Review Article

Potential of plant based metallophytes for phytoremediation in agriculture

Abstract

Remediating heavy metal contaminated places with plants is an effective choice due to phytoremediation, an environmentally friendly method that uses plants to mitigate the pollution.

Metallophytes are the unique group of plants that have evolved to thrive in metal rich environments and have drawn plenty of attention. Metallophytes are ideal options for phytoremediation applications due to their inherent traits such as hyper-accumulation, efficient metal absorption and tolerance mechanisms impacting both the plant and soil. These plants absorb and translocate heavy metals, detoxifying the soil while accumulating them in tissues. This reduces metal toxicity in soil and holds potential for resources recovery. The role of metallophytes in phytoremediation is analysed in this review with particular focus given to their ways of metal absorption, translocation and detoxification. Metallophytes have high metal tolerance and accumulation capacities due to their unique physiological and biochemical adaptations including enhanced metal sequestration in vacuoles, metal chelation by phytochelatins and activation of anti-oxidant defence systems. This review also highlights the significance of metallophytes in enhancing the soil health, reducing metal bioavailability, and promoting the ecological sustainability as well as their potential for restoring contaminated ecosystems. Utilizing the unique capabilities of metallophytes obtained from plants possesses enormous possibilities to minimise the negative effects of heavy metal pollution, protect ecosystems, and promote sustainable development for future generations. Eventually, it outlines future research approaches that aim to enhance metallophytes based phytoremediation strategies, widen their implementation and include them in holistic approaches for environmental restoration and sustainable land management.

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Keywords: Metallophytes, phytoremediation, environmental restoration, heavy metals, soil health, ecosystem

Introduction

Due to massive economic development and quick expansion in numerous industries including agriculture, the environment is becoming more polluted (Shubham et al., 2023). Toxic metals which originate from natural and man-made sources might be referred to as environmental contaminants. Abiotic factors chiefly soil, water, air and biotic communities such as plants, animals and anthropogenic activities are put at risk by a number of environmental processes including burning trash, converting coal and creating synthetic businesses. A major issue preventing plants from growing in many situations is metal toxicity in soils. Certain metals like zinc and copper are considered to be micronutrients in low concentrations but become hazardous if present in larger concentrations, whereas, other

Comment [b4]: You need to talk a bit about “bioaccumulation’ metals like lead and aluminium are exclusively recognized for their toxicity. Certain soils naturally contain high traces of metals. For instance, serpentinite regions are found contaminated with enormous amount of trace metals which includes high level of Cr, Ni and associated metals (Mg, Pb, Co and Zn) with other elements (Pal *et al.*, 2005). In addition, acid rains can cause metal poisoning indirectly by increasing the availability of most metals for plant absorption due to low soil pH. The Pb and Zn were mainly adsorbed on colloidal particles and were transported during simulated acid rain. The mobility of Zn was increased at low pH (Singh & Agrawal, 2007). Therefore, a significant constraint on agriculture may arise from the elevated availability of aluminium in some acidic soils.

The world is facing several challenges today due to rapid and reckless industrialization, intense farming practices, hazardous mining operations and waste disposal (Bhatti *et al.*, 2018; Shubham et al., 2021). The health of people, animals and plants is also impacted by the continuous accumulation of metals in terrestrial systems. According to a Central Pollution Control Board (CPCB) research, 80 per cent of hazardous waste in India including heavy metals is produced in the states of Gujarat, Maharashtra and Andhra Pradesh (Marg, 2011).
The usage of pesticides, fertilisers, municipal and compost wastes, as well as, the emission of heavy metals from metalliferous mines and smelting businesses have all resulted in the contamination of large regions of land with heavy metals (Yang *et al.*, 2005). Even though the earth's crust contains a large number of heavy metals at different concentrations by nature, the issue comes when these metals are released into the environment in excess as a result of man-made or natural processes. Based on their density (>5 g/cm^3), the 53 elements that make up the D-block have been classified as "heavy metals" (Jarup, 2003). Only 19 elements, including the macronutrients C, O, H, Mg, S, N, Ca, P, and K and the micronutrients Cu, Zn, Mn, Fe, Mo, B, Ni, Co, Cl, and B, were chosen for basic metabolism during the development of angiosperms (Ernst, 2006). Furthermore, silicon (Si) is regarded as a helpful element and has been implicated in certain plants structural preservation (Epstein, 1999). Plant physiological and biochemical activities, including chlorophyll production, photosynthesis, DNA synthesis, protein modifications, redox reactions in the chloroplast and mitochondrion, sugar metabolism and nitrogen fixation are significantly influenced by macro and micro-nutrients. In many plants, visual symptoms are caused by metal poisoning. Leaves may get discoloured and root development is frequently inhibited. Deficiencies in some nutrients (e.g., magnesium or calcium deficiency due to aluminium competition for root absorption) may appear as symptoms. Toxic metals can also be harmful when they attach to proteins and other substances because they share similarities with essential metals. Both essential and non-essential heavy metals often have similar harmful effects on plants including reduced biomass accumulation, chlorosis, growth and photosynthetic inhibition, altered water balance and nutrient absorption and senescence which eventually results in plant death. Since, heavy metals are so persistent in nature they not only have negative effects on plants but also constitute a hazard to human health. One of the most hazardous heavy metals is lead (Pb) which has around 150–5000 year soil retention period and has been shown to sustain high concentrations for up to 150 years (Yang et al., 2005).

