

Phytomining: a sustainable approach for heavy metal removal

Ehitua Julius Oziegbe ^{a,*}, Olubukola Oziegbe ^b and Ibrahim Ajibola Oladeni ^c

^a Department of Geosciences, Faculty of Science, University of Lagos, Nigeria.

^b Department of Biological Sciences, Covenant University, Ota, Nigeria.

^c Department of Geology, Georgia State University, USA.

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ABSTRACT

Researchers are learning more about how plants fight off the harmful effects of heavy metal pollutants as the environment gets worse with these pollutants. Also, investigation on how to better manage these pollutants sustainably are on the rise. Phytomining is a phytoremediation technique that utilizes plants to extract precious heavy metals from mineralized or contaminated soils to generate revenue. This can be achieved by recovering valuable levels of metals from the biomass of plants. Aside, being a sustainable and cost-effective technique, phytomining financial viability depends on valuable biomass of obtained from the contaminated environments. Natural heavy metal hyperaccumulators are currently attracting attention due to the enormous opportunities presented by phytomining. Hyperaccumulator plants such as *Berkheya coddii*, *Eleocharis acicularis*, and *Myriophyllum aquaticum* are some of the efficient plants for phytomining of heavy metals. Genetic engineering of specific species of hyperaccumulators of certain heavy metals could improve the efficiency of phytomining technology. Potential biorefineries using phytomining techniques could be supported by the circular bioeconomy of heavy metals. Thus making appropriate the reuse of high-value heavy metals (Au, Co, Cu, and Ni) from polluted sites and also concentrating valuable heavy metals within the plants from mines with low concentration. This review highlights the potential use of phytomining in the cleanup of heavy metal contaminated sites as well as wealth creation. Thereby, making heavy metal phytomining a promising bioremediation strategy.

Keywords: Bioeconomy; Biorefineries; Genetic engineering; Hyperaccumulator plants; Wealth creation.

1. Introduction

The earth's crust by nature contains heavy metals, which vary in concentration depending on the location [1]. High concentrations of heavy metals have been reported in the overburdens and soils in karst regions [2-4]. Phytomining a phytoremediation technique make use of phytoextraction, which is the process of using plants to extract metals from soils. In phytoremediation, plants absorb and eliminate toxic metals from heavy metal polluted sites [5-7]. Phytomining offers plant the potential to extract commercial heavy metals from overburdens, low-grade ores, mill tailings or mineralized soil that is not profitable by conventional mining methods [8, 9], as shown in Figure 1. Thus, Phytomining offers both economic and environmental benefits [10]. This technique involves the production of heavy metal "crop" by cultivating high-biomass plants that could extract high metal concentrations [11]. Drying, and combustion of the harvested biomass yields high-grade bio-ore [12]. For example, in soils with nickel levels much below the threshold level for traditional mining, *Alyssum Bertolonii* and *Berkheya coddii* might extract more than 100 kg of nickel per hectare annually [13]. This newer and more sophisticated phytoremediation technique creates low volume and sulphide-free "bio-ore" that can melt and retrieved for economical purpose target metal [8]. A plant that can accumulate heavy metal to a concentration 100 times higher than "normal" plants growing in the same environment is considered a hyperaccumulator [13, 14]. Table 1 shows different hyperaccumulators of some heavy metals. Some species of hyperaccumulator show greater growth possibility in environment with

higher levels of heavy metals in comparison to their close or distant family [15]. As a consequence, a number of natural plants have been classified as the natural accumulators of heavy metals. Phytoremediation which is a developing technique uses green plants to remove pollutants from the environment [16, 17]. It is thought to be a sustainable and more affordable option than traditional remediation techniques [18, 19]. Planting in a contaminated matrix by Phytomining helps to eliminate environmental toxins by promoting the pollutants' sequestration and/or breakdown [17]. For in situ metal removal, hyperaccumulator plants outperform traditional technologies at a lower cost [20].

Heavy metal cleanup is a huge industry; in fact, based on the report from European Environment Agency (EEA), the overall estimated cost of cleaning up polluted sites in Europe might vary from EUR 59 to EUR 109 billion [21]. Phytomining is a 34–54 billion US dollar worldwide phytoremediation business that is growing in wealthy nations, offering this green technology a chance [20]. It has been an effective economical method of removing gold from low-grade ores at residual dumps, which are piles of tailings [22, 23]. Plant species such as *Kalanchoe serrata* L. and *Helianthus annuus* L. are both employed in the phytoextraction of Au and Cu from mine tailings [24]. Despite the fact that numerous plant species have exceptional ability for metal biosorption, hyperaccumulators have significant benefit of being able to thrive in excessive levels of external metals [25]. Heavy metal hyperaccumulators are capable of extracting significant levels of contaminants without exhibiting any sign of toxication [26]. The soil's metal composition,

* Corresponding author. E-mail address: eziegbe@unilag.edu.ng (E. J. Oziegbe).

plant assimilation of metal, plant biomass, and above all, the metal price all affect how profitable Phytomining is [8, 9, 27].

Even though soil naturally contains heavy metals, their quantity has grown due to human activities [28, 29]. Rocks contain heavy metals because they are present in both primary and secondary minerals as trace constituents [30].

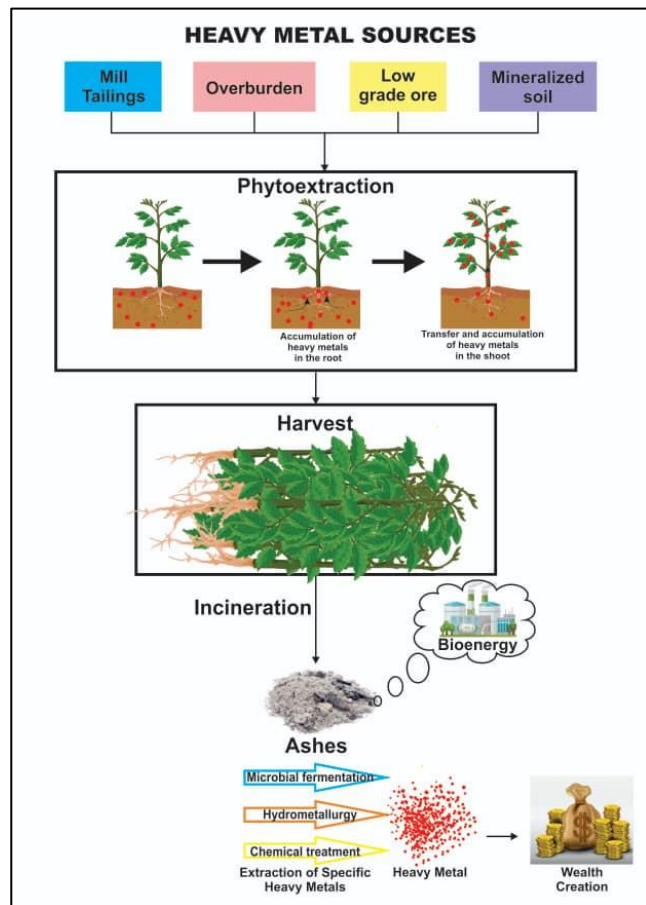


Figure 1: Schematic summary of phytomining.

