

## Arsenic distribution in environment and its bioremediation: A review

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Paper No. 309

Received: 14 January 2015

Accepted: 4 March 2015

Published: 25 March 2015

### ABSTRACT

Arsenic (As) is a naturally occurring toxic metalloid which is introduced into the environment through natural geochemical processes and several anthropogenic actions. Since it is a carcinogen, there is an urgent need to efficiently remove As from contaminated soil and water. This review elaborates the chemistry and environmental distribution of As along with several bioremediation approaches to alleviate As pollution.

### Highlight

- Arsenic is a ubiquitous element and ranks 20<sup>th</sup> in earth's crust and is widely distributed in a variety of minerals, commonly as arsenide of iron, copper, lead, silver and gold or as sulphide minerals
- Arsenic is also introduced into the environment through various anthropogenic activities
- Microorganisms control the environmental fate of Arsenic through various mechanisms resulting changes in solubility and/or toxicity of different Arsenic species

**Keywords:** Arsenic, Bioremediation, Carcinogen, Contamination

### An Omnipresent Environmental Pollutant

Toxic inorganic and organic chemicals are the main reasons for environment contamination and pose a major health threat to the human population. Deterrence of future contamination from these compounds presents an immense technical challenge (Evans *et al.*, 2004). Arsenic (As, Atom Number 33, Atom. Wt. 74.9216), the 20<sup>th</sup> most abundant element in the earth crust (National Research Council 1977), is a naturally occurring toxic metalloid. With an electron configuration of 3d<sup>10</sup>4s<sup>2</sup>4p<sup>1</sup>4py<sup>1</sup>4pz<sup>1</sup>, it belongs to group V and period 3 in the periodic table of elements. It readily changes its oxidation state and bonding configuration, producing four oxidation states: 0 (elemental), -3 (arsine), +3 (arsenite), and

+5 (arsenate) with the predominant forms being As (III) and As (V) (Cullen and Reimer 1989). Arsenic occurs naturally in soils as a result of the weathering of igneous and sedimentary rocks (Boyle *et al.*, 1973). The mean concentration of As in igneous rocks ranges from 1.5 to 3.0 mg kg<sup>-1</sup>, whereas in sedimentary rocks, it ranges from 1.7 to 400 mg kg<sup>-1</sup> (Smith *et al.*, 1998). More than 300 As containing minerals are found in nature with approx. 60% being arsenates, 20% being sulphides and sulphosalts, 10% being oxides and the rest being arsenites, arsenides, native elements and metal alloys (Bowell and Parshley, 2001). The most abundant and widespread As containing mineral is arsenopyrite (FeAsS) which is commonly found in pegmatites, high-temperature gold-quartz and tin veins, and also in contact with metamorphic sulfide

deposits (Anthony *et al.*, 2003). As bonds to oxygen and sulphur to produce a multitude of aqueous species and minerals like Arsenolite ( $\text{As}_2\text{O}_3$ ), Arsenopyrite ( $\text{FeAsS}$ ), Realgar ( $\text{As}_4\text{S}_4$ ), Orpiment ( $\text{As}_2\text{S}_3$ ) etc (O'Day 2006). Moreover, via biomethylation certain groups of microorganisms produce a large number of organoarsenic compounds (Stolz *et al.*, 2006), namely dimethylarsinate (DMA) and monomethylarsonate (MMA), generated by replacing a hydroxyl (-OH) ligand by a methyl group (-CH<sub>3</sub>) in inorganic As (III) and As (V) structures (Cullen and Reimer 1989).

Redox potential (Eh) and pH are the main drivers of As speciation in natural water, where the predominant chemical forms include oxyanions of As (III) ( $\text{H}_3\text{AsO}_4^-$  or  $\text{H}_2\text{AsO}_3^-$ ) and As (V) ( $\text{H}_2\text{AsO}_4^-$  or  $\text{HAsO}_4^{2-}$ ) (Suttigarn and Wang 2005; Rhine *et al.*, 2006). Generally, As (III) occurs in anoxic condition, exhibiting greater toxicity and mobility than As (V) which mainly occurs in aerobic conditions (Clifford 1990; Ehrlich 1996). Relative to the other oxyanion-forming elements (e.g. Se, Sb, Mo, V, Cr, U, Re), As is the most problematic in the environment because of its relative mobility over a wide range of redox conditions (Smedley and Kinniburgh 2002).

### Origin and sources of As

Arsenic is a ubiquitous element in the environment. It ranks 20th in earth's crust, 14th in sea water and 12th in the human body as an element (Woolson 1975). A range of As compounds, both organic and inorganic, are introduced into the environment through natural and anthropogenic sources.

