A review on phytoremediation of arsenic-contaminated soil

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Abstract
Arsenic contamination of soil is drastically increased by extensive industrialization, mining, use of pesticides, smelting of non-ferrous metals which have become alarming concern for environment worldwide. The arsenic accumulation in the soil is a severe health concern, unlike organic compounds it is not degraded thus has to be removed from the soil. Most of the conventional remedial technologies are expensive and destroy the soil properties rendering it inferior for growing plants. Such issues draw attention worldwide to calls for environmentally friendly remediation techniques for acute. Presently, phytoremediation being solar-driven effective and affordable solution to remove heavy metal contaminants from soil has gained popularity. The hyper-accumulator plants play a key role in reducing the amount of waste from going to landfills and while also utilizing both other organic and inorganic contaminants making the soil reusable. This review is a compilation of studies associated with effects of Arsenic accumulation, the efficacy of phytoremediation technology including mechanisms for uptake and factors affecting the process.

Keywords: Soil contamination, heavy metals, arsenic, phytoremediation, hyper-accumulators.

Introduction
Soil contamination by heavy metals has raised alarm because toxic elements reach to food grown in such soil and also to the water which is utilized for human consumption1. The heavy metals contamination by Cd, Cu, As, Ni, Pb and Hg is distress signal on the environmental threat to man and animals, requiring special attention. Although metals are natural constituents of soil, some of which also required by plants as micronutrients. However, the unplanned industrial revolution has drastically polluted the biosphere to the extent that making metal pollution as one of the most severe environmental problem today2.

Arsenic Element
Arsenic is the 20th most abundant mineral in the Earth’s crust and interestingly, 12th most abundant mineral in the human body. It is a ubiquitous metalloid found in all natural media in a low concentration occurring at an average concentration of 2 mg kg-1. The toxicity of Arsenic is powerful to earn the title of ‘the king of poison’ and has influenced human history more than by any other toxic compounds3. This metal occurs in organic and inorganic forms having four oxidation states of -3, 0, +3 and +5. The organic form of arsenic refers to carbon base which mainly contains covalently-bonded arsenic atom, whereas inorganic form mostly occurs in pure and metallic forms usually bonded with non-carbon elements. The toxicity of arsenic largely depends on its chemical form to which the organism is exposed and its speciation are of considerable interest. Inorganic arsenic (Arsenite +3) is more toxic as compared to that of organic arsenic (Arsenate +5) mainly because of the later being more soluble4.

Biotransformation is the major metabolic pathway for inorganic arsenic (iAs) in humans and in most of the animal species. Methylation of inorganic arsenic mainly occurs in liver but other organs also have the arsenic methylation activity5. In this process inorganic arsenic is enzymatically biotransformed to methylated arsenicals including MMA and DMA, these are the end metabolites and the biomarker of chronic arsenic exposure6,7.

\[ \text{iAs (V) } \rightarrow \text{iAs (III) } \rightarrow \text{MMA (V) } \rightarrow \text{MMA (III) } \rightarrow \text{DMA (V)} \]

Firstly, reduction of iAs (V) to iAs (III) is mediated by glutathione, acts as reducing agent and then methyl group is transferred to iAs (III) from S-adenosyl methionine to form MMA (V). Then MMA (V) is reduced to form an intermediate metabolite monomethylarsonous acid (MMAIII) in methylation process and during the second methylation, MMA (III) is oxidized to DMA (V)8,9. Glutathione and S – adenosyl-methionine acts as co-substrate10. The activity of first methylation step is represented by the ratio of iAs / MMA, if the ratio is high which indicate poor methylation and activity of thesecond step is denoted by the ratio of MMA / DMA, if the ratio is low which indicate good methylation11,12. Children are poor methylator and good excretor in comparison to the adults. Thus children are less susceptible to arsenicism13,14.
Sources and Effect on the Environment

Natural processes like weathering of rock and volcanic eruption release arsenic in the surroundings. However, the present elevated arsenic level in soil attributed to major anthropogenic activities including mining, application of pesticides and fertilizers to the agricultural land, smelting of non-ferrous metals, burning of fossil fuels and much more. Both natural and anthropogenic sources raised the arsenic level of soil from normally below 20 mg.kg$^{-1}$ to 250,000 mg.kg$^{-1}$ in extreme cases$^{15}$. From the soil, the arsenic contaminants get leached deeply to contaminate groundwater. Apart from crop and water, humans can be get exposed to arsenic through animal products$^{16}$.

