



Advancements in assisted phytoremediation of arsenic contaminated soils with an emphasis on biochar

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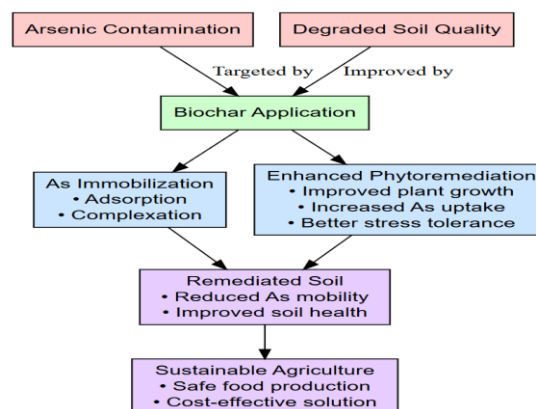
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Abstract

Arsenic (As) contamination of soil is a developing concern in numerous countries worldwide, as it is discharged into the soil environment through both geological and anthropogenic processes. The presence of high concentrations of As in soil may result in a decrease in the yield and safety of food commodities, as well as a reduction in nutritional quality. Consequently, it is essential to establish sustainable, cost-effective, and publicly acceptable methods for the remediation of soils that have been contaminated with As. Phytoremediation is a low-cost and environmentally sustainable technology that is used to remediate As-contaminated soils and sediments. However, its application may be impeded by the time required for remediation, climatic constraints, and low-nutrition-induced harm to plants. While assisted phytoremediation using various agents (e.g., microbes, nanoparticles, inorganic and organic materials) has shown efficient progress to remediate As-contaminated soils, biochar-enabled As phytoremediation has seen less attention until now. For phytoremediation, biochar improves soil physical and chemical qualities, which help plants grow. Biochar may enhance phytoextraction of As anions from soil. In this review, we briefly discussed sources of As, As speciation, and (phyto)remediation methods in soil; elaborated phytoremediation and various assisted phytoremediation approaches for As, and how biochar is helpful in phytoremediation of As-contaminated soil by immobilizing As in soil or via phytoextracting As from soil.

1. Introduction

The deterioration of soil and water resources due to various contaminants under a climate change scenario is a major challenge for humans to protect the planet Earth and its environment, to produce safe food for billions of people globally. Among many types of contaminants, arsenic (As) release into the terrestrial and aquatic systems is an ecological, agricultural, and human health issue worldwide (Zhao & Wang 2020). Since the industrial development and urbanization, hazardous substances like As are added into terrestrial environments both by anthropogenic activities (e.g., mining, smelting, arsenical pesticides application, fertilizers) (Zheng et al 2019a) and natural processes, for instance, volcanic eruptions, and weathering of parent material. Arsenic is the 20th most prevalent element in the



Graphical Abstract

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geosphere, and it is thought to be extremely damaging to all types of biota.

Arsenic occurs as inorganic arsenite (As^{III}) and arsenate (As^{V}) species, which are several-fold more poisonous than the organic ones. Being the analogue of phosphate, As^{V} can be harmful to plants and humans when it is replaced with phosphate in different processes, such as during the synthesis of adenosine triphosphate (ATP). Conversely, As^{III} toxicity begins due to its inherent attachment with thiol groups in the plants and other living organisms (Wan et al 2020) As-S complexes. In numerous areas, As concentration in the environment has surpassed the safe limit in soil (agriculture purpose: 20 mg kg^{-1}) and groundwater (drinking water As: $10 \mu\text{g L}^{-1}$) (WHO 1993). Naturally, As concentration in the soils differs from $1\text{--}40 \text{ mg kg}^{-1}$ depending on the type of parent material, however, high As concentrations have been observed with the As-rich waste disposal, mining activities, application of pesticides and fertilizer, and sewage irrigation (Wan et al 2020).

Being a non-essential for humans, As ingestion can cause harm to the kidneys, lungs, and liver, and even death of people through consumption of As-containing food or drinking water (Althobiti et al 2018; Irem et al 2019). Conventional remediation approaches have been employed to clean up metalloid-contaminated areas, including As-contaminated soils, but they are expensive, time-consuming, risky, and can damage the ecosystem. Due of the high expense of conventional treatment methods, phytoremediation is being pursued (Abbas et al 2018; Amiri et al 2021).

Niazi et al 2016; Niazi et al 2012). Arsenic by fern species, such as *Pteris vittata*, has been elucidated in various previous studies (Abbas et al., 2020; Bashir et al.,. In contrast to phytoremediation, assisted phytoremediation has evolved as a strategy to support plant species for high biomass production where various agents (e.g., carbon-based materials, bacteria, nanoparticles, biochar) are employed to enhance metal(loid) uptake and plant growth. In assisted phytoremediation, natural or chemical additives may alter soil characteristics, increase As bioavailability in soil for increased uptake by plants (Bhargava et al 2012; Gupta et al 2022).

