

Review Article

Bioreclamation of Arsenic in the Soil-plant System: A Review

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Abstract

Arsenic becomes a serious problem in this era. Being a carcinogenic it causes severe damage to living being. Several methods are developed for its remediation and jeopardize its toxicity. Among the physical, chemical and biological methods, bioremediation of arsenic contaminated soils, submerged soil and groundwater shows an immense potential for future development due to its effectiveness, environmental compatibility and cost-effectiveness. Bioremediation relies on microbial activity to remove, immobilize, change oxidation-reduction status, sorption, complexation, biomethylation, demethylation, coprecipitation and complexation of arsenic from the contaminant sites. Bioleaching can effectively eliminate bulk arsenic from polluted soils. Bioaugmentation such as addition of effective microbial strain in the contaminant areas or biostimulation such as adding up of food materials like carbon sources, mineral nutrients or specific elements can be applied to encourage the leaching rate. Apart from this an *ex-situ* treatment technology is biovolatilization, several microbes are capable to volatilize toxic arsenic species from the environment and methylation-demethylation mechanism are employed here. In phytoremediation techniques, various arsenic hyper accumulating plants are responsible to remove arsenic from impure soils and shallow groundwater. Engineering genetic strategies may become the future way to boost the arsenic-hyper accumulating faculty of the plants. In this review paper, it is found that bioremediation techniques are superior to other conventional methods.

Key words: Bioremediation, phytoremediation, speciation, chelation, arsenic oxidizing and reducing genes

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INTRODUCTION

Arsenic is a widely dispersed and ubiquitous in environment. Average concentration of As in earth's crust is approximately 5 mg kg^{-1} . Under oxidizing conditions such as those prevailing in surface waters, the principal species is pentavalent arsenic and under reduce condition trivalent arsenic is dominant. Arsenic, the king of poison, a non-threshold carcinogen and 20th most abundant element in the earth's crust is commonly found in various types of minerals mainly sulfide, copper, lead, nickel, cobalt or other metals. It has been reported in recent years from several parts of the world, in diversified agro ecology of Bangladesh, India, China, USA, Chile, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, Japan and India^{1,2}. A number of studies have reported by Pontius *et al.*³ that arsenic is a carcinogen and its belongings are primarily due to consumption of arsenic contaminated drinking water at concentrations around 100 mg L^{-1} . As(V) can replace phosphate in various biochemical reactions, whereas, As(III) possibly react with critical thiols in proteins and inhibit their activity⁴.

GRAVITY OF PROBLEM

Arsenic is mobile in the soil environment thus can enter in the soil plant atmospheric continuum. During dry periods, irrigation through Arsenic contaminated ground water will enhance the formation of more toxic As(III) from 40-60 times than the less toxic As(V) species and thus cause is a serious threat to mankind all over the world. It has a immense potential to get entered in food chain and thus cause biomagnifications as well as bioaccumulation. Among the different food items, fruits and vegetables primarily contain organic arsenic compare to inorganic As that is less than 10%, but in other case of milk and dairy products, cereals, poultry, beef and pork, inorganic As shared the 65-75%. Humans are suffering from the toxic effects of arsenic mainly from ground water, industrial effluents, food and faulty drainage system and even through in the form of suspended particulate matter from air. Arsenic present in human body mainly in the form of mono methyle arsenate (MMA) and is transported to the different organs in the body by the blood circulation system. Important hazards to human include black foot disease, arsenicosis, pigmentation (Fig. 1), dermatosisulceration and hyperkeratosis and disorder in respiratory, pulmonary, cardiovascular, gastrointestinal, hematological, hepatic, renal, neurological, developmental, reproductive, immunologic, genotoxic and mutagenetic system in human physiology. Naujokas *et al.*⁵ in the year of 2013 reported that about 200 million people worldwide are exposed to arsenic

concentrations in drinking water that exceed the recommended limit of $10 \text{ } \mu\text{g L}^{-1}$ as set out in the guidelines of the World Health Organization (WHO). People in more than 70 countries are probably affected by arsenic poisoning of drinking water. Geogenic arsenic contamination of groundwater has been recognized in 105 countries with an estimate of the exposed population of above 200 million worldwide⁶. Currently more than 100 million people are potentially at risk from groundwater arsenic contamination in Ganga-Meghna-Brahmaputra (GMB) plain⁷. Cancer probability for arsenic is calculated as per the equation below according to Rahman *et al.*⁸ is:

$$R_i = \frac{1}{5000} \sum_{i=1}^{5000} C_{ij} \times K_j$$

where, the subscript "i" represents the sampling regions, C_{ij} is the average concentration of arsenic in groundwater that was estimated by the bootstrap method, "j" is the sampling times in the bootstrap method and K_j is the random sampling number from the distribution for cancer slope of arsenic for drinking water.

