 >800	Daily	Skin lesion	1.5(M); 0.4(F) 10.7(M); 8.3 (F)	Not reported	
Smith et al. [98]	Chile	750–800	Daily	Skin lesion	66.6(M); 16.6(F)	Not reported	Male and female below 20 years of age are equally affected
Guo et al. [99]	Inner Mongolia, China	>50		Skin lesion	44.8%; 37.1%	–	No gender effect but residents over 40 years old showed higher prevalence
Watanabe et al. [100]	Bangladesh	1–535	Daily	Skin lesion	80 (M); 50 (F)	Creatinine adjustment	Males are more susceptible than female, urinary arsenic concentration was taken as dose indicator
Lama et al. [101]	133 US Countries	3–60	Ecological study	Bladder cancer mortality	SMR 0.73	–	No dose–response relationship was observed
Steinmaus et al. [102]	Nevada and California	0–1000	Daily	Bladder cancer mortality	SMR 0.73	–	Overall, there was no association between bladder cancer and arsenic intake even in the highest exposure category of >80 $\mu\text{g/day}$
Moore et al. [103]	Churchill country Nevada	10–90	Ecological study	Childhood cancer	SMR 1.37	–	No evidence of excess childhood cancers for any of the exposure levels. Also no association between arsenic and leukemia was established for higher exposure group
Lewis et al. [104]	Millard Country Utah	3.5–620	Ecological study	Malignant cancers	SMR 0.82	–	No dose–response relationship

M = male, F = female, SMR = standard mortality ratio.

concentration in drinking water and cancer risks [101–104]. The reports are summarized in Table 3 below.

In 2003, the Environmental Protection Agency, USEPA proposed a draft of the final guidelines for cancer risk assessment [105]. The revised document advocates the use of nonlinear relationship between arsenic carcinogenesis and its dose in drinking water. Schoen et al. have reported that the arsenic carcinogen-

esis is also influenced by factors in the cellular environment [106].

Prospective studies in large area of endemic arsenic poisoning like Bangladesh, India or China, where the rate of malignancies is expected to increase within the next several decades, will help to clarify the dose–response relationship between arsenic exposure levels and adverse effects with enhanced accuracy.

Table 4
Relationship between nutritional factors and arsenic toxicity

Nutritional factors	Effect	Source of information	Reference
Undernourishment, under weight	Increases toxicity	Epidemiological studies	Mazumder et al. [97]; Hsueh et al. [107]
β -Carotene deficiency	Increases toxicity	Epidemiological studies	Hsueh et al. [108]
Selenium deficiency	Increases toxicity	Epidemiological and animal studies	Biswas et al. [109]; Nyon et al. [110]
Choline and methionine deficiency	Increases toxicity	Animal studies	Gebel [111]; Vahter et al. [112]
Anti oxidants (Vitamin C and E) superannuation	Decreases toxicity	Animal studies	Chattopadhyay et al. [113]; Rabbani et al. [114]
Folic acid superannuation	Decreases toxicity	Animal studies	Rabbani et al. [114]

4.4. Nutritional factors on arsenic toxicity

Furthermore, nutrition and overall health may play important roles in modulating arsenic toxicity and influencing individual susceptibility. There are also contradictory reports on the role of nutrition on arsenic induced skin lesions. Mazumder et al. [97] by their study in Bangladesh and West Bengal in 1998 reported that underweight individuals were disproportionately more susceptible to arsenic induced skin lesion. Similarly, after the survey of Taiwanese diet [107,108], it was found that under nourishment and low β -carotene levels were associated with increased incidence of arsenic induced skin lesion. Nutritional factors that may modulate arsenic toxicity is summarized in Table 4.

Study by Smith et al. [98] indicated that arsenic induced skin lesions were as frequent in well-nourished individuals from northern Chile as they were in a malnourished area of West Bengal [97]. However, these studies are not comparable for several reasons, the most significant discrepancy being that Smith et al. examined skin lesion in a sample population of only 44 individuals while in the study conducted in West Bengal more than 7500 subjects were examined. Further, study designs were so vastly different that relating exposure assessments between the two studies are difficult [106].

In the 2001 analysis [88], the National Research Council (NRC), USA, indicated that the nutritional status has the potential to modulate arsenic toxicity. However, because the carcinogenic effects of arsenic are relatively consistent across several different geographical locations, NRC concluded that it was unlikely that nutrition has a substantial role in the etiology of arsenic-related diseases. NRC specifically refers to two studies that suggest arsenic is equally toxic to populations with good nutrition [115,116]. These two experiments were done within well nourished Chilean and Taiwan Population, respectively.

5. World scenario of arsenic poisoning

The arsenic poisoning of ground water was first reported in Taiwan in 1968. Acute and chronic arsenic exposure through water has been reported in the countries like Argentina, Bangladesh, India, Pakistan, Mexico, Mongolia, Germany, Thailand, China, Chile, USA, Canada, Hungary, Romania, Vietnam, Nepal, Myanmar, Cambodia [3,43,44,117–119]. Arsenic associated with geothermal waters has been found in Japan, New Zealand, Kamchatka, France Dominica [3]. Many parts of European countries are also having arsenic concentration $\geq 10 \mu\text{g/l}$

in ground water [120]. As per the report [44] in USA, 5% of all its community water supply system will have to make corrective action to lower the current arsenic level. According to a recent survey carried out by School of Environmental Studies (SOES), Jadavpur University, Kolkata, ground waters of 2700 villages in 9 districts out of a total of 18 in West Bengal, India, are arsenic contaminated (arsenic content $>50 \text{ ppb}$). About 6 million people from these districts having a total population of 42 million are consuming arsenic contaminated water and about 30,000 of them are threatened with visible symptoms of arsenic poisoning [2]. Recently, in India, arsenic poisoning due to contaminated ground water has also been reported in Sahebgunj district of Jharkhand [2], Bhojpur district of Bihar [121], Dhemaji district and Karimganj district of Assam [122], Rajnandgaon District of Chattisgarh [123] and Balia district of Uttar Pradesh [122]. Many places of Punjab and Haryana like Ropar, Manimajra, Chandigarh, N. Garh, Patiala and Ambala, etc. have also been reported to have higher arsenic level in wells and springs water ($50\text{--}545 \mu\text{g/l}$) [124].

In Bangladesh, ground waters of 2000 villages in 50 districts out of a total of 64 districts have been identified as containing arsenic above permissible level of 50 ppb. Twelve worst affected districts of south and east Bangladesh are Chandpur, Madaripur, Munshiganj, Gopalganj, Lakshmipur, Noakhali, Bagerhat, Shariatpur, Comilla, Faridpur, Satkhira and Meherpur where arsenic concentrations in tube wells have been found maximum. Arsenic concentrations in the ground water of about 76% of shallow wells of these districts exceed the Bangladesh standard for arsenic. The median arsenic concentration is $135 \mu\text{g/l}$ and 60% or more of the wells in each of these worst affected districts contain arsenic concentrations exceeding $50 \mu\text{g/l}$ and occasionally concentrations exceed $1000 \mu\text{g/l}$ [4]. It is estimated in 2003 that more than 50 million people in Bangladesh are drinking water with arsenic concentrations exceeding the current Bangladesh standard of $50 \mu\text{g/l}$ [91].

Recently, arsenic above $50 \mu\text{g/l}$ has been found in the ground water of Muzaffargarh district of southwestern Punjab, central Pakistan. Maximum arsenic content has been found to be $906 \mu\text{g/l}$. The arsenic concentrations in the shallow tube wells of urban area have been found more than that of rural area. During the 1980s, the endemic arsenicosis was found successively in many areas on mainland China such as Xinjiang Uygur A.R., Inner Mongolia, Shanxi, Liaoning, Jilin, Ningxia, Qinghai, and Henan provinces [5]. The scenario of arsenic poisoning around the world is summarized in Table 5.