Exposure to arsenic causes a number of health hazards to humankind. Long-term exposure to low concentration skin lesions, cancer of lung, prostate and bladder, as well as cardiovascular and neurological diseases. At high concentration, arsenic acts in a deleterious manner blocking the essential functional groups displacing other metal ions or by modifying the biological molecules$^{1,15}$. Also, high arsenic level I drinking water affected the visual perception of children but not the visual-motor integration, are confirmed by visual-motor integration test [VMIT] and motor-free visual perception test (MVPT)$^{17}$. Chronic ingestion of arsenic causes characteristics melanosis, keratosis, basal cell carcinoma and squamous cell carcinoma$^{18}$. Presence of both melanosis and keratosis is the conformational sign of chronic arsenic toxicity. Researchers have reported association of arsenic with lung cancer to the workers of mining unit and peoples linked with the industries of arsenic-containing pesticides, chemicals and metals smelting area. The trivalent (AsⅢ) form of inorganic arsenic has shown the activity of carcinogenesis$^{19}$. The adverse effects of chronic exposure to drinking arsenic water on the nervous system are reversible peripheral neurological damage. Exposure to inorganic arsenic for a long period can cause the peripheral neuropathy, which is similar to the Guillain-Barre syndrome syndrome$^{20}$.

Depending on the chemical species, the lethal dose can range between 1.5-500 mg.kg$^{-1}$. Symptoms of low-level of arsenic exposure include abdominal pain, vomiting and diarrhea; whereas acute oral poisoning affects the respiratory and cardiovascular system. Long-term exposure affects skin causing darkening and development of ‘corns’ on the palms, soles and torso. The carcinogenic effects of the arsenic have also been reported$^{21}$. The arsenic derivatives monoethylarsonous acid (MMA) and dimethylarsinous acid (DMA) are more toxic compared to inorganic forms and has thegenotoxic capability$^{4}$. These transformants being immutable, remain unchanged even after years, this invited research interest to find immediate action plan against this hazards$^{22}$. The quest for a most suited method for remediation of arsenic from the power source of contamination – soil, is warranting development of technology to combat the huge environmental issue.

Conventional Methods

Removal of arsenic from contaminated soil by means of treatment on- or off-site (and returning the treated soil) to restore. The ex-situ methods include physical treatment such as soil excavation, landfills, and capping. Chemical approaches includetreatment with strong acids and chelators to clean the polluted soil. However, these techniques are not cost-effective and destroy soil properties hampering the fertility$^{23,24}$. Search for environmental friendly remedial alternatives to decontaminate the damaged soil without affecting its quality is need of the hour.

Phytoremediation

Phytoremediation, promising alternative so far, involves the use of plants for decontamination and thereby improving the soil quality. Plants used for the purpose are called hyper-accumulator which absorbs a lot of toxic metals from the soil and store within different tissues. This method remained widely acclaimed as anecologically friendly alternative to currently practiced physical and chemical remediation methods$^{25}$. Metal phytoremediation, also referred to as ‘phytoextraction’ encompasses a number of processes in which plants can remove, stabilize and transfer the pollutants from the soil and water$^{26,27}$.