ENTRY OF ARSENIC IN THE ENVIRONMENT

Many terrestrial as well as aquatic ecosystems have been subjected to heavy metal toxicity in recent years. Organic and inorganic both contaminations are coming from industrial waste discharge, domestic and agricultural pollution, these leading to widespread contamination of both surface and groundwater by runoff (Fig. 2). Metals are introduced into the agro ecosystems as a result of weathering of minerals and rocks, volcanic eruptions, mining, processing and use of metals. Remobilization of these heavy metals may also result from soils due to the changes in redox conditions and the corrosion of structures due to extended submergence under acidic groundwater. Broad origin of arsenic may be classified into following heads.

Geogenic: There are various As bearing minerals and among these As found mainly as arsenopyrite and as a constituent in sulfide minerals. Arsenic-containing bedrock formations in Arsenic affected areas such as Bangladesh (Chittagong), India (West Bengal), Taiwan (Taiwan city), Pakistan (Lahore) and China (Shaanxi) is the main cause of As pollution. Various As bearing minerals are sulfides, sulfosalts such as arsenopyrite (FeAsS), lollingite (FeAs_2), tennantite ($\text{Cu}_6[\text{Cu}_4(\text{Fe}, \text{Zn})_2]\text{As}_4\text{S}_{13}$), orpiment (As_2S_3), realgar others are Andryobertsite ($\text{KCdCu}_5(\text{AsO}_4)_4(\text{H}_2\text{AsO}_4) \cdot 2\text{H}_2\text{O}$), Annabergite ($\text{Ni}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$), Arakiite ($[(\text{Zn}, \text{Mn}^{2+})(\text{Mn}^{2+}, \text{Mg})_{12}(\text{Fe}^{3+}, \text{Al})_2(\text{As}^{3+}\text{O}_3)(\text{As}^{5+}\text{O}_4)_2(\text{OH})_{23}]$,

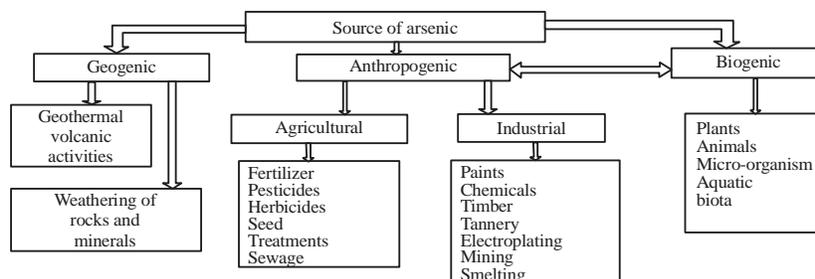


Fig. 1: Pigmentation resulting from the toxic effects of arsenic mainly from ground water, industrial effluents in Varanasi, India

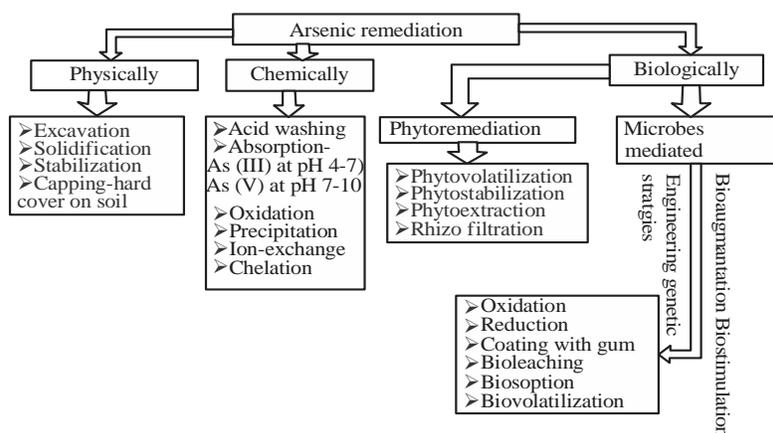
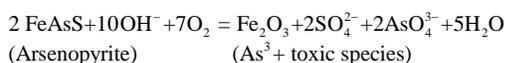


Fig. 2: Source of arsenic

Arsenosiderite ($\text{Ca}_2\text{Fe}^{3+3}(\text{AsO}_4)_3 \cdot \text{O}_2 \cdot 3\text{H}_2\text{O}$), Arsenoclasite ($\text{Mn}_5(\text{AsO}_4)_2(\text{OH})_4$), Arthurite [$(\text{AsO}_4, \text{PO}_4, \text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$], Austinite [$(\text{CaZnAsO}_4(\text{OH}))$] etc. Weathering of these minerals potentially cause As hazard in the environment.