Heavy metals and metalloids are continuously released into the environment at different rates and amounts from natural materials due to their existence in minerals and the breakdown of minerals brought on by chemical weathering [31]. From the soils, heavy metals eventually enter groundwater and surface waters through leaching and surface runoffs [29, 32]. Heavy metals can also reach the aquatic environment from atmospheric deposition as well as human activity brought on by mining waste, home sewage, and industrial effluents [29, 33]. The environment contains these heavy metals such as Cr, As, Ni, Cd, Pb, Hg, Zn, and Cu in varying degrees in soil, water, food and even the air [34]. When these heavy metals exceed the permissible levels, they alter soil characteristics and damage plants, which lowers crop yield [35]. Heavy metals cause oxidative stress in cells, which damages organelles, and they are very poisonous and have a propensity to accumulate in organisms [36]. Since heavy metals are persistent environmental contaminants, it is difficult to remove them after they have entered ecosystems [37]. Instead, they typically travel through the environment through processes like adsorption, desorption, and leaching [38]. There is therefore an urgent need for some efficient environmental management techniques to reduce the threats to ecosystems and human health because of these increased accumulations in these different habitats. Controlling the risk of heavy metal contamination and lowering the dangers of heavy metal exposure requires sustainable methods for proper waste disposal, and heavy metal recovery. This review provides a detailed solution to the total elimination of heavy

metals from polluted sites without further endangering the ecosystem. Potential biorefineries using phytomining techniques could be supported by the circular bioeconomy of heavy metals, thus making appropriate the reuse of high-value heavy metals without producing secondary damage [39, 40].

2. Effects of some heavy metals on plants

Plants need heavy metals as vital micronutrients, but it may become toxic when it exceeds a certain threshold [41]. Heavy metals toxicity causes high accumulation of reactive oxygen species (ROS) and methylglyoxal (MG) [42]. This can cause peroxidation of lipids, oxidize proteins, inactivate enzymes, damage DNA, and/or interact with other essential components of plant cells [42]. By producing reactive oxygen species (ROS), which impede the majority of cellular activities at various metabolic levels, exposure to heavy metals (HMs) may cause a variety of harmful effects in plants [43]. Oxidative stress results from an increase in ROS production in cells [44]. ROS are extremely reactive molecules that are significantly harmful to all sorts of cells and cell forms [45]. Plants, which are subjected to biotic and abiotic stresses, produce, scavenge and utilize ROS as an adaptive mechanism of overcoming such stresses [46] which can serve both positive and negative purposes. They mediate signal transduction that helps maintain cellular homeostasis and promotes plant acclimatization to stressors [47]. When their production surpasses threshold levels, they cause oxidative stress in plants [47]. Thus, plants use antioxidants to keep the balance between the production of ROS and their quenching [48]. It must be noted that in plant's biological system, heavy metals are either redox active or inactive metals in the plant cells. Free heavy metal cations, whether redox active or inert, may play a major role in the development and maintenance of oxidative stress in mitochondria [49]. For example, Cu, Cr, and Mn are known to partake in plant's redox reactions while Ni, Al and Zn, are non-redox active metals [50]. Plants are capable of using their antioxidative defense system to control ROS levels in both non-stress and stress settings, such as exposure to excess metals [51]. Excessive quantities of heavy metals cause abscisic acid (ABA) to accumulate and impact root functioning on several levels [52]. And according to research, plants use a network of pre-existing signalling cascades to "report" cellular homeostasis abnormalities to the nucleus, which will then trigger a wide range of reactions [52]. Multi-metal hyperaccumulators could be used in the situation of multi-metal contaminated soils. For example, field trials showed that the *Pelargonium Attar* cultivar has the capability to extract Pb, Zn, Cu, Cd, and As from a heavily polluted soil without exhibiting any signs of morphophytotoxicity [53]. To resist metal toxicity, plants have unique cellular mechanisms such as vacuolar compartmentalization and chelation of metals [54]. Sequestration within vacuoles play a pivotal role in regulating heavy metal balance in plants [55]. This rely on vacuolar proton pumps like V-PPase and V-ATPase, alongside tonoplast transporters energized by the proton electrochemical gradient as well as ATP-fueled primary pumps [55]. Common structural alterations in the vacuoles of plants exposed to heavy metal stress highlight the role of vesicle transport in this sequestration mechanism [56, 57]. Amino acids are essential for sequestering, translocating, and detoxifying heavy metals in plants [58, 59]. The use of amino acid-based chelates in place of traditional organic chelators or fertilizers serves as an economical, potent, and evidence-based strategy to enhance agricultural productivity, photosynthetic efficiency, and nutrient quality for crops cultivated in heavy metal-polluted environments [60].

Heavy metals inhibit plant growth, dry matter buildup, and yield by disrupting physiological processes such as photosynthesis, nutrient absorption and gaseous exchange [76-78]. Photosynthesis is hampered by heavy metal stress-induced Mg^{2+} substitution *in vivo* in the chlorophyll by heavy metals [79]. Also, alleviated seed germination, decreased plant biomass, decreased root elongation and inhibition of chlorophyll production are all consequences of heavy metal deposition in plant tissue [53]. Since the leaf area is the primary organ for transpiration, the presence of Pb impacts a number of plant mechanisms [80, 81].

Table 1: Hyperaccumulators (both natural and engineered) suitable for phytomining applications.

Heavy metal	Plant	Source
Zn	<i>Arabidopsis halleri</i> , <i>Thlaspi</i> , <i>Brassicaceae</i> , <i>Sedum alfredii</i>	[61, 62]
Cd	<i>Solanum nigrum</i> , <i>A. halleri</i> , <i>T. caerulescens</i> ,	[63 - 65]
Ni	<i>B. coddii</i>	[66, 67]
In, Ag, Pb, Cd, Cu, and Zn	<i>Eleocharis acicularis</i>	[68]
Zn	<i>Myriophyllum aquaticum</i>	[69]
Zn	<i>Thlaspi caerulescens</i>	[70, 71]
Au	<i>Brassica juncea</i>	[72]
Ni	<i>Odontarrhena chalcidica</i>	[73]
Ni	<i>Alyssum murale</i>	[74]
Ni	<i>Phyllanthus rufuschaneyi</i>	[75]

This includes the reduction of leaf growth and surface area, which in turn reduces the plant transpiration process [80, 81]. The effect of Cd on leaf shape was the indirect cause of *P. divaricata's* photosynthetic efficiency being inhibited under high Cd concentrations in a study by Hu et al. [78]. Heavy metal (HM) ions, in addition to extreme temperatures, reactive molecules and other stresses interfere with the folding of freshly synthesized proteins and also cause pre-existing plant proteins to misfold [82, 83].