### Natural Sources

In nature, As occurs rarely in its elemental form and is widely distributed in a variety of minerals, commonly as arsenide of iron, copper, lead, silver and gold or as sulphide minerals, for example arsenopyrite (O'Day 2006). Weathering of these As bearing minerals, volcanic activity as well as mining waste resulted in occurrence of As in aquatic and terrestrial environment under both oxic and anoxic condition (Rhine *et al.*, 2006). A list of some of the most common As minerals along with their place of occurrence is given in Table 1.

**Table 1. Major As mineral occurring in nature (Smedley and Kinniburgh 2002)**

Mineral	Composition	Occurrence
Native As	As	Hydrothermal veins
Niccolite	NiAs	Vein deposits and norites
Realgar	AsS	Vein deposits, often associated with orpiment, clays and limestones, also deposits from hot springs
Orpiment	As <sub>2</sub> S <sub>3</sub>	Hydrothermal veins, hot springs, volcanic sublimation product
Cobaltite	CoAsS	High-temperature deposits, metamorphic rocks
Arsenopyrite	FeAsS	The most abundant As mineral, dominantly mineral veins
Tennantite	(Cu,Fe) <sub>3</sub> As <sub>4</sub> S <sub>13</sub>	Hydrothermal veins
Enargite	Cu <sub>3</sub> AsS <sub>4</sub>	Hydrothermal veins
Arsenolite	As <sub>2</sub> O <sub>3</sub>	Secondary mineral formed by oxidation of arsenopyrite, native Arsenic and other As minerals
Claudetite	As <sub>2</sub> O <sub>3</sub>	Secondary mineral formed by oxidation of realgar, arsenopyrite and other As minerals
Scorodite	FeAsO <sub>4</sub> ·2H <sub>2</sub> O	Secondary mineral
Annabergite	(Ni,Co) <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O	Secondary mineral
Hoernesite	Mg <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O	Secondary mineral, smelter wastes
Conichalcite	CaCu(AsO <sub>4</sub> )(OH)	Secondary mineral
Pharmacosiderite	Fe <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH) <sub>3</sub> ·5H <sub>2</sub> O	Oxidation product of arsenopyrite and other As minerals

The greatest concentrations of these minerals occur in mineralised areas and are found in close association with the transition metals as well as Cd, Pb, Ag, Au, Sb, P, W and Mo (Smedley and Kinniburgh 2002). Oxidation and dissolution of the most common As bearing minerals such as arsenian pyrite [ $\text{Fe}(\text{AsS})_2$ ],



arsenopyrite (FeAsS), realgar (AsS), and orpiment (As<sub>2</sub>S<sub>3</sub>), are the major natural sources of As release in ground water (Nordstrom 2002; Wang and Mulligan 2006).

Arsenic concentration in most igneous rock types averages at 1.5 mg kg<sup>-1</sup>, whereas, in volcanic gases, As level is around 5 mg kg<sup>-1</sup> (Ure and Berrow 1982; Smedley and Kinniburgh 2002). In metamorphic rocks, As concentration is generally 5 mg kg<sup>-1</sup> with Pelitic rocks exhibiting the highest concentration of 18 mg Kg<sup>-1</sup> (Boyle and Jonasson 1973). Arsenic typically ranges between 5-10 mg kg<sup>-1</sup> (Webster 1999) in sedimentary rocks. The baseline As concentration in soils generally ranges between 5-10 mg kg<sup>-1</sup>. Boyle and Jonasson (1973) estimated the average baseline As concentration of 7.2 mg kg<sup>-1</sup>, whereas, Ure and Berrow (1982) quoted a higher average value of 11.3 mg kg<sup>-1</sup>.

Arsenic is generally present at very low concentration in natural waters. However, Smedley *et al.*, (1996) reported As concentration in the range of 100 – 5,000 µg L<sup>-1</sup> in unpolluted fresh waters located in areas of sulfide mineralization and mining.

### Anthropogenic Sources

Arsenic is also introduced into the environment through various anthropogenic activities originated from primary and secondary industries. Nriagu and Pacyna (1988) estimated that the total worldwide anthropogenic As discharge onto land is 64,000-132,000 t year<sup>-1</sup>. They estimated the major sources of As discharged onto land were originated from commercial wastes (about 40%), coal ash (about 22%), and atmospheric fallout from the production of steel (about 13%). Other anthropogenic sources of pollution associated with the mining industry (about 16%) also greatly contributed to As emissions onto land.

Industrial uses of As include the manufacture of ceramics and glass, electronics, pigments, antifouling agents, cosmetics, and fireworks (Leonard 1991). As trioxide (As<sub>2</sub>O<sub>3</sub>) is the major form of As that is produced from various industries. As has excellent

wood-preserving properties and is used in the timber industry in conjunction with Cu and Cr. Chromated copper arsenate (CCA) and ammonical copper arsenate (ACA) in conjunction with 99% of the arsenical wood preservatives (Perker 1981) are the most common wood preservatives used in the industry. Also the use of As in colouring agents such as Scheele's green (CuHAsO<sub>3</sub>) or Paris green [Cu (AsO<sub>2</sub>)<sub>2</sub> Cu(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>] (Azcue and Nriagu 1994) adding to the anthropogenic sources of As contamination.