Table 5
World scenario of arsenic poisoning from drinking water

Country name	Poisoning effect	Permissible national limit (ppb)	Reference
Bangladesh	2000 villages in 50 out of a total of 64 districts have been identified as containing arsenic above permissible level of 50 ppb and 50 million people are drinking water with arsenic concentrations exceeding the current Bangladesh standard of 50 $\mu\text{g/l}$. Aresnic available in the range of 10–1000 $\mu\text{g/l}$	50	[3,4,6]
India	2700 villages in 9 districts out of a total of 18 in West Bengal, India, are arsenic contaminated (arsenic content >50 ppb). About 6 million people from these districts having a total population of 42 million are consuming arsenic contaminated water and about 30,000 of them are threatened with visible symptoms of arsenic poisoning. Available arsenic concentration is 0.003–3700 $\mu\text{g/l}$. Arsenic poisoning has also been reported in Bihar, Punjab and Haryana	50	[3,2]
Pakistan	Ground water from shallow tube wells of Muzaffargarh District of south-western Punjab, central Pakistan has been found to have arsenic concentration upto 906 $\mu\text{g/l}$	50	[17]
Taiwan	Chronic arsenicism is observed in a population of 40,421 in 37 villages, and 7418 cases of hyper pigmentation, 2868 of keratosis, 360 of BFD patients, and some cases of cancer (liver, lung, skin, prostate, bladder, kidney) are observed. Arsenic concentration in endemic area is 400–600 $\mu\text{g/l}$	50	[3]
China/Mongolia	The arsenic concentration in the groundwater in affected areas is in the range of 220–2000 $\mu\text{g/l}$ with the highest level at 4440 $\mu\text{g/l}$. At present, the population exposed to high amounts of arsenic is estimated to be over 2 million and more than 20,000 arsenicosis patients are confirmed	50	[3,5,7]
Mexico	The range of total arsenic concentration is 8–624 $\mu\text{g/l}$. The symptoms observed in this area are cutaneous manifestations (skin pigmentation changes, keratosis and skin cancer), peripheral vascular disease (BFD), gastrointestinal disturbances and alteration in the coporphyrin/uroporphyrin excretion ratio		[3,8]
Thailand	Arsenic in the range of 1.25–1032 $\mu\text{g/l}$ is available in water		[3,9]
Chile	Average arsenic concentration is >100 $\mu\text{g/l}$. In a survey of 27,088 school children, 12% are found to have the cutaneous changes of arsenicism; one-fourth to one-third of these has suggestive systematic symptoms. Eleven percent has acrocyanosis. Of the Antofagastan residents, 144 have abnormal skin pigmentation, compared with none in the 98 control subjects		[3,10]
USA	The range of arsenic in the well water is 1–490 $\mu\text{g/l}$. Five percent of all its community water supply system will have to make corrective action to lower the current arsenic level	10	[3,13]
Germany	Arsenic concentration <10–150 $\mu\text{g/l}$		[11]
Canada	Arsenic in water varies from 100 to 410 $\mu\text{g/l}$ as As_2O_3	25	[3]
Argentina	The arsenic content of nearly 50% of the water samples from Pampa Province of Cordoba, southeast Argentina ranges from 100 to 316 $\mu\text{g/l}$ with a maximum value of 3810 $\mu\text{g/l}$		[3]
Hungary	1–174 $\mu\text{g/l}$ arsenic is available in water. A few thousand people are affected and several symptoms of arsenic poisoning i.e. melanosis, hyperkeratosis, skin cancer, internal cancer, bronchitis, gastroenteritis, haematologic abnormalities are found among them		[3,14]
Finland	Arsenic concentration in well water is 17–980 $\mu\text{g/l}$		[18]
Vietnam	Elevated arsenic concentration, 1–3050 $\mu\text{g/l}$ over a large rural and sub-urban area of the Vietnamese capital of Hanoi has been reported	50	[15]
Nepal	Arsenic concentration in some sources exceeding 50 $\mu\text{g/l}$ although documentation of the affected aquifers is so far limited		[3]
Myanmar	Arsenic concentration in some sources exceeding 50 $\mu\text{g/l}$ although documentation of the affected aquifers is so far limited		[34]
Cambodia	Arsenic concentration in some sources exceeding 50 $\mu\text{g/l}$ although documentation of the affected aquifers is so far limited		[37]
Japan	The highest concentration found is 293 $\mu\text{g/l}$	10	[3,16]
New Zealand	Effluents from the Kawerau geothermal field in New Zealand contains 38 $\mu\text{g/l}$ arsenic	–	[3,12,19]
Kamchatka	Arsenic associated with geothermal waters has also been reported in several areas, including hot springs	–	[3]
France	Arsenic associated with geothermal waters has also been reported in several areas	–	[3]
Dominica	Arsenic associated with geothermal waters has also been reported in several areas	–	[3]

BFD: Black foot disease.

6. Remediation techniques

There are some conventional as well as advanced techniques, which can be applied for the removal of arsenic from contaminated water. These techniques are discussed below.

6.1. Conventional techniques

Arsenic removal in the conventional techniques are performed by oxidation of soluble As(III) to less soluble As(V) followed by separation of As(V) by exploiting any of the physico-chemical properties like coagulation–precipitation, adsorption, ion exchange, reverse osmosis, electro dialysis, etc. The conversion of As(III) to As(V) is done by using some oxidizing chemical agents like chlorine, potassium permanganate, etc. Addition of chemicals in the oxidation step increases the cost of these techniques. These physico-chemical techniques can be classified as below.

1. *Coagulation–precipitation*. In this process chemicals transform dissolved arsenic into an insoluble solid which is precipitated. Dissolved arsenic may also be adsorbed on the surface and be co precipitated with other precipitating species. Suspended/colloidal arsenic may also be separated by coagulation and flocculation. The pH of the process highly influences the efficiency of removal. Commonly used chemicals in this technique are ferric salts, alum, manganese sulphate, ammonium sulphate, copper sulphate, etc.
2. *Lime softening*. It is similar to precipitation where limes (lime stone, calcium hydroxide) are used for the removal.
3. *Adsorption*. In this technique arsenic species is attached on the surface of the adsorbent by physical as well as chemical forces. The active surface area of adsorbent, its surface energy and the pH of the solution highly influence the removal efficiency. Conventionally used adsorbents are activated alumina, activated carbon, greensand (KMnO₄ coated gluconite), granular ferric hydroxide, iron oxide coated sand, copper-zinc granules, etc.
4. *Ion exchange*. In this technique arsenic ions held electro statically on the surface of a strong base anion exchange resins are exchanged for ions of similar charge in the solution from the resin.
5. *Membrane filtration*. In this technique arsenic is separated from water by passing it through a semi permeable barrier or membrane. Pressure difference is the driving force for the separation. The removal efficiency depends on the pore size in the membrane and the particle size of arsenic species. Pre oxidation step improves the removal efficiency. Various types of membrane filtration techniques are mentioned in Table 6.

However, certain drawbacks make these processes inefficient in some cases, especially when Fe and Mn are available in water. Small pores of these membranes are more prone to fouling. Fe and Mn promote fouling of membrane due to co-precipitation that might be ir-reversible. It needs pretreatment of water, monitoring of operational pressure and skilled operator, which makes the process costly.

Table 6

Various types of membrane filtration

Membrane process	Operating structure (pore size)	Operating range (μm)
Microfiltration	Macro pores (>50 nm)	0.08–2.0
Ultrafiltration	Mesopore (2–50 nm)	0.005–0.02
Nanofiltration	Micro pore (<2 nm)	0.0001–0.001
Reverse osmosis	Dense (<2 nm)	0.0001–0.001

6. *Electro dialysis*. It is similar to reverse osmosis except the driving force; an electric field applied across a semi permeable membrane in the contaminated water generates the driving force for separation.

These conventional techniques have some limitations i.e. (i) use of chemicals, its handling and impact on water quality; (ii) production of large volume of high arsenic contaminated sludge; (iii) need of secondary treatment in some cases (iv) interference of sulfates and other ions on removal efficiency and (v) high installation and operation cost and lower efficiency in many cases. A comparison among some conventional processes of typical cases is summarized in Table 7.

The success of a particular removal technology depends upon the following factors.

- (i) MCL target,
- (ii) Influent arsenic concentration,
- (iii) Population,
- (iv) Region where the system is located,
- (v) Source water,
- (vi) Whether a system has existing treatment in place,
- (vii) Co-occurrence of solutes and
- (viii) Waste disposal issues.

All the processes mentioned in Table 7 except electro dialysis and adsorptions on activated carbon have been applied to solve arsenic problems in real fields. These technologies are suitable for all of the nine system size categories (based on population) made by EPA as shown below:

- 25–100,
- 101–500,
- 501–1000,
- 1001–3300,
- 3301–10,000,
- 10,001–50,000,
- 50,001–100,000,
- 100,001–1,000,000 and
- greater than 1,000,000.

6.2. Best available technologies (BATs)

Among the conventional techniques the following techniques have been defined as the best available technologies (BAT) for arsenic removal [44,125,130]:

- (i) Anion exchange,

Table 7
The comparison amongst the conventional processes

Process	Salient features	Advantages	Disadvantages	Reference
Precipitation with alum	pH \leq 6.5, E.R.S. = lower as well as higher As_0 , A.O.A.C \leq 20 $\mu\text{g/l}$, R.E. = 20–90%, OPC = medium	Well established; suitable for home use	Use of chemicals; high arsenic contaminated sludge; dose of oxidizing chemicals highly influence the removal efficiency	[44,125]
Precipitation with iron	pH 6–8, E.R.S. = lower as well as higher As_0 , A.O.A.C \leq 20 $\mu\text{g/l}$, R.E. = 60–90%, OPC = medium	Proven and reliable	Use of chemical; high arsenic contaminated sludge; dose of oxidizing chemicals highly influence the removal efficiency	[44,45,125,126]
Precipitation with Fe/Mn	pH $>$ 7, E.R.S. = lower as well as higher As_0 , A.O.A.C \leq 10 $\mu\text{g/l}$, R.E. = 40–90%, OPC = medium	Proven and reliable	Higher and lower pH reduces efficiency; use of chemical; high arsenic contaminated sludge; dose of oxidizing chemicals highly influence the removal efficiency	[44,45,125]
Lime softening	pH \geq 10.5, E.R.S. = lower As_0 , A.O.A.C \leq 10 $\mu\text{g/l}$, R.E. = 80–90%, OPC = high	Proven and reliable; reduces corrosion	Sulfate ions influence efficiency; secondary treatment is required; use of chemicals	[44,45,125]
Reverse osmosis	E.R.S. = lower As_0 , A.O.A.C \leq 2 $\mu\text{g/l}$, R.E. \geq 90%, OPC = high	Highest water quality; treats wide range of dissolved salts, minerals; turbidity	Expensive to install and operation; frequent membrane monitoring; pH, temperature and pressure control to meet membrane tolerance	[44,45,125]
Electro dialysis	pH 7–9, E.R.S. = lower As_0 , A.O.A.C \leq 3 $\mu\text{g/l}$, R.E. \geq 95%, OPC = high	Pure quality water	Less proven; costly; needs oxidizing agents	[44,120,125]
Ion exchanges	pH 7.5, E.R.S. = lower As_0 , A.O.A.C \leq 2 $\mu\text{g/l}$, R.E. \geq 90%, OPC = high	Can produce treated water with As concentration less than 2 $\mu\text{g/l}$	Efficiency affected by sulfate, nitrates, fluorides ions, TDS, selenium, etc	[44,45,125,127]
Adsorption in activated alumina	pH 5.5–6.0, E.R.S. = lower As_0 , A.O.A.C \leq 1 $\mu\text{g/l}$, R.E. \geq 90%, OPC = low	Well established; suitable for home use; typically inexpensive with simple replacement requirements; improves test and odour	Careful monitoring; effectiveness is based on contaminant type; concentration and rate of water usage; bacteria may grow on alumina surface	[44,45,125]
Adsorption on activated carbon	pH 2–9, E.R.S. = lower As_0 , A.O.A.C \leq 7 $\mu\text{g/l}$, R.E. = 30–90%, OPC = low	Typically inexpensive with simple replacement requirements; improves test and odour	Efficiency depends on the ash content in the carbon and on the metal concentration; not proven	[44,128,129]

A.O.A.C: attainable outlet arsenic concentration, R.E.: removal efficiency, E.R.S.: effective range of separation, OPC: operating cost.

- (ii) Activated alumina (AA),
- (iii) Reverse osmosis (RO),
- (iv) Modified coagulation/filtration,
- (v) Modified lime softening and
- (vi) Oxidation/filtration (including greensand filtration).

But the level of iron in the raw water affects greensand filtration. It works well when iron: arsenic ratio exceeds 20:1. Surface waters typically have low iron content whereas ground waters often have levels in excess of 300 mg/l; accordingly, greensand filtration is not considered as a viable removal technology for surface water systems but is viable for ground water systems. The Safe Drinking Water Act (SDWA) identifies point of entry (POE) and point of utilization (POU) treatment units as potentially affordable technologies for the two smallest categories of groundwater systems out of nine categories made by EPA. The

available POU technologies for arsenic removal are essentially smaller versions of reverse osmosis and activated alumina.

It is difficult to compare the costs of various treatment techniques as the efficiency depends on different parameters. However, a cost comparison has been done in the report [130] where average cost has been calculated assuming a public won ground water system with a single contaminated entry point. The system compliance technology cost of various BET processes for a system size category of 501–1000, assuming inlet concentration of 50 $\mu\text{g/l}$ and treated water arsenic concentration of 10 $\mu\text{g/l}$ is shown in Table 8.

Similarly base cost of treatment plants based on the above stated techniques have been calculated based on water and water cost models [131]. As per this report the cost comparison for treating 1 million gallon water of same quality per day by some of these processes is shown in Table 9.

Table 8
Comparison of treatment costs of various treatment processes [130]

Processes	Treatment cost (US\$)
Coagulation–filtration	11325
Lime softening (LS)	19681
Reverse osmosis (RO)	143199
Ion exchange (IX)	169273
Activated alumina (AA)	83871

By a comparison among these processes it is evident that coagulation–filtration and lime softening techniques are cheaper but the removal efficiency of these techniques are low (<90%). Hence, the adsorptive process with activated alumina seems to be the most inexpensive among the techniques with higher efficiency ($\geq 95\%$). For ground water systems without pre treatment in-place, the most suitable treatment technologies are ion exchange and activated alumina.

Activated alumina process can also remove some organic chemicals, pesticides, chlorine, etc. and is capable of improving taste and smell. But effectiveness is dependant on contaminant type, concentration and rate of water usage. Adequate water flow and pressure requirement for backwashing/flushing requires careful monitoring. Further, bacteria may grow on alumina surface.

6.3. Developments in the area of arsenic removal techniques

In recent years, efforts have been directed to improve the efficiency and cost effectiveness of arsenic removal techniques either by modification of the conventional techniques mainly adsorption or by inducing new technology where chemical oxidation of As(III) to As(V) is avoided. Replacement of conventional chemicals like chlorine and KMnO_4 by other chemicals like ozone is also a recent research trend on arsenic removal from contaminated water. These are discussed below.

6.3.1. Modification of conventional techniques

Although adsorption by alumina is a low cost efficient treatment option for arsenic removal from contaminated water, this technique is still not affordable by the common people of poor countries. Hence, search for more efficient and cost effective

Table 9
Approximate cost comparison of various treatment processes [131]

Processes	Treatment cost (US\$)	Model used
Coagulation–filtration	–	–
Lime softening (LS)	310500/1 mgd	Water model for package lime softening
Reverse osmosis (RO)	775820/1 mgd 1157600/1 mgd	Water cost model Water model for package reverse osmosis
Ion exchange (IX)	253930/1.1 mgd	Water cost model
Activated alumina (AA)	90400/0.7 mgd	Water cost model

mgd: million gallons per day.

alternate adsorbents are in progress. Some of such alternatives are the surface coated adsorbents. Recently some adsorbents like coconut husk carbon, iron oxide coated polymeric materials, low cost ferruginous manganese ore, iron oxide coated sand, Mn greensand, etc., have been reported [27,43,132,133] for effective adsorption. Relatively very little information is published on the adsorption of As(III) by activated carbon; however, As(V) is adsorbed by commercially available activated carbon (ash content around 16%) with lower removal efficiency. The high ash containing charred carbon (ash content around 29%), obtained from fly ash has been reported to have 90% removal efficiency [129]. Similarly, coconut husk carbon has been reported to have more than 95% removal efficiency with optimum adsorption at pH 12.0. Adsorbent dose, contact time and initial concentration of arsenic have been found to affect removal efficiency [132]. Iron-hydroxides coated polymeric materials (polystyrene and poly HIPE) have been reported to show more than 95% removal efficiency with the optimum pH at 7.0 and empty bed contact time (EBCT) of 125 min. The efficiency has been found dependent on initial concentration, pH, EBCT, presence of competitive ions in solution [131].

A low cost ferruginous manganese ore (FMO), US\$ 50–56 per tonne, has been used as effective adsorbent to remove arsenic, this material is able to treat water without pretreatment and at optimum conditions it is able to remove arsenic by 98.5–99.8%. The presence of Ni^{+2} , Co^{+2} , Mg^{+2} enhances the adsorption capability of FMO [27]. Manganese greensand (MGS) and differently prepared iron oxide coated sands have been reported as adsorbents for the removal of organic arsenic from water [43]. Arsenic removal by some recently used adsorbents is summarized in Table 10.

Recently, the suitability of ozone as oxidizing agent over chlorine for the oxidation of As(III) to As(V) has also been studied. More than 96% conversion has been reported by using ozone in place of chlorine for arsenic oxidation at pH 7.6–8.5 [141].

6.3.2. Advances in arsenic removal technology

To meet the challenge of reducing arsenic concentration to the MCL value of $10 \mu\text{g/l}$ and its treatment cost, apart from the conventional removal processes, search for new developed technique has been initiated in the last decade of the 20th century. Recently, some techniques have been reported where conventional chemical oxidizing agents are not used for oxidation of As(III) to As(V). UV ray, living plants and microbes are responsible for oxidation of arsenic in these cases. In 2002, oxidation of arsenic by UV ray and sunlight in presence of iron and oxidation of arsenic by UV ray in presence of sulfite has been reported [118]. The reported conversion in both the cases was more than 95%. In the first case residues passed the USEPA leach test with or without solidification. In the second case no residue was obtained. These technique of arsenic removal are patented and the filters based on oxidation by photo-absorber is used in rural areas of Bangladesh where as the filters based on the oxidation of arsenic using UV ray is used in USA.