Since organic materials are eco-friendly, supply plant nutrients, and sequester carbon in soil, they have gained popularity (Mehmood et al 2021). Because of its porosity, biochar (BC) is a carbon-rich (black) substance with exceptional efficiency and adaptability (Gholami et al 2020; Igalavithana et al 2017). Due to its soil conditioning and health advantages, BC has garnered interest as a soil supplement (Lehmann et al 2015; Liu et al 2019). Biochar has a high pH that may reduce the contaminants' bioavailability and toxicity (Lu et al 2017; Paz-Ferreiro et al 2017). Also, the association among BC, microbes, and plants might change the behavior of As and bioavailability in soil, depending on the soil and plant nature (Kiran & Prasad 2019). Biochar's impact on plant growth and microbial activity is expected to enhance hyperaccumulator phytoremediation. (Gong et al 2019).

This chapter provides key information, albeit brief, related to As sources and geochemistry and speciation of As

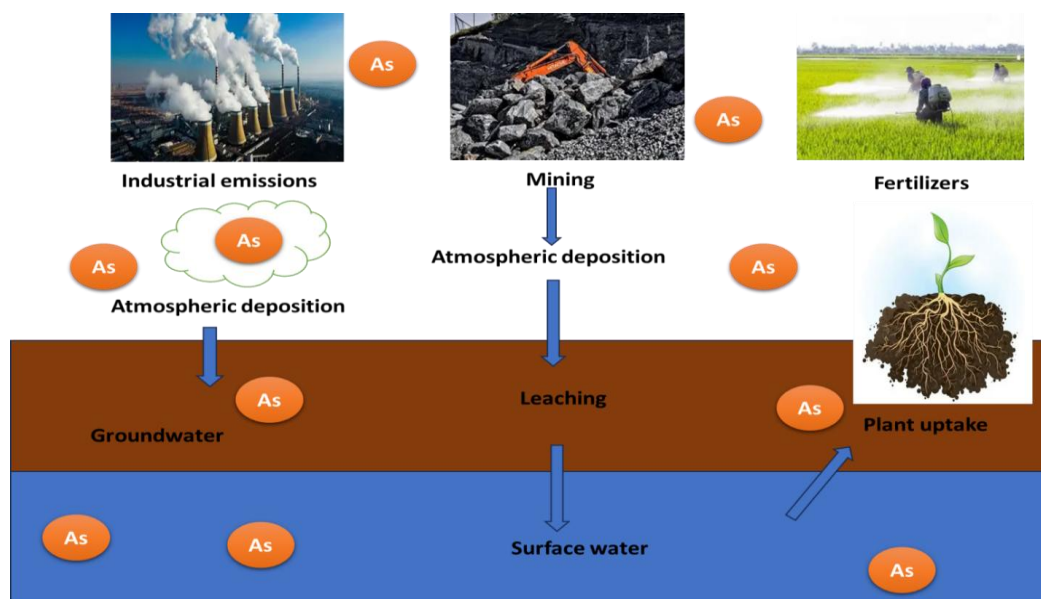


Figure 1: Sources and biogeochemical cycling of arsenic

Phytoremediation is a sustainable, ecologically safe, and cheaper soil repair strategy than other physicochemical procedures. As-hyperaccumulating ferns collect high quantities of As in above-ground plant tissues (Ma et al 2001;

in soil; As remediation methods used for soil; and discusses the potential of assisted-phytoremediation for the restoration of As-contaminated soils. Moreover, we discuss specifically

BC-assisted phytoremediation of As-contaminated soils, with its possible advantages and limitations.

2. Sources and biogeochemical cycling of arsenic

Arsenic is a poisonous metalloid that can occur in the forms of realgar (AsS), arsenical pyrite (FeAsS), orpiment (As₂S₃), and As-bearing iron (Fe) oxides minerals in soil and sediments (Bibi et al 2021; Khosravi et al 2019). Geogenic and anthropogenic sources of As are major contributors to agricultural soil contamination. Arsenic minerals can be released into the soil-water system from either dissolution of Fe-As minerals (FeAsS) or from As-bearing Fe oxides (Hussain et al 2021), where rice and other food crops are cultivated as staple food, most importantly in developing countries. Nevertheless, human activities such as arsenical pesticides, paints, mineral extraction processes, and burning of fossil fuels contaminate the soil environment with As (Khosravi et al 2019) (Figure 1).

In sandy sediments, the concentration of As is usually less than 10 mg kg⁻¹, but in peat and clay-rich residuals, it may reach up to 100 mg kg⁻¹ (Hussain et al 2019). The As speciation can show its toxicity and bioavailability regardless of the total As concentration in soil (Niazi et al 2011; Pierart et al 2015). Arsenic acid (As(OH)₃) is the most common As species in flooded soils, with a pKa of 9.2 (Zhang et al 2020) or can be present in different soil fractions to render it unavailable or to make it more bioavailable.

3. Remediation approaches for soil arsenic

3.1. Physical methods

3.1.1. Soil excavation and covering

To remove As from soil, many approaches are employed (Table 1). The soil cover method is employed where the original soil has lower levels of As than the neighboring soils. Soil replenishment (excavation) is used if the original soil level is similar to nearby soil. Clean soil replaces contaminated soil in soil replacement to diminish the quantity of As in the original soil (Wan et al 2020). Although it has significant expenditures and energy needs, this method is widely utilized on highly polluted soil. Soil replenishment is usually considered while recovering mining sites in China. Obtaining suitable clean soil is usually a key challenge for this remediation procedure. Another problem to consider is secondary contamination during the transportation of As-contaminated soil. Soil cover is a proficient method for accomplishing the decrease of metalloids like As in soil. The polluted soil is covered with unpolluted soil, and a hardpan layer is created between the polluted and unpolluted soils (Wan et al 2020).