Anthropogenic: Although, the As present in earth crust is in very low amount, but its activity can elevate following human intervention. Natural weathering process is not so fast to create As contamination but it is our imperfect practices in different sector that gradually increases As concentration in environment. Industrial activity has led to 100-1000 fold higher heavy metal concentrations on the environment, than present in the earth's crust. In agriculture, havoc use of ground water for irrigation causing ground water deficit and create vacuum in the underground. In the vacuum part As bearing minerals get oxidize and release the As specially during the dry periods. Likewise consecutive irrigation from that area will surely endanger As toxicity:



With reference to industry, atmospheric arsenic emissions from copper smelting stand for the largest input of arsenic

from the mining and metals industry⁹. Cyanide or acid rock drainage also responsible for As leaching out and deposited into the environment¹⁰. Mining industry share the major part for As release in the environment. Gibaud and Jaouen¹¹ stated that during the 18th, 19th and 20th centuries, arsenic compounds were used as medicines, together with arsphenamine-A ($\text{C}_{12}\text{H}_{24}\text{N}_2\text{As}_2\text{O}_2$) by Ehrlich¹² and arsenic trioxide (As_2O_3) by Hindmarsh *et al.*¹³ in 1986, so even hospital waste also possess As.

Biogenic: Some organism are responsible for transformation of less toxic form of arsenic to more toxic form, many arsenic reducing bacteria actually convert As(V) to As(III) under anaerobic condition. Cai *et al.*¹⁴ isolated three of anaerobic As(v) reducing bacterial strains (strains JQ, DJ-3 and DJ-4) from soil samples containing 48.7% of total As(III) collected in Chifeng, Inner Mongolia, China. Among these strains JQ, DJ-3 and DJ-4 were phylogenetically closely related to Bacillus, Desulfitobacterium and Exiguobacterium, respectively. They are capable to reduce As because they possess As reducing genes. Strains, JQ and DJ-3 possess the *arsC* gene, DJ-4 have the *arrA* gene. The three strains efficiently resist and reduce high concentrations of As(V) under anoxic conditions.

Among these *DJA* may play an important role in the mobilization and transformation of As in soil. In plant mechanisms, arsenate reductase reduces arsenate to arsenite with the help of electron donors that are thioredoxins (variable formula) or glutaredoxins (variable formula) subsequently Arsenite could be stored in the plant vacuole.

SPECIATION OF ARSENIC AND THEIR REACTIVITY

The element arsenic exists in different chemical species (Table 1, 2) in soil, water, biological tissues and minerals, many of which are biotically and abiotically inter-convertible under different conditions pragmatic in terrestrial and marine environments¹⁵. Arsenic has both organic and inorganic species. Organic species of As are mono-methyl arsenic acid (MMA), di-methyl arsenic acid (DMA) tri-methyl arsine, tetra-methyl arsonium, arsenocholine, arsenosugar and arsenobetaine. Arsenosugar, nontoxic species present in marine algae and creature which feed on them a small amount of trimethylarsine oxide and arsenobetaine present in a heavily contaminated soil due to arsenopyrite (FeAsS) mineralisation. The inorganic species are arsenate [As(V)] and arsenite [As(III)] these are redox sensitive, under reduced condition arsenite predominating and under oxidized

conditions arsenate is dominant species. This interchange of species can be driven chemically through altering pH and Eh, or presence of chemical oxidants, reductants, or sometimes enzymatically. As has variety of oxidation state like -3, 0, +3, +5. As(III) is more toxic and has been shown to hold back various dehydrogenases e.g., yruvate-ketoglutarate nd dihydrolipolate)¹⁶. Arsenite has the ability to bind to sulfhydryl groups of proteins and dithiols such as glutaredoxin. Arsenate (AsO₄³⁻) acts as a structural analog of phosphate and inhibits oxidative phosphorylation by generating unstable arsenylated derivatives¹⁷. In case of plant uptake and transport, protonated arsenic species (arsenite, MMA and DMA) can behave like silicic acid analogues¹⁸ and arsenate and potentially deprotonated DMA, as phosphate analogues¹⁹.

AVAILABLE OPTIONS FOR REMEDIATION

Various remediation methods are available for arsenic mitigation (Fig. 3). Irrigation with arsenic contaminated groundwater has emerged as a danger to the health and livelihoods of people in the arsenic affected areas. Mitigation of arsenic can be done physically, chemically or biologically. Different mitigation techniques are as follows:

Physically: Different types of clays like kaolinite (Si₄Al₄ (OH)₈ O₁₀) and illite ((K,H₃O) (Al, Mg, Fe)₂ (Si, Al)₄O₁₀ [(OH)₂, (H₂O)]) have been shown to adsorb and increase the oxidation of arsenite to arsenate and arsenite adsorption maximized between pH 7.5 and pH 9.5²⁰. Organic matter is also known to influence arsenic's mobility: Insoluble humic (variable formula) acids sturdily adsorb arsenic in the pH range 5-7, whereas, soluble fulvic (variable formula) acids can