Arsenic is a natural component of Pb, Zn, Cu, and Au ores. Consequently, As contamination of the atmosphere, soils, sediments, streams, and groundwater is possible during mining and/or smelting processes. As concentration as high as 1,628 mg L<sup>-1</sup> have been reported in the effluent of industrial discharges from metallurgical industries involved in smelting operations for mining metals (Basha *et al.*, 2008). The smelting operations of Cu, Ni, Pb, and Zn have emitted 62, 000 tons of As with 80% generated alone through copper smelters (Bissen and Frimmel 2003). Sadler *et al.*, (1994) reported As level in soil near a lead smelter was 0.2 g Kg<sup>-1</sup>, whereas, near a copper smelter, the concentration was 0.55 g Kg<sup>-1</sup>. Unlike many heavy metals such as Cr, Cd and Hg As has been detected in groundwater especially at sites contaminated by mill tailings. Bernard (1983) investigated the contamination of groundwater and the subsequent contamination of Lake Moira, Canada, and found that haphazard disposal of mill tailings and other slag wastes resulted in considerable leaching of As from these sites.

As concentration in coal varies from 2 to 82 mg As kg<sup>-1</sup>, depending on geological origin (Adriano *et al.*, 1980). However, very high concentrations of As (1500 mg As kg<sup>-1</sup>) have been recorded in brown coal from the former Czechoslovakia (Bencko and Symon 1977). The volatilization of As hexoxide (As<sub>4</sub>O<sub>6</sub>) during coal combustion leads to the emission of As in the environment which eventually condenses in the flue system (Bhumbla 1994). Fly ash from the thermal power plants may also contribute to As contamination of the soil.



Arsenic contamination of the environment can also occur through the use of arsenical fungicides, herbicides, and insecticides in the agriculture (Bissen and Frimmel 2003). Soil contamination due to the use of organoarsenical herbicides such as monosodium methanearsonate (MSMA) and disodium methanearsonate (DSMA) was also reported (Gilmore and Wells 1980; Smith *et al.*, 1998). The use of sodium arsenite ( $\text{NaAsO}_2$ ) to control aquatic weeds has contaminated small fish ponds and lakes in several parts of United States with As (Adriano 2001).

### Impacts on Agriculture and Food Chain

Long term use of As based fungicides, pesticides and insecticides as well as irrigation with As contaminated ground water had led to elevated concentration of As in soil. Bioavailability of As to plant species is highly influenced by several soil factors including redox potential, pH, the contents of organic matter, iron, manganese, phosphorus, calcium-carbonate, soil microbes and the speciation of As in soil (Mahimairaja *et al.*, 2005). Marin *et al.*, (1992) reported that the order of As availability to rice (*Oryza sativa*) is as follows:  $\text{As(III)} > \text{MMA} > \text{As(V)} > \text{DMA}$ . Although plants exhibit certain degree of tolerance to As, at higher concentration As is toxic to all forms of life. An average toxicity threshold of  $40 \text{ mg As kg}^{-1}$  biomass has been established for crop plants (Sheppard 1992). Arsenic is known to alter and disturb uptake and transport of nutrients in plants (Päivöke and Simola 2001) leading to yield loss. Various other symptoms of phytotoxicity include retardation of root and shoot growth (Macnair and Cumbes 1987; Meharg and Macnair 1991), inhibition of root water uptake and ultimately resulting in death from wilting (Woolson *et al.*, 1971). Rice being produced in As contaminated soil showed symptoms of straight head disease which included increased sterility (Wells and Gilmour, 1977). There is significant evidence that exposure to inorganic As species results in the generation of reactive oxygen species (ROS) which leads to oxidative stress in plants (Hartley-Whitaker *et al.*, 2001).