3.1.2. Electrokinetic

An emerging approach to remediate As from contaminated soils is electrokinetic, which is an in-situ approach with more promising and easy field application (Li et al 2020a; Li et al 2020b). Expulsion techniques, such as

water electrolysis, electrophoresis, electro migration, and electroosmotic stream, with the help of an electrical field, can remediate As by moving it from the soil due to electric potential (Xu et al 2019b). Electrokinetic techniques to remediate As in soils have been researched, although the field application in the real world needs future studies (Yang et al 2016). This method has its restrictions in eliminating As since As in its disintegrated stage is challenging to deal with, and it increases the mobility of As and some other metals. By adding or coupling it with different procedures, it can bring effect to the ecosystem, improve its viability and productivity, and make it a financially reasonable alternative remediation option for As (Li et al 2020a; Li et al 2020b).

3.1.3. Turnover and attenuation

To lessen the total As amount in the soil, the turnover and attenuation technique is used, which involves mixing As-contaminated topsoil with clean deep soil. It is a broadly used technology in Japan, but in China, it is not widely utilized since it is not cost-effective and may have an impact on crop development (Wan et al 2020). Over 50% of As can be reduced in the top soil (0–20 cm). Furthermore, local soil conditions must meet the following criteria: 1) soil must be only slightly polluted; 2) pollutants (As) must be widely spread in the topsoil; 3) clean deep soil must be present. Also, this rehabilitation region must be suitable for machine farming because turnover machines are necessary. The depth can be calculated by the maximum cost and contaminant dispersion that can be set from 40, 60, or 80 cm (Wan et al 2020).

3.2. Chemical remediation methods

3.2.1. Soil washing

Chemical reagents are used in soil washing or soil leaching to enhance the solubility or movement of soil contaminants such as As and collect the contaminated leachate, and remove them from the soil. (Beiyuan et al 2017). In soils containing varying As levels, soil washing has been proven to be a promising method. Inorganic acids and inorganic bases, chelating agents, organic ligands, and bio surfactants may be used as washing reagents. (Wang et al 2017; Wei et al 2016) (Table 1). Phosphoric acid can solubilize As-adsorbed to Fe oxides or clay minerals and replace As^V because both As^V and PO₄³⁻ occupy the same sorption sites (Mukhopadhyay et al 2017; Zhao et al 2016). The main issues of soil washing are the deterioration of soil properties and the cost to nature.

3.2.2. Soil arsenic immobilization

In this technique, a range of chemical reagents is used to immobilize soil pollutants, such as As, thereby reducing the danger of contamination in the soil. Immobilization agents for As include solid wastes, biochars, and Fe oxides (Arenas-Lago et al 2019; Doherty et al 2017; Gil-Diaz et al 2017). Positively charging Fe-oxide with a positive charge can

Table 1: Various techniques used for remediation of arsenic (As)-polluted soils, with potential advantages and disadvantages.

Remediation techniques	Advantages	Disadvantages	References
Adsorption	Highly discriminatory towards As ^V ; beneficial for pilot scale treatment; communities and households	Moderate efficacy: regeneration needed	(Ahmad et al 201; Ahmad et al 201; Litter et al 201; Luong et al 2018)
Electrokinetic processes	Removing a wide range of HMs at a low cost	At any given time, only work on a small section of the soil	(Li et al 2019; Mao et al 2016; Xu et al 2019a)
Chemical precipitation	Increases soil fertility; Simple and effective; elements have been eliminated	Invariably forms silt; high processing costs	(Senn et al 2018; Vega-Hernandez et 2019)
Ionic exchange	Operative; Not dependent on pH; Not dependent on influent concentration	Sulfates, TDS, Se, F ⁻ and NO ³⁻ interfere; Suspended solids and iron precipitates cause clogging pretreatment can be required	(Ahmad et al 2018; Ahmad et al 2017; Litter et al 2019; Luong et al 2018)
Phyto-remediation	Phytoaccumulation: Plants used to absorb contaminants from the contaminated soil; widely utilized for metallic and radionuclide wastes Phytovolatilization: Plants used to uptake the contaminants from the contaminated soil; and then release these contaminates in the environment in less toxic form Phytodegradation: Plants used to take up the contaminants from the contaminated soil and break them into simpler, less toxic forms Phytostabilization: Plants used to immobilize the contaminants at contaminated sites through accumulation by roots through root hairs	Time taking process; microbes produce additional toxic materials; Hazardous pollutants interact with metabolic processes of plants	(Karakurt 2019; Muthusaravanan et 2018; Niazi et al 2016; Shakoor et al 2017; Shukla & Srivastava 2019; Y. et al 2019)

reduce As mobility by forming complexes that ultimately bind As in the soil solution, thereby decreasing its mobility.