3. Mechanisms of heavy metal chelation in plants

There are numerous options for dealing with the plant's metal pollution issue. Some plants escape metal contamination by suppressing its entry into their bodies through defensive morphological adaptations [84, 85]. On the other hand, some successfully compartmentalize uptaken heavy metals in intracellular organelles, resulting in a limited toxicity reaction [55, 86]. Chelation is a chemical phenomenon in which a central metal atom or ion links with a ligand, resulting in the creation of a stable, cyclic coordination compound [87]. And it is the primary detoxification mechanism deployed by plants to withstand high levels of heavy metals [88]. Phenolic antioxidants perform important role in the distribution and binding of metals, as well as heavy metal detoxification in the plant [89]. Additionally, it's likely that multiple mechanisms work together to lessen a given metal's toxicity [90]. In general, plants' response to high environmental concentrations of heavy metals tries to prevent the accumulation of excess metal levels in the cytosol, which would delay the onset of poisoning symptoms [90].

3.1. Mechanism of mycorrhiza in binding to cell wall and extracellular exudates

Fungi have some excellent qualities that allow them to tolerate heavy metal stress and mitigate its negative effects on both the plant growth and the environment [91]. Mycorrhizal fungi are crucial for metal accumulation and tolerance because they cover the root system of numerous plant species that grow in soil contaminated with metals [92]. *Arbuscular mycorrhizal* (AM) fungus have developed a number of defense mechanisms against almost all harmful metals when metal ions are present in excess usually through plasmid encoded means [93]. The ability of AM fungus to accumulate heavy metals may vary, and *Glomus mosseae* species have been found to have high metal accumulating capacity [94]. Using Redundancy Analysis (RDA), researchers found that AM symbioses made heavy metal accumulation more effective [95, 96]. Although, Arbuscular mycorrhizal fungi (AMF) are promising biotechnological technique for enhancing the resistance of plants to heavy metal-contaminated soils and the effectiveness of phytostabilization [97]. Plants exhibit a variety of changes as a result of AMF's influence, including an increase in antioxidant response and changes in root shape, and their symbiotic relationships promote plant growth by improving nutrient acquisition [91]. They also serve as a biofertilizer for plants and a biosorbant for heavy metals, enhancing plant performance through distinct intrinsic molecular pathways [98, 99]. Microorganisms, particularly fungi, also have a protective function in plants, increasing defense system responses and playing an important role in conditions involving soil iron deficiency or phosphorus

solubilization [100]. For instance, in the study of Adeyemi et al. [101] arbuscular mycorrhizal fungi (AMF) was discovered to be more tolerant in decreasing heavy metal toxicity in soybeans grown in contaminated soils. This was achieved by retaining the heavy metals in the roots, thus reducing translocation of Pb, Zn and Cu. Plant-associated microorganisms, such as AMF, can thus boost plant growth in both natural and severe environments [102, 103].

3.2. Efflux pumping and reduced uptake of metals at the plasma membrane

Membrane transporters known as efflux pumps are responsible for the particular export of harmful substances from cells [104]. One could argue that the first "living" structure that heavy metals can harm is the plasma membrane of plants. Heavy metals can quickly alter plasma membrane function, as evidenced by increased cell leakage when metal concentrations are high [105]. The major facilitator superfamily (MFS), small multidrug resistance (SMR), ATP-binding cassette (ABC transporter), resistance nodulation division efflux pumps (RND HAE), and the multidrug and toxic compound extrusion (MATE) transporters are the five families into which these efflux pumps are divided [106]. The interaction between plants and microorganisms especially bacteria in heavy metal contaminated environment facilitate plant's heavy metal resistance [107]. Efflux pumps maintain the bacterium's internal balance by expelling harmful substances, quorum-sensing signals (autoinducers), biofilm-forming compounds, and virulence factors. (Figure 2). As a result, efflux pumps can provide heavy metal resistance by exporting metal ions [108].

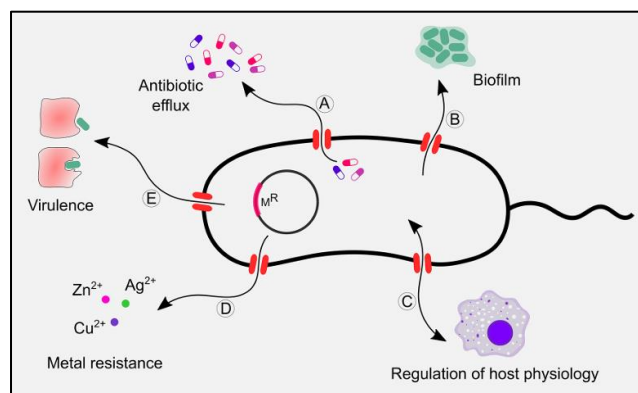


Figure 2: Diagram illustrating the biological roles of bacterial efflux pumps. These pumps are crucial for (a) expelling antibiotics, (b) promoting biofilm development, (c) modulating host physiology, (d) conferring resistance to metals, and (e) enhancing virulence [108].

Copper (Cu) and silver (Ag), highly toxic to bacterial cells, have been noted for potential beneficial roles in the initial phases of biofilm development [108, 109]. The CusABC pump, a heavy metal RND efflux pump (HME-RND), reduces their intracellular levels [110], which appears essential for bacterial survival and maintaining biofilm integrity.

Examination of plasma membrane vesicles from the roots of Cu-

of misfolded or denatured proteins [150, 151]. This help to maintain cellular homeostasis. By favorably controlling the system of antioxidant enzymes, HSP also detoxifies reactive oxygen species and improves membrane stability [152, 153]. Among main antioxidants, glutathione (GST) supports reduced glutathione (GSH) to minimize metals/metalloids toxicity by conjugating with them [154]. The proportion of reduced to oxidized glutathione (GSH/GSSG) is a key soluble redox pair critical to bioenergetics and the metabolism of reactive oxygen species (ROS) [155].