Plants take up As from soil and are known to accumulate in different parts depending on the species and variety. Arsenic accumulated in the edible parts of plants may result food chain contamination and pose serious health risk to humans (Abedin *et al.*, 2002). The World Health Organization (WHO 1993) has set a value of  $2 \text{ g As kg}^{-1}$  bodyweight/day as the tolerable daily intake. However, in countries where most of the basic diet consists of cereals and vegetables, the stated value is not observed when cropland or irrigation water contain high levels of As (Sengupta *et al.*, 2006; Signes-Pastor *et al.*, 2008). The As content of rice grain is an important concern because of the large daily intake of rice by people in many parts of S and SE Asia (commonly assumed to be  $450 \text{ g day}^{-1}$  for a 60 kg adult in Bangladesh). Duxbury and Zavala (2005) pointed out that, when As in rice grain exceeds  $0.11 \text{ mg kg}^{-1}$ , it is possible for adults consuming 450 g of rice and 4 L of water per day at the 10 ppb WHO As water standard to exceed the FAO and WHO provisional tolerable dietary intake standard of  $130 \text{ } \mu\text{g As per day}$  for a 60 kg adult. Williams *et al.*, (2006) measured As contents of 37 vegetables, pulses and spices commonly grown in Bangladesh and found that As levels were highest in radish leaves ( $0.79 \text{ mg kg}^{-1}$ ), arum stolons, spinach and cucumber, and lowest ( $0.2 \text{ mg kg}^{-1}$ ) in most fruits, vegetables, and spices. Besides As intake from cereals and vegetables, consumption of certain seafood and fish can be potential sources of As intake (Peralta-Videa *et al.*, 2009). According to Rose *et al.*, (2007), As is first accumulated in phytoplankton from sea water and transformed into arsenosugar compounds and DMA, which are taken up by algae. Arsenosugar compounds are then transformed to arsobetaine by methylation of As (V), MAA, and DMA by microbial organisms (Peralta-Videa *et al.*, 2009). The As levels can be magnified 1000–10,000-fold in marine animals that ingest algae (Borak and Hosgood 2007). Furthermore, bivalves such as oysters, mussels and clams were found to accumulate arsenosugar- $\text{PO}_4$  and arsenobetaine, which are less toxic than inorganic As compounds. The dietary intake of organoarsenic compounds via seafood pose little health risk to animals and humans, because



the ingested As compounds are rapidly excreted in uncharged forms (Tamaki and Frankenberger 1992).

### The Extent of Arsenic Pollution

As contamination in groundwater and its subsequent health effects has become a worldwide concern over the past two to three decades. Untreated, highly toxic As in soil and effluent has been disposed of in rivers and has ended up in groundwater, leading to toxicity to humans and other biota. Groundwater is more vulnerable to As contamination than surface water because of the interaction of groundwater with aquifer minerals and the increased potential in aquifers for generating the physiochemical conditions favourable for As release (Smedley 2006). Arsenic in drinking water is one of the topmost environmental threats worldwide, based on the potential exposure of people to As and the numerous diseases with which it has been associated (Smith *et al.*, 1992; Abernathy *et al.*, 2003; Watanabe *et al.*, 2003; Tapio *et al.*, 2006). Long term use of As enriched groundwater for drinking has resulted in severe health problems in majority of As affected regions across the world. The United States Environmental Protection Agency (US EPA) drinking water standard for As was set at 50 µg L<sup>-1</sup> in 1975, based on a Public Health Service standard originally established in 1942 (USEPA, 1996). On the basis of investigations initiated by the National Academy of Sciences, it was concluded that this standard did not eliminate the risks of skin, lung, and prostate cancer from long-term exposure to low As concentrations in drinking water. In order to achieve the EPA's goal of protecting public health, recommendations were made to lower the safe drinking water limit to 5 µg L<sup>-1</sup>, slightly higher than what is considered the technically feasible measurable level (3 µg L<sup>-1</sup>) (National Research Council 1999). However the current drinking water guideline for As adopted by both the World Health Organisation (WHO) and the US EPA is 10 µg L<sup>-1</sup>. This is higher than the proposed Canadian and Australian maximum permissible concentrations of 5 and 7 µg As L<sup>-1</sup>, respectively. The ground water As contamination problem has been recognized and documented across the world over the last decade.

Review works covering the As contamination scenario around the world have reported many countries with As concentration in drinking water greater than the WHO Guideline Value of 10 µg/L or the prevailing national standards. These incorporate Afghanistan, Argentina, Australia, Bangladesh, Brazil, Bulgaria, Canada, Cambodia, Chile, China, Germany, Ghana, Greece, Hungary, India, Iran, Japan, Mexico, Myanmar, Nepal, New Zealand, Pakistan, Romania, Switzerland, Taiwan, the United States of America, and Vietnam (Mukherjee *et al.*, 2006). The first incidence of As poisoning was reported in Chile in 1962. It was estimated that about 7% of the deaths were caused by previous exposure to As in this country (Borgono and Greiber 1972; Zaldivar 1974). The Natural occurrence of As in groundwater (>10 µg L<sup>-1</sup>) is reported from many parts of the United States, such as California, Alaska, Arizona, Indiana, Idaho, Nevada, Washington, Missouri, Ohio, Wisconsin, and New Hampshire (Moncure *et al.*, 1992; Frost *et al.*, 1993; Welch *et al.*, 1998; Welch *et al.*, 2000; Chiou *et al.*, 2001). With the discovery of newer sites in the recent past, the As-contamination scenario around the world, especially in Asian countries, has changed considerably. Before 2000, there were five major incidents of As contamination in groundwater in Asian countries: Bangladesh, West Bengal, India, Inner Mongolia (PR China) and Taiwan. Between 2000 and 2005, As-related groundwater problems have emerged in different Asian countries, including new sites in China, Mongolia, Nepal, Cambodia, Myanmar, Afghanistan, DPR Korea, Iran, Pakistan and Viet Nam (Suk *et al.*, 2003; Mukherjee *et al.*, 2006). Arsenic problem was reported in 1968 in Taiwan. More than 19% of tube wells among 83,000 tested tube wells were reported to be contaminated with As with concentrations above 50 mg L<sup>-1</sup> (Tseng 1977; Thornton and Farago 1997; Tsai *et al.*, 1998). Blackfoot disease due to As contamination is of common occurrence in this country (Tseng 2003). An estimated 5.63 and 14.66 million people in 29 out of 32 provinces of China are drinking water which contains As exceeding 50 and 10 mg L<sup>-1</sup>, respectively. More than 30,000 cases of Asosis have been diagnosed in China (Borgono and