Upcoming waves of biotechnology also attracted the researchers to investigate for alternative cost effective and eco-

Table 10
Arsenic removal by recently used adsorbent/surface modified adsorbents

Adsorbent	Operating conditions	Nature of work	Remarks	Reference
Iron oxide coated cement	pH 4, temperature = $27 \pm 2^\circ\text{C}$, $\text{As}_0 = 2000 \mu\text{g/l}$, particle size of adsorbent = 0.212 mm	Column study	Percentage removal = 99.5%. The efficiency of the adsorbent after regeneration by 10% NaOH was not decreased much	[134]
Bead cellulose loaded with iron oxy hydroxide	pH 7, temperature = $25 \pm 0.5^\circ\text{C}$, $\text{As}_0 = 500 \mu\text{g/l}$, particle size of adsorbent = 20–60 mesh	Column study	Percentage removal for arsenite = 95%, for arsenate = 80% SO_4^{-2} had no effect on arsenic removal but PO_4^{-3} influenced the removal greatly. Silica decreases only arsenite adsorption	[135]
Granular titanium dioxide	pH 7 ± 0.1 , temperature = 24°C , $\text{As}_0 = 300 \mu\text{g/l}$, particle size of adsorbent = 0.15–0.6 mm	Batch study	Percentage removal = 95%, Silica has shown no obvious effect	[136]
Natural iron ores	pH 4.5–6.5, temperature = 24°C , $\text{As}_0 = 0\text{--}100 \mu\text{g/l}$, particle size of adsorbent = 75–63 μm	Batch study	Percentage removal = >95%	[137]
Zero-valent iron and filter sand	pH 6, temperature = 24°C , $\text{As}_0 = 8500 \mu\text{g/l}$, Fe = $200 \mu\text{g/l}$, DO = 8 mg/l, $\text{SiO}_2 = 560 \text{mg/l}$, particle size of Fe(o) = 100 and 40 mesh, for filter sand = 0.35–0.45 mm	Batch study	Percentage removal = >99%	[138]
Hardened paste of Portland cement	pH 4–5, temperature = 24°C , $\text{As}_0 = 200 \mu\text{g/l}$ (batch), $\text{As}_0 = 400\text{--}500 \mu\text{g/l}$ (column), particle size of adsorbent = 4.88–4.92 mm	Batch and column study	Percentage removal for As = >90%	[139]
Polymetallic sea nodule	pH < 6, temperature = 20°C , $\text{As}_0 = 100\text{--}240 \mu\text{g/l}$, particle size of adsorbent = 75 μm , shaking time 30 min	Batch	Percentage removal for As = >90%	[140]

friendly removal processes by the help of biochemical engineering. Phyto remediation and bio-filtration using living microbes have recently been identified as two main biological treatment techniques for removing arsenic from contaminated water in an eco-friendly way [28,142–150].

In phyto remediation technique plant/fungal biomass is used as adsorbent. The removal mechanism is similar to that of adsorption techniques. The fungal/plant biomass is susceptible to chemical and engineering improvements and regeneration of their capabilities [142]. It has recently been observed that the capability of fungal biomass for treating metal contaminated effluents is better than activated carbon (F-400) or the industrial resin Dowex-50 [142].

The pre treatment of biomass of *P. chrysogenum* with common surfactants (as hexadecyl-tri-methyl ammonium bromide and do-decyl amine) and a cationic-polyelectrolyte was found to improve the bio-sorption efficiency. The reported improvement in bio-sorption efficiency was 37.85, 33.31% and 56.07%, for hexadecyl-trimethyl ammonium bromide, dodecyl amine and polyelectrolyte, respectively [143]. Moreover, this biosorptive process reduces capital cost by 20%, operational; cost by 36% and total treatment cost by 28% when compared with conventional processes [144].

The tea fungus, a waste produced during black tea fermentation has been examined for its capacity to sequester the metal ions from ground water samples. Autoclaved tea fungal mat and

autoclaving followed by FeCl_3 pretreated tea fungal mat were exploited for removal of As(III), As(V) and Fe(II) from ground water sample collected from Kolkata, West Bengal, India. The biosorption rate tends to increase with the increase in contact time and adsorbent dosage. FeCl_3 pretreated and autoclaved fungal mats removed 100% of As(III) and Fe(II) after 30 min contact time and 77% of As(V) after 90 min contact time. The optimum adsorbent dosage was 1.0 g/50 ml of water sample. The results revealed that the FeCl_3 pretreated fungal mat could be used as an effective biosorbent for As(III) and As(V); autoclaved fungal mat for Fe(II) removal from ground water sample [145]. Living plants like Brake fern (*Pteris vittata*) may also be used to take up arsenic from contaminated water, which is accumulated into the plant body [146].

The mechanism of arsenic removal by using living microbes differs from that of phyto remediation technique. Like other heavy metals, in this case the conversion of As(III) to As(V) may be performed by an extra cellular enzyme and the oxidized species may be adsorbed or precipitated/co precipitated onto the bio layer formed on the solid support medium. Or, by a trans membrane protein the arsenic may be entered into the microbial cell where methylation or oxidation–reduction of arsenic species may take place. It has been reported that in most of the cases the removal efficiency of this technique is controlled by plasmid gene. Hence, there is a high possibility for improving the efficiency by genetic modification of the microbes. However, the

Table 11
A comparison amongst some recently reported major techniques

Process	Parameters	Removal efficiency (%)	Advantage(s)	Disadvantage(s)	Reference
Oxidation by UV ray and sun light in presence of iron	As ₀ = 10 mg/l, pH 1.5–3, Fe ₀ = 180 mg/l, Fe(II) to As(III) ratio = 24	>96	No use of chemicals; The residues with or without solidification passed the standard of USEPA leach test for disposal	pH is lower	Zaw and Emmett [118]
Oxidation by UV ray in presence of sulfite	As ₀ = 0.47 mg/l, pH 9, air bubble supplied	>96	Effluent amenable to all techniques for As(V) removal	Sulfite content influences the efficiency	Zaw and Emmett [118]
Oxidation by iron oxidizing bacteria in presence of iron and Mn	As ₀ = 35.60 µg/l, pH 7.2, Fe ₀ = 2.8 mg/l, Mn ₀ = 0.6 mg/l, ORP = 280–290 mV, DO = 2.7 mg/l	>80	No use of chemical; cheaper and eco-friendly; indigenous microbes	Not well established	Katsoyannis et al. [28,148]
Oxidation by sulfate reducing bacteria	As ₀ = 10 mg/l, pH 4.5–7, Fe ₀ = 20 mg/l	>78	No use of chemical; cheaper and eco-friendly; indigenous microbes	Not well established	Jong and Pany [149]

Fe₀ = initial iron concentration, Mn₀ = initial manganese concentration, As₀ = initial arsenic concentration, ORP = oxidation reduction potential.

evaluation of the removal efficiency and the reliability of these processes are yet to be found out.

In a study of iron removal through sand filters of three different fresh water plants, two biotic and one abiotic, in the same area of Denmark, the rate of iron precipitation in biotic and abiotic conditions has been compared [147]. As per this report, biotic iron precipitation is 60 times faster than abiotic precipitation and biotic sludge is 7–9 times denser than abiotic one. The microbe used in this study was *Gallionella ferruginea*. The morphology of the iron precipitates has been investigated by using light, X-ray, scanning electron and transmission electron microscopy. The physico-chemical conditions governing precipitation and precipitated iron sludge has also been investigated.

This report seems to be of interest to the bio-engineers to develop new technique to remove iron and other metals that can be co-precipitated with iron. In 2002, the biological oxidation of As(III) to As(V) by iron and Mn oxidizing bacteria has also been reported. It has also been confirmed that trivalent arsenic can be efficiently treated without any additional use of chemicals in this bioprocess, the optimum conditions have also been reported [28,148].

Similarly in 2003, microbial sulfate reduction and subsequent precipitation of Cu, Zn, Ni, Ce and As has been reported. The experiment has been done with a mixed population of sulfate reducing bacteria (SRB) in an up-flow anaerobic packed bed reactor (UPAB) containing silica sand [149].

In 2003, Casiot et al. by their study on the mobilization of arsenic in acid mine drainage from Carnules creek in France, have suggested that the immobilization of indigenous bacteria in the precipitates which cover the bottom of the creek, is responsible for oxidation of arsenic. More than 75% Arsenic removal in presence of bacteria as living cell and 22% arsenic removal in absence of bacteria have been observed [150]. Out of six indigenous bacteria in the creek two have been found mainly responsible for As(III) oxidation, and one for iron oxidation.

An arsenic oxidizing bacteria has been reported as *Thiomonas Ynys1*. The role of other bacteria is not known. The experiment was carried out at pH 2.73–3.37 and through out the year, creek temperature was varied from 13.2 to 16.5 °C. No influence of UV and photo oxidation on the arsenic removal has been reported in this study.

Kostal et al. [151] has shown that by the genetic modification of *E. coli* the arsenite and arsenate removal efficiency can be improved by 60 and 5-folds, respectively.

A comparison among some major recently reported techniques are summarized in Table 11.

6.3.3. Scopes and limitations of advanced techniques

The advanced techniques have been able to oxidize As(III) to As(V) successfully without the use of any chemicals. By these oxidation techniques the cost effectiveness may be increased, but there are some limitations of these techniques too. The pH of the iron photo absorber process is very low i.e. 1.5–3, which needs to be increased to 6–8 to satisfy drinking water standard. In sulfite absorber process the oxidation rate is highly influenced by the concentration of sulfite. Similarly the only limitation of the biological oxidation processes is that the reported oxidation efficiency is only 80%. Although, the genetic modification of some microbes improves its arsenic removal efficiency [152], these genetically engineered bacteria may alter eco system [153].