4. Phytoremediation and its types

Phytoremediation is a cheap, effective, and ecologically friendly technique used to eliminate contaminants from soil (Jasrotia et al 2017). The plants utilized for phytoremediation must be capable of tolerating As or removing As and controlling its adverse impacts (Bhattacharya et al 2021). Plants are utilized to eliminate contaminants in phytoremediation techniques, and the procedure requires relatively slight nutrient input. It is easy to implement and is an ecologically sustainable method (Manoj et al 2020). Plants

having a broad root system, strong resistance, fast growth with high biomass output, flexibility, and the capability to digest and eliminate As from polluted soil are used in phytoremediation (Manoj et al 2020; Niazi et al 2017). From the soil solution, the As hyperaccumulators can absorb As and allow it to transfer at the root surface (Suman et al 2018). Few plant species use carrier proteins to transfer metal(loid)s, whereas others take in water directly from the air, activating adsorption and promoting aerial metal aggregation. Phytoextraction, phytostabilisation, phytofiltration, and phytovolatilization are all phytoremediation techniques that are dependent on metal take-up and transportation routes. (DalCorso et al 2019).

Hyperaccumulating plants have high remediation capacity because of their significant capacity to accumulate metalloids in their tissues. Phytoremediation, which includes chelators, can be assisted to improve elimination efficacy (Irshad et al 2020), soil amendments (Irem et al 2019) and nanotechnology (Moameri & Abbasi Khalaki 2019). *Pteris vittata* has seen success for the treatment of As-contaminated soil and is being used for the purification of As-polluted soils and water (Ye et al 2011). Leao et al (2017) stated that *Azolla caroliniana* can take up As up to 386 mg kg⁻¹ dry weight of As without saturation.

4.1. Phytostabilization

Phytostabilization or phytoimmobilization is a plant-enabled inactivation of toxic metalloids such as As in contaminated soil (Ramanjaneyulu et al 2017) (Figure 2). The goal is to decrease the mobility and bioavailability of As and restrict its mobility to groundwater by reducing As leachability, surface water, and finally to the food chain (Khalid et al 2017). Soil amendments like biochars, manures, and agri-waste peels act as secondary associates when used in the phytostabilization process along with plants. Sorption and surface complexations are two major processes followed in the phytostabilization process, along with the inner and outer layer complexes (Ashraf et al 2019b). However, more detailed research work is thus needed to understand the physiological and morphological changes that occur in plants and soil after the ameliorant applications.

microbes, redox-sensitive PTEs, such as As can be converted from poisonous As^{III} to immobile As^V (Ashraf et al 2019b).

4.3. Phytovolatilization

Phytovolatilization is the discharge of some metalloids, such as As, selenium, or other volatile chemicals into the air through plant transpiration. Plants absorb soil pollutants by phytovolatilization, converting the toxic contaminants into less toxic species and making them volatile, thus releasing them into the environment through aerial parts. However, the major limitation is confined only to organic compounds like mercury and selenium (Kumar & Gunasundari 2018).

4.4. Phytofiltration

The plant's mechanism to remediate the As (low levels) from ground and surface water or from wastewater by using roots, thus making complexes and other strong bonds using root exudate (high-low molecular weight compounds) (Ashraf et al 2019b). This method involves the transplanting of plants that are being grown under As-contaminated water irrigation to the soil contaminated with As, later on harvested and analyzed. Phytofiltration can be done through caulofiltration (plant shoots) or blastofiltration (seedlings) (Da Conceicao Gomes et al 2016).

4.5. Phytoextraction

Fast-growing plants with strong biomass yield and the capacity to remove hazardous ions are utilized in

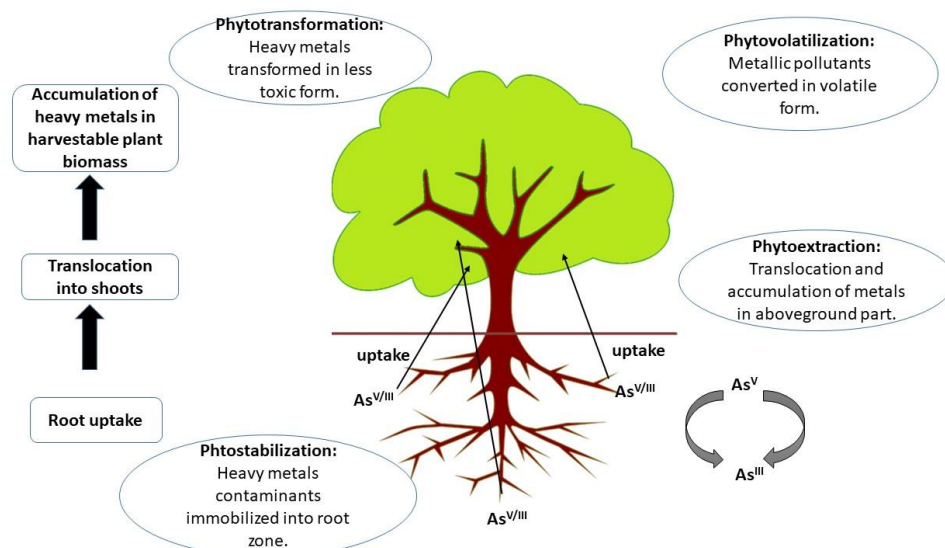


Figure 2: Schematic diagram of phytoremediation pathways of As-polluted soils

4.2. Phytotransformation

Phytodegradation, also known as phytotransformation, is the breakdown of harmful (organic or inorganic) chemicals by the plant's metabolic cycles or enzymes (Kumar et al 2018). Phytodegradation is helpful for the breakdown of organic compounds or, in certain cases, in association with

phytoextraction to extract PTEs, most notably in terms of polluted soil (Niazi et al 2017; Niazi et al 2012; Pajevic et al 2016). Before being disposed of in landfills, plant biomass could be collected for biogas production or combusted to make ash (Niazi et al 2012). Plant biomass that has been burned can be recycled, incorporated into bricks, or placed on poor soil. This new green technique will be 10 times less

expensive than conventional remedial methods (Wan et al 2016).