Mechanism of Phytoremediation

Contaminants found in the soil can be organic carbon-based and are released by a number of activities. To remediate such contaminants, the substance needs to be broken down into the non-toxic compound by the process of degradation$^{25}$. Plants take-up the substances into their roots through active and passive transport, wherein the former involves specific transporters such as carrier proteins$^{28}$. The ‘xenobiotic’ organic pollutants being manmade, no transporter for its uptake in bio system have evolved, so are taken up to by diffusion as determined by its hydrophobic or hydrophilic nature to that extent$^{29}$. Uptake of the organic pollutants by plants within the tissues depends on the type of compounds, so significant differences exist in uptake byplant species within both roots and shoots$^{30}$. Inorganic contaminants are those that are mineral based as compared to that of the organics$^{31,34}$. Inorganic pollutants generally not degraded into simple forms, but can be fully removed from the environment and transported, transformed into less toxic forms or are ‘stabilized’. In phytoremediation process, plants can be exploited to accumulate the inorganic compounds from the soil and mainly depend upon the ability of plants to tolerate and accumulate high concentration of such contaminants.

Heavy metals like arsenic cannot be destroyed, but are transformed from one oxidation state to another$^{35}$. Researchers have examined As– metabolizing bacteria and indicated remediation by oxidation of As (Ⅲ)as pollutant. Phytoremediation holds promise for the most effective tool for recovery of Arsenic contaminated soil$^{16}$.
Response of plants: Plant response to soil arsenic concentration divide plants into three strategies: i. Excluders, maintain the concentration of the heavy metal in roots to a critical value. These plants prevent metal from entering their aerial parts or maintain low and constant metal concentration over a broad range of metal concentration in soil. ii. Hyper-accumulators, concentrate metal in their aerial parts to levels far exceeding that in the soil. These plants absorb high levels of contaminants and concentrate it either in roots, shoots and/or leaves. iii. Indicator, deposits internal concentration of heavy metals reflecting the external levels in the soil. They accumulate metal in their aerial tissues.

The other plants called non hyper-accumulator shows a high concentration of heavy metals in roots only (and little in shoots), as compared to hyper-accumulators which shows transport of heavy metal from roots to shoots as well.

Characteristics of Hyper-accumulators

The plants usable for phytoextraction of soil contaminants is expected to have the characteristic of rapid growth, produce high biomass, profuse root-system, adaptation of weather and climatic variation, and easily cultivated; in addition to accumulating a high level of soil contaminants.

Trees as Hyperaccumulators

Apart from plants, trees are hyper-accumulators of heavy metal contaminants of soil, are low-cost plant type so can be used for phytoremediation. Commonly used hyper-accumulator of organic compounds are willows, poplars and various grasses.

It is reported that the mined soil which is considered to be the major source of air and water pollution, can also be cleared up by phytoremediation by phytostabilization and phytoextraction to stabilize the toxic mine spots and removing the toxic metals from the contaminated soil suggesting the beneficial option of recovering rather than disposing of the contaminants in soil. Also pollutant-enriched biomass of plants can easily be disposed of off than contaminated soil mass, because low mass limits the disturbance especially when the compounds are not degraded but are simply extracted from the soil.

Arsenic hyper-accumulators

A number of plants are reported to hyper-accumulate arsenic to an extremely high concentration of about 23,000 µg arsenic g⁻¹ in its shoots. Chinese brake fern, Pteris vittata L., is the first reported arsenic hyper-accumulator. Study on mechanism of arsenic accumulation in brake fern furnished useful information to improve phytoremediation attempt and hence the report prompted an outburst of similar research. P. vittata absorbs Arsenate and Arsenite by a different mechanism. When the only arsenate was present in the soil, the percentage of the arsenic present as arsenate in the roots was 100% and 91%.

Limitations of phytoremediation

Phytoremediation approach for inorganic arsenic is less successful than that for its organics form. Although the results in the pot trials remained successful, success for removal in field trials is lower than expected, mainly due to the complexity of soil and availability of the pollutants curtailed. Within the sites containing both the organic and inorganic pollutants.
present, the interaction among the substance affects the availability of the pollutants. The on-site remediation charged with mixed contaminants (organics and inorganics) becomes very complex phenomena and the key for such remediation includes the selection of an appropriate mix of the plant species which could degrade the organics or stabilize the inorganics, while being able to tolerate the presence of mixed contaminants. Plant species like *Brassica juncea*, *Helianthus annuus*, *Festucaarundinacea* and *Loliumperenne* can be used to remediate such site with an admixture of contaminants. Plants roots are having the indirect capacity to degrade the organic substance by means of releasing root exudates that promote in microbial activities in the vicinity. The direct release of catalytic enzymes capable of biotransformation of organic compounds has also been attempted.