Greiber 1971). Occurrence of As in groundwater of the Bengal Delta Plain in West Bengal, India and Bangladesh, is the region's single largest emerging societal and environmental problem of the present century (Bagla and Kaiser 1996; Dhar *et al.*, 1997). According to a study led by the British Geological Survey in 1998, shallow tube wells in 61 of the 64 districts in Bangladesh had As concentration above 0.010 mg L<sup>-1</sup> in 46% of the samples and above 0.050 mg L<sup>-1</sup> in 27% of the samples. When combined with the estimated 1999 population, it was speculated that the number of people exposed to As concentrations above 0.05 mg L<sup>-1</sup> was 28-35 million and the number of those exposed to more than 0.01 mg L<sup>-1</sup> was 46-57 million (British Geological Survey 2000). In India, As contamination was first discovered as late as 1982. By then 6.97 million people were estimated to be exposed to high As content in drinking water. At present some 3, 00,000 people are likely to be suffering from various stages of Arsenosis (Chakraborti *et al.*, 2002; Mukherjee *et al.*, 2006). The first report of As groundwater contamination and its health effects in the Ganga plain from West Bengal was published in 1984 (Garai *et al.*, 1984). As affected areas in West Bengal have been classified into three zones: highly affected (9 districts mainly in eastern side of Bhagirathi River), mildly affected (5 districts in northern part), and unaffected (5 districts in western part).

### Toxicity and Human Health Effects

Toxicity and Health effects associated with significant exposure to As are dependent on the duration and dose of exposure. Depending on that As induced toxicity can be classified as acute toxicity and chronic toxicity (Ratnaïke 2013). Acute toxicity involves harmful effects in an organism through a single or short-term exposure. Acute As poisoning mainly occurs in two distinct forms acute paralytic syndrome and acute gastrointestinal syndrome (Brouwer *et al.*, 1992; Civantos *et al.*, 1995). Other clinical features of acute poisoning include nausea, vomiting, profuse watery diarrhoea, and diffuse skin rash etc (Ratnaïke 2013). Chronic As poisoning occurs usually upon repeated or continuous exposure to

small amount of As (Ratnaïke 2013). The chronic effects of inorganic As exposure via drinking water include skin lesions, such as hyperpigmentation, and respiratory symptoms, such as cough and bronchitis and reproductive disorders (Smith *et al.*, 2000; Ahsan *et al.*, 2000; Milton and Rahman 2002, Sen and Chaudhuri 2008). The cardiovascular, gastrointestinal, neurological and urinary systems are some of the other systems most affected in humans (Lee *et al.*, 2002; Mukherjee *et al.*, 2003). Arsenic is known to have mutagenic and genotoxic effects on humans, and it has been associated with increased risk of skin, lung, liver and other cancers, type 2 diabetes, and reproductive and developmental problems (Hopenhayn-Rich *et al.*, 1998; Steinmaus *et al.*, 2000; Karagas *et al.*, 2001; Bodwell *et al.*, 2006; Navas-Acien *et al.*, 2006; Liu *et al.*, 2008; Prozialeck *et al.*, 2008). The International Agency for Research on Cancer (IARC) has listed As as a human carcinogen since 1980. Due to toxic and carcinogenic effects of As World Health Organization has set the permissible limit of As in drinking water as 0.01 mg L<sup>-1</sup>, which is equivalent to 10 ppb (Chakraborti *et al.*, 2002; Prozialeck *et al.*, 2008). Recently, however, it has been reported that there is an increased risk of As toxicity, even at the low and permissible dose of 10 ppb (Prozialeck *et al.*, 2008). In certain areas in the Indian subcontinent, the maximum As concentration in ground water was found to be around 3700 ppb to 4700 ppb (Chakraborti *et al.*, 2002), leading to several physiological damages to human beings. Presently, the extent of groundwater As contamination in West Bengal has reached an alarming situation as nine districts of West Bengal have been reported to have groundwater As concentrations above 0.05 mg L<sup>-1</sup> and several people have been affected by As poisonings (Chakraborti *et al.*, 2009).