5. What is assisted phytoremediation?

Toxic metal phytoextraction began with hyperaccumulators, plants that collect metalloids in their aerial parts. Hyperaccumulators cannot handle many pollutants due to their low biomass production and capacity to absorb just one element (Barbafieri et al 2017). To address these challenges, an assisted phytoremediation technique might be used for the treatment of As-polluted soils. Plant species with high biomass production are combined with natural or chemical additives that may alter soil characteristics, enhance the As bioavailability for accumulation, and provide nutrition to plants (Bhargava et al 2012; Gupta et al 2022). In addition to chemical additions, organic material is popular due to its eco-friendliness and capacity to nourish plants (Mehmood et al 2021). It covers an extensive range of uses of plants and different techniques for the remediation of environmental pollutants. It includes coverage of different technologies for rapid phytoremediation of metals and enhancing phytoremediation capabilities (Deb et al 2020).

6. Assisted phytoremediation approaches

6.1. Nano-phytoremediation

Nano-phytoremediation shows the effectiveness of combining nanomaterials with plants to reduce pollution issues such as toxic metals like As, chromium, and other pollutants (organic and inorganic ones) (Song et al 2019). While this interaction needs time, a few studies have demonstrated nanomaterial efficiency in developing the phytoremediation system (Hou et al 2019; Rady & Romeh 2019; Yadav et al 2017). There are few studies on As removal using nano-phytoremediation and the fundamental mechanisms that lead to synergistic expulsion, but current data suggest that nanomaterials combined with plants and organisms are in an early stage and will improve traditional bioremediation practices (Hou et al 2019).

As-contaminated soils require an innovative approach that combines nanotechnology and phytoremediation for an eco-friendly method (Jesitha & Harikumar 2018). New nanomaterials that reduce treatment time, speed cleanup, and remove harmful pollutants from polluted soils (Pillai & Kottekottil 2016). Recently, several nanomaterial classes have been developed and employed to remove As, most notably Fe oxide nanoparticles, which can remove substantial levels of As from soil and aquatic settings (Maity et al 2019; Pariona et al 2015). Arsenic removal with nano-sized adsorbents is promising and operational. Various nano-adsorbent materials, such as Fe₂O₃, nanocube-impregnated graphene aerogel (Yu et al 2019), α - and γ -Fe₂O₃, Cu/Fe, CeO₂-CNT, Ceria, and magnetite, have been developed for As (Maity et al 2021).

6.2. Microbial-assisted phytoremediation

Plant-microbe interactions alter metal absorption and accumulation due to various methods of plants and microbes to deal with metal-like contaminants. Inoculation of rhizosphere bacteria with selected microorganisms can enhance phytoremediation. According to Wang et al (2011) *Populus japonicus* LH05-17 inoculated with *Agrobacterium* D14 strain can eliminate 54% As compacted in 300 mg kg⁻¹ As-contaminated soil, compared to 43% in uninoculated plants. Stems, roots, and leaves gained 113%, 229%, and 291%, respectively. Plant growth-promoting rhizosphere bacteria remove arsenic from the environment and restrict its transfer from roots to lessen its negative effects (Mallick et al 2018; Mallick et al 2014).

Microbes in the rhizosphere eliminate pollutants. Plant growth-promoting rhizosphere bacteria (PGPR) are identified and employed for As phytoremediation. Plant growth-promoting bacteria provide several benefits for plant development and immunology, including: B. Changes in rhizosphere-metal plant consumption processes and synthesis of extracellular polymers like indole-3-acetic acid and siderophores that boost plant growth and biomass for phytoremediation (Vocciante et al 2022). Subcellular distribution and As chemical forms may affect plant As decontamination and tolerance following extraction (Aljerf & AlMasri 2018). In As remediation, *Lysinibacillus* sp. in *P. vittate*'s rhizosphere may remediate up to 1136 mg L⁻¹ (As^{III}) and 3256 mg L⁻¹ (As^V) and accumulate 5.65 mg L⁻¹ and 23.43 mg L⁻¹ (Singh et al 2015). Genetic transformations for phytoremediation have been studied. Transgenic canola expressing a bacterial ACC deaminase germinated faster in As^V than non-transformed canola (Jan & Parray 2016). Plant-microbe interaction is another environmentally benign approach that speeds up soil As phytoremediation.