Table 1: Major two arsenic species and their pK values

Arsenite (H _n As(III)O ₃ ⁽³⁻ⁿ⁾⁻ while n = 1, 2	pK1	pK2	pK3
H ₃ AsO ₃ = H ₂ AsO ₃ ⁻	9.2	-	-
H ₂ AsO ₃ ⁻ = HAsO ₃ ²⁻	-	12.1	-
HAsO ₃ ²⁻ = AsO ₃ ³⁻	-	-	12.7
Arsenate (H_nAs(V)O₄⁽³⁻ⁿ⁾⁻ while n = 1, 2			
H ₃ AsO ₄ = H ₂ AsO ₄ ⁻	2.22	-	-
H ₂ AsO ₄ ⁻ = HAsO ₄ ²⁻	-	6.98	-
HAsO ₄ ²⁻ = AsO ₄ ³⁻	-	-	11.53

Table 2: Speciation of Arsenic

Arsenic species	Formula	Toxicity
A. Inorganic arsenic species		
Arsine	AsH ₃	Highest toxicity
Trivalent	As(OH) ₃	Highly toxic
Pentavalent Arsenate	H ₃ AsO ₄	Less toxic
B. Organic arsenic species		
Methylarsine	CH ₃ AsH ₂	Less toxic
Dimethylarsine	(CH ₃) ₂ AsH	Less toxic
Trimethylarsine	(CH ₃) ₃ As	Less toxic
Monomethylarsonic acid	CH ₃ AsO(OH) ₂	Cytotoxicity
Monomethylarsenous acid	CH ₃ As(OH) ₂	Highly acutely toxic as higher affinity to thiol ligands
Dimethylarsinic acid	(CH ₃) ₂ AsO(OH)	Cytotoxicity
Dimethylarsenous acid	(CH ₃) ₂ AsOH	Highly acutely toxic
Trimethylarsinic oxide	(CH ₃) ₃ AsO	mutagenesis and DNA damage
Tetramethylarsonium ion	(CH ₃) ₄ As ⁺	mutagenesis and DNA damage
Arsenobetaine	CH ₃) ₃ As ⁺ CH ₂ COO ⁻	Found in see food
Arsenocholine	(CH ₃) ₃ As ⁺ CH ₂ CH ₂ OH	-



Fig. 3: Different approaches of remediation of arsenic

boost its leaching and mobility²¹. Arsenic remains adsorbed to FeOx as long as the sedimentary environment is sufficiently oxidized. High inputs of organic carbon to the sediments, however, usually give rise to oxygen depletion and lowering of redox potentials. As(V) uptake on goethite [(FeO(OH))] and ferrihydrite [(Fe³⁺)₂O₃·0.5H₂O] have suggested that arsenic ions are strongly bound to these surfaces, perhaps as inner-sphere complexes.

Chemically: Arsenic also can be removed by chemical treatments. There are several mechanisms which lead to the reduction of As toxicity. When the toxicity of As is controlled by a chemical reagent, the prime emphasis is given on oxidation and precipitation reactions. Ion exchange on chemically inert materials also proves significant results. Some oxidizing agents are potassium permanganate (KMnO₄), chlorine (Cl⁻), ozone (O₃), hydrogen peroxide (H₂O₂) or manganese oxides (MnO₂) which are very much effective to diminish As toxicity.

Biochemically mediated: Microorganisms are very much important for As remediation. Microbes have different genes that are responsible for generating proteins and reduce As toxicity. Arsenic oxidase gene is *aoxB* found in *Bacillus flexus* ASO-6, Arsenic reductase gene is *arrA* and *arsC* found in *Pseudomonas putida* 46 (ABY 19333).

Bioremediation of arsenic: Two toxic inorganic forms of As are usually found in aquatic systems: arsenite, As(III), which is found mainly under anaerobic conditions; it is more mobile than arsenate, As(V), which classically occurs under aerobic conditions and tends to connect with oxyhydroxides and clay minerals^{22,23}. As(III)-oxidizing bacteria can make a payment to

a natural attenuation of As pollution by decreasing its bioavailability and can help to eradicate As from mine wastewaters through bioprocessing²⁴. Many As(III) oxidizers have been isolated from various environments, particularly mesophilic ecosystems; they belong to more than 25 genera, mainly of the *Proteobacteria* phylum²⁵. As oxidation functional *aoxB* gene encoding the large molybdenum-bearing catalytic subunit of As(III)-oxidase (EC 1.20.98.1), an enzyme of the dimethyl sulfoxide (DMSO) reductase family^{26,27}. As(III)-oxidizing Alpha, Beta and Gamma proteobacteria and *Chloroflexi* strains, formerly used as positive controls²⁸. The developed *aoxB* gene-targeting qPCR and DGGE tools proved to be capable for evaluating diversity pattern and abundance of aerobic As(III)-oxidizing bacteria. In view of their abundance, broad distribution and large-scale diversity, these bacteria play the key roles in As transformation and mobility in the Upper Isle river basin²⁹.