This significantly impacts many processes through which plants adapt to environmental stresses and variations, including exposure to major heavy metals and metalloids [155]. Plants control the amounts of ROS by an assortment of enzymatic and non-enzymatic antioxidants [47, 156]. ROS also regulate the expression of a lot of genes, thus controlling numerous activities, including growth, cell cycle, programmed cell death (PCD), abiotic stress responses, pathogen defines, systemic signalling, and development [157]. Thus, the role of signalling molecules in altering antioxidant defences provides unique insights into techniques for increasing plant resilience [158].

Recent studies on plants showed that glutathione (GSH) and its related enzymes, such as glutathione S-transferase, dehydroascorbate reductase, glutathione reductase, glutathione peroxidase, glyoxalase I, and glyoxalase II, work together to protect against damage from ROS and methylglyoxal (MG), while also helping to remove and manage heavy metals (HMs) [42, 159].

3.6. Metal binding to cell wall

The plant cell wall represents a material with remarkable mechanical performance and which is utilized as a model for the synthesis of materials with better qualities [160]. Strains and stresses in the growing cell wall are increasingly recognized as feedback to cellular mechanisms that controls the cytoskeleton, auxin transporter vesicular trafficking, and the cellular machinery involved in cellulose deposition [161]. It is well recognized that this cell wall accumulates harmful divalent and trivalent metal cations both when the cell absorbs them from the surroundings and when they are finally sequestered from the protoplast [162]. The cell wall's pectic sites, histidyl groups, and extracellular carbohydrates immobilized heavy metals and prevented them from entering the cytoplasm [163]. Pectins can enhance cell wall rigidity during sudden deformations, but their viscous nature leads to rapid dissipation of pectin-related stresses, transferring forces to more inflexible cell wall component [161]. The structural variety of pectins, along with the diverse array of enzymes involved in their synthesis and modification, are essential for enabling precise and adaptable cell wall restructuring across various cell types and environmental conditions [164-166]. Research has shown that the cell wall's chemical characteristics influence metal uptake as well as metal tolerance [160]. Nishizono et al. [167] in a study found that the cell wall of *Athyrium yokoscense* contributes to copper tolerance by binding excess copper ions. According to studies, higher pectin content and demethylation boosted Cd chelation onto root cell walls while decreasing Cd levels entering organelles [168-170]. Yu et al. [169] found that abscisic acid might mitigate Cd toxicity by boosting Cd uptake, improving Cd binding to the root cell wall, and triggering defense mechanisms. Pectinous cell wall thickening is a common plant defensive response for dealing with Pb [171]. Studies has shown that in copper-tolerant plant cells, the cell wall acts as a barrier, preventing copper from interfering with cell metabolism [172]. Thus, at this interface, copper binds with organic compounds to form a complex, which is then discharged into the surrounding medium.

3.7. Mechanism involved in the compartmentation of metals in the vacuole via tonoplast - located transporters

Tolerance plants have evolved a variety of defense mechanisms that are activated upon exposure to heavy metals in order to prevent the negative effects of heavy metal toxicity. Sequestration or accumulation of poisonous heavy metals in a cellular compartment like the vacuole or

apoplast, which helps in the detoxification, that is, transformation into nontoxic forms [173].

Tonoplast transporters and their roles in heavy metal homeostasis, calcium signaling, guard cell motions, cellular pH homeostasis, nitrogen storage, and salt tolerance have been identified by recent research, including proteome investigations for a number of plant species [174]. Although heavy metal ions disrupt the cellular and molecular processes involved in the traffic of the membrane, the structure and makeup of membranes let them withstand the impacts of heavy metals [56, 175]. This offers more resources for future advancements in phytoremediation techniques. Plants have developed protective strategies against Cd toxicity, such as synthesizing phytochelatin and metallothioneins,

sequestering metals in vacuoles, and increasing antioxidant enzyme activity to mitigate Cd-related stress [176]. It should be mentioned that vacuoles are the largest organelles in plants [177]. This makes them ideal for storing metal ions and chemical compounds, as they occupy more than 90% of the cellular volume in vegetative tissues [177]. Therefore, the "buffering pool" function of vacuolar sequestration capacity (VSC) in plants is to dynamically mediate long-distance metal transport [178]. A system known as "overflow" takes over when exposed to large concentrations of hazardous metals, notably when a metal's VSC is depleted, and the excess metal undergoes long-distance root-to-shoot transfer [179]. Park et al. [180] identified two ABC-type transporters, AtABCC1 and AtABCC2, which are crucial for arsenic detoxification. These transporters have also been found to be significant vacuolar transporters that provide tolerance to cadmium and mercury, in addition to their role in arsenic detoxification [180, 181]. For instance, rice (*Oryza sativa*) uses phytochelatin and vacuolar sequestration to detoxify cadmium, while root exudates like oxalate reduce arsenic uptake [182].

4. Effects of climatic conditions on the efficiency of phytomining strategies

Global warming poses a grave danger to plants of different species across the globe [183]. It manifests through escalating temperatures, shifting rainfall regimes, more frequent severe weather occurrences, and higher levels of atmospheric ozone (O₃) and carbon dioxide (CO₂) [184]. All these severely endanger biodiversity and the balance of ecosystems [185, 186].

4.1. Temperature

Temperature affects plant physiology, enzyme activity, and metal mobility in soils [187], which can either enhance or hinder phytomining. The impact of temperature on plant growth and development varies by species, and under escalating climate change, air temperatures are more likely to surpass the optimal range for numerous species [188]. With rising global temperatures, alterations in soil temperature and moisture levels could influence the mobility and chemical reactions of heavy metals within the soil [189]. Heat stress above 30 °C hampers uptake, and temperatures below 20 °C hinder metabolism, but around 27 °C, phytoextraction is optimized by enhancing biomass growth and metal transport [190]. Thus, impaired function from heat stress, decreased heavy metal absorption, and suppressed microbial and enzymatic activities [191]. Optimal temperatures around 27 °C support efficient heavy metal uptake by hyperaccumulator plants, as they promote growth and metabolic processes involved in phytoextraction [192]. According to Kudo et al. [193], Cd movement from roots to shoots in *Arabidopsis halleri* ssp. *gemmifera* was strongly influenced by temperature, with the highest translocation rate observed at 25 °C. Also, atmospheric temperature can influence soil moisture levels, which may alter organic matter decomposition and, consequently, the availability of heavy metals within the soil ecosystem [194].

