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Approaches for Remediation of Arsenic Contamination from Soil and Water: A Review

Dheeraj Pandey[1], Ifra Zoomi[1], Ovaid Akhtar[2], Pragya Srivastava[1], Harbans Kaur Kehri[1*]

[1]Sadasivan Mycopathology Laboratory, Department of Botany, University of Allahabad, Allahabad- 211002, India.

[2]Department of Botany, Kamla Nehru Institute of Physical and Social Sciences, Sultanpur – 228118, India.

[*] Corresponding author Email id – *Kehrikaurhk@gmail.com*

Abstract: **Arsenic (As) is semi metallic compound (metalloid). Beside the elemental form, As exists in four oxidation states; -3, 0, +3 and +5 and As (0) as an elemental form. Arsenic exists in environment since long back, but present acceleration of its exposure leads to cancer, which is increasing day by day. During recent years, several technologies are developed to remediate As physically and chemically from drinking water, but least effort is seen in case of healthy crop production in As contaminated areas. In this regard, there is a hope with bioagents as they can be suitable and convenient for ecological sustainability in As contaminated soils.**

Keywords: **Remediation, microbes, phytoremediation, Arsenic.**

1. INTRODUCTION

Arsenic (As) is semi metallic compound (metalloid) existing in environment in solid gray, yellow and black color. Its structure consists of many interlocked ruffled, six-membered ring which is double layered but brittle and relatively low mohs-hardness. As was discovered in early Bronze Age (2500 BC) but for the first time isolated as arsenic sulfide by Albertus Mannus (1250). Death of Napoleon Bonaparte was suspected to be due to As poisoning. It is a carcinogenic, toxic heavy metalloid (Huysman and Frankenberges, 1990; Phillips, 1990). As exists in four oxidation states; -3, 0, +3 and +5. According to ATSDR, (1999) elemental form of As is as As (0). Solubility of arsenate (As V), arsenite (As III), arsenic (As 0) and arsine depends on the pH and ionic condition. Amongst all its oxidation states, As(V) is the most stable form (Sharma and Sohn, 2009; Zhao *et al*. 2010; Gupta *et al*. 2011). As resembles with phosphorus (P), which occupies the same group 15 in periodic table.

As exists in environment since long back, but present acceleration of its exposure leads cancer which is considerably increasing day by day. IARC (International Agency for Research on Cancer) recognized it as a group-I carcinogenic. EU (European Union) directive 67/548/EEC declared As as a toxic and dangerous for the environment. Exposure of As induces adverse effects on human health and causing cancer. As reaches in human body directly from water and indirectly from food products which are grown at As contaminated areas (Huq *et al*. 2006; Srivastava *et al*. 2013). In agriculture deep water irrigation accelarate As toxicity in agricultural crops and drinking water. FAO (Food and Agriculture Organization) declared permissible limit of As in irrigation water as 0.10 mg/l. Whereas different organizations set different permissible limit of As in drinking water such as 0.01 mg/l by WHO, 10 ppb by EPA (US), 5 ppb by Department of Environmental Protection New Jersay etc. as there is no average of As content global food products however, WHO advisory conference of As scheduled to consider 200-300 ppb for rice and China sets 150 ppb As for food products in china. Under normal conditions, As concentrations in terrestrial plants are usually less than 10000 ppb (Matschullat, 2000). During recent years, several technologies are developed to remediate As physically and chemically from drinking water, but least effort are seen in case of healthy crop production in As contaminated areas. In this regard, there is a hope with bioagents, which may be suitable and convenient for ecological sustainability in As contaminated soil.

In living bodies As present in many forms like mono methyl arsenic acid [MMA; $CH_3AsO(OH)_2$], dimethyl arsinic acid [DMA; $(CH_3)_2AsOOH$], tri-methyl arsineoxide [TMAO; $(CH3)_3AsO$], arsenobetaine [AsB; $(CH_3)_3$AsþCH$_2$COOH], arseno-choline (AsC), arsenosugars (AsS), arsenolipids etc. (Tangahu *et al*. 2011). As (III) is usually more toxic than As(V) (Abedin *et al*. 2002a and b; Schat et al. 2002) and dimethyl arsinous acid and mono methyl arsonous acid are more toxic than other related compounds (Petrick *et al*. 2000; Mass *et al.* 2001). Toxicity of As is because of its affinity to As (III) oxidies for thiols ($^-$SH). Thiol is important in cysteine residues and act as a cofactor like lipoic acid cofactor in citric acid cycle. As(III) inhibits ATP production and also inhibit succinate dehydrogenase activity because of that it leads to inhibition of mitochondrial activity. As can compete with Phosphorus during oxidative phosphorylation and by inhibiting the reduction of NAD^+ (Saha *et al*. 1999; Mazumder, 2005).