Phytoremediation: Phytoremediation is an alternative and cost-effective way to reduce As contamination. Various hyperaccumulator plant species are used for this technique. According to Robinson *et al.*³⁰ plants that accumulate >1 g contaminant per kg of dry weight are hyperaccumulator plants (Table 3). They have a high bio-concentration factor (BF) of more than 1, which is the ratio of plant to soil concentration of the element. Translocation factor (TF) that is the ratio of above-ground biomass and root concentration of elements is also more than 1 for those plants. Hyperaccumulator plants possess high accumulation capacity for a particular element that may be more than 100 times compared with a non-hyperaccumulator plant. This technique reduces the remediation time as well as decreases the volume of contaminant biomass.

Table 3: Plant species tailored for bioreclamation

Crops	Mechanism	Agro-ecosystem
<i>Pteris vitata</i>	phytoextraction	Moist, swampy areas ³¹
<i>Eichornia crassipes</i>	hyper accumulation	170-340 gAs/dry wt. ³²
<i>Trichosanthes dioica</i>	phytostabilization	At normal pH ³³
<i>Hydrilla verticillata</i>	hyper accumulation	Water bodies ³⁴
<i>Pteris cretica</i>	phytoextraction	Humid condition ³⁵
<i>Pteris longifolia</i>	hyper accumulation	Humid condition ³⁵
<i>Pteris umbrosa</i>	hyper accumulation	Humid condition ³⁵
<i>Daucus carota</i>	hyper accumulation	Aerobic field ³⁶

Through chelation: Clelate means “claw”. When ligand share its lone pair electron to a central cation forming a ring like structure is known as chelate. In chelation mechanism As play the role of central cation and different ligand share lone pair electron poly dentally and reduces toxicity of arsenic. Some examples are Dimercaprol [C₃H₅ (OH) (SH)₂] (British Anti Lewisite), Dimercaptosuccinic acid [C₃H₂ (COOH)₂ (SH)₂], Dimercapto-Propane Sulphonate [C₃H₅ (SO₃H) (SH)₂], Penicillamine (C₅H₁₁NO₂S).

Microbial: Pentavalent arsenic, which is mainly present with the oxyanionic forms (H₂AsO₄, HAsO₄) with pKa 2.19; pKb 6.94, respectively. As(III) is the thermodynamically stable form in groundwaters, which at pH values of most natural waters is present as non-ionic form of arsenious acid (H₃AsO₃, pKa 9.22)¹⁵. Thus, As(III) may interact in smaller extent with most solid surfaces, therefore, it is more difficult to be removed by the conventional treatment methods, such as adsorption, precipitation, etc.³⁷. Several treatment technologies have been applied in the removal of arsenic from waters, such as lime softening, coagulation, filtration and ion exchange, adsorption on activated alumina or iron oxides and reverse osmosis³⁸⁻⁴⁰. Most of these technologies are not efficient enough for the removal of As(III). Therefore, a preoxidation step is usually required to transform the trivalent form to pentavalent. The oxidation procedure is mainly performed by the addition of chemical reagents, such as chlorine, ozone, potassium permanganate, manganese oxides or hydrogen peroxide^{41,42}. Although these reagents are active in oxidizing trivalent arsenic, As(III) and they may cause numerous secondary problems arisen mainly by the presence of residuals or from by-products formation, inducing also a significant increase to operational costs of the methods. From the above discussion as a matter of fact it is evident that most effective way of arsenic remediation is to adopt microbes (Table 4).

Bacteria: Arsenic Oxidizing bacteria-As early as 1918, *Bacillus arsenoxidans* a bacteria from cattle-dipping tanks were reported to both oxidize and reduce arsenic⁴³. Other bacteria such as *Pseudomonas arsenoxidans*, *Xanthomonas*