6.4. Alternate options for arsenic free water

Some alternate safe water options applied in West Bengal and Bangladesh are clay filters, deep tube well, dug well, surface water, rainwater harvesting and solar distillation. Solar distillation technique uses the sun's energy to evaporate water, which then re-condenses. The process of evaporation and re-condensation separates all chemicals, including arsenic, from the water. In Bangladesh, where solar energy is plentiful, this

approach may be especially suited for application in crisis areas [154].

7. Conclusion

Based on the above discussions the following conclusions are made:

1. Recovery of the arsenic related cancers by medication are difficult as the arsenic metabolism and mechanism of carcinogenicity are poorly understood. In this situation proper treatment of contaminated drinking water plays a vital role for eradicating the arsenic health risk by reducing the arsenic level well below the MCL value of arsenic in drinking water.
2. Conventional treatment processes are neither cost effective nor affordable by the common people of poor countries like Bangladesh, India, etc., as a result, the MCL value in these countries are still at 50 $\mu\text{g/l}$ and a large number of people in the world are under the threat of arsenic.
3. In near future surface coated adsorbents might play a role in decreasing treatment cost of arsenic contaminated water.
4. Out of the advances reported in cost effective arsenic removal techniques, the microbial oxidation of arsenic draws maximum attention because it requires no chemicals and the microbes are indigenous to the contaminated water. The percentage oxidation has already been reported as 80%. In spite of the low oxidation efficiency it can be applicable to reduce arsenic concentration in the lower contaminant level successfully. More over, genetic modification of microbes by microbial cloning technique might improve the efficiency of this technique in near future.

References

- [1] Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), USEPA, 2003.
- [2] S. Bhattacharjee, S. Chakravarty, S. Maity, V. Dureja, K.K. Gupta, Metal contents in the ground water of Sahebgunj district, Jharkhand, India, with special reference to arsenic, *Chemosphere* 58 (2005) 1203–1217.
- [3] P.L. Smedley, D.G. Kinniburgh, A review of the source, behaviour and distribution of arsenic in natural waters, *Appl. Geochem.* 17 (2002) 517–568.
- [4] C.F. Harvey, C.H. Swartz, A.B.M. Badruzzaman, N. Keon-Blute, W. Yu, M.A. Ali, J. Jay, R. Beckie, V. Niedan, D. Brabander, P.M. Oates, K.N. Ashfaq, S. Islam, H.F. Hemond, M.F. Ahmed, Arsenic mobility and groundwater extraction in Bangladesh, *Science* 298 (2002) 1602–1606.
- [5] J.C. Nga, J.P. Wanga, B. Zheng, C. Zhaib, R. Maddalena, F. Liua, M.R. Moorea, Urinary porphyrins as biomarkers for arsenic exposure among susceptible populations in Guizhou province, China, *Toxicol. Appl. Pharmacol.* 7 (2005) 176–184.
- [6] Y. Zheng, M. Stuteb, A. van Geenb, I. Gavrielib, R. Dhara, H.J. Simpsonb, P. Schlosserb, K.M. Ahmed, Redox control of arsenic mobilization in Bangladesh groundwater, *Appl. Geochem.* 19 (2004) 201–214.
- [7] J. Yinlong, Progress on arsenic research in China, in: M. Kabuto (Ed.), *Proceedings of the First International Workshop on Arsenic Pollution of Drinking Water in South Asia and China*, National Institute of Environmental Studies, R-166-2001, Tokyo, Japan, 2001, pp. 35–39.
- [8] A. Albores, M.E. Cebrian, I. Tellez, B. Valdez, Comparative study of chronic hydroarsenicalism in 2 rural communities of the Laguna region of Mexico, *Bol. Sanit. Panam.* 86 (1979) 196–205.
- [9] M. Williams, F. Fordyce, A. Pajitrapapon, P. Charoenchaisri, Arsenic contamination in surface drainage and groundwater in part of the south east Asian tin belt, Nakhon Si Thammarat Province, southern Thailand, *Environ. Geol.* 27 (1996) 16–33.
- [10] E. Astolfi, A. Maccagno, J.C.G. Fernandez, R. Vaccaro, R. Stimola, Relation between arsenic in drinking water and skin cancer, *Biol. Trace Elem. Res.* 3 (1981) 133–143.
- [11] G. Heinrichs, P. Udluft, Natural arsenic in Triassic rocks: a source of drinking water contamination in Bavaria, Germany, *Hydrogeol. J.* 7 (1999) 468–476.
- [12] M.J. Ellwood, W.A. Maher, Arsenic and antimony species in surface transect and depth profiles across a frontal zone: The Chatham Rise, New Zealand, *Deep-Sea Res. Part I* 49 (2002) 1971–1981.
- [13] G. Matisoff, C.J. Khourey, J.F. Hall, A.W. Varnes, W.H. Strain, Nature and source of arsenic in Northeastern Ohio ground water, *Ground Water* 20 (1982) 446–456.
- [14] I. Varsanyi, Arsenic in deep groundwater, in: D.L. Miles (Ed.), *Proceedings of the Sixth International Symposium on Water–Rock Interaction (WRI-6)*, Malvern, Publisher AA Balkema, Otterdam/Brookfield, 1989, pp. 715–718.
- [15] M. Berg, H.C. Tran, T.C. Nguyen, H.V. Pham, R. Schertenleib, W. Giger, Arsenic contamination of ground water and drinking water in Vietnam: a human health threat, *Environ. Sci. Technol.* 35 (2001) 2621–2626.
- [16] H. Nakahara, M. Yanokura, Y. Murakami, Environmental effects of geothermal waste water on the near-by river system, *J. Radioanal. Chem.* 45 (1978) 25–36.
- [17] R.T. Nickson, J.M. McArthur, B. Shrestha, T.O. Kyaw-Myint, D. Lowry, Arsenic and other drinking water quality issues, Muzaffargarh District, Pakistan, *Appl. Geochem.* 20 (2005) 55–68.
- [18] P. Kurttio, E. Pukkala, H. Kahelin, A. Auvinen, J. Pekkanen, Arsenic concentrations in well water and risk of bladder and kidney cancer in Finland, *Environ. Health Perspect.* 107 (1999) 705–710.
- [19] E.K. Mroczek, Contributions of arsenic and chloride from the Kawerau geothermal field to the Tarawera River, New Zealand, *Geothermics* 34 (2005) 218–233.
- [20] D.E. White, J.D. Hem, G.A. Waring, Data of Geochemistry, 6th ed. In: M. Fleischer (Ed.), *Chapter F. Chemical Composition of Sub-surface waters*. US. Geol. Surv. Prof. Pap. 440-F, 1963.
- [21] WHO, Guidelines for drinking water quality. World Health Organisation, Geneva, P-41, 1993.
- [22] NHMRC Australian Drinking Water Guidelines. National Health and Medical Council, Agriculture and Resource Management Council of Australia and New Zealand, Commonwealth of Australia. PF S93, 1996.
- [23] European commission Directive. 98/83/EC, related with drinking water quality intended for human consumption. Brussels, Belgium, 1998.
- [24] EPA Office of Ground water and drinking water. Implementation guidance for the arsenic rule. EPA report-816-D-02-005, Cincinnati, USA, 1998.
- [25] D.K. Nordstrom, Worldwide occurrence of arsenic in ground water, *Science* 296 (2002) 2143–2145.
- [26] S. Chakraborty, V. Dureja, G. Bhattacharya, S. Maity, S. Bhattacharjee, Removal of arsenic from ground water using low cost ferruginous manganese ore, *Water Res.* 36 (2002) 625–632.
- [27] S. Mohammad, Arsenic chemistry in soils: an overview of thermodynamic predictions and field observations, *Water Air Soil Poll.* 93 (1997) 117–136.
- [28] I. Katsoyiannis, A. Zouboulis, H. Althof, H. Bartel, Arsenic removal from ground waters using fixed bed up flow bioreactor, *Chemosphere* 47 (2002) 325–332.
- [29] J.G. Hering, P. Chen, J.A. Wilkie, M. Elimelech, S. Liang, Arsenic removal by ferric chloride, *J. AWWA* 88 (1996) 155–167.