2. APPROACHES TO REMEDIATE ARSENIC CONTAMINATION

Remediation of As from contaminated water is necessary to reduce its adverse effects on human health. Most of the physical and chemical tools have been applied for As remediation, from drinking water, but these are costly and less affordable (Mukherjee *et al*. 2010). However, Many bacteria, fungi and accumulating plant have potentialiy to remediate the As contamination by various mechnisms (Su *et al*. 2010; Srivastava *et al*. 2011) and that could be used as a bio-agents in stressful environmental condition.

As contaminated soil is being remediated via various methods, which are physical excavation and transport for landfills, solvent extraction techniques, electrokinetic separation, chemical oxidation, soil stabilization/solidification (Bento *et al*. 2005; Gong *et al*. 2005; Collins et al. 2009). Now a days, bioremediation technique received much attention, because it enhances the establishment of vegetation at reasonable cost along with sustainability. Phytoremediation (Phytoextraction, Phytostabilization and Rhizofiltration) of contaminated soils has been widely accepted as a cost-effective and environmentally friendly (Yu *et al*. 2003) tool for As remediation.

2.1 Physical approaches for Arsenic remediation

In the physical approaches, As contaminated and non-contaminated soils are mixed together and washed with sulfuric acid, nitric acid, phosphoric acid, and hydrogen bromide. This leads to As dilution at an accepetable level (Mahimairaja *et al*. 2005). However, application of physical approach at large scale is not possible as it uneconomical and non eco-friendly. (Mahimairaja *et al*. 2005).

Treatment of As residue by cow dung, reduces As into gaseous (AsH_3) and release it into atmosphere (Mudgal, 2001). As a pre-landfill waste treatment technology, stabilisation/solidification processes cab be done, which make the As waste safe for disposal (Conner, 1990). The process involves mixing the waste, either in the form of sludge, liquid or solid into a cementitious binder system. Stabilisation/solidification is most suitable for treating inorganic wastes, as these are considered more compatible with the cementitious binders. Use of Stabilisation/solidification technologies inhibit leaching of hazardous components by reducing waste/leachant contact and by forming a stable pH environment (Sullivan *et al*. 2010). Mixing of As sludge into construction materials is common in urban areas of South Asian countries e.g. Bangladesh and India (Sanchez *et al*. 2000). Calcium silicate hydrate (C–S–H) matrix co-precipitation of As ions homogeneously dispersed with Ca and Si compounds present in the cement (Halim *et al*. 2004). Portland cement with lime is appropriate for treating waste from sorptive filters but not oxidised precipitative sludges because of high pH (Sullivan *et al* 2010). On applying soil flushing in the field, efficiency can vary from 0% to almost 100% and use of more complex methods with polymer injection leads to higher efficiencies (Atteia *et al.* 2013; Lin *et al*. 2014).

In As removal technology an important aspect is membrane technology that depends on selective pores and driven force. This technology is efficient to reduce As concentration of less than 50 mg/l. Microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) are high pressure techniques efficient in removal of dissolved As from the contaminated water (Figoli *et al.* 2010). Pore size in UF is 10-1000 Å whereas in NF size of membrane 1 nm and molecular weight of NF is typically less than 1000 Da. In NF membrane have slightly charged surface and charge intraction plays a important role in separation of molecule (Waypa *et al.* 1997).

Reverse Osmosis (RO) membrane contains extremely small pores size i.e., <0.001 (Schneiter and Middlebrook 1983). Farword Osmosis (FO) is another membrane process that used in treatment plants for industrial waste (Cath *et al.*2006), where water is filtered through osmotic pressure difference and driven force.