4.2. Precipitation and water availability

Intense precipitation may cause metals to dissolve and migrate

downward through the soil profile, thereby elevating their levels in the soil liquid phase and promoting greater absorption by plants [195]. On the other hand, dry conditions may limit the mobility of metals, thereby limiting their availability for plant uptake [195, 196]. Adequate water availability is essential for plant growth and metal uptake, as drought stress reduces biomass production and limits the plants' ability to accumulate metals, thereby lowering the efficiency of phytomining. But excessive flooding may disrupt ecosystems and dilute metal concentrations and reduce heavy metal bioavailability by accelerating the migration process of heavy metals [189]. Variable patterns, such as drying-rewetting cycles, release bound metals, increasing their inhibitory effects on soil enzymes and plant health [197, 198]. In seasonal snow-covered areas like Northeast China, altered precipitation leads to higher metal contents in tillage layers, elevating pollution risks but possibly aiding extraction in suitable plants [199, 200].

4.3. Elevated CO₂ levels

Elevated atmospheric CO₂ levels boost photosynthetic carbon fixation, leading to enhanced carbohydrate synthesis and storage, which can result in increased biomass, yield, and carbohydrate output under optimal environmental conditions [201, 202]. In multiple Free-Air CO₂ Enrichment (FACE) studies involving diverse plant species, exposure to heightened CO₂ levels between 475 and 600 ppm boosts leaf photosynthesis rates by 40% on average [203]. Plants primarily capture carbon through photosynthesis, converting atmospheric CO₂ into organic compounds such as carbohydrates [204]. This serves as both structural elements of biomass and energy sources for soil microbial communities [205]. However, these benefits can be offset by accompanying warming or drought, leading to variable metal bioavailability and multi-stress conditions that reduce plant tolerance [206, 207]. But genetic modification has produced diverse transgenic plants with introduced genes linked to stress adaptation, demonstrating significant resilience to both drought and heavy metal exposure [122]. In aquatic-adjacent systems, higher CO₂ causes acidification, increasing metal solubility from sediments [208], which could indirectly benefit coastal phytomining. As carbon dioxide levels rise, the pH in the water body becomes higher, causing a shift in the chemical forms of heavy metals [189].

4.4. Humidity and other interactive effects

Plants cultivated in environments with elevated relative air humidity exhibit dysfunctional stomata that fail to close when exposed to darkness, abscisic acid (ABA), or drying conditions. [209, 210]. Broader climate change interactions, including combined warming and altered precipitation, can alter soil properties (e.g. pH and structure) and rhizosphere microbe-metal interactions [189, 211, 212], complicating phytomining. For instance, in ultramafic soils suitable for nickel phytomining, climate change may reduce viable areas for hyperaccumulators like *Alyssum murale* by up to 48% by 2070 in regions like Albania, limiting overall strategy deployment [213]. Sunlight exposure, tied to weather patterns, is also crucial, with sufficient levels required for optimal performance.

Overall, while some climatic shifts (e.g. moderate CO₂ elevation) can improve efficiency through increased growth and metal availability, extreme changes often pose challenges by inducing plant stress and reducing suitable habitats. Site-specific factors like soil type and plant species selection are critical for mitigating these effects, and further research is needed for predictive modeling in phytomining applications.

5. Bioeconomy of heavy metals

Toxic plant biomass derived from phytoremediation can be recycled and repurposed using the circular bioeconomy strategy to create various circular bioeconomy byproducts, including charcoal, biogas, bioethanol, and biodiesel [40]. Through a variety of processes, including anaerobic digestion, nanomaterial synthesis, incineration, gasification, and

pyrolysis, the residues from phytoremediated biomass can be transformed into gaseous (biogas/methane), liquid (biodiesel, bioethanol, and bio-oil), or solid energy forms (biochar, hydrochar) [214]. The key mechanisms for converting biomass into biofuels are summarized in Figure 4. For example, crop residue (CR) is regarded as a sustainable and renewable carbon-rich resource for a range of bio-based products, energy sources, and fuels [215]. Recently, phytoextraction has become the most popular and effective way to clean up polluted soil. Nanomaterials can help the phytoremediation system by making pollutants more available to plants, encouraging plant growth, and directly getting rid of pollutants [216]. In order to properly remediate heavy metal-polluted soils, plants that can produce large amounts of biomass and tolerate numerous heavy metals are needed [217, 218]. Plants grow extremely slowly and produce little biomass, therefore the process takes a long time. Both plants and rhizosphere microorganisms, such as plant growth-promoting bacteria and arbuscular mycorrhizal fungus (AMF), can be used to further improve this plant-based remediation approach [219]. With the aid of plant growth-promoting rhizobial (PGPR) bacteria and arbuscular mycorrhizal fungus (AMF) in their rhizospheres to boost biomass output, vetiver grass seems to be the answer to achieving this aim [220]. In Cd-contaminated soil, *Trifolium repens* grew more when TiO₂ nanoparticles (NPs) and PGPR were applied together. This also improved the plant's ability to absorb and accumulate Cd [221]. Therefore, there is a lot of potential for using PGPR, nanomaterials, and plants uniquely to remediate soil. According to recent studies, the use of plant growth-promoting rhizobacteria (PGPR) for bioremediation activities is becoming more and more significant among the various microorganisms because of their unique capacities to break down and detoxify pollutants as well as their beneficial impacts on boosting plant growth [222]. This can go a long way in boosting bioeconomy. Table 2 shows harvested heavy metal energy output from phytomining of some plant species. The combination of phytoextraction and thermochemical biofuel production can enhance phytomining through the recovery of heavy metals and the production of bioenergy [223].

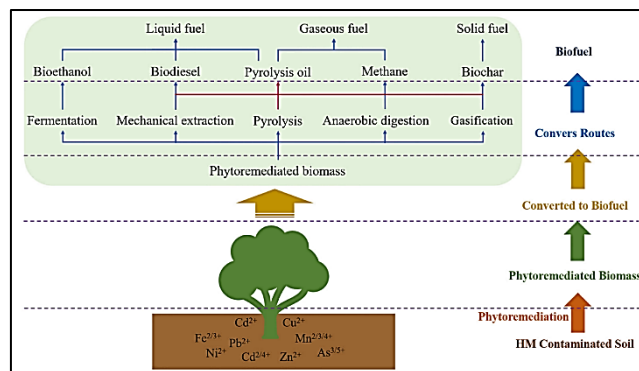


Figure 4: Primary methods for transforming biomass into biofuels [214].

5.1. Anaerobic digestion (AD)

According to studies, anaerobic digestion offers a lot of potential for getting rid of contaminated plants and could be a way to employ the resources of plants used in restoration [227]. According to Cao et al. [227] using *Oenothera biennis* L. in remediation with high Cu levels (100 mg kg⁻²) not only speed up anaerobic digestion and made it easier than using plants with low Cu levels, but it also increased the amount of methane in biogas. However, researches indicates that heavy metals have impact on the activity of microorganisms involved in the digestion of biogas [228 - 230]. The study by Alrawashdeh et al. [230] indicated that when the concentrations of Fe, Zn, Cr, Pb, Ni, and Cu are less than 2.9, 0.335, 1.211, 0.297, 0.082, and 1406.25 mg/L, respectively, they can safely enhance the anaerobic digestion (AD) process (with regard to

Table 2: Phytomining and energy output profit.

