Review

Sustainability of phytoremediation: Post-harvest stratagems and economic opportunities for the produced metals contaminated biomass

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ABSTRACT

Heavy metals (HMs) are indestructible and non-biodegradable. Phytoremediation presents an opportunity to transfer HMs from environmental matrices into plants, making it easy to translocate from one place to another. The ornate features of HMs' phytoremediation are biophilia and carbon neutrality, compared to the physical and chemical remediation methods. Some recent studies related to LCA also support that phytoremediation is technically more sustainable than competing technologies. However, one major post-application challenge associated with HMs phytoremediation is properly managing HMs contaminated biomass generated. Such a yield presents the problem of reintroducing HMs into the environment due to natural decomposition and release of plant sap from the harvested biomass. The transportation of high yields can also make phytoremediation economically inviable. This review presents the design of a sustainable phytoremediation strategy using an ever-evolving life cycle assessment tool. This review also discusses possible post-phytoremediation biomass management strategies for the HMs contaminated biomass management. These strategies include composting, leachate compaction, gasification, pyrolysis, torrefaction, and metal recovery. Further, the commercial outlook for properly utilizing HMs contaminated biomass was presented.

1. Introduction

The research in phytoremediation has improved significantly, and there has been an increase in practical field applications (Afzal et al., 2019; Ujang et al., 2021). This sustainable treatment method removes numerous contaminants, including petroleum hydrocarbon, antibiotics, toxic metals, emerging pollutants like polychlorinated hydrocarbon, pesticides, and many others (Mushtaq et al., 2020; Qurban et al., 2021). In relation to these biotechnological interventions to manage heavy metal-containing post-phytoremediation biomass, however, some major concerns exist (Khan et al., 2021).

The preparation of instruments such as laws and policies are necessary to maintain a proper disposal mechanism for contaminated biomass. Phytoremediation has been successfully implemented from pilot to field scale, however, policies against the contaminated biomass produced are becoming more restrictive. Among the notable acts that specifically mention controlled mobility of hazardous biowaste in the

developing and developed world are "Hazardous Substances Rules, 2003" in Pakistan, "Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016" in India, "Sludge and biosolids (NOM-004-SEMARNAT-2002)" in Mexico, "Wastes Control Act (Act Number 13038)" in South Korea, "Environmental liability with regard to the prevention and remedying of environmental damage" (2004/35/CE) in Europe, and "Solid Waste Disposal Act (Public law 89–272)" and "Resource Conservation and Recovery Act (Public law: 94–580)" in the USA. It is therefore vital to improve the management of contaminated biomass. Additionally, specific legislations are needed to be prepared. If national or international environmental quality standards are set directly or indirectly, they need to address the expected problem of post-phytoremediation biomass management.

In this review post-phytoremediation biomass was discussed as a problem. However, as it is well known that one organism's waste is the raw material of another, and most non-infectious biological waste is biodegradable, the same principle applies here. It is necessary to find

innovative ways to recycle waste biomass. Thus, the discussion focuses on novel and exciting biomass waste management strategies. The environmental sector of land reclamation using phytoremediation can play a significant role in the circular economy model, which is among the hot topics in global politics.

2. Method

The authors utilized the Scopus database to perform the systematic literature review and scientific data extraction. The search keywords were biomass OR Phytoremediation AND LCA OR "Life cycle assessment" AND metal OR heavymetal OR "heavy metal". The database searches identified 82 studies in total. This results in a total of 63 articles for the examination. The database was then manually checked for the removal of irrelevant literature. Between 2013 and 2022, 37 specific articles were published. The specific screening criteria were a) the exclusion of reviews, conferences, surveys, and books, b) original research reported the combination of phytoremediation or biomass, LCA, and metal or heavy metal. Data from the screened publications was downloaded and used in the review article. The same bibliographic data was also used to produce a map with VOS viewer Software (version 1.6.18). For this investigation, the binary counting of keyword co-occurrence was employed, with the minimum number of occurrences of the term set to "3." A total of 107 keywords out of 769 fits the criteria. 14 irrelevant keywords were manually removed, yielding a total of 93 keywords for network and overlay visualization analysis (Fig. 1). In all, 93 elements were grouped into five clusters. There were a total of 2372 links generated, with a total link strength of 227.2. The majority of the articles were written during the previous five years. Out of which the term "Life cycle assessment" was in the 1st cluster, making a total of 90 links with 20.0 link strength, "Phytoremediation" and "Heavy metal" were in cluster 3, making 48 links, with a link strength of 6, while biomass was in cluster 4, with total 89 links and total link strength of 19.