Arsenite can bind to sulfhydryl groups and dithiols groups of proteins, whereas arsenate can act as a chemical analog of phosphate and can inhibit oxidative phosphorylation (Ordon *et al.*, 2005). Arsenic does not directly react with DNA or cause gene mutations, except to a small extent at high doses. However, it does cause gene amplification and chromosomal damage at lower doses and can



enhance mutagenesis by other agents, apparently by inhibiting DNA repair (Li and Rossman 1989). Arsenite can also cause aneuploidy. Unlike spindle poisons, arsenite does not inhibit spindle fiber formation; instead, it deranges the spindle apparatus, possibly by accelerating microtubule polymerization. Arsenite may act as carcinogen by causing DNA hypomethylation leading to aberrant gene expression (Zhao *et al.*, 1997). Chronic exposure to arsenite caused a progressive increase in CpG methylation within the p53 promoter, which would be expected to block transcription of the p53 gene (Mass *et al.*, 1997). The p53 gene is an important tumor-suppressor gene whose protein product plays an important role in cell cycle control, apoptosis, and control of DNA repair.

#### **Remediation of as contaminated soil and water**

There have been increasing needs of removal of As from contaminated soils and groundwater to limit the detrimental impacts of As on living beings. There are a plenty of remediation methods have been developed based on physical, chemical and biological approaches that may achieve complete or partial removal of As from soil and groundwater or the reduction of its bioavailability in order to minimize toxicity.

#### **Conventional Methods**

The most commonly used conventional methods include oxidation, co-precipitation and adsorption, ion exchange and membrane techniques such as filtration, reverse osmosis etc (Shen 1973; Cheng *et al.*, 1994; Kartinen and Martin 1995; Hering *et al.*, 1996; Joshi and Chaudhuri 1996).

Most conventional treatment methods are effective in removing As in pentavalent form and hence include an oxidation step as pretreatment to convert arsenite to arsenate. Arsenite can be oxidized by oxygen, ozone, free chlorine, hypochlorite, permanganate, hydrogen peroxide, and fulton's reagent (Ahmed 2003). Chemical oxidation of As (III) to As (V) is currently being used in most conventional treatments. The chemical oxidation of As (III) to As

(V) was first studied by Frank and Clifford (1986) utilizing chlorine, monochloramine, and oxygen. Solid phase oxidants such as birnessite ( $\delta$ -MnO<sub>2</sub>) have also proven to be very useful in the oxidation of As (III) to As (V) at a optimum pH of about 6.5 (Manning *et al.*, 2002).

Coagulants such as aluminium alum, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.18H<sub>2</sub>O, ferric chloride, and ferric sulfate are effective in removing As from water by utilizing the electrostatic attachment of negatively charged ions to the flocs. As (III) occurs in non-ionized form, it is not subject to significant removal. Oxidation of As (III) to As (V) is thus required as a pretreatment for efficient removal (Ahmed 2003). Other adsorption techniques such as activated alumina, activated carbon (Ghosh and Yuan 1987) and activated bauxite (Gupta and Chen 1978) are also proved to be efficient technologies.

Ion exchange is a physico-chemical process by which an ion in the liquid medium is exchanged for saturated ion on the solid phase. Synthetic resin saturated with the preferred anion is most widely used for exchanging As anions in contaminated water (Johnston and Heijnen 2001). Generally strong-base resins (SBA) and sulfate-selective resins are found to be most efficient in As removal over a broader pH range (USEPA 2000). The biggest disadvantage of using the ion exchange process is the non-removal of As (III) species because of its uncharged behavior until pH of about 9 (pK<sub>a</sub> =9.22). This characteristic of As (III) anions necessitates a pre-oxidative step for the conversion of As (III) to As (V) prior to removal from water. The removal of As (V) is independent of the initial concentration and pH of the liquid medium (Johnston and Heijnen 2001).

Membrane techniques like Reverse osmosis (RO), Nano-filtration (NF), Ultra-filtration (UF), microfiltration (MF), membrane distillation (MD) are proved to be capable of removing dissolved As from water with a high efficacy. Membranes are typically synthetic materials with billions of pores or microscopic holes that act as a selective barrier allowing the passage of certain constituents with the rejection or exclusion of others in the water (Uddin

*et al.*, 2007). RO membrane contains extremely small pores ( $< 0.001 \mu\text{m}$ ) (Schneiter 1983) and a very high (often close to 100%) rejection of low-molecular mass compounds and ions can be achieved. With the invent of cellulose acetate RO membrane in the 1980's, arsenate removal efficiency of above 90% have been achieved with the RO system operated at high-pressure around 400 psi (Fox 1989). However, arsenite removal efficiency is less than 70%.