arsenoxidans, *Achromobacter arsenoxidans*⁴⁴, *Alcaligenes faecalis*⁴⁵ and *Pseudomonas arsenitoxidans*⁴⁶ also has the capacity to oxidize and reduce arsenic. Direct adsorption or co-precipitation on the preformed biogenic iron oxides, can remove arsenic and there was an sign of As(III) oxidation through iron oxidizing bacteria, leading to enhanced overall removal efficiency⁴⁷. It is well established that As(V) tends to be adsorbed on iron oxides⁴⁸. The biotic oxidation of iron by the microorganisms *Gallionella ferruginea* and *Leptothrix ochracea* was found to be an emerging technology for effective removal of arsenic from ground waters. Throughout this process, iron oxides were left in the filter medium, with the microorganisms, which tender a favourable environment for arsenic to be adsorbed and removed from the aqueous streams. Under optimized conditions, trivalent arsenic was found to be oxidized by these microorganisms, contributing to increased overall arsenic removal (upto 95%) even when initial arsenic concentrations were as high as 200 mg L⁻¹. According to Katsoyiannis and Zouboulis⁴⁹ the pentavalent arsenic content, under the same experimental conditions was removed effectively, having residual concentrations below the newly enforced limit of 10 mg L⁻¹. *Pseudomonas* and *Bacillus* are largely represented among arsenic-resistant bacterial strains isolated from other arsenic polluted sites⁵⁰⁻⁵². *Pseudomonas* sp. utilized D-xylose (C₅H₁₀O₅), glucose (C₆H₁₂O₆), mannose (C₆H₁₂O₆), galatose (C₆H₁₂O₆), melibiose (C₁₂H₂₂O₁₁), gentiobiose (C₁₂H₂₂O₁₁) and D-fucose (C₆H₁₂O₆), as carbon sources. The AR-5 was also partially positive for L-arabinose (C₅H₁₀O₅), fructose (C₆H₁₂O₆) and ribose (C₅H₁₀O₅) and strain *Enterobacter* sp. grew in the presence of high concentrations of As(III) (upto 5 mM) and As(V) (upto 200 mM). This characteristic allows these bacteria to deal with the excess arsenic concentrations in natural groundwater. The isolated bacteria were grouped into the following genera: *Pseudomonas*, *Bacillus*, *Psychrobacter*, *Vibrio*, *Citrobacter*, *Enterobacter* and *Bosea*. *Pseudomonas arsenitoxidans*, was found to grow chemolithoautotrophically with arsenite, carbon dioxide and oxygen⁵³. Different arsenic resistant heterotrophic bacteria isolates were augmented from the sediment samples and analysis of the 16S rRNA gene sequence of these bacteria exposed them to be members

Table 4: Microbe mediated bioremediation of arsenic

Micro-organism	Mechanism	Agro-ecosystem
<i>Sphaerotilus</i> <i>Leptothrix ochracea</i> <i>Gallionella ferruginea</i>	Iron oxidization and thus arsenic precipitation	Groundwater ⁶⁰
A. Bacteria		
<i>Thiobacillus acidophilus</i> , <i>Acidithiobacillus ferrooxidans</i> <i>Acidithiobacillus ferrooxidans</i>	Arsenic precipitation as ferric arsenate and arsenate-sulfate under acidic and high (SO ₄) ₂ conditions Formation of schwertmannite under acidic and high sulphate conditions concentrated arsenic up to several 10,000 mg kg ⁻¹ because of sorption and incorporation into the structure	Acidic mine waters ⁶¹ Mining drainage water ⁶²
<i>Leptothrix ochracea</i>	Residual arsenic concentration below 10 mg L ⁻¹ was resulted when the initial concentrations were 35 for As(III) and 42 mg L ⁻¹ for As(V)	As(III) oxidation and subsequent As(V) removal from groundwater ⁶³
<i>Ralstonia eutropha</i> MTCC 2487 <i>Pseudomonas putida</i> MTCC 119 <i>Bacillus indicus</i> MTCC 4374	Arsenic concentration of 15 mg L ⁻¹ prolongs the stationary phase of these strains. Arsenic removal capacities were 67, 60 and 61%, respectively	Arsenic removal from wastewater ⁶⁴
Tea fungus (a symbiont of two yeasts viz., <i>Pichia</i> sp. NRRL Y-4810 and <i>Zygosaccharomyces</i> sp. NRRL Y-4882 and a bacterium <i>Acetobacter</i> sp. NRRL B-2357)	FeCl ₃ pretreated and autoclaved fungal mats efficiently removed 100% of As(III) after 30 min and 77% of As(V) after 90 min ⁶⁵	Arsenic sequestration from groundwater
Scytonema	At pH 6.9, the sorbent exhibited a 100% affinity for As(III) and demonstrated a recycle-ability of up to 59 cycles of sorption-elution	As(III) removal from water ⁶⁶
<i>Methanobacterium formicicum</i> <i>Closterium aciculare</i>	As methylation and demethylation ⁶⁷ As(V) methylation into methylarsenic(III) ⁶⁸	
B. Fungi		
<i>Aspergillus niger</i>	At pH 6, 95% of As(V) and 75% of As(III) removed	Arsenic removal by oxidecoated fungal biomass ⁶⁹
<i>Penicillium chrysogenum</i>	The removal capacities ranged from 33.3 to 56.1 mg g ⁻¹ arsenic under common surfactants and a cationic polyelectrolyte at pH 3	As(V) removal from wastewaters ⁷⁰
Mn oxide-depositing fungus, strain KR21-2	As(V) sorption decreased as Mn oxide formation progressed biogenic Mn oxide with a high amount of bound Mn ²⁺ oxidizes As(III) less successfully than with a low proportion of bound Mn ²⁺	As(III) oxidation and adsorption of As(III/V) by biogenic Mn oxide ⁷¹
<i>Penicillium</i> sp. <i>Penicillium</i> sp. <i>Ulocladium</i> sp.	Methylarsonic and dimethylarsinic acid methylation to trimethylarsine As(V) methylation to arsine	Aerobic condition ⁷² Aerobic condition ⁷³
C. Algae		
<i>Fucus gardneri</i> <i>Spirogyra hyaline</i>	As(V) methylation into dimethylarsine ⁷⁴ dried biomass is used for removal of these heavy metals	Humid areas ⁵⁵