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According to McLaughlin *et al.* (1999) a contaminated food chain serves as the main pathway for the heavy metals to enter the tissues of animals and humans and thus increasing their susceptibility to a variety of illnesses including dermatitis and cancer. If appropriate action is not done at the appropriate time, this issue might get worse. Heavy metal toxicity in plants can occur in four different ways. These comprise: (a) Structural and functional

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similarities that cause competition for absorption at the root surface *e.g.* As and Cd compete with P and Zn, respectively (b) Direct interactions between heavy metals and the sulfhydryl groups (-SH) of functional proteins which disrupt and degrade the structure and function of the proteins (c) Removal of necessary cations from specific binding sites that results in a collapse in function (d) Production of reactive oxygen species (ROS) which in turn damages the macromolecules. It has been well documented that plants may adapt to soils that are enriched in heavy metals (Antonovics *et al.,* 1971). Plants that have modified their metabolism to enable growth and reproduction in metalliferous soils, such as *Agrostis capillaries* and *Silene vulgaris* have found success. It is possible for heavy metals like Cd, Pb, Al and Ag to be non-essential micronutrients in metal-enriched soils, yet necessary micronutrients like Mn, Zn, Cu, Fe and Mo may be present (Woolhouse, 1983). The soil characteristics at a certain location influence the kind and level of resistance to heavy metals. High atomic weight elements with a density at least five times that of water are known as heavy metals. These elements generally occur naturally. It is non-biodegradable and continues to accumulate in the environment, reaching toxic levels in the soil as a result of various natural processes like soil formation, rock weathering, volcanic eruptions as well as anthropogenic activities like excessive application of chemicals in agriculture, industry, mining and effluents from various sources etc. In the environment, heavy metals are quite persistent. Because of their slow movement and restricted breakdown once they are incorporated into the soil, they tend to accumulate over time. As a result, areas exposed to heavy metals over prolonged periods of time are becoming more contaminated, which presents long-term risks to crop production (Pehoiu *et al*., 2020). Such soils are remediated by various methods such as removal, isolation, incineration, solidification/stabilization, thermal treatment, solvent extraction and chemical oxidation. Currently, in situ techniques, phytoremediation techniques are preferred because they are more cost-effective and cause less environmental disruption (Favas *et al*., 2014). Using plants and associated soil microbes to reduce the harmful effects of pollutants (HM's) in the environment is known as phytoremediation. This technique uses metal accumulating plants referred as Metallophytes. Some metallophytes are Indian mustard, broad leaf plant like *ribwort plantain*, *Arabidopsis arenosa* (Singh *et al*., 2016).There are many pros of using metallophytes in phyto-remediation of heavy metal pollute soils as they are economically feasible, eco-friendly, prevents erosion and establishment of vegetation in barren lands.