6.3. Chemical-assisted phytoremediation

To increase the uptake of As by plants, many additives are often employed, including chelating agents like ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA), as well as weak acids like citric acid (Barbafieri et al 2017). To improve Chelate-assisted phytoextraction, use organic and synthetic chelating agents to increase plant bioavailability (Guo et al 2019; Meers et al 2009). This method uses hyperaccumulator and non-accumulator plants. These chemicals may remain harmful in soil. And the potential of Consider seeping into groundwater (Pedron et al 2014). Low molecular weight organic acids, including oxalic, acetic, citric, malic, and humic acids, can chelate As and dangerous metals instead of costly synthetic chemicals. Low to moderate metal complex production by these organic acids. Made chelators decay more slowly than organic acids in soil (Souza et al 2013).

6.4. Phosphate-assisted phytoremediation

Phosphate has two fundamentally essential effects on As uptake by plants (Table 2). It may compete with adsorbed As on soil mineral exchange sites and enhance As availability

Table 2: Phytoremediation efficiency of different plant species against arsenic.

Plant species	Arsenic accumulation (mg kg ⁻¹)	Metal-accumulated part of plant	Type of phytoremediation	Medium	References
<i>Horedeum vulgare</i>	126 469	Shoots, Roots	Phytoaccumulation	Soil	(Mains et al 2006a; Mains et al 2006b; Muthusaravanan et al 2018)
<i>Pteris cretica</i>	2200–3030	Frond and roots	Phytoaccumulation	Compost	(Muthusaravanan et al 2018; Zhao et al 2002)
<i>Pteris longifolia</i>	5000	Frond and shoots	Phytoaccumulation	Soil	(Shagol et al 2011; Zhao et al 2002)
<i>Pityrogramma calomelanos</i>	8000	Frond and shoots	Phytoaccumulation	Soil	(Francesconi et al 2002; Shagol et al 2011)
<i>Pteris vittata</i>	8331	Frond and roots	Phytoaccumulation	Soil	(Kalve et al 2011; Muthusaravanan et al 2018; Yan et al 2020)
<i>Corrigiola telephiiifolia</i>	2110	Above-round plant plants	Phytoaccumulation	Soil	(Garcia-Salgado et al 2012; Muthusaravanan et al 2018; Yan et al 2020)
<i>Eleocharis acicularis</i>	1470	Shoots	Phytoaccumulation	Water	(Muthusaravanan et al 2018; Sakakibara et al 2011; Yan et al 2020)
<i>Solanum tuberosum</i> L.	-----	-----	Phytostabilization	-----	(Baghour et al 2001; Muthusaravanan et al 2018)
<i>Lupinus albus</i>	-----	-----	Phytovolatilization	-----	(Muthusaravanan et al 2018; Vazquez et al 2006)
<i>Typha latifolia</i> L.	-----	-----	Phytovolatilization	-----	(Muthusaravanan et al 2018; Varun et al 2011)
<i>Pteris vittata</i>	-----	-----	Phytodegradation	-----	(Muthusaravanan et al 2018; Sakakibara et al 2010)
<i>Arundo donax</i> L.	-----	-----	Phytodegradation	-----	(Mirza et al 2011; Muthusaravanan et al 2018)
<i>Canna glauca</i> L., <i>Colocasia esculenta</i> L. Schott, <i>Cyperus papyrus</i> L. and <i>Typha angustifolia</i> L.	-----	-----	Phytodegradation	-----	(Jomjun et al 2010; Muthusaravanan et al 2018)

(Kumar et al 2013; Niazi et al 2017). It may nourish As-stressed plants. Plants take arsenate through phosphate transporter channels, producing reactive oxygen species that kill them. Arsenate can substitute P in biological components like ATP, DNA, and proteins, interfering with important biological processes (Niazi et al 2017). Phosphate added to a hydroponic system decreased the ability of *P. vittata* to remove arsenic. Young ferns with less initial phosphate or split-phosphate were more effective in removing As than elderly ferns with single or greater initial phosphorus (Niazi et al 2016). Significantly, during As stress, phosphorus

availability to plants has been described as one of the primary elements that positively influences plants, allowing them to withstand hazardous As concentrations (Han et al 2016). Table 2 shows the phytoremediation efficiency of different plant species against arsenic.

7. Biochar-assisted phytoremediation

Biochar is a porous carbonaceous substance made from the pyrolysis of bio-waste such as plant residues and industrial and agricultural solid waste, under oxygen-limited conditions. It has physicochemical features such as a huge

surface area for adsorption, which allows it to immobilize potentially toxic metals (Niazi et al 2018; Shaheen et al 2019). It has been used to improve the physicochemical and biological qualities of soil, resulting in increased plant yield (Figure 3) (Prendergast-Miller et al 2014). Biochar-assisted phytoremediation can be utilized to remove As from soil (Table 3). Furthermore, because of its sorption ability and impacts on soil characteristics, recent research has shown the capacity of BC to minimize the harmful effects of As present in soils (Simiele et al 2020b). Biochar has been widely identified as enhancing soil As mobility because of its alkaline nature, creating possible concerns for ecological security (Zeng et al 2018). Application of BC-assisted phytoremediation for arsenic remediation is explained in Table 3.

translocation to the upper plant. This method improves metal bioadsorption in bioremediation and phytoremediation (Liu et al 2013).