3. Life cycle assessment of phytoremediation

The notable reasons for the ever-increasing acceptability of green remediation methods are the public's awareness related to carbon footprints and climate change issues (Lin et al., 2021). Though the footprint approach (based on carbon, water, or land) is attractive, they have the limitation that they only focus on one issue relevant to a process or product at any specific time (Yue et al., 2020). In this regard, the

Life Cycle Assessment (LCA) approach is much more holistic. It allows comparing 2 or more of the products, processes, services, or activities related to quantification/assessment of the potential risk that can impact the immediate environment, starting from the extraction of resources (removal of metals/metalloid from environmental matrices, in the present case) to final fate, which can be disposal, treatment, recovery of resources (biological, chemical, or physical nature) (Jin et al., 2021). The application of LCA with phytoremediation could provide insight into the optimal strategy for phytoremediation of HMs, compare the regulatory feasibility of each application methodology versus the conventional treatment method, determine the potential impact hotspot among the extended application cycles, and identify prevention and corrective measures to minimize resource losses, including chemicals, electricity, water, and biomass (Jia et al., 2022; Lin et al., 2021; van der Ent et al., 2015). According to some comparative analyses, there has always been a keen interest among the scientific and environmental communities to determine whether these green technologies are feasible, viable, and sustainable. However, in-depth investigations are necessary for LCA in studies related to phytoremediation and bioremediation. Table 1 summarizes a few studies that perform the LCA to study the efficacy of phytoremediation with other conventional applied remediation techniques or between different options for phytoremediation.

Understanding LCA requires having a few key fundamental concepts. Technically the LCA studies come within the scope of ISO 14040:2006, covering the life cycle inventory (LCI) studies (Barjoveanu et al., 2020; Ögmundarson et al., 2020). The LCA can be applied to determine the environmental performance of a product, process, or service. The LCA is a four-step approach: a) goal and scope definition, b) inventory analysis, c) impact assessment, and d) interpretation (Zahid Gill et al., 2021).

3.1. Goal, scope, and definition

The first step of an LCA study defines the reason for the study and the intended use of the results. It is also known as the goal and scope of the LCA study. It is equally essential to compare 2 or more systems having the same functional unit. The primary goal of a life cycle assessment of remediation of a contaminated site is to compare the environmental performance of the various remediation techniques. This step defines the systems under investigation, the functional unit, and the boundaries. Based on the system boundary, a strategy or applied technique can be a closed loop or open loop. A close loop occurs when all the inputs and
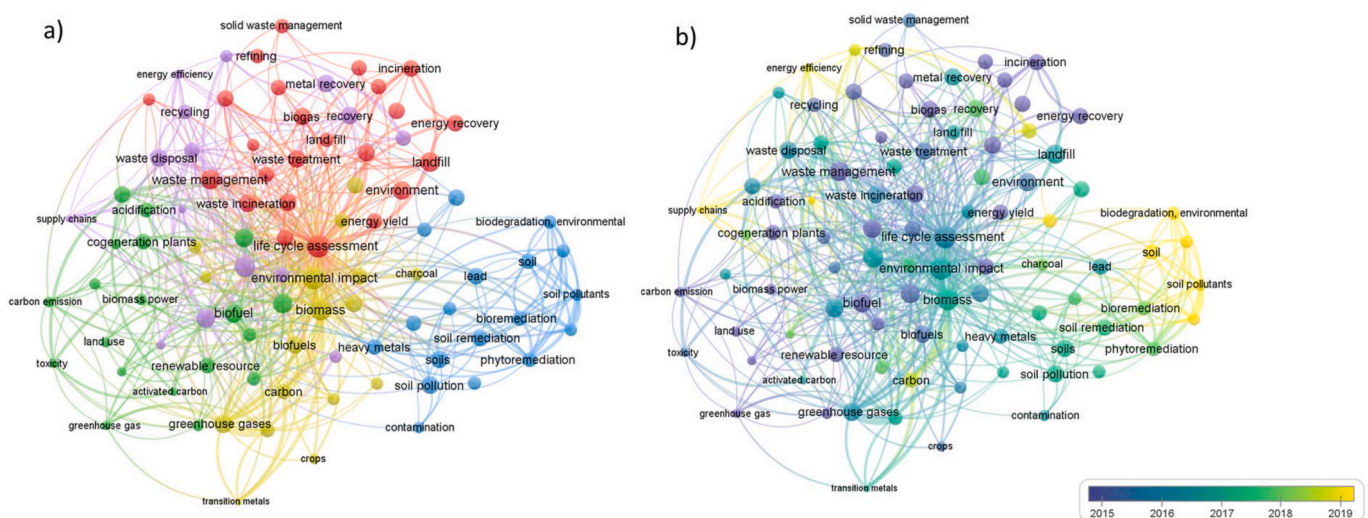