Metallophytes

Metallophytes plants can be used in phytoremediation because of their capacity to absorb the significant concentrations of heavy metals from the soil. The capacity of metallophytes to withstand and even accumulate the dangerous concentrations of heavy metals in their tissues without suffering noticeably negative consequences is one of their most remarkable characteristics.There are different categories of metallophytes named metal excluders, metal hyper-accumulators and metal indicators (Devi & Kumar, 2020).Metal excluders are such metallophytes which accumulates heavy metals in the root from the particular contaminated soil, but the metals movement into the aerial plants components is restricted (Sheoran *et al.,* 2011; Malik *et al.,* 2012; Shubham *et al.,* 2023). According to Baker and Walker, (1990), plants that accumulate metals in their above ground tissues are known as metal indicators and the amounts of metals in these tissues typically corresponds to the levels of metals in the soil .Plant species classified as hyper-accumulators are capable of absorbing and utilizing large concentrations of heavy metals >100 to 10,000 µg/g (or much higher) relative to the plants dry weight without facing any harmful effects.

Metallophytes are classified into two types *i.e.* hyper-accumulators and non-hyper accumulators. Heavy metals from soils can be absorbed by hyper accumulators through their roots and then transferred to shoots and leaves. On the other hand, plant species classified as non-hyper accumulators are capable of storing heavy metals in their underground parts and are unable to transfer them to their shoots or leaves with a few species allowing restricted translocation. The heavy metals that these hyper accumulators take up from the soil are not stored in the roots instead they go up the shoots and build up in the above ground organs at concentrations that are 100–1000 times higher than those found in non-hyper accumulating species. Three characteristics mark them apart from non-hyper accumulators. These include increased heavy metal absorption capacity, root-to-shoot heavy metal translocation and detoxification and the storage of heavy metals (Singh *et al*., 2016*)*.Approximately, 45 per cent of hyper accumulators are members of angiosperm families of these, 25 per cent are members of the *Brassicaceae* family. Members of the *Asteraceae*, *Caryophyllaceae*, *Fabaceae*, *Cyperaceae*, *Poaceae*, *Cunoniaceae*, *Lamiaceae* and numerous other families are among the other families. Research indicates that the rhizosphere and endosphere of hyper-accumulator plants have a high diversity of bacteria and fungus (Kaflee*t al*., 2022; Gani*et al*., 2024).There is lots of research supporting *E. crassipes*ability to remove the heavy metals (Sarkar *et al*., 2017).

Comment [b7]: You can as well give the English/common names of these plants for the benefit of a layman.

Heavy metals toxicity in soil due to agronomic practices

Comment [b8]: This sub section could have been " HEAVY METAL CONTAMINATION, HEALTH IMPLICATIONS AND MITIGATION"

a) **Sources of contamination:** Two prominent ways that heavy metals might end up in agricultural soils are through chemical fertilisers and insecticides that contain the metals. Using contaminated irrigation water from industrial or municipal sources. The concentration of heavy metals (HM's) in agricultural soil grew in the following order, according to a study conducted in the agricultural soils of Jhansi, India: Cd, Co, Mn, Cu, Pb, Ni, and Zn. The Food and Agriculture Organisation/World Health Organisation (FAO/WHO), the United States Environmental Protection Agency (USEPA), and Indian norms are the research areas for concentrations of Cu, Zn, Pb, and Ni. The mean Cd content in the studied region was greater than the allowed limits established by the FAO/WHO and USEPA (Gupta *et a*l., 2021).Use of sewage sludge, also known as bio-solids, which may include significant levels of heavy metals from human waste and industrial discharge. Heavy metals are released into the atmosphere by industry and vehicle emissions.

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b) **Accumulation and persistence:** Because of their slow rates of degradation and restricted mobility, heavy metals have a tendency to accumulate in soil over time. Heavy metals may accumulate gradually and may contaminate crops after being added to the soil, where they can remain for extended periods of time.

c) **Impacts on soil health:** High levels of heavy metals in soil can have detrimental effects on soil health through two different processes: disrupting soil microbial communities and nutrient cycle mechanisms. Lowering water retention and penetration as well as reducing the soil's structure. Decreasing the fertility of the soil and impeding plant growth.

d) **Heavy metal absorption by plants:** Plants raised in polluted soils have the potential to absorb heavy metals through their roots, which can result in a build-up of the metals in edible plant parts. A study indicated that the concentration of DTPA-extractable and total heavy metals in flood plain soils around the Sutlej River was