8. Effect of biochar on soil arsenic

Most likely owing to soil pH increases, BC increased arsenic bioavailability and pore water concentration (Namgay et al 2010; O'Connor et al 2018; Simiele et al 2020a). Beesley et al (2013) unveiled the potential for As mobilization when BC is useful to As-contaminated soils. Because of its strong affinity for As, iron sulphate may be used to effectively immobilize As when using BC.

Biochar can remove As by surface complexation, precipitation, electrostatic attraction, and ion exchange, depending on soil type. As for many surface functional

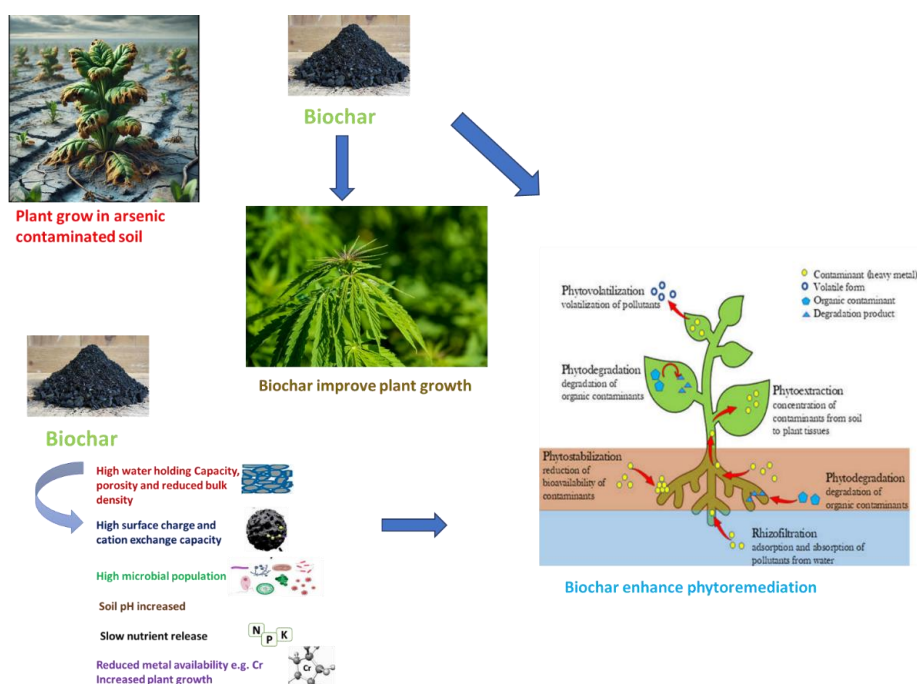


Figure 3: Illustration of biochar improves soil properties and supports assisted phytoremediation

Biochar promotes soil microbial activity when it is added to the soil. Combining BC with phytoremediation methods can boost their efficacy. Since BC boosts plant growth and biomass by 10% (Liu et al 2013). Biochar, plants, and bacteria may interact to change the behavior of As in soil. Biochar affects the microbial population in soil by favoring beneficial bacteria and inhibiting pathogens, as several chemical components in BC suppress the pathogens in the soil (Arafa et al 2019). Lebrun et al (2020) studied which tissue from the oak trunk is responsible for the positive effect on As immobilization. Results showed that bark appears to be the best trunk portion for producing BC that can immobilize As in soil. Lebrun et al (2019) examined how BC, compost, and Fe improve soil As stability. Biochar-compost increased soil conditions, plant development, and As

groups (mostly $-OH$, $-COOH$, and thiol ($-SH$)), electrostatic attraction, ion exchange, and surface complexation attract As (Niazi et al 2018). At low pH, BC may have a larger amount of protonated functional groups, which could enhance As^V sorption via electrostatic interaction at acidic pH levels (Alkurdi et al 2019). On changing the pH of the solution, the surface area of BC is also changed. Negative charges have been observed on the BC surface at higher pH levels.

9. Advantages of assisted phytoremediation

Phytoremediation is affordable, eco-friendly, and socially acceptable. Plants may be cultivated and monitored easily (Qadir et al 2021). This emerging technology is 60–80% cheaper than physical and chemical procedures (Ashraf et al 2019a). After phytoextraction, plant biomass may be

Table 3: Application of biochar-assisted phytoremediation for remediation of arsenic-contaminated soils.

Feedstock	Pyrolysis conditions	Plant	Result	Reference
<i>Hibiscus cannabinus</i> , sewage sludge and chicken manure	500 °C for 3 h	<i>Cassia alata</i> (Candle bush)	Biochar @ 3% (w/w) decrease As 54.9-77.5%	(Huang et al 2018)
Wood biomass	500 °C	<i>Phaseolus vulgaris</i>	Biochar 5% (w/w) reduced the As (24%) concentration in the pore water	(Lomaglio et al 2017)
Rice husk	500 °C for 2 h	<i>Typha latifolia</i>	64% As removed	(Irshad et al 2021)
Oak , Beech and Hornbeam	500 °C	<i>Phaseolus vulgaris</i>	Biochar 2% (w/w) increased the As concentration	(Nandillon et al 2019a)
Rice straw	450 °C for 1 h	<i>Pteris vittata L</i>	Biochar @1% (w/w) reduced 33.25% As in soil	(Zheng et al 2019b)
Hardwood biomass (oak, beech and charm wafers and chips)	500 °C for 3 h	<i>S. purpurea</i> <i>P. euramericana</i> <i>S. viminalis</i>	Biochar 1% (w/w) reduced the As by 30%	(Simiele et al 2020b)
Rabbit manure waste	450°C and 600°C for 1 h	<i>Brassica napus</i>	Biochar 2% (w/w) reduced the As concentration 98%	(Gasco et al 2019)

used to make bioenergy (Dhiman et al 2016; Tripathi et al 2016).