The concept of employing select species of plants hyperaccumulator for removal of the soil contaminants was introduced by Chaney in 1983. The idea lately brought to public attention is presently regarded as the most suited cost-effective and environmentally friendly means for soil clearing. The naturally occurring metal hyperaccumulator plants have the tendency to accumulate 10-500 times higher level of elements from the contaminated soil. For successful development of the usable technique of phytoremediation, it is an extremely important consideration that each of the metal and elemental pollutants, owing to its unique soil and plant chemistry, need to be addressed separately.

A major concern in phytoremediation approach is the safe disposal of the harvested biomass of *P. Vittata*. Public support plays an key role in disposing of contaminated biomass with adequate care and economically viable mode. Various methods available for the safe disposal contaminated harvest including incineration, composting, washing, compaction, pyrolysis, liquid disposal and direct disposal. But arsenic residue in the plant biomass undergoing thermal processing can emit arsenic directly back to the environment make it unsafe to practice. Safer alternative methods for safe disposal of contaminated biomass may include sub-and super-critical water treatment method where the biomass of the arsenic contaminated fern fronds was reduced by 70-77%, and the excess arsenic is further reduced by sorption over hydrous iron oxides. The by-products of such methods can be used as materials for fragrance, antiseptics and herbicide precursors, once commercialized can make the process economic. Fern fronds can also be composted before treatment to reduce the weight of biomass up to 38% in 120 days cutting down the overall cost of final disposal.

**Factors Affecting Phytoremediation**

The Phytoremediation technology influenced by factors that include the degree of contamination, metal bioavailability and the ability of the plant to absorb and accumulate the metals from the soil. The application of the technique can be confined to small habitat range or size of plants which expresses the remediation potential and is further marred by the insufficient abilities of plants to tolerate, detoxify and accumulate the contaminants from the soil. An important factor considered in planting hyper-accumulators is pH of the soil. The plant's take-up maximum amount of contaminants from the soil with low pH due to its enhanced solubility. The high affinity of arsenic for oxide surfaces affects biogeochemical factors such as soil texture, organic matter, a constituent of minerals, pH, redox potential and ions. The activity of arsenic in the soil is also controlled by surface reactions on oxides/hydroxides of Al, Mn and Fe. The toxicity and chemical behavior of arsenic compounds are largely influenced by the speciation of As. As (III) is more mobile than As (V). Using soil with pure Fe-hydroxides, the As (V) solubility increases as the pH increases, whereas the opposition reaction takes place in case of As (III) with high pH in soil. With *P. vittata*, the As hyperaccumulator was referred to the calcareous soil of neutral to slightly alkaline pH which says that changes of rhizosphere pH would be no prerequisite for Ashyper-accumulation due to high pH buffer power of calcareous soils. There is a correlation between dissolved Fe and As, describing that Fe oxides/hydroxides represent the major sorbing agents for as in soil.

As carboxylic acid is released by the plant roots, other organic and inorganic anions may compete with adsorption sites where the phosphate ion plays an important role in anion-As interaction due to its similarity to As(V). The result from pot, field and laboratory experiments shows different conclusions, where phosphor addition at high rate enhances As leaching in lab studies, increase in extractable fraction of As in batch experiments, and reduced sorption of As (V) and As (III) onto the soil. After application of *P. As uptake of the plant is increased* and also at field experiments. The hyper-accumulating plants *P. vittata* and *P. calomelanos* shows large biomass production and hence are the best suited for Ashyper-accumulation. Many of the plants used as hyper-accumulators have evolved on the soil that is highly infertile with scarce water holding capacity and climate that is extremely cool with mist winters or hot and dry summers. It is reported that many hyper-accumulators have the capacity to survive in the metal rich soils and when grown in low metal soil, the plants die rapidly from fungal infection by *Pythium* or *Phythoperca* using root disease bringing death or decline of the plant.