of the genera *Exiguobacterium*, *Aeromonas*, *Bacillus*, *Pseudomonas*, *Escherichia* and *Acinetobacter*.

Algae: Algae have different mechanism for arsenic tolerance like exclusion, compartmentalization, synthesis of binding proteins such as metallothioneins (Mts) or phytochelatins (PCs) and making complexes, translocate them into vacuoles⁵⁴. *Spirogyra hyaline* has capacity to remove As, but specially dried biomass is used for removal of these heavy metals. According to Kumar and Oommen⁵⁵ maximum As was absorbed when initial heavy metal concentration was 40 mg L⁻¹. Irgolic *et al.*⁵⁶ reported that *Tetraselmis chuil* and *Daphnia magna* tolerant to heavy As load. Sibi reported that the living biomass of *Scenedesmus* and *Chlorella* has adsorbed utmost As (III) from the aqueous solution followed by *Spirogyra* and *Pandorina* at 30 mg L⁻¹ initial

concentrations. Dried biomass of *Scenedesmus* uptake of 25 mg g⁻¹ was recorded followed by *Chlorella* and *Pandorina* (24 mg g⁻¹) under similar conditions.

Fungi: *Glomus mosseae* and *Glomus caledonium* were isolated from *H. lanatus* growing on an arsenic-contaminated mine-spoil soil and these are highly resistance to As⁵⁷. The influence of *Glomus mosseae* inoculation on plant growth, As uptake, phosphorus (P) nutrition and plant competitions showed that both plant species extremely depended on mycorrhizas for surviving the As contamination. Mycorrhizal inoculation not only markedly decreased root to shoot As translocation and shoot As concentrations but also substantially improved plant P nutrition⁵⁸. The biomass and As uptake of *Medicago truncatula* colonized by the arbuscular mycorrhizal (AM) fungus of *G. mosseae* external mycelium

was unchanged by the highest addition level of As 200 mg kg⁻¹, but shoot and root biomass declined in both mycorrhizal and nonmycorrhizal plants, representative that the AM fungus was more tolerant than *Medicago truncatula* to arsenate⁵⁷. The As-resistant fungi *Penicillium janthinellum*, *Trichoderma asperellum* and *Fusarium oxysporum* were exposed to 50 mg L⁻¹ of As(V) and the biotransformation of As was studied and fresh weights of all three isolates increased⁵⁹.

PRESENT STATUS OF BIOREMEDIATION OF ARSENIC

Present bioremediation approaches are based on two principles, i.e., absorption of hazardous compounds by living organisms. One particular microorganism alone is unable to degrade an environmental pollutant due to lack of diversity of metabolic processes. A group of diverse organisms have diverse metabolic processes for bioremediation of a different heavy metals. Bioremediation emphasized that microbes have capability to degrade contaminant by their enzymatic mechanism or absorb pollutant in their biomass in both in-situ and ex-situ conditions. Throughout the world, different kinds of heavy metals remediation strategies are adopted according to various agro ecological conditions. Even the techniques are changes according to the site of application. Arsenite As(III) oxidizing and arsenate As(V) reducing bacterial strain that is *Pseudomonas* sp. HN-2 which is a mesophilic, Gram-negative, bacteria was isolated from an As-contaminated soil. Phylogenetic analysis based on 16S rRNA gene sequencing resulted that the strain was closely related to *Pseudomonas stutzeri*. Within 3 h of incubation this strain oxidized 92.0% (61.4 μmol L⁻¹) of arsenite to arsenate under aerobic condition and this bacteria has both the arsenic oxidize and reducing capacity⁷⁵. The bioremediation status of various continents is as follows:

USA: According to a USEPA⁷⁶ report it is predictable that there are almost half a million contaminated sites throughout the United States and more than 217,000 of them are need of remediation. Sites included in this estimate are those that have either contaminated by battery manufacturers, metal finishing, electroplating and mining companies. Also included producers of solvents, paints, coated glass, leather and chemicals. Phytoremediation is providing an economical, innovative and environmentally responsive tactic to remove toxic metals from dangerous waste sites³¹.