- [30] J.G. Hering, P.-Y. Chen, J.A. Wilkie, M. Elimelech, Arsenic removal from drinking water during coagulation, *J. Environ. Eng.* 123 (1997) 800–807.
- [31] L.S. McNeill, M. Edwards, Arsenic removal during precipitative softening, *J. Environ. Eng.* 123 (1997) 453–460.
- [32] L.S. McNeill, M. Edwards, Predicting arsenate removal during metal hydroxide precipitation, *J. AWWA* 89 (1997) 75–86.
- [33] K. Duquesne, S. Lebrun, C. Casiot, O. Bruneel, J.C. Personne, M. Leblanc, F.E. Poulichet, G. Morin, V. Bonnefoy, Immobilization of arsenite and ferric iron by *Acidithiobacillus ferrooxidans* and its relevance to acid mine drainage, *Appl. Environ. Microbiol.* 69 (10) (2003) 6165–6173.
- [34] S. Banga, M.D. Johnson, G.P. Korfiatis, X. Meng, Chemical reactions between arsenic and zero-valent iron in water, *Water Res.* 39 (2005) 763–770.
- [35] S. Oremland, J.F. Stolz, Ecology of arsenic, *Science* 300 (2003) 939–944.
- [36] H. Onishi, Arsenic, in: K.H. Wedepohl (Ed.), *Handbook of Geochemistry*, Vol. II, Springer-Verlag, New York, 1969 (Chapter 33).
- [37] B.K. Mandal, K.T. Suzuki, Arsenic round the world: a review, *Talanta* 58 (2002) 201–235.
- [38] S. Goldberg, C.T. Johnston, Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling, *J. Colloid Interf. Sci.* 234 (2001) 204–216.
- [39] L.C.D. Anderson, K.D. Bruland, Biochemistry of arsenic in natural waters: the importance of methylated species, *Environ. Sci. Technol.* 25 (1991) 420–429.
- [40] M.O. Andreae, Determination of arsenic species in natural waters, *Anal. Chem.* 49 (1977) 820–823.
- [41] K. Banerjee, R.P. Helwick, S. Gupta, A treatment process for removal of mixed inorganic and organic arsenic species from ground water, *Environ. Progress* 18 (1999) 280–284.
- [42] S.L. Chen, S.J. Yeh, M.H. Yang, T.H. Lin, Trace element concentration and arsenic speciation in the well water of Tiwan area with endemic Blackfoot disease, *Biol. Trace Elements Res.* 48 (1995) 263–274.
- [43] O.S. Thirunavukkarasu, K.S. Subramanian, S. Tanjore, Organic arsenic removal from drinking water, *Urban Water* 4 (2002) 415–421.
- [44] Report, Bureau of reclamation, Technical Service Center, Water treatment Engineering and Research Group, Denver, 2001.
- [45] M. Leist, R.J. Casey, D. Caridi, The management of arsenic wastes: problems and prospects, *J. Haz. Mater.* 76 (2000) 125–138.
- [46] N.E. Korte, Q. Fernando, A review of arsenic(III) in groundwater, *Crit. Rev. Environ. Control* 21 (1991) 1–39.
- [47] D.K. Nordstrom, C.N. Alpers, Negative pH, efflorescent mineralogy, and consequences for environmental restoration at the Iron Mountain Superfund Site, California, *Proc. Natl. Acad. Sci. U.S.A.* 96 (1999) 3455–3462.
- [48] D. Sengupta, S.S. Banerjee, A. Chakraborti, Radon and Arsenic measurements in Ground waters around south 24th Parganas, West Bengal, *I. J. Environ. Protec.* 21 (2001) 961–967.
- [49] F.J. Peryea, R. Kammereck, Phosphate-enhanced movement of arsenic out of lead arsenate contaminated topsoil and through uncontaminated sub-soil, *Water Air Soil Pollut.* 93 (1997) 117–136.
- [50] S.J. Hug, L. Canonica, M. Wegelin, D. Gechter, U.V. Gunten, Solar oxidation and removal of arsenic at circumneutral pH and Iron containing waters, *Environ. Sci. Technol.* 35 (2001) 2114–2121.
- [51] W.R. Cullen, K.J. Reimer, Arsenic speciation in the environment, *Chem. Rev.* 89 (1989) 713–764.
- [52] J. McArthur, P. Ravenscraft, S. Safiulla, M.F. Thirwall, Arsenic in ground water: testing population mechanisms for sedimentary aquifer in Bangladesh, *Water Res.* 37 (2002) 109–117.
- [53] S.K. Acharyya, P. Chakraborty, S. Lahiri, B.C. Raymahashay, S. Guha, A. Bhowmik, Arsenic poisoning in the Ganges delta, *Nature* 401 (1999) 545.
- [54] J.M. Santini, L.I. Sly, R.D. Schnagl, J.M. Macy, A new chemolithoautotrophic arsenite-oxidizing bacterium isolated from a gold mine: phylogenetic, physiological, and preliminary biochemical studies, *Appl. Environ. Microbiol.* 66 (2000) 92–97.
- [55] D.K. Nordstrom, *Minor Elements 2000: Processing and Environmental Aspects of As, Sb, Se, Te, and Bi*, in: C. Young (Ed.), Society for Mining, Metallurgy, Exploration, Littleton, CO, pp. 21–30.
- [56] D. Stuben, Z. Berner, D. Chandrasekharan, J. Karmakar, Arsenic enrichment in groundwater of West Bengal, India: geochemical evidence for mobilization of As under reducing condition, *Appl. Geochem.* 18 (2003) 1417–1434.
- [57] M.A. Hossain, A. Junji, S. Hiroshi, Mobilization of arsenic from subsurface sediments by effect of bicarbonate ions in ground water, *Chemosphere* (2004) 753–762.
- [58] Central Ground Water Board Report, Ministry of Water Resources, Govt of India, <http://cgwb.gov.in/arsenic.htm>.
- [59] N. Melitas, J. Wang, M. Conklin, P.O. Day, J. Farrell, Understanding soluble arsenate removal kinetics by zerovalent iron media, *Environ. Sci. Technol.* 36 (2002) 2074–2081.
- [60] M. Bauer, C. Blodau, Mobilization of arsenic by dissolved organic matter from iron oxides, soils and sediments, *Sci. Total Environ.* 354 (2006) 179–190.
- [61] P.R. Barry, Biochemistry of arsenic detoxification, *FEBS Lett.* 529 (2002) 86–92.
- [62] A.M. Bode, Z. Dong, The paradox of arsenic: molecular mechanisms of cell transformation and chemotherapeutic effects, *Crit. Rev. Oncol. Hematol.* 42 (2002) 5–24.
- [63] P.J. Craig, in: F.R. Harley (Ed.), *The Chemistry of the Metal–Carbon Bond*, vol. 5, Wiley, London, 1989, pp. 437–463.
- [64] L.L. Hall, In vitro methylation of inorganic arsenic in mouse intestinal cecum, *Toxicol. Appl. Pharmacol.* 147 (1997) 101–109.
- [65] D. Thomas, S.B. Waters, M. Styblo, Elucidating the pathway for arsenic methylation, *Toxicol. Appl. Pharmacol.* 198 (2004) 319–326.
- [66] B.C. McBride, R.S. Wolfe, Biosynthesis of dimethylarsine by *Methanobacterium*, *Biochemistry* 10 (1971) 4312–4317.
- [67] S. Honschopp, N. Brunken, A. Nehrkorn, H.R. Breunig, Isolation and characterization of a new arsenic methylating bacterium from soil, *Microbiol. Res.* 151 (1996) 37–41.
- [68] K.A. Francesconi, D. Kuehelt, in: W.T. Frankenberger Jr. (Ed.), *Environmental Chemistry of Arsenic*, Dekker, New York, 2002, pp. 51–94.
- [69] H.V. Aposhian, A.Z. Zakharyan, M.D. Avram, M.J. Kopplin, M.L. Wollenberg, Oxidation and detoxification of trivalent arsenic species, *Toxicol. Appl. Pharmacol.* 193 (2003) 1–8.
- [70] B.P. Rosen, Biochemistry of arsenic detoxification, *FEBS Lett.* 86 (2002) 529.
- [71] H.W. Langner, W.P. Inskeep, Microbial reduction of arsenate in the presence of ferrihydrite, *Environ. Sci. Technol.* 34 (2000) 3131.
- [72] J.M. Macy, J.M. Santini, B.V. Pauling, A.H. O’Neill, L.I. Sly, Two new arsenate/sulfate-reducing bacteria: mechanisms of arsenate reduction, *Arch. Microbiol.* 173 (2000) 49–57.
- [73] H. Rosenberg, R.G. Gerdes, K. Chegwidden, Two systems for the uptake of phosphate in *Escherichia coli*, *J. Bacteriol.* 131 (1977) 505–511.
- [74] G.R. Willsky, M.H. Malamy, Characterization of two genetically separable inorganic phosphate transport systems in *Escherichia coli*, *J. Bacteriol.* 144 (1980) 356–365.
- [75] O.I. Sanders, C. Rensing, M. Kuroda, B. Mitra, B.P. Rosen, Antimonite is accumulated by the glycerol facilitator GlpF in *Escherichia coli*, *J. Bacteriol.* 179 (1997) 3365–3367.
- [76] R. Wysocki, C.C. Chéry, D. Wawrzycka, M. Van Hulle, R. Cornelis, J.M. Thevelein, M.J. Tamás, The glycerol channel Fps1p mediates the uptake of arsenite and antimonite in *Saccharomyces cerevisiae*, *J. Microbiol.* 40 (2001) 1391–1401.
- [77] Z. Liu, J. Shen, J.M. Carbrey, R. Mukhopadhyay, P. Agre, B.P. Rosen, Arsenite transport by mammalian aquaglyceroporins AQP7 and AQP9, *Proc. Natl. Acad. Sci. U.S.A.* (2002) 6053–6058.
- [78] P. Martin, S. Demel, J. Shi, T. Gladysheva, D.L. Gatti, B.P. Rosen, B.F. Edwards, Insights into the structure, solvation, and mechanism of ArsC arsenate reductase, a novel arsenic detoxification enzyme, *Structure* 9 (2001) 1071–1081.