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higher along the trans-boundary. In soil samples, 18 per cent of samples surpassed the limits of total Cd during both pre and post-monsoon seasons. The PLI values for total metal concentration were above one in 60 per cent of the soil samples. The concentration of Co, Pb and Cd were higher in rice and wheat grains in contrast to their safe limits (Setia et al., 2021). Because heavy metals can bio-accumulate and bio-magnify throughout the food chain, eating polluted crops can put humans and animals at risk for health problems.

e) **Implications for human health:** Exposure to heavy metals can be harmful to human health if they ingest polluted food, drink contaminated water, or breathe in contaminated dust. In India, high concentrations of As and Cr in urban soils exceed threshold values and represent serious non-carcinogenic health concerns for both adults and children. Residents may be at risk for cancer from Cr and As, while Pb levels usually remain within advised ranges. These health risks in urban areas require immediate attention as well as preventative measures (Adimalla, 2020).

f) **Mitigation measures:** A number of measures such as soil testing to determine heavy metal levels and direct remediation activities can be used to lessen the pollution of agricultural soils with heavy metals. Adoption of integrated pest control and organic farming as sustainable farming methods to lessen the dependency on chemical inputs. Heavy metal immobilisation, extraction or degradation in polluted soils can be achieved using soil amendments and phytoremediation methods; it is a plant-based remediation which is an affordable and environment friendly approach to remove heavy metal and organic pollutant contamination from soil and water. Implementing the suitable waste management procedures to reduce the amount of heavy metals that are introduced into agricultural systems.

Effects of heavy metals on crops

The intricate reactions between the main harmful ions and other necessary or non-essential ions produce toxic damage to cells and tissues when plants assimilate and accumulate high concentrations of heavy metals. Plant development does not require heavy metals (Ahmadpour *et al*., 2012; Shubham *et al.*, 2022). Research from Northern India suggests that leafy vegetables, such as fenugreek and spinach, have a higher concentration of heavy metals than fruit vegetables, including eggplant and chilli (Gupta *et al*., 2021). Since arsenic-polluted groundwater has been used to irrigate crops, especially rice crops (*Oryza sativa L*.), Bangladesh has greater soil arsenic levels. Amin *et al*., (2013) conducted a study to examine the accumulation of Cu, Ni, Zn, Cr, Fe, Mn, Co, and Pb in waste water-irrigated red onions (*Allium cepa*), garlic (*Allium sativum*), tomatoes (*Solanum lycopersicum*), and eggplants (*Solanum melongena*). Waste water irrigation significantly increased the degree of heavy metal pollution in crops when compared to tube well water. *A. cepa* that was irrigated with tube-well water did not have a manganese build up 50 times greater (28.05 mg/kg) than the severely polluted onions (Kgopa *et al*., 2018).

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Effects of heavy metals on soils in India

Heavy metals such as lead, mercury, cadmium, arsenic and chromium pose a major danger to the stability of ecosystems and the health of the soil. Heavy metal accumulation can negatively impact crop productivity, soil quality and agricultural product quality all of which have an impact on the health of people, animals and the environment (Nagajyoti et al., 2010). Large areas of land might get contaminated by heavy metals released by waste incinerators, industrial smelters, municipal compost or sludge, pesticides, fertilisers, and industrial effluent. In the Surat industrial region, soil samples were extracted from the top 10 cm of the soil. The study revealed that the soils in the area were highly polluted, with a greater amount of toxic elements than normally seen. The study area's soils had heavy metal loadings of 139.0 mg/kg for Zn, 317.9 mg/kg for Sr, 380.6 mg/kg for V, 51.3 mg/kg for Co, 137.5 mg/kg for Ba, 305.2 mg/kg for Cr, and 51.3 mg/kg for Ni (Krishna & Govil, 2007). In another study conducted at Andhra Pradresh, environmental geochemistry studies were carried out in and around the Patancheru industrial growth region so as to determine the extent of chemical contamination in the soil. The data indicate how severely contaminated the area's soils are, with quantities of harmful substances two to three times higher than average. Above their usual distribution, a number of heavy metals, such as Cr, V, Fe, As, Cd, Se, Ba, Zn, Sr, Mo, and Cu, are discovered in the soil. The research region's soils showed heavy-metal loadings of 240 mg/kg, 235 mg/kg, 1,350 mg/kg, and 500 mg/kg for Cr, V, Ba, Cd, and Cu, respectively (Govil *et al*., 2001).To determine the impact of pollution in the study region in and around the Pali industrial growing area of Rajasthan, an environmental geochemistry study was conducted. Soil samples around the Pali industrial district were evaluated for Pb, Cr, Cu, Zn, Sr, and V using a Philips PW 2440 X-ray fluorescence spectrometer. Most of the samples were taken in the vicinity of the Bandi River and small streams that surrounded industrial areas. The soil around the industrial zone was found to contain significantly higher amounts of the metals Pb (293 mg/kg), Cr (240 mg/kg), Cu (298 mg/kg), Zn (1,364 mg/kg), Sr (2,694 mg/kg), and V (377 mg/kg) than their typical distribution in soil (Krishna &Govil, 2004).The microbial population in the Baula-Nuasahi mining belts in Keonjhar District, Orisaa, was found to be decreased and the overburden soils exhibited low concentrations of nutrients (N, P, and K). It turns out that the agricultural lands nearby had become unsuitable for crop production due to the metal ions that had seeped into them (Dal *et al*., 2011). It was found that the main sources of chromium contamination were seepage water and overburden dumps (Dhal and Pinaki, 2014).