2.2 Chemical Approaches for Arsenic remediation

Remediation of As through Chemical approaches are carried out by various methods, like oxidation, electrokinetics, iron-exchang, coagulation flocculation, Adsorption etc. Oxidation of more toxic As(III) to less toxic As(V) and after oxidation As(V) is precipitated (Masscheleyn *et al*. 1991). In this process many chemical oxidants like chlorine, chlorine dioxide, ozone, hydrogen peroxide, chloroamine, permagnate and ferrate are utilized (Johnston *et al*. 2001; Lee *et al*. 2003; Vasudevan *et al*. 2006; Sharma *et al*. 2007; Mondal *et al*. 2013). Photochemical oxidation uses UV irradiation in presence of oxygen, which helps to generate hydroxyl radicals through the photolysis of $FeOH^{2+}$ (Yoon and Lee, 2005). In situ oxidation also helps to reduce As content in ground water (Sen Gupta *et al*. 2009). Coagulant such as Alum, ferric oxide, sulfate are efficient in removal of As from water by coagulation flocculation process (Mondal *et al*. 2006; Singh *et al*. 2014). In electrocoagulation application of iron and effluent water generates loosely clumped mass of fine particles (Van Genuchten *et al*. 2012). ECAR (Electrocoagulation-chemical Arsenic Remediation) model is based on electrocoagulation principle (Amrose *et al*. 2013). Iron Based Sorbents (IBS) is an emerging treatment technique for As remediation. In this adsorption principle hydroxyl groups are present as absorbent (Selvin *et al*. 2000). This trend shifts to Zero valent iron method over the last decade because of non-toxic, abundant, cheap and easily available resource. In Zero valent iron , the oxygenated water comes in contact with Z(VI), Fe(II) and Fe(III) hydroxides produces that oxidies As and help in removal (Farrel *et al*. 2011; Leupin and Hug, 2005). In recent trend wide variety of absorbent like activated carbon fly ash and aluminium loaded coral limestone (Huang and Fu 1984; Ohki *et al*.1996; Diamadopulos *et al*. 1993), modified fly ash, nanoparticles or hydrous iron oxide (Goswani and Das, 2000; Sylvester *et al*. 2007) are used for the removal of As. Electrokinectics (EK) remediation is also a technique based on electro-osmosis, electromigration and electrophoresis (Virkutyte *et al*. 2002). During this remediation process, various chemicals such as chelating agent, surfactant and gasoline (Bhatacharya, 1996) are used.

2.3 Biological Approaches for Arsenic remediation

Remediation of heavy metals through biological means is termed as bioremediation. This includes flora and fauna utilized in remediation process. The process is as old as 100 years when first biological plant established in 1891 at Sussex, UK (NABIR primer,2003), however, its history began from back 6000 BC (NABIR Primer 2003). Bioremediation technology became more popular because of its sustainability with ecology and environment. However, there are many physical and chemical techniques, but these are not much efficient, costly and hard to apply at a large scale. Principle involved in the process of bioremediation is to change in redox reactions, increasing/decreasing the solubility, pH changing and adsorption or uptake of substance through complex enzymatic reaction by living organisms. Smith *et al*. (1994) reported that many microbes reduces As content for obtaining their energy by oxidizing various fuel while reducing Arsenate to Arsenite under oxidative environmental conditions. In some cases As act as a source of electron donar too. It has been reported that marine polychaete species like *Australonuphis parateres* could accumulate As up to 2739 mg/kg dry weight (Kaise *et al*. 1997; Waring and Maher, 2005). Takeuchi *et al.* (2007) reported that *Marinomonas communis* cells accumulated up to 2290 mg/kg of dry weight. As hyperaccumulation up to 22,630 mg/kg was recorded in a fern *Pteris vittata* (Ma *et al.* 2001). Biosorption of As by microbial biomass may be helpful to remove As from groundwater. Bioaccumulation method found in certain plants and micro-organisms (for example, *Gallinonella furruginea*, *Leptothrix ochracea*) help in remediation of metal concentration (Katsoyiannis and Zouboulis 2004; Singh *et al*. 2014). Bioleaching process also used in remediation of As contaminated soils (Wang S and Zhao X, 2009). As transformation in environment is mostly biotic (Meng *et al*. 2003). There are different As mobility forms such as [methyl As (III)>>methyl As (V)>As(III)>As(V)] (Lafferty and Loeppert, 2005; Abedin *et al*. 2002). *Thermus aquaticus* and *Thermus thermophiles* have been shown to 100 times more oxidation than abiotic oxidation rate (Gihring *et al*. 2001).