- [79] R. Mukhopadhyay, J. Shi, B.P. Rosen, Purification and characterization of Acr2p, the *Saccharomyces cerevisiae* arsenate reductase, *J. Biol. Chem.* 275 (2000) 21149–21157.
- [80] N. Scott, K.M. Hatlelid, N.E. Mackenzie, D.F. Carter, Reactions of arsenic(III) and arsenic(V) with glutathione, *Chem. Res. Toxicol.* 6 (1993) 102–106.
- [81] T.R. Radabaugh, H.V. Aposhian, Enzymatic reduction of arsenic compounds in mammalian systems: Reduction of arsenate to arsenite by human liver arsenate reductase, *Chem. Res. Toxicol.* 13 (2000) 26–30.
- [82] T.R. Radabaugh, A. Sampayo-Reyes, R.A. Zakharyan, H.V. Aposhian, Arsenate reductase II. Purine nucleoside phosphorylase in the presence of dihydrolipoic acid is a route for reduction of arsenate to arsenite in mammalian systems, *Chem. Res. Toxicol.* 15 (2002) 692–698.
- [83] S. Dey, B.P. Rosen, Dual mode of energy coupling by the oxyanion-translocating ArsB protein, *J. Bacteriol.* 177 (1995) 385–389.
- [84] M. Ghosh, J. Shen, B.P. Rosen, Pathways of As(III) detoxification in *Saccharomyces cerevisiae*, *Proc. Natl. Acad. Sci. U.S.A.* 96 (1999) 5001–5006.
- [85] R. Wysocki, P. Bobrowicz, S. Ulaszewski, The *Saccharomyces cerevisiae* ACR3 gene encodes a putative membrane protein involved in arsenite transport, *J. Biol. Chem.* 272 (1997) 30061–30066.
- [86] C. Rensing, M. Ghosh, B.P. Rosen, Families of soft-metal-ion-transporting ATPases, *J. Bacteriol.* 181 (1999) 5891–5897.
- [87] S.V. Kala, M.W. Neely, G. Kala, C.I. Prater, D.W. Atwood, J.S. Rice, M.W. Lieberman, The MRP2/cMOAT transporter and arsenic–glutathione complex formation are required for biliary excretion of arsenic, *J. Biol. Chem.* 275 (2000) 33404–33408.
- [88] National Research Council (NRC). Arsenic in Drinking Water: 2001 update. National Academy Press, Washington, DC, 2001.
- [89] T. Yoshida, H. Yamanchi, G.F. Jun, Chronic health effect in people exposed to arsenic via the drinking water: dose–response relationship in review, *Toxicol. Appl. Pharmacol.* 198 (2004) 243–252.
- [90] J.K. Wieneke, J.W. Yager, A. Varkonyi, M. Hultner, L.H. Lutze, Study of arsenic mutagenesis using the plasmid shuttle vector pZ189 propagated in DNA repair proficient human cells, *Mutat. Res.* 386 (1997) 335–344.
- [91] T. Helledy, R. Nilsson, D. Jenssen, Arsenic(III) and heavy metal ions induce intrachromosomal homologous recombination in the hprt gene of v79 Chinese hamster ovary cells, *Environ. Mol. Mutagen.* 35 (2000) 114–122.
- [92] T.K. Hei, M. Filipic, Role of oxidative damage in the genotoxicity of arsenic, *Free Radic. Biol. Med.* 37 (2004) 574–581.
- [93] J. Cuzick, P. Sasieni, S. Evans, Ingested arsenic, keratosis and bladder cancers, *Am. J. Epidemiol.* 136 (1992) 416–417.
- [94] National Academy of Science, USA, Risk estimate, 1999.
- [95] National Research Council, Arsenic in Drinking Water, National Academy Press, Washington, DC, 1999.
- [96] M. Tondel, M. Rahman, A. Magnuson, L.A. Chowdhury, M.H. Faruquee, S.A. Ahmed, The relationship of arsenic levels in drinking water and the prevalence rate of skin lesions in Bangladesh, *Environ. Health Perspect.* 107 (1999) 727–729.
- [97] D.N.G. Mazumder, R. Haque, N. Ghosh, B.K. De, A. Santra, D. Chakraborty, A.H. Smith, Arsenic levels in drinking water and the prevalence of skin lesions in West Bengal, India, *Int. Epidemiol. Assoc.* 17 (1998) 871–877.
- [98] A.H. Smith, A.P. Arroyo, D.N.G. Mazumdar, M.J. Konsnett, A.L. Hernandez, E.O. Lingas, M. Beeris, M.M. Smith, L.E. Moore, Arsenic induced skin lesions among Atacamenos people in northern Chile despite good nutrition and centuries of exposure, *Environ. Health Perspect.* 108 (2000) 617–620.
- [99] X. Guo, Y. Fujino, S. Kaneko, K. Wu, Y. Xia, T. Yoshimma, Arsenic concentration of ground water and prevalence of arsenic dermatosis in the Hetao plain area, Inner Mongolia, China, *Mol. Cell. Biochem.* 222 (2001) 85–94.
- [100] C. Watanabe, T. Inaoka, M. Nagano, S. Nakamura, K. Ushijima, N. Murayama, K. Miyazaki, R. Ohtsuka, Males in rural Bangladeshi communities are more susceptible to chronic arsenic poisoning than female: analysis based on urinary arsenic, *Environ. Health Perspect.* 109 (2001) 1265–1270.
- [101] S.H. Lamm, A. Engel, M.B. Kruse, M. Feinleib, D.M. Byrd, S. Lai, R. Wilson, Arsenic in drinking water and bladder cancer mortality in the US: an analysis based on 133 US counties and thirty years of observation, *J. Occup. Environ. Med.* 46 (2004) 298–306.
- [102] C. Steinmaus, Y. Yuan, M.N. Bates, A.H. Smith, Case-control study of bladder cancer and drinking water arsenic in the western United States, *Am. J. Epidemiol.* 158 (2003) 1193–2001.
- [103] L.E. Moore, M. Lu, A.H. Smith, Childhood cancer incidence and arsenic exposure in drinking water in Nevada, *Arch. Environ. Health* 57 (2002) 201–206.
- [104] D.R. Lewis, J.W. Southwick, R. Onellet-Hellstrom, J. Rench, R.L. Caldero, Drinking water arsenic in Utha: a cohort mortality study, *Environ. Health Perspect.* 107 (1999) 359–365.
- [105] US Environmental Protection Agency (USEPA) Draft final Guidance for Carcinogen Risk Assessment Forum, 2003.
- [106] A. Schoen, B. Beck, R. Sharma, E. Dube, Arsenic toxicity at low doses: epidemiological and mode of action considerations, *Toxicol. Appl. Pharmacol.* 198 (2004) 253–267.
- [107] Y.M. Hsueh, G.S. Cheng, M.M. Wu, H.S. Yu, T.L. Kuo, C.J. Chen, Physiological factors and environmental carcinogenesis: multiple risk factors associated with arsenic induced skin cancer: effects of chronic liver disease and mal-nutritional status, *Hum. Exp. Toxicol.* 14 (1995) 464–465.
- [108] Y.M. Hsueh, H.Y. Chiou, Y.L. Huang, W.L. Wu, C.C. Huang, M.H. Yang, L.C. Lue, G.S. Chen, C.J. Chen, Serum b-carotene level, arsenic methylation capability, and incidence of skin cancer, *Cancer Epidemiol. Biomarkers Prev.* 6 (1997) 589–596.
- [109] S. Biswas, G. Talukdar, A. Sharma, Prevention of cytotoxic effects of arsenic by short term dietary supplementation with selenium in mice in vivo, *Mutat. Res.* 441 (1999) 155–160.
- [110] E.M. Kenyon, M.F. Hughes, O.A. Levonder, Influence of dietary selenium on the disposition of arsenate in the female B6C3F1 mouse, *J. Toxicol. Environ. Health* 51 (1997) 279–299.
- [111] T.W. Gebel, Arsenic methylation is a process of detoxification through accelerated excretion, *Int. J. Hyg. Environ. Health* 205 (2002) 505–508.
- [112] M. Vather, E. Marafante, Effects of low density intake of methionine, chlorine or proteins on the bio-transformation of arsenic in the rabbit, *Toxicol. Lett.* 37 (1987) 41–46.
- [113] S. Chattopadhyay, S. Bhaumik, M. Purkayastha, S. Basu, S.A.N. Chaudhuri, S.D. Gupta, Apoptosis and necrosis in developing brain cells due to arsenic toxicity and protection with antioxidants, *Toxicol. Lett.* 136 (2002) 65–76.
- [114] G.H. Rabbani, S.K. Saha, M. Akhtar, F. Manni, A.K. Mitra, S. Ahamed, M. Alauddin, M. Bhattacharjee, G. Sultana, A.K. Chowdhury, Protective role of ascorbic acid and alpha-tocopherol on arsenic induced oxidative injury in rabbits: preliminary results, *J. Environ. Sci. Health. Part A: Toxic/Hazard. Subst. Environ. Eng. A* 38 (2003) 273–287.
- [115] C. Ferreccio, C. Gonzalez, M. Milosavljevic, G. Marshall, A.M. Sancha, A.H. Smith, Lung cancer and arsenic concentrations in drinking water in Chile, *Epidemiology* 11 (2000) 673–679.
- [116] H.Y. Chion, S.T. Chion, Y.H. Hsu, Y.L. Chon, C.H. Tseng, M.L. Wei, C.J. Chen, Incidence of transitional cell carcinoma and arsenic in drinking water: a flow up study of 8102 residents in an arseniasis endemic area in Northeastern Taiwan, *Am. J. Epidemiol.* 153 (2001) 411–418.
- [117] R.K. Dhar, B.K. Biswas, G. Samanta, B.K. Mondal, D. Chakraborty, S. Roy, A. Jabar, A. Islab, G. Ara, S. Kabir, A.W. Khan, S.A. Ahamed, S.A. Hadi, Ground water arsenic calamity in Bangladesh, *Curr. Sci.* 73 (1997) 48–59.
- [118] M. Zaw, M.T. Emmett, Arsenic removal from water using advanced oxidation processes, *Toxicol. Lett.* 133 (2002) 113–118.
- [119] T. Viraraghavan, K.S. Subramania, J.A. Aruldoss, Arsenic in drinking water problems and solutions, *Water Sci. Tech.* 40 (1999) 69–76.
- [120] H.R. Pfeifer, A.G. Girardet, D. Reymond, C. Schlegel, E. Temgona, D.L. Hesterberg, J.W. Chou, Dispersion of natural arsenic in the Malcantone Watershed South Switzerland: field evidence for repeated