Plant	Harvested Metals	Phytomining and Energy output Profit	Source
<i>Aeolanthus biformifolius</i>	Cu	USD 1592 ha ⁻¹	[27]
<i>Streptanthus polygaloides</i>	Ni	USD 513 ha ⁻¹	[8]
<i>Berkheya coddii</i>	Ni	11,500 AU\$/ha/harvest	[224]
<i>Brassica juncea</i>	Au	26,000 AU\$/ha/harvest	[224]
<i>Haumaniastrum robertii</i>	Co	6723 USD / ha/ annum	[27]
<i>Streptanthus polygaloides</i>	Ni	USD 513 ha ⁻¹	[27]
<i>Alyssum murale</i>	Ni	Biomass yield of 9 t ha ⁻¹ (USD 1,055)	[225]
<i>Alyssum murale</i>	Ni		[226]

increasing biogas and methane production and increasing total chemical oxygen demand (TCOD), soluble chemical oxygen demand (SCOD), volatile solids (VS), and polyphenols removal). Controlling the amount of heavy metals throughout the digestion process is therefore advised in order to produce biogas [231]. Lee et al. [232] demonstrated that the presence of endogenous heavy metals in crop residues did not impede the anaerobic bacterial activities for the formation of methane gas. According to their findings, anaerobic digestion may be a viable substitute disposal technique for phytoremediated wastes from heavy metal-contaminated areas in terms of energy recovery potential. A study by Zhang et al. [233] using sludge from anaerobic digestion showed excellent resistance to heavy metals and may be a viable treatment solution for wastewater that contains heavy metals.

5.2. Nanomaterial synthesis

Engineered nanoparticles have been found to significantly lessen the negative effects of heavy metal exposure on various plant species. For example, nanoscale particles can markedly alleviate the detrimental impacts of heavy metal toxicity through bolstering enzymatic and non-enzymatic antioxidant systems, and facilitating metal detoxification mechanisms [234, 235]. In contrast to other disposal methods, nanoparticle synthesis can completely eliminate phytoremediation biomass [236]. The feasibility of employing hyperaccumulator biomass in the phytoremediation of cadmium has been shown by the manufacture of nickel oxide nanoparticles using an extract from *Lactuca sativa* L. [237]. Selecting the appropriate plant species and nanoparticles for toxin absorption is also essential for the high-quality and effective cleanup procedure.

5.3. Incineration

One practical method for treating the plants that are enriched with heavy metals is incineration. Incineration of plant tissues produces a 'bio-ore' with high residual metal level, which can then be smelted [238]. As thermal processes, such as fluidized bed incineration, appear to be an effective way to dispose of phytoextraction crops, willow trees composition permits them to burn in a fluidized bed [239]. The first method to increase the amount of heavy metals that are volatilized in the thermal utilization of contaminated biomass is to raise the operating temperature of the hot cyclone. Co-incineration with other fuels that contain more sulfur and chlorine can also help increase the amount of metals that are volatilized [239].

5.4. Gasification/ Pyrolysis

Gasification is a heat-driven chemical reaction that occurs in an oxygen-limited setting to transform carbon-rich substances, such as biomass [240, 241]. Compared to incineration under oxidizing settings, gasification (also known as pyrolysis) under reducing conditions proved a more effective way to improve volatilization and, consequently, recovery of Cd and Zn from plants [242]. Biomass gasification and pyrolysis are preferred over combustion because they lower fly ash levels [243]. The gasification process involves incomplete combustion of biomass at high temperatures (700-1200 °C) [244]. Biomass

gasification thus converts diverse biomass fuels into combustible gases (producer gas) in the presence of a restricted supply of oxygen or appropriate oxidants like carbon dioxide (CO₂) or steam [245]. Advanced gasification of biomasses can be utilized to promote sustainable development, thereby decreasing the current dependence on non-renewable energy resources [246].

Pyrolysis is receiving increasing attention in recent years as a potentially effective and adaptable method of turning biomass into useful resources. Since it avoids complex processes and dangerous or flammable substances, the pyrolysis of biomass tainted with heavy metals, using catalytic effects from metals like copper, nickel, zinc, and cobalt, to produce carbon-supported metal nanoparticles is more cost-effective and environmentally friendly [247]. Lignocellulosic biomass (LB), a renewable carbon resource, can generate green chemical products during the pyrolysis process, making it a valuable resource for environmental remediation and energy recovery [248].

6. Process of metal recovery in phytomining

Hyperaccumulator plants, which accumulate valuable metals in quantities similar to conventional metal ores, can be considerably enhanced through incineration. There is a motivation to recover these metals as valuable products to help offset the expenses of handling contaminated biomass from polluted soils, mine residues, and industrial byproducts, while also creating income. The dried biomass is burned and smelted, enabling the processing of resources that would otherwise remain unused. And in some cases, such as hydrothermal carbonization (HTC), metals can be recovered without going through the drying process [249]. Studies have suggested that the adsorption-pyrolysis procedure is viable for recovering Cd and Cu in solution by concentrating metals in the bio-ore by predominantly the redox reaction of Cd and Cu salts, as well as element volatilization [250]. While hyperaccumulators excel at concentrating heavy metals, their low biomass production reduces the total metal removal capacity, and their limited survival in harsh environments like minefields restricts their practical application [251].

Different methods such as microbial fermentation, hydrometallurgy and chemical treatments can be utilized for extracting heavy metals from harvested biomass [252-254]. Studies have shown that *Aspergillus niger* and *Penicillium simplicissimum*, are efficient in the recovery of heavy metals [255]. Rasoulnia and Mousavi [255] demonstrated that the metal extraction efficiency of *Aspergillus niger* surpassed that of *Penicillium simplicissimum* for V and Ni. Filamentous fungi, capable of producing organic acids to dissolve metal ions from solution, can be used for recovering valuable metals under specific conditions such as pH, temperature, substrate type, and incubation duration [253]. Zhang et al. [252] was able to extract sulfate and ammonium nickel double salt hexahydrate from *Alyssum murale* biomass ash hydrometallurgical process.

6.1. Ashing

Ashing is a thermal transformation method that converts gathered biomass into a reduced amount of ash. According to Krisnayanti et al.