To assess the extent of heavy metal pollution carried by urbanisation and industrial development, the soils of Hyderabad's Balanagar industrial area were examined. Significant contamination was found with amounts of toxic substances higher than those present in soils with a normal distribution. Copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), cobalt (Co), vanadium (V) and chromium (Cr) concentrations ranged from 82.2 to 2,264 mg/kg, 31.3 to 1,040 mg/kg, 34.3 to 289.4 mg/kg, 57.5 to 1,274 mg/kg, 67.5 to 5,819.5 mg/kg, 8.6 to 54.8 mg/kg, and 66.6 to 297 mg/kg, respectively (Machendar *et al*., 2011).Toxic heavy metals pose a major danger to many countries worldwide in Karnataka's chromite mining districts, where mining operations have historically occurred. The soil pollution around chromite mines was analysed in this study using a variety of indicators to evaluate contamination levels. The heavy metal concentrations in soil samples from 57 locations close to Tagdur and Jambur, two closed and active chromite mines, and residential areas near Chikkondanahalli in the Nuggihalli Schist Belt of Karnataka, India, were examined using wavelength dispersive X-ray fluorescence spectrometry. The studied area showed elevated levels of cobalt (Co), nickel (Ni), and chromium (Cr) compared to the Soil Quality Guideline's recommended limits. The higher enrichment factor of these metals indicates an increased risk of heavy metal contamination, perhaps as a result of past mining operations (Krishna et al., 2013).

Conclusion

The utilization of metallophytes derived from plants in phytoremediation is a sustainable and long-term way of minimizing the degree of heavy metal contamination in soils. These unique adaptations enable these specialized plants to thrive in metalliferous situations and effectively eliminate the metals from the environment around them. By reducing the bio-availability and toxicity of heavy metals, metallophytes significantly contribute to environmental restoration through processes such as the absorption of metals, translocation and increased antioxidant defences. Also the metallophytes offer a variety of benefits over conventional remediation techniques when used in phytoremediation. Phytoremediation is an environmentally friendly method that does not add to the existing pollutants in the environment, in contrast to chemical treatments. Metallophytes are excellent options for cleaning up the extremely contaminated regions that are challenging to restore using traditional approaches, as they are able to survive in hard environments where other plants might struggle. Their ability to adapt and bounce back from heavy metal contamination makes metallophytes a vital asset in efforts to restore ecosystems. Phytoremediation capability helps to ensure the sustainability of natural resources and lowers the environmental pollution, thus being consistent with the aims of the circular economy and sustainable resource management. The implementation of metallophytes into phytoremediation strategies offers a holistic approach to environmental conservation, emphasising the importance of biodiversity conservation and ecosystem resilience, in addition to offering an effective approach for cleaning the contaminated environments. As this field of research advances, further study of metallophyte species and their interactions with metals will help us better understand phytoremediation processes and enhance the effectiveness of this strategy for the global issue of heavy metal pollution.

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