Biochar and phytoremediation may clean up mined areas. *Brassica juncea* (Ali et al 2017; Rodriguez-Vila et al 2014; Rodriguez-Vila et al 2015), *Zea mays* (Gonzaga et al 2020) and bioenergy crops such as *Jatropha* (Gonzalez-Chavez et al 2017) have been employed in BC-assisted phytoremediation. Due to its high adsorption capacity, BC lowered soil HM bioavailability and leachability, whereas botanical extractants reduced polluted regions' HM levels. Forjan et al (2017) found that hardwood BC and canola reduce plant-available Cu, Pb, Ni, and Zn in mine-degraded soils. Nandillon et al (2019b) found that BC treatment decreased phytoavailable Pb and As concentrations and increased *Populus nigra* plant growth in technosols.

Biochar-assisted phytoremediation has several advantages, including the ability to fix PTEs and enhance

crop development, making it the best alternative for crop stabilization. The most practical application of combining BC with botanical extractants is in multi-contaminated soils, where both target different components and can aid in long-term cleanup. In acidic, polluted, mining-damaged soils, BC acts as a soil amendment before colonization by plants (Ghosh & Maiti 2021).

10. Disadvantages of assisted phytoremediation

Phytoremediation is generally slower than other normal treatment methods and relies on climatic conditions. For better outcomes, sites should be adequately enormous to develop and use agricultural machinery for planting and harvesting. Plants can assimilate harmful As, which can be dangerous and pose a threat to wildlife and contaminate the food chain (Qadir et al 2021).

Consequences can be diverse under greenhouse and field conditions (Ji et al 2011; Niazi et al 2011; Niazi et al 2012). This method must be studied in the field before commercialization, since gross distribution, soil pH, pathogens, moisture, temperature, and nutrients can impact phytoremediation (Vangronsveld et al 2009). Plant exudates may enhance the solubility of As, resulting in greater contaminant movement or environmental damage. Some plants could be involved with numerous toxic materials, making them a possible hazard to the food chain and toxic to animals that feed on them (Qadir et al 2021).

On-site batch production and long-term results are two key limitations to the use of BC at mine sites. Biochar may increase PTE toxicity, according to certain research. Due to high PTE content in raw materials. The disposal of phytoremediation biomass is another concern. Field studies are needed to identify As hyperaccumulators and BC-derived fuels (Ghosh & Maiti 2021).

Another issue is that, because of the high amount of PTE in the starting material, using BC enhances PTE toxicity. Phytoremediation of biomass disposal is also a concern. Plant selection for hyperaccumulators and feedstocks for BC synthesis must also be studied in the field. Long-term studies on the usage of trees and shrubs should be fortified since they can reduce disposal costs. Environmental cost-benefit analyses should be widely distributed, and strategies for disposing of polluted biomass should be developed (Ghosh & Maiti 2021).

11. Conclusions and future perspectives

Arsenic soil contamination is a major ecological and human health hazard all over the world. Arsenic in food causes health problems in humans. Biological methods and phytoremediation seem to be the best solutions for remediating such sites. This method is both cost-efficient and environmentally friendly, and it produces effective results. Arsenic-accumulating plants, both aquatic and terrestrial, can be utilized to reduce and excerpt As from the soil and water. Due to sluggish accumulator development and lower aboveground biomass output, traditional phytoremediation technologies are less cost-effective on a broad scale. To circumvent these restrictions, three to four new solutions are deployed to one polluted site.

One of the most important remedial approaches for As-polluted soils may be BC-assisted phytoremediation. Biochar may be an effective technique for immobilizing As in soil or help the plants to extract As when applied to As-contaminated soils. Biochar can recover soil contaminated with As by improving soil health, nutritional status, carbon pool, and microbial diversity.

- The majority of BC-based research is short-term, raising concerns about the long-term fate of As. Long-term research with perineal tree species could lead to the production of multipurpose trees that meet the societal needs of a reclaimed site.

- As pH and redox potential affect As sorption, biochars must be designed depending on soil properties like flooded (reduced) or unflooded (oxidized) soil conditions and acidity or alkalinity.
- Genetic engineering research is needed to enhance phytoremediation of transgenic plants and understand their mechanics and efficiency for successful, cost-effective solutions.

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14. Authors' Contribution

Amna Zulfqar, and Madiha Batool: Writing original draft, visualization and data collection; Nabeel Khan Niazi, Hamna Bashir: Supervision and Writing reviews; Muhammad Jahandad Khan, and Muhammad Hassan Bashir: Writing reviews

15. Conflict of Interest

Authors declare no conflict of interest.

16. Sustainable Development Goals

This review supports SDG 3 (Good Health and Well-being), SDG 12 (Responsible Consumption and Production), and SDG 15 (Life on Land).

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