[256], the ashing temperature for polluted biomass ranges from 300 to 550 °C. Most dry plants are burned to create ash with a high Ni content, which is subsequently leached into an aqueous solution [257]. For instance, Zhang et al. [258] found that the best conditions of biomass combustion for Ni recovery were ashing at 550 °C for a duration of 3 hours. Biomass in its dry form may be processed similarly to activated carbon, then incinerated within a clay vessel utilizing forced air as a supplementary oxidizing agent; thorough combustion of every organic component in the biomass ought to produce a weight decrease exceeding a factor of 10 [256].

Precipitation is used to recover Ni, which is then converted into salts or oxide. The energy generated by biomass incineration might be valorized [259], making phytomining useful for both metal recovery and energy generation. Combining phytoremediation with the valorization of plant biomass and the extraction of metals presents viable and sustainable options over the outright discarding of contaminated plant material which results in secondary contamination [260]. Pyrolysis of biomass serves as a critical energy transformation process that unlocks diverse valorization pathways for biomass laden with heavy metals [261].

6.2. Pyrometallurgy

Pyrometallurgy involves the thermal chemical treatment of metals at elevated temperatures, incorporating processes like calcining, roasting, smelting, and converting [257, 262, 263]. Smelting heavy metal biomass and bio-ores entails heating them to high temperatures with a reducing agent to extract metals, a technique used in pyrometallurgy to remove metals such as iron, copper, and zinc from ores [264]. “Bio-ores” contain essentially no sulfur, and processing them in a smelter consumes far less energy compared to sulfide ores [265]. A “bio-ore” exhibits a substantially higher metal concentration than traditional ores, thus requiring considerably less storage volume; furthermore, its negligible sulfur levels ensure that smelting produces minimal contributions to acid rain [11].

A study by Boominathan et al. [266] used a bench-scale horizontal tubular furnace to produce nickel-enriched bio-ore from dried biomass of nickel hyperaccumulator species (*Alyssum bertolonii* and *Berkheya coddii*). This study reported that both the overall mass reduction during heating and the nickel concentration factor were markedly reduced under nitrogen purging conditions, underscoring the critical role of oxidation reactions in nickel enrichment. Nickel metal was easily extracted from the ash of *Alyssum* biomass by loading 500 kg of the ash into a “revert bag” and introducing it into an electric arc furnace [226].

6.3. Hydrometallurgy and biohydrometallurgy

Hydrometallurgy refers to the water-based chemical extraction and refinement of metals, performed at comparatively mild temperatures, encompassing leaching, solution purification and concentration, and final metal recovery [257, 267]. On the other hand, biohydrometallurgy provides a straightforward and efficient approach to recovering precious metals (e.g. Cu, Au, Zn, Ni etc.) from low-grade ores, rocks, and waste streams by harnessing the metal-dissolving and metal-concentrating capabilities of microbes [268-270]. Zhang et al. [271] developed a technique for synthesizing a nickel salt, ammonium nickel sulfate hexahydrate, from the biomass of the hyperaccumulator plant *Alyssum murale*. The process involves drying and incinerating the biomass, removing potassium by rinsing the ash with purified water in a cross-current method, and extracting nickel through acid leaching. A bispicolylamine-based chelating resin can be used to extract Ni from hyperaccumulator plant bio-ores and very acidic bio-ore leachate [272]. Hydrometallurgy and biohydrometallurgy have been discovered to deliver markedly efficient higher metal recovery yields than pyrometallurgy [273, 274]. Certain biohydrometallurgical techniques for metal extraction and site remediation demand lower energy inputs than conventional approaches, thus potentially lowering industrial expenses while bypassing net smelter royalties, refining fees, and impurity-related penalties tied to smelting operations [273].

6.4. Hydrothermal carbonization (HTC)

Hydrothermal carbonization (HTC), a type of thermochemical procedure that uses subcritical water at an average temperature range (160-260 °C), can transform biomass into valuable carbon-enriched hydrochar [274, 275]. Lee and Park [276] investigated transforming heavy metal-containing sunflower wastes into hydrochar, a carbon-rich substance that might be used as an alternate solid fuel. The HTC method reduced heavy metal concentrations in raw sunflower biomass. HTC has the considerable advantage of not requiring dry starting material and not requiring large energy input to remove water by evaporation [277].

7. Economical perspective of phytomining

Demand for the key metals needed by the contemporary society to make goods in order to meet up with the current technological trend has expanded considerably over the last few decades [278]. This has resulted in increase of heavy metal extraction to supply this demand, thereby leading to a depletion of the existing ore grade [278]. Decline ore grades has been confirmed by several studies [279-282]. Currently, scientists have predicted that some heavy metal, including Zinc, Silver, and Gold, will be exhausted over the next 50 years if the present consumption rate persists [283].

Some metals including heavy metals play critical role in shifting from today's fossil fuel-dependent society to a sustainable, non-fossil-based future supporting green energy technologies like wind turbines and electric vehicles (EVs) [284]. The future demand for EVs appears to elevate the load on the geological reserves of metals used in the manufacture of components of electric vehicles [285, 286]. The current (2025) prices per metric ton are high for Au, Co, Cu and Ni. Nickel, cobalt, and platinum group metals hold immense value owing to their wide array of uses and critical contribution to sustainable technologies [287]. Therefore, based on the current and future projections, phytomining may be feasible for Au, Co, Cu, and Ni. According to the London Metal Exchange (LME), copper (Cu) prices are approximately US\$9,884.00 per ton as of March 27, 2025, while nickel (Ni) prices are around US\$15,785.00 per ton. The cost of a metric ton of cobalt as of March, 2025, is US\$29,742.54. The metal Co can be used as alloys and superalloys [288]. It is used in the manufacture of lithium-ion batteries [289], which are a significant component of electric vehicles.

Mine waste, known as tailings, comes from mining around the world and usually includes clay, sand, crushed rock, and sometimes water, along with large amounts of leftover heavy metals [290, 291] that are too small or difficult to extract using regular methods. The global total volume of metal-containing mine tailings is estimated to be over 18 billion m³/year [292]. A research project by Mohan [22] revealed that 33 million tonnes of accumulated tailings, with gold concentrations of 0.7–0.8 mg/kg, could serve as a viable resource for phytomining, potentially yielding 24 tonnes of gold. The Kolar Gold Fields (KGF) in India span 12,500 acres and hold about 33 million tonnes of leftover material from past gold mining [293], which means it could be a good place for phytomining. Additionally, phytomining for gold could offer a practical approach to managing tailings at artisanal and small-scale gold mining (ASGM) sites, where plants absorb residual gold into their aboveground biomass [256]. Phytomining of heavy metals from mine tailing will prevent them from being leached down into the groundwater system. Mine tailings, often lacking sufficient organic matter or macronutrients, may hinder the growth and survival of various organisms, including bacteria, resulting in unvegetated areas [294, 295]. And for phytomining to be effective might require the addition of organic fertilizer to enhance growth [296, 297].