- sorption-desorption and oxidation–reduction processes, *Geoderma* 122 (2004) 205–234.
- [121] D. Chakraborti, S.C. Mukherjee, S. Pati, M.K. Sengupta, M.M. Rahman, U.K. Chowdhury, D. Lodh, C.R. Chanda, A.K. Chakraborti, G.K. Basu, Arsenic groundwater contamination in middle Ganga Plain, Bihar, India: a future danger? *Environ. Health Persp.* 111 (2003) 1194–1201.
- [122] <http://www.soesju.org/arsenic/uttarpradesh.htm>.
- [123] D. Chakraborti, B.K. Biswas, T. Roy Chowdhury, G.K. Basu, B.K. Mandal, U.K. Chowdhury, S.C. Mukherjee, J.P. Gupta, S.R. Chowdhury, K.C. Rathore, Arsenic groundwater contamination and sufferings of people in Rajnandgaon district, Madhya Pradesh, India, *Curr. Sci.* 77 (4) (1999) 502–504.
- [124] D.V. Datta, M.K. Kaul, Arsenic content of drinking water in villages in northern India: a concept of arsenicosis, *J. Assoc. Phys. Ind.* 24 (1976) 599–604.
- [125] E. Kartinen, J.C.J. Martin, An overview of arsenic removal processes, *Desalination* 103 (1995) 79–88.
- [126] A.J. Jenny, K.B. Nicole, F.H. Harold, L.D. John, Arsenic-sulfide conformed anion exchange resin speciation of aqueous arsenic, *Water Res.* 38 (2004) 1155–1158.
- [127] B. Volesky, Detoxification of metal-leaching effects: bio sorption for the next century, *Hydrometallurgy* 59 (2001) 203–216.
- [128] S.K. Gupta, K.Y. Chen, Arsenic removal by adsorption, *J. Water Poll. Control Fed.* 50 (1978) 493–506.
- [129] J. Pattanayak, K. Mondal, S. Mathew, S.B. Lalvani, A parametric evaluation of the removal of As(V) and As(III) by carbon based adsorbents, *Carbon* 38 (2000) 589–596.
- [130] Final Report of the Arsenic Cost Working Group to the National Drinking Water Advisory Council USA, 2001.
- [131] Technologies and Costs for Removal of Arsenic from Drinking Water EPA 815-R-00-028 December, 2000.
- [132] G.N. Manju, C. Raji, T.S. Anirudhan, Evaluation of coconut husk carbon for removal of arsenic from water, *Water Res.* 32 (1998) 3062–3070.
- [133] I.A. Katsoyiannis, A.I. Zouboulis, Removal of arsenic from contaminated water sources by sorption onto iron oxide coated polymeric materials, *Water Res.* 36 (2002) 5141–5155.
- [134] S. Kundu, A.K. Gupta, Analysis and modeling of fixed bed column operations on As(V) removal by adsorption onto iron oxide-coated cement (IOCC), *J. Colloid Interf. Sci.* 290 (2005) 52–60.
- [135] X. Guo, A. Chen, Removal of arsenic by bead cellulose loaded with iron oxyhydroxide from groundwater, *Environ. Sci. Technol.* 39 (2005) 6808–6818.
- [136] S. Bang, M. Patel, L. Lippincott, X. Meng, Removal of arsenic from groundwater by granular titanium dioxide adsorbent, *Chemosphere* 60 (2005) 389–397.
- [137] W. Zhang, P. Singh, E. Paling, S. Delides, Arsenic removal from contaminated water by natural iron ores, *Min. Eng.* 17 (2004) 517–524.
- [138] Sunbaek Bang, P. George, Korfiatis, Xiaoguang Meng, Removal of arsenic from water by zero-valent iron, *J. Haz. Mater.* 121 (2005) 61–67.
- [139] S. Kundu, S. Paul, S. Kavalakatta, A. Pal, S.K. Ghosh, M. Mandal, T. Pal, Removal of arsenic using hardened paste of Portland cement batch adsorption and column study, *Water Res.* 38 (2004) 3780–3790.
- [140] S. Maity, S. Chakravarty, S. Bhattacharjee, B.C. Roy, A study on arsenic adsorption on polymetallic sea nodule in aqueous medium, *Water Res.* 39 (2005) 2579–2590.
- [141] J.K. Myoung, N. Jerome, Oxidation of arsenate in ground water using ozone and oxygen, *Sci. Total Environ.* 247 (2000) 71–79.
- [142] L. Coulibaly, G. Courene, N.S. Agathos, Utilization of fungi for biotreatment of raw waste waters, *Afr. J. Biotechnol.* 2 (2003) 620–630.
- [143] M.X. Loukidou, K.A. Matis, A.I. Zouboulis, M.L. Kyriakidou, Removal of As(V) from waste water by chemically modified fungal biomass, *Water Res.* 37 (2003) 4544–4552.
- [144] J.K.R. Yang, C.H. Wu, A. Mulchandani, W. Chen, Enhanced arsenic accumulation in engineered bacterial cells expressing ArsR, *Appl. Environ. Microbiol.* 70 (2004) 4582–4587.
- [145] G.S. Murugesan, M. Sathishkumar, K. Swaminathan, Arsenic removal from groundwater by pretreated waste tea fungal biomass, *Biores. Technol.* 97 (2006) 483–487.
- [146] N. Singh, L.Q. Ma, M. Srivastava, B. Rathinasabapathi, Metabolic adaptation to arsenic-induced oxidative stress in *Pteris Vittata* and *Pteris ensiformis* L, *Plant Sci.* 170 (2006) 274–282.
- [147] G.S. Erik, R. Medenwaldt, V.A.P. Joanna, Conditions and rates of biotic and abiotic iron precipitation in selected Danish fresh water plants and microscopic analysis of precipitate morphology, *Water Res.* 34 (2002) 2675–2682.
- [148] I.A. Katsoyiannis, A.I. Zouboulis, Application of biological processes for the removal of arsenic from ground water, *Water Res.* 38 (2004) 17–26.
- [149] T. Jong, D.L. Pany, Removal of sulfate and heavy metals by sulfate reducing bacteria in short term bench scale up flow anaerobic packed bed reactor runs, *Water Res.* 37 (2003) 3379–3389.
- [150] C. Casiot, G. Morin, F. Jullot, O. Burneel, J.C. Personne, M. Leblanc, K. Duquesne, V. Bonnefoy, F.E. Poulichet, Bacterial immobilization and oxidation of arsenic in acid mine drainage (Carnoules Creek, France), *Water Res.* 37 (2003) 2929–2936.
- [151] J. Kostal, R. Yang, C.H. Nu, A. Mulchandani, W. Chen, Enhanced arsenic accumulation in engineered bacterial cells expressing ArsR, *Appl. Environ. Microbiol.* 70 (8) (2004) 4582–4587.
- [152] P. Nimfodora, V. Edita, N. Valentine, K. Anthony, M. Ludovit, Removal of fixation of arsenic in the form of ferric arsenates. Three parallel experimental studies, *Hydrometallurgy* 41 (1996) 243–253.
- [153] A.K. Chatterjee, Introduction to Environmental Biotechnology, Prentice-Hall, New Delhi, India, 2002, pp. 151–152.
- [154] R. Johnston, H. Heijnen, Safe water technology for arsenic removal, in: M.F. Ahmed, et al. (Eds.), Technologies for Arsenic Removal from Drinking Water, Bangladesh University of Engineering and Technology, Dhaka, Bangladesh, 2001.