Fig. 1. The VOS viewer Software based graphical representation of keyword co-occurrence in the examined papers. a) Overlay visualization, and b) network visualization. The connecting lines between phrases show co-occurrences in the same article, and the keywords contained in the same cluster reveal that they have been analyzed frequently in the same publications.

Table 1
LCA studies related to phytoremediation.

Targeted problem*	Compared scenarios	Functional unit	Process inputs	Process outputs	Methods used	Studied impacts per function unit	Conclusion
Disposal of HMs contaminated biomass[1]	Landfilling, phytoremediation + disposal, phytoremediation + Incineration, and phytoremediation + pyrolysis	1 m² of contaminated site	Energy and resources for site preparation and operation and crop cultivation	Emission to air, water, and soil, and solid waste	GaBi-LCA & CML 2001	Climate Change (kg CO_2)	Phytoremediation showed the least environmental impact in all combined scenario compared to landfilling
Cd, Co, Cu, Ni, Pb, and Zn in soil[2]	Excavation and landfilling, phytoremediation, phytoremediation + landfilling, phytoremediation + co-digestion, and no action	1 ha of contaminated site	Energy and resources for site preparation, operation, transportation for biomass management	Emission to air, water, and soil, solid and biomass waste, biogas, digestate (depending on the approach adopted)	GaBi-LCA & ReCiPe	Urban land occupation (m² yr), Agricultural land occupation (m² yr), Natural land transformation (m² yr), Particulate matter formation (kg PM$_{2.5}$), Fossil resource depletion (kg Sb), Climate change (kg CO_2)	Phytoremediation without biomass valorization was not sustainable, while only sustainable with conversion of produced biomass into energy compared to other scenarios. Choice between phytoremediation or ex-situ treatment depends on the distance between the site and management faculty
BTEX in soil[3]	Excavation and landfilling, phytoremediation and biofuel production using *Salix viminalis* biomass	5000 m² of site	Energy and resources for site excavation, refilling, operation, and transportation for excavation-and-refill, while *Salix* cultivation, monitoring, operation, transportation for phytoremediation and biofuel production	Emission to air, water, and soil	ReCiPe & EPD	Global warming (kg CO_2), Ozone layer depletion (kg CFC-11), Photochemical oxidation (kg C_2H_4), Acidification (kg SO_2), Eutrophication (kg PO_4), Gross caloric values (MJ), Ecotoxicity (kg 1,4 DB), Water resource depletion (m³ water), Fossil resource depletion (kg Sb), Urban land occupation (m² yr), Agricultural land occupation (m² yr), Natural land transformation (m² yr)	The excavation-and-refill showed a primary impact in the traditional categories of global warming, ozone layer depletion, photochemical oxidation, acidification, eutrophication, gross calorification value. The Phytoremediation and biofuel production showed large importance of land occupation and biodiversity.
Cu, Cr, and Ni in soil[4]	In situ excavation-and-refill, phytoremediation with energy recovery from biomass of Taiwanese chenopod or Napier grass	1-time operation of excavation-and-refill, and one-year operation of phytoremediation	Energy and resources for excavation, transportation and refilling for in situ excavation-and-refill, while energy and fertilizer for phytoremediation scenarios	Emission to air, water, and soil, and biomass	IMPACT 2002+ (v2.12)	Human health (Pt), Ecosystem quality (Pt), Climate Change (Pt