**Genetic Engineering to improve phytoremediation**

Remediation performance by the plant can be improved by selective breeding, and by current research focusing on the use of transgenic technique. Biotechnology is used extensively to transfer the foreign genes from the...
microorganisms into plants to enhance the process of phytoremediation. Using this approach, the traits like an extensive root system, high water uptake, rapid growth and large biomass production in the transgenic poplar (Populus) tree was improved with a better capacity to detoxify the contaminants from the soil.

Exploration of recent advanced techniques applied for phytoremediation is aimed at improving the plants with the help of genetic engineering. Identification of genes involved in hyper-accumulation in terms of uptake, transport and sequestration can help understanding and improve the natural process. Also the risk due to such heavy metal contamination must be first identified, quantified, managed and communicated with the help of phytoextraction in broad public acceptance related to the use of genetically modified plants. Further biotechnology approaches are being developed to increase the level of metal-binding proteins in plants. The transgenic plants could be developed to secrete metal-selective ligands into the rhizosphere, where it could solubilize elements from the site. Improved hyper-accumulator plants tend to increase the annual rate of phytoextraction and further the metals can be recycled which are accumulated in harvestable organs of the plants.

**Precautions and Regulations**

The best remediation system is chosen considering the characteristics of soil and the site, suitable method of remediation and the estimated cost. After exploring all the possible avenues of the existing technologies, the most suited remediation tool is selected. The problem of soil contamination is seen as a recent issue, but has begun a long time ago soon after the industrial revolution, however, mankind became familiar to its dimension and persistence only after its harmful impacts were seen. For economic benefits, man has been dumping every kind of organic and inorganic waste directly in the soil, assuming that the soil has great assimilation capacity in the soil, assuming that the soil has great assimilation capacity ignoring the fact that soil is a support of our ecosystem. The soil must be regarded as a non-renewable resource, as the estimated time for originating 1 cm of soil is about 200-400 years. Thus it is inevitable to take care of this precious resource and conserve it for the future generation. The soil is not only the habitat for humans, animals, plants and other living organisms; but it also supports the water and nutrient cycles that provide protection for the groundwater, conserve the mineral resources, food production, and also social and economic activities for humans.

There are ample laws and environmental regulations on water and air pollution in developed countries, but very few countries have regulations related to soil pollution. The method to get rid of contaminated soil until the last decade was to only to excavate and put it into a landfill or isolate it with different types of barrier leaving behind a scope for the contaminant to flow in the surrounding sites. This approach, although good to risk management controlling the danger for the surrounding, is incapable to treat the contaminated soil attending the risk of leachate spread o further contaminates the groundwater also. Thus Phytoremediation is aforesaid very promising in situ and clean biological technique that uses different species of plants having the capacity to ‘fix’ the contaminants from soil.

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**Figure-1:** Schematic diagram illustrating the link between (in) mobilization, bioavailability and remediation of heavy metal.
Conclusion

The problem of soil contaminated by heavy metals, most importantly the arsenic have increased the risk of entering to ground water prominent worldwide, is also a potential threat of spreading the food chain via oral consumption also. It becomes critical to clean up the soil at the earliest to minimize the risk of contamination spreading, and phytoremediation by hyper-accumulators plants which accumulate the heavy metal from the soil and store it in the biomass offers an appropriate method to achieve this. This environmentally friendly and cost-effective approach is extensively used on large scale replacing conventional physical and thermal methods. Although it takes longer time for reduction of soil contamination, is simple to implement and reduces the amount of waste destined to landfills. The most importantly, the method allows selection of appropriate plant species that accumulate the maximum amount of contaminants from the soil sediments, also allows generation of valuable biomass controlling carbon emission. Better knowledge and understanding of this alternative technique expect the best outcome to improve the quality of soil by cleaning up the metal and toxic elements from the contaminated soil.

References


plants to remove contaminants from polluted areas. *Reviews on environmental health*, 17(3), 173-188.