Large-scale commercial phytomining of nickel is actively taking place in Europe (e.g. the Balkans and France) with Brassicaceae species, notably *Odontarrhena chalcidica* (previously *Alyssum murale*), while significant trials are ongoing in Malaysia using *Phyllanthus rufuschaneyi* [298]. The majority of nickel-hyperaccumulating plants can concentrate over 1,000 mg of nickel per kilogram in their shoot dry biomass [299].

A recently documented nickel phytomining operation in Malaysia

was projected to produce an annual production of 170–280 pounds of nickel per acre, with a gross profit of \$3800 per acre [300]. In regions with low fertility and low farmer productivity, phytomining agroecosystems can provide a new, fully integrated agromining agriculture that might span hundreds of km² and improve soil resource efficiency [301]. Originating from ultramafic rocks like serpentinite and peridotite, ultramafic soils are devoid of plant nutrients, unsuited for agriculture, and extremely concentrated in heavy metals such as Ni, Cr, and Co [302]. Though laterite and ultramafic soils may contain elevated nickel levels, they typically support limited plant diversity because of a low calcium-to-magnesium ratio and deficient phosphorus content in the soil [301, 303]. For instance, the quantity and extent of mine or ore processing waste at the Sudbury smelters increased gradually, yet these areas remained unproductive due to infertility and elevated soil acidity from sulfide oxidation, which heightened nickel solubility and plant toxicity [304–306]. Fertilization and limestone treatment resulted in revegetation on these sites [307]. Many among the world's greatest surface exposures of ultramafic bedrock are found in Indonesia (the Sulawesi and Halmahera Islands), where successful lateritic nickel mining activities are located [299].

The Barberton Greenstone Belt (BGB) is a geologically significant region renowned for its unique ultramafic soils derived from ultramafic rocks [308, 309]. These soils, derived from ultramafic rocks such as peridotite and serpentinite, are characterized by high concentrations of magnesium, iron, and heavy metals like nickel, chromium, and cobalt, but low levels of essential nutrients like phosphorus and potassium [310]. This mix creates a challenging environment for plant growth, leading to specialized flora adapted to these extreme conditions, and has already yielded hypernickelophore plants [251]. Hyperaccumulator Gardens such as that in Sabah, Malaysia, Malaysia's Kinabalu Park, have been established to grow and protect high and rare hyperaccumulator species [311]. Harris et al. [224] found that using the plant *Berkheya coddii* to extract nickel from nickel-rich serpentinite soils and producing energy from the collected biomass could earn about 11,500 AU\$ for each hectare per harvest in Australia, while using a method with thiocyanate on a *Brassica juncea* crop could potentially earn around \$26,000 per hectare per harvest for Au. Furthermore, the use of heavy metals contaminated biomass for bioenergy is promising because it minimizes the release of CO₂ [18]. Studies have shown that some plants, such as the Co/Cu hyperaccumulators of former Zaire in Central Africa, can accumulate both metals and extract them simultaneously [66].

Heavy metal phytomining will create new economic opportunities, optimize land usage, lead to the establishment of biomass processing factories and also help solve the problem of pollution. In addition to extracting valuable metals from waste, phytomining enhances soil carbon levels, nutrient content, and microbial activity, supporting the long-term rehabilitation of mining sites, ecological recovery, and regrowth of vegetation on degraded soils caused by traditional mining practices [312].

8. Future perspective

By modifying genes linked to antioxidant defenses, genetic editing can improve a plant's resistance to heavy metal stress [313]. As a multigenic trait that is regulated at several levels, plant heavy metal tolerance might be combined with other desirable traits to create plants that are more suited to heavy metal-polluted soils once the mechanisms underlying its genetic regulation are understood [145]. By transferring metal hyperaccumulating genes from low-biomass wild species to the higher-biomass-producing farmed species, recent biotechnology advancements are also anticipated to play a promising role in the generation of new hyperaccumulators in the future [314]. Determining the phytochelatin–metal complex transport pathway's origin and destination can help with the design and/or advancement of phytoremediation technologies [137].

An alternative approach is to use nanoparticles (NPs) to trigger substantial modifications in plant biochemical processes, gene activity, and epigenetic DNA configurations [315, 316], thus promoting the

creation of enhanced stress response mechanisms. Nanoparticles (NPs) interact with plants through various mechanisms, influenced by their chemical makeup, dimensions, surface characteristics, and reactivity [317]. These interactions lead to significant changes in the plants' structure, anatomy, and physiological processes, which are essential for enhancing crop plant development [318]. Certain benefits of employing nanoparticles in managing abiotic stress involve enhanced plant growth, increased biomass, higher chlorophyll levels, elevated sugar content, greater osmolyte buildup, and boosted antioxidant activity [319]. Specific genes associated with aluminium tolerance were found to have different DNA methylation frequencies in tolerant and susceptible rice cultivars [320]. Differential methylation patterns may be connected with epigenetic regulation of rice responses to aluminium stress, emphasizing epigenetics' importance in specific abiotic stress responses. Epigenetic alterations, such as deoxyribonucleic acid (DNA) methylation, histone modifications, and small ribonucleic acid (RNA) engineering, provide novel approaches for modifying plant responses to minimize the impact of heavy metal and metalloids stress [321].

9. Conclusion

In the wake of ore reserve depletion, phytomining is a promising method for recovering important metals from secondary deposits or low-grade ores. Economically, in recent times, phytomining has generated income and opened up new study areas for the production of biofuel which is eco-friendly. If phytomining is connected to the creation of important biomass products as specified above, it will always be a potential method for cleaning heavy metal contaminants. One could argue that the viability of phytomining depends on a number of resources, including the availability of heavy metals in a given location, the efficiency of hyperaccumulators, and the type of heavy metal available. Genetic engineering of specific species of hyperaccumulators could improve the efficiency of phytomining technology. This could be achieved by modifying genes linked to antioxidant defenses, genetic editing to improve plant's resistance to heavy metal stress. Despite phytomining being an effective and promising method of phytoremediation, this method has a limited reach because of its delayed metal extraction, low biomass output, and metal recovery process. However, current trend of technological advancements could be of great advantage. Phytomining should target species of plants with high levels of hyperaccumulation, typically those with high percentages of metals in foliar dry matter, for wealth generation. This review suggests that further extensive research be conducted on the selection of appropriate plant taxa for various sets of conditions, such as environmental risk assessment, and heavy metal-enriched biomass. Phytomining technologies should be embraced, most especially by mining industries, because they have the potential to improve mine site rehabilitation and provide sustainable post-mining incomes.

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