Despite the development of numerous conventional methods, the application of these techniques is not very economical and requires very high tech operation and maintenance. Many of these processes remove As partially and the byproducts resulted from these physiochemical processes can be harmful and difficult to remove from soil and water.

### **Bioremediation of As**

Bioremediation is defined as degradation of environmental pollutant to less toxic form using living organisms like bacteria, fungi or plant.

#### **Microbial Bioremediation of As**

Currently bioremediation of heavy metals using microorganisms has received immense interest for its potential, cost effectiveness, and environmental friendly way for heavy-metal removal (Valls and Lorenzo 2002, Rakshit and Ghosh 2009). Microorganisms control the environmental fate of As through various mechanisms resulting changes in solubility and/or toxicity of different As species (Ghodsi 2011, Rakshit *et al.*, 2009). Researchers have successfully isolated and characterized As resistant bacteria from different environmental samples and concluded that they have evolved several mechanisms to tolerate the uptake of heavy metal such as As. Microorganisms have evolved several strategies for dealing with the toxicity of As which could be utilized as attractive approaches for removal of As from contaminated sites. It mainly involves efflux of heavy metal ions outside the cell, accumulation and complexation of the metal ions inside the cell and oxidation-reduction of the heavy metal ions to a less toxic state (Nies 1999). Arsenic-

resistant strains also utilizes As in their metabolism, either as a means of generating energy through chemoautotrophic arsenite oxidation (Santini *et al.*, 2000) or using arsenate as a terminal electron acceptor in an aerobic respiration (Ahmann *et al.*, 1994; Stolz *et al.*, 1999). Moreover microbes are also capable of transforming inorganic As compounds by biomethylation into monomethylarsonic acid (MMA), dimethylarsenic acid (DMA), trimethylarsine (TMA) and trimethylarsine-oxide (TMAO) (Ridley *et al.*, 1977; Woolson 1977; Cullen and Reimer 1989; Gadd 1993). Methylation of inorganic arsenic has actually been described as the most important detoxification process in the human body since it reduces the affinity of the compound for tissue (Vahter and Marafante 1988). The three main approaches used in bioremediation of As are as follows.

### **Bioaccumulation**

Microorganisms exhibit a strong ability to accumulate (bioaccumulation) As from a substrate containing very low concentrations of this element. Bioaccumulation is activated by two processes, namely biosorption of As by microbial biomass and its byproducts and physiological uptake of As by microorganisms through metabolically active and passive processes. Factors such as soil pH, moisture and aeration, temperature, concentration and speciation of As, soil amendments, and rhizosphere are known to influence the process of bioaccumulation of As in microbial cells (Mahimairaja *et al.*, 2005). Scientists have isolated a non-genetically engineered potent As accumulating bacteria *Marinomonas communis* from marine and non marine environment in Japan with high removal efficiency (Takeuchi *et al.*, 2007). Furthermore, Ghodsi *et al.*, (2011) concluded that the cellular accumulation of As could be a result of higher uptake and lower efflux by a regulatory protein of the *ars* operon that has a specific binding site available for arsenite (Ghodsi *et al.*, 2011). In addition to bioaccumulation of As by bacterial and fungal species, some algal species (*Fucus gardneri* and *Chlorella vulgaris*) are also known to accumulate (Granchinho *et al.*, 2001; Maeda *et al.*, 1985).





### Microbial Redox Reaction

Microbial mediated redox reactions mainly act upon As (III) and As (V) species. Researchers have successfully isolated and characterized As resistant bacteria from different environmental samples and concluded that these bacteria have the capability to grow chemolithotrophically with oxygen as an electron acceptor and As (III) as an electron donor (Santini *et al.*, 2000; Duquesne *et al.*, 2008). Furthermore, Ilyaletdinov and Abdrashitova (1981) concluded that bacteria derive metabolic energy from As (III) oxidation. Strains of *Bacillus* and *Pseudomonas* spp. (Frankenberger and Losi 1995) and *Alcaligenes faecalis* (Phillips and Taylor 1976) and *Alcaligenes* spp. (Osborne and Ehrlich 1976) were found capable of oxidizing As (III) to As(V). Gihiring *et al.*, (2001) explored the As (III) to As (V) oxidizing ability of *Thermus aquaticus* and *Thermus thermophilus*. Because As (V) is strongly adsorbed onto inorganic soil components, microbial oxidation could result in the immobilization of As. On contrary, some strains use As (V) as a terminal electron acceptor in an aerobic respiration, resulting in dissimilatory reduction of As (V) (Ahmann *et al.*, 1994; Stolz and Oremland 1999). Examples are: *Sulfurospirillum barnesii*, *S. arsenophilum*, *Desulfotomaculum auripigmentum*, *Bacillus Asoselenatis*, *B. selenitireducens*, *Crysiogenes arsenatis*, *Sphingomonas* spp., *Pseudomonas* spp. and *Wolinella* spp. (Ahmann *et al.*, 1994; Lovley and Coates 1997; Newman *et al.*, 1998; Stolz and Oremland 1999). In addition, a plasmid-encoded, detoxifying reductase (arsC enzyme) present in the cytoplasm of certain bacteria (e.g. *Escherichia coli* and *Staphylococcus aureus*) reduces As (V) to As (III) for its quick extrusion from the cell, resulting in As resistance (Ji *et al.*, 1994; Diorio *et al.*, 1995).