Europe: As compared with USA and Canada use of phytoremediation technologies in Europe is limited, in those countries, private companies have been very much involved. Due to limited knowledge and poor broadcasting there are doubts in the public opinion and limited acceptance, unfavorable competition with standard clean-up methods, which can give a long record of success. Initiatives targeted at dissemination, training and education should be activated in order to increase the confidence and familiarity of the public opinion and of stakeholders in these fresh sustainable technologies⁷⁷.

Africa: In South Africa, AngloGold Ashanti has planted approximately half a million trees over the last decade for research on by means of phyto (plant) technologies to prevent environmental effects from the company's tailings storage facilities (TSFs) in South Africa. Most TSFs release seepage and dust containing metals and salts which can pollute the surrounding environment. Anglo Gold Ashanti started the "Ecological Engineering and Phytoremediation Research Programme". It is predicted that around 200 plant species will finally be used for phyto remediation.

Oceania: Pioneering work on Phytoremediation in Australia was done by Professor R.R. Brooks. His work was on plant that hyperaccumulate heavy metals. Australia has over 2 million ha of open cast mining and many contamination sites associated with smelting and processing⁷⁸. In Australia the most vital role of phytoremediation is to degrade organic pollutants and reduce contaminant mobility rather than the phytoextraction of heavy metals.

Asia: In Indonesia one study aimed to define the best type of aquatic plants for phytoremediation in acid mine water management system with a passive model that testing several kinds of local plants as a medium of Phytoremediation. The best phytoremediation plants to remediate acid levels by raising the pH is *Ipomea aquatic* that raise pH of 53%. Iron levels also reduced by 70% in acid mine water by using of *Eleocharis dulcis*. *Pistia stratiotes* also lower the levels of manganese (Mn) as much as 55%⁷⁹. In another study in Bangladesh, chromium is present in the wastes from tanneries have been studied which became a threat to the environment. Present research in Bangladesh, conducted greenhouse pot experiments on several plant species having phytoextraction potential to eliminate Cr from polluted soils. A common nettle *Urtica dioica*, proved to be the best plant for this purpose with

less addition of nutrient like potassium (K)⁸⁰. In China, phytoremediation technique for controlling of water hyacinth in Dianchia eutrophic lake in China is adopted. A comparison was made on the current approach at Dianchi lake of water hyacinth through, fill and collection⁸¹.

In India various strategies are adopted for bioremediation of arsenic which are as follows:

Arsenic hyper accumulator plants: The first known arsenic hyperaccumulating plant is Chinese brake fern (*Pteris vittata*). It was discovered from an arsenic affected site, using chromated-copper-arsenate a number of other arsenic hyper accumulating plants have been reported, those are *Pityrogramma calomelanos* and *Pteris longifolia* and *Pteris umbrosa*.

Phosphate fertilization: Phosphate fertilization seems to be one of the feasible strategies for successful phytoremediation of arsenic impure soils. Arsenic is toxic to plant, but phosphorus is essential for plants, having similar electron configurations and chemical properties. Therefore, arsenate and phosphate will fight with each other for similar soil sorption sites. Thus their sorption on soil decrease and solution concentrations increase. Phosphate appreciably suppressed the sorption of arsenate and arsenate may replace phosphate in in various phosphorolysis reactions or ATP synthesis.

Arbuscular mycorrhizal fungi: *Glomus mosseae* has capacity to reduce toxicity of arsenic in the environment. It also formed a stable association with Chinese brake fern (*P. vittata* L.) and resistance to arsenic toxicity. Mycorrhizal colonization increased the biomass of hyperaccumulator thus amplified the quantity of arsenic removed from the soil.

Grasses: Grass belongs to *Poaceae* such as *A. delicatula*, *Agrostis castellana* and *Holcus lanatus* have played an important role in remediation of arsenic toxicity. A perennial grass vetiver with large biomass production, strong ecological adaptability, easy to manage was found to accumulate arsenic in all parts of the grasses with different levels of concentration.

CONCLUSION

Arsenic remediation is necessary for mankind; arsenic can create both acute and chronic toxicity not in human, plants, animals but also in the environment. It has a long persistence in environment especially in the areas where anaerobic

condition prevails. Toxic form of arsenic is very much mobile in nature therefore it easily moves towards the soil-plant-atmospheric continuum and shows its toxicity. Out of several techniques most efficient, ecofriendly and economically viable method is to adopt biologically remediation techniques. Various hyper accumulator plants have proven their efficiency towards jeopardize the toxic effect of arsenic under different agro ecosystems. Microorganism having arsenic oxidation and reduction genes is also capable in reducing arsenic toxicity under their favorable conditions. Microbes prove the most effective way of detoxification of arsenic. They can immobilize toxic form of arsenic and side by side precipitation in arsenic contaminant soil. The only exceptional that microbes can only do is bioleaching of arsenic from the contaminant field. Where arsenic present in high quantity but in immobile state that is As(V) then the only way is to remobilize through arsenic reducing bacteria and subsequent bioleaching.

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