2.3.1 *Bioaccumulation of Arsenic*

Bioaccumulation refers to accumulation of As inside the cell of organism (Joshi *et al*. 2009). These organisms may be bacteria, fungi, algae and plants. As can enter and accumulate through pores of cell membrane and stored in vacuole and cytoplasm (Xie *et al.* 2013). In microbes As operon peptide with thiol group play role in binding of As and detoxification by increase tolerancy. Ars R gene has high affinity towards As(III) (Kostal *et al.* 2004). As(V) uptake takes place through phosphate transporters (Rosen, 2002). *Bacillu*s sp. strain DJ-1 accumulates As upto 9.8 mg/g of dry weight (Joshi *et al*. 2009). In an experiment Adeyemi, (2009) reported that *Trameter versicolor* accumulate As from arsenic sulfide amended agar medium. Algal biomass such as, *Scytonema* also have the ablility to remove As from water (Prasad *et al*. 2006).

2.3.2 *Biosorption of Arsenic*

Biosorption is a retention of metal on the cell surface by cationic elements (Gadd, 2009). Hydroxyl, amino and amide groups (present in prokaryotic cell membrane) and pH are responsible for sorption of As (Giri *et al*. 2013; Prasad, 2011). Bacteria, like, *Bacillus subtilis* (Hossain and Anantharaman, 2006), *Bacillus cereus* (Giri *et al.* 2013) and many fungus like *Penicillium chrysogenum* , *P. purpurogenum* and *Aspergillus niger* (Loukidou *et al*. 2003; Pokharel and Viraraghavan, 2006)showed sorption activity with As(III), As(V) and MMA (monomethylarsonic acid). 15^0 and 20^0 to 40^0 temperature favor sorption in *B. cerus* and *A. ferrooxidance* BY-3. (Giri *et al*. 2013; Yan *et al*. 2010). Whereas, increase temperature 30^0 to 60^0 C decrease sorption in *Bacillus cereus* W2 (Miyatake and Hayashi, 2011). Physical or chemical pretreatments can improve the biosorption (Wang and Zhao, 2009). Recent findings indicate that presence of nanopartical amorphous Fe(III) may increases As(III) and As(V) sorption (Yang *et al*. 2012).

Byproduct of *Penicillium chrysogenum* pretreated with surfactants hexadecyl trimethylammonium bromide and dodecylamine can improve the biosorption and at pH 3 (Loukidou *et al*. 2003). Tea fungus, a waste product is also able to remove As from groundwater (Murugesan *et al*. 2006). *Aspergillus niger* coated with iron oxide showed efficiency to remove As from water (Pokharel and Viraraghavan, 2006; 2008).

2.3.3 *Adsorption of Arsenic*

Mineral weathering microbes shows adsorption of metal on the surface of cell (Dong, 2010). Haque *et al*. (2007) reported that *Sorghum* biomass in adsorbing As from water. The equilibrium time for As adsorption in the biomass was 12 hr. The maximum removal of arsenic was found at an initial pH value of 5.0 and maximum adsorption capacity for the biomass was 2.4–2.8 mg/g of As. Fungal biomass of *Penicillium purpurogenum* showed maximum adsorbance in noncompetitive conditions (Say *et al*. 2003) and Mn oxide-depositing fungus, strain KR21-2, Mn phase shows a transiently high accumulation of As(V) during the early stage of manganese oxide formation (Tani *et al*. 2004).

2.3.4 *Oxidation of Arsenic*

Many Chemolithoautotrophic microbes derived energy by oxidation of As(III) to As(V) aerobically, in this process As(III) oxidizers couple the oxidation of As(III) (e.g., electron donor) to the reduction of either oxygen or nitrate and use the energy derived to fix CO_2 into organic cellular material to achieve growth (Wang Z. and Zhao X, 2009). Arsenite and arsenate are normally occurs in waters. As(III) is oxidize to As(V) for prior to its removal (Inskeep et al. 2004; Sun 2008). Anaerobic As (III) oxidation applied in contaminated soil treatment in waste industries where inorganic carbon added as source and nitrate as electron acceptor. (Rhine *et al*. 2006).

2.3.5 *Reduction of Arsenic*

In anaerobic reduction, microbes utilizeses As(V) through respiratory reduction as terminal electron acceptor (Lloyd and Oremland 2006; Mukhopadhyay *et al*. 2002; Stolz *et al*. 2002, 2006). Reduction of As indicate the increases As mobility, detoxification and resistance (Silver and Phung, 2005). In microbes, cytoplasmic As(V) reductase, (ArsC) is protein of small-molecular mass (13 to 16 kD) that mediates the reduction of As(V) to As(III) and detoxify by transported outside of the cell by ArsAB As chemiosmotic efflux system (Silver and Phung, 2005; Macur *et al*. 2001). Another detoxify mechanism are ATPase membrane system or sequestered in intracellular compartments, either as free As(III) or as conjugates with glutathione or other thiols As(V) reduction under aerobic conditions (Macur et al. 2001). Many microbes like *Sulfurospirillum barnesii*, *Bacillus arsenicoselenatis*, *Bacillus selenitireducens*, *Sulfurospirillum arsenophilum*, *Desulfotomaculum auripigmentum*, *Chrysiogenes arsenatis* and *Desulfomicrobium* strain Ben-RB (Macy et al. 2000; Newman et al. 1998; Stolz and Oremland,1999) and hyperthermophilic archaea (*Pyrobaculum arsenaticum* and *Pyrobaculum aerophilum*) (Huber et al. 2000) utilizes As(V) as terminal electron acceptor.

2.3.6 *Methylation of Arsenic*

Methylation of As allows the transformation of aqueous- or solid-associated inorganic As into gaseous arsines. Gaseous arsines are highly mobile in comparison to aqueous As and aqueous trivalent and pentavalent methyl As was considered mobilization because of lower adsorption affinity (Mukai *et al*. 1986; Huang and Matzner, 2006; Lafferty and Loeppert, 2005). Lower value of redox potentials (i.e. reducing conditions) promote the production and mobilisation of As (Frohne *et al*. 2011). Some methanogenic bacteria under anaerobic conditions proceeds to dimethylation of As, which is stable in the absence of oxygen but can be rapidly oxidized under oxygenated conditions (Takamatsu *et al*. 1982). However, As methylation was demonstrated by both aerobic and anaerobic microorganisms (Kuehnelt and Goessler, 2003). There are many enzymes present in microbial system which are involved in methylation such as, As(V) reductase, monomethylarsonic acid reductase, As(III) methyltransferase and monomethylarsonous acid methyltransferase (Wu, 2005). Extracellularly methylation was as follows: inorganic As→monomethylarsonic acid→dimethylarsinic acid→trimethylarsine oxide in microbes like *Apiotrichum humicola* and *Scopulariopsis brevicaulis* whereas in *Trichoderma asperellum, Penicillium janthinellum* and *Fusarium oxysporum* intracellular methylation (Su *et al*. 2012). Methylation of As in biological system term as biomethylation. It may be inorganic to organic forms like MMA, DMA or TMAO, MMA (III), DMA(III) or some time gaseous arsines (Takamatsu *et al*. 1982; Sanders, 1979; Oremland and Stolz, 2003; Jia *et al*. 2013).

2.3.7 *Demethylation of Arsenic*

In natural conditions, microbial As demethylation occurs under both aerobic as well as anaerobic conditions (Huang *et al*. 2007). Demethylation of As is apparently not suitable for the purpose of remediation. There is comparatively less number of microbes involved in demethylation (Millward *et al*. 1996; Sierra-Alvarez *et al*. 2006). In an experiment of mixed culture of *Burkholderia* and *Streptomyces* species could perform the complete process of demethylation by two-step process (Yoshinaga *et al*. 2011). *Mycobacterium neoaurum* was found to demethylate both monomethylarsonic acid and monomethylarsonous acid (Lehr *et al*. 2003) and degradation of aqueous methylated As usually occurs *via*. demethylation but gaseous As demethylation is still an open question (Mestrot *et al*. 2011).

2.3.8 *Bioleaching of Arsenic*

As contaminated soil reclamation by the transformation ability of microbes, from solid to soluble extractable forms is called bioleaching (Deng and Liao, 2002; Wiertz *et al*. 2006). Transformation ability of some microbes for conversion of As in extractable forms, they may help to detoxify As toxicity. Acidophilic Fe oxidation microorganism usually prefered As containing sulphide minerals, e.g. arsenopyrite (FeAsS), enargite (Cu3AsS4) and realgar (As4S4) (Acevedo *et al*. 1998). Conversion of ferrous to ferric ions with the subsequent chemical oxidation of sulphides by Fe3+ help in As bioleaching. (Marquez *et al*. 2012). Secondary mineral precipitates such as jarosite [$KFe_3(OH)_6(SO4)_2$], magnetite (Fe_3O_4), ferric arsenate [$Fe_2(AsO_4)_3$], scorodite ($FeAsO_4{\cdot}2H_2O$), schwertmannite [$Fe_8O_8(OH)_6(SO_4){\cdot}\ nH_2O$], ferric hydroxide [$Fe(OH)_3$] and ferric phosphate [$Fe_2(PO_4)_3$] may suppress by bioleached As (Acevedo *et al*. 1998; Chen *et al*. 2011; Corkhill *et al*. 2008; Duquesne *et al*. 2003). Bayard *et al*. (2006) experimentally evaluated the As mobilization and found that upto 35% of the As was mobilized over 84 days with sulfur at 30^0 C under very acidic (pH <1) and oxidative conditions. Dopson and Lindstrom, (1999) reported that *Thabacillus caldus* may support bioleaching. Deng and Liao (2002) reported that mixed cultures containing *Thiobacillus ferrooxidans* and *Lepptospirillum ferroxidans* could extract As from a complex flotation concentrate up to 95% was bioleached from the concentrate after 6 days under optimal conditions. The introduction of Fe(II) increased As leaching in *Acidithiobacillus ferrooxidants* but showed insignificant effect in *Acidithiobacillus thiooxidants* (Zhang *et al*. 2007). In *Desulfuromonas palmitatis* As removal increased up to 90% in the presence of an iron reducing microorganism (Vaxevanidou *et al*. 2008).

2.3.9 *Biostimulation of Arsenic*

Biostimulation is to stimulate existing bacteria to be capable or become more capable for bioremediation. This can be done by addition of various forms of rate limiting nutrients and electron acceptors. In an experiment, element sulfur added as an energy substrate in aerobic conditions to stimulate Arsenic bioleaching. (Seidel *et al*. 2002; Bayard *et al*. 2006). Carbon sources also act as energy donor and can be use for stimulate bacteria growth promotion in As bioleaching from soils (Mc Lean *et al*. 2006). Chatain *et al*. (2005) found that the anaerobic As bioleaching from soils by indigenous bacteria could be increased by 28-folds through addition of carbon sources. Chen *et al*. (2017) reported that biostimulation with 5% rice straw amendment and bioaugmentation with genetic engineered *Pseudomonas putida* KT2440 enhanced efficiency of As volatilization (483.2 μg/kg/year).

2.3.10 *Biominiralization of Arsenic*

Living microorganisms involved in the hardening or stiffening of the mineralized materials and there are more than 300 As minerals known to occur in nature (Drahota and Filippi, 2009). Some biogenic minerals like iron, mangnese and sulphide can immobilise As in solution such as precipitation of calcium arsenates [$Ca_5H_2(AsO_4)_4{\cdot}cH_2O$] in Ca-rich environments is example of As mineralization (Martinez-Villegas *et al*. 2013). It has been a common practice to stabilize

As wastes as metal arsenate compounds (Bothe and Brown, 1999; McNeill and Edwards, 1997). Freire *et al*. (2014) investigated that the pH would also impact on the mineralogical composition of the arsenic-sulfide minerals and As(V) and $SO4^{2-}$ reducing bacteria can stimulate the immobilization of As ground waters by the process of mineralization.

2.3.11 *Biofilm formation for Arsenic*

Microorganisms attach and grow on a surface irreversibly and produce extracellular polymers that facilitate attachment and matrix formation, resulting to growth rate and gene transcription (Donlan, 2001) and 99% of all microorganisms can form biofilms (Costerton *et al*. 1987). Biofilm formation may role in As biogeochemistry was evidenced by the potential enrichment of As in biofilm and As in rock biofilm reached up to 60 mg kg^{-1} (dry weight) (Drewniak *et al*. 2008). In As rich environment microbes might stimulates oxidation and reduction, redox transformation and As methylation (Huang, 2014). Mallick Ivy *et al*. (2017) reported that As-resistant halophilic bacterial strains *Kocuria flava* AB402 and *Bacillus vietnamensis* AB403 from mangrove rhizosphere of Sundarban, both isolates, AB402 and AB403, can tolerate 35 mM and 20 mM of arsenite, respectively.

2.3.12 *Biovoltlization of Arsenic*

Volatile As-species generated during biomethylation through process of biovolatlization. biovolatilization might be developed as an ex-situ method for As removal under controlled conditions (Wang and Zhao, 2009). Many filamentous fungi and some bacteria involve in such processes. Visoottiviseth and Panviroj (2001) Reported that *Penicillium* sp. were capable of volatilizing 25.8–43.9 mg of As during a 5-day cultivation period. Edvantoro *et al*. (2004) found that augmenting contaminated soils (1390 mg As/kg) with methylating fungi (*Penicillium* sp. and *Ulpcladium* sp.) significantly increased the As volatilization rates (up to eight-fold increase). Cernansky *et al*. (2009) found in his comperative study that *Neosartorya fischeri* is more efficient in comparison to *Aspergillus clavatus* and *A. niger* whereas *A. niger* is least capable out of three species. Genetic engineered (GE) *Pseudomonas putida* KT2440 bearing arsM gene exhibited high capacity of As volatilization (Chen *et al*. 2013, 2014) and with the application of rice straw (RS) and GE P. putida, arsine fluxes were also the highest in Dayu soil (483.2 μg/kg/year), followed by Zhuzhou soil (79.3 μg/kg/year) and Qiyang soil (29.3 μg/ kg/year) and the combination of RS + GE *P. putida* significantly enhanced the As flux in different soils except Qiyang soil, which is lower than RS amendment alone, (Chen *et al*. 2017).

2.4 Phytoremedial Approches for Arsenic Remediation

Phytoremediation is eco-friendly approach to remediate As contamination from soils and water bodies, many of land and macroaqutic plants are efficiently perform this action (Favas *et al*. 2014). Phytoremediation of As can be done through the process of phytostablization, phytoextraction and phytovolatilization. As tolerancy and accumulation is common type which included compartmentation and translocation of As in plants. (Zhu. and Rosen, 2009). Plants accumulate As in their root, shoot biomass and attend significant attention for phytoextraction (Barbafieri *et al*. 2013). Several study concluded that the plant-associated growth-promoting bacteria (PGPB) contribute in phytoremediation and the application of resistant-accumulatory microbes with Plants has been accelerate cleanup of metal contaminated soils (He *et al*. 2007; Glick, 2010).

2.4.1 *Phytostablization of Arsenic*

Phytostablization is the mobility of heavy metal into immobilization form in order to minimize bulk erosion, leaching and transport of heavy metals (Singh 2008, Porter and Peterson, 1975). In the under ground parts, phytostablization reduces bioavailability and mobility into ground water and food chain (Erakhrumen, 2007). Root exudates also stimulate microbial activity and releasing redox enzymes shows the ability to stabilization of heavy metals and converts them into complex immobilizing forms in rhizosphere (Wuana and Okieimen, 2011; Rocovich and West, 1975; Benson *et al*. 1981) and improve biological and chemical characteristics of contaminated soil (Arienzo *et al*. 2004). Some acids like acetic, butyric, citric, fumaric, lactic, malic, malonic, oxalic, propionic, tartaric, succinic acids etc. shows effects on the dynamics of metal(loid)s in soils *via.,* acidification, chelation, complexation, precipitation, redox reactions and microbial activity (Bolan *et al*. 2011).

2.4.2 *Phytoaccumulation of Arsenic*

Metal accumulating plants are able to accumulate heavy metals from contaminated soils and water and accumulated metals can be extracted and translocate in different storage parts (Fitz and Wenzel, 2002). As hyperaccumulator plants are

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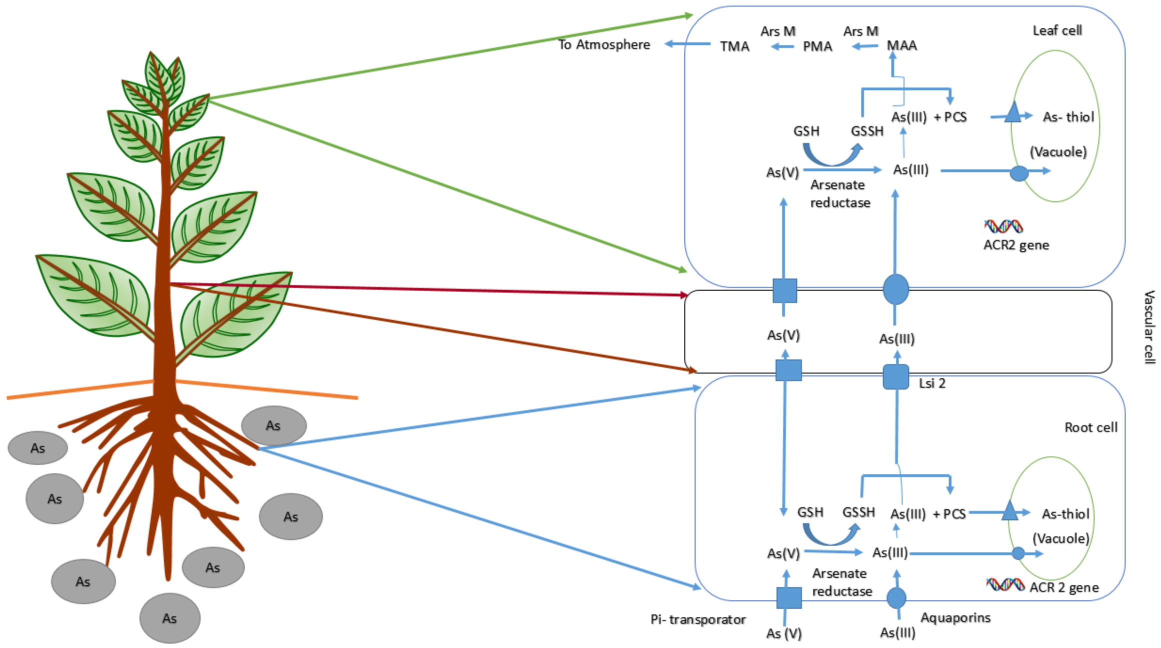
mainly fern species and first As accumulation discovered in *Pteris vittata* (Fitz and Wenzel *et al*. 2002) and followed by *Pityrogramma calomelanos* (Francesconi *et al*. 2002) but phytoextraction of As has not yet been applied (Sun *et al*. 2001). These hyperaccumulator plants are actively take up and translocate heavy metals into above-ground tissues but in tolerant plant species tend to restrict soil–root and root–shoot transfers, and therefore have much less accumulation in biomass.

2.4.3 *Phytovolatilization of Arsenic*

Phytovolatilization is process to convert non volatile As to volatile As-species in plants and emits to environment (Rugh *et al*. 1996). There is two way for first direct in which volatilization of the compound from the stem/trunk and leaves (Guenther *et al*. 1994) and indirect is the increase in volatile contaminant flux from the subsurface resulting from plant root activities (Jasechko *et al*. 2014). Direct volatization differ from transpiration that produce moderately hydrophobic, able to diffuse across hydrophobic barriers such as cutin in the epidermis or suberin in woody dermal tissues (Guenther *et al*. 1994).



Asenite efflux carrier- Lsi-2 , As- thiol transporter, PSC – Phytochelatin synthase, Ars M- As(III)-S-adenosylmethionine methyltransferase.

Figure 1: Diagrammatic representation of Arsenic uptake, metabolism of phytoaccumulation and phytovolatilization in As-tolerant plants (After Zhu & Rosen, 2009).

2.4.4 *Mechanism of Phytoremediation of Arsenic*

Phytoremediation of As depend on its bioavailability and tolerancy of plant. Complexity of As tolerance and accumulation in plant is managed by some functional gene and their expression (Zhu and Rosen, 2009). Uptake of As(V) and As(III) by phosphate and aquaporin transport channel pathway are utilized (Catarecha *et al*. 2007; Wu *et al*. 2011). Aquaporin also provide channel for other methylated As species in different plant parts (Ma *et al*. 2008; Li *et al*. 2009a, b). However Lsi 2 transporter found only in cells of root, responsible for As translocation to xylem (Yamaj and Ma, 2011). Arsenate reductase convert As(V) to As(III) in cytosol of root and shoot with utilization energy by conversion of GSH into GSSH. These As(III) accumulated in vacuole by two way,first directly cross the tonoplast membrane (Zhu and Rosen., 2009) and other as form of As-thiol which form the rection of phytochelatin synthatase (PCS) and utilize As-thiol transporter to accumulate in vacuole (Guo et al. 2008). Remaining As reach upto shoot parts by vascular translocation like xylem. In aerial region volatilized form of As forms like monomethyl arsonicacid (MMA), dimethylarsinic acid (DMA), trimethylarsineoxide (TMA) in presence of arsM [As(III)-S–adenocylmethionine methyltransferase] and these forms volatilizes to environment in gaseous forms (Qin *et al*. 2006). Nahar *et al*. (2017) cloned At ACR2 gene (arsenic reductase 2) of *Arabidopsis thaliana* and proof by experiment its role in As reduction in plant cell.

3. CONCLUSION

There are many bioremediation mechanisms applied to remediate As toxicity from contaminated water and soils. They transform more toxic to less toxic forms sustainabally in minimum cost. Conversion and release of volatile As species into environment is very safe due to dilution effect. Isolation of indigenous microbes from contaminated sites shows more efficiency to bioaccumulation, bioabsorption and tolerancy. Many indigenous filamentous fungi shows more efficiency for volatilization of As. Recent study revealed that application of microbes with accumulator plant shows increased As accumulation in different parts of plant.

Efficient microbes have hope to cost effective remediation in accelerating As contamination with sustainable approach.

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