**Table 2. Phytoremediation techniques (Vidali *et al.*, 2001)**

Technique	Plant mechanism	Surface medium
phytoextraction,	Uptake and concentration of metal via direct uptake into the plant tissue with subsequent removal of the plants	Soils
phytotransformation,	Plant uptake and degradation of organic compounds	Surface water, groundwater
phytostabilization,	Root exudates cause metal to precipitate and become less available	Soils, groundwater, mine tailing
phytodegradation,	Enhances microbial degradation in Rhizosphere	Soils, groundwater, within rhizosphere
Rhizofiltration	Uptake of metals into plant roots	Surface water and water pumped

### Biovolatilization of As

Microbes are able to biomethylate inorganic As species to monomethylarsine and dimethylarsine (Ridley *et al.*, 1977; Woolson 1977; Cullen and Reimer 1989; Gadd 1993). Due to their low boiling point and/or high vapor pressure, these compounds are susceptible for volatilization and could easily be lost to the atmosphere (Braman and Foreback 1973). The conversion of As (V) to small amounts of volatile methylarsines was first described in a pure culture of a methanogen, *Methanobacterium bryantii* (McBride *et al.*, 1971). Recently, several pure cultures of anaerobes, including a methanogen (*Methanobacterium formicicum*), a fermentative bacterium (*Clostridium collagenovorans*) and sulfate-reducing bacteria (*Desulfovibrio vulgaris* and *D. gigas*), were also implicated in the formation of methylarsines (Michalke *et al.*, 2000. As (V) can be converted to monomethylarsine and dimethylarsine by *Achromobacter* sp. and *Enterobacter* sp., and to monomethylarsine, dimethylarsine and trimethylarsine by *Aeromonas* spp. and *Nocardia* spp. (Cullen and Reimer 1989).



## Phytoremediation of As

Along with microbes based bioremediation, vegetation-based remediation shows potential for accumulating, immobilizing, and transforming a low level of persistent contaminants. Phytoremediation is an emerging technology that employs plants and their associated root-bound microbial community to remove, contain, degrade, or render environmental contaminants harmless (Robinson *et al.*, 2003). Based on the contaminant fate phytoremediation has been classified into phytoextraction, phytotransformation, phytostabilization, phytodegradation, rhizofiltration (Vidali *et al.*, 2001). An overview of these techniques has been given as follows (Table 2).

A number of plants have been identified as hyperaccumulators for the phytoextraction of a variety of metals as well as metalloids such as As. The hyperaccumulation of metalloids involves uptake of the soluble metalloid species by the root system, translocation to the aerial parts, and storage in a nontoxic form in the aerial portions (Mahimairaja *et al.*, 2005). The first reported As hyperaccumulator is the Chinese brake fern *Pteris vittata* (Ma *et al.*, 2001). It can accumulate 12–64 mg As kg<sup>-1</sup> in its fronds from uncontaminated soils containing 0.5–7.5 mg As kg<sup>-1</sup>, and up to 22,630 mg As kg<sup>-1</sup> from a soil amended with 1500 mg As kg<sup>-1</sup> (Ma *et al.*, 2001). Several other fern species, including *Pityrogramma calomelanos*, *Pteris cretica*, *Pteris longifolia* and *Pteris umbrosa* and some plant species such as *Agrostis tenuis*, *A. stolonifera*, *A. tenuis* have also been reported to be able to hyperaccumulate As (Visoottiviseth *et al.*, 2002; Zhao *et al.*, 2002). An accumulation of As up to 2000 mg kg<sup>-1</sup> (dry mass) in *Lemna gibba* (duckweed) was observed in the tailings water of abandoned uranium mine sites in Saxony, Germany (Mkandawire and Dudel 2005). As hyperaccumulator fern *Pteris vittata* L. produces large amounts of root exudates that are hypothesized to help *P. vittata* to mobilize As directly from soils also help sustain a rhizosphere microbial community, which indirectly mobilizes As from soil (Huang *et al.*, 2010).

## Acknowledgements

This work was supported by integrated rural development and management (IRDM) faculty centre under school of agriculture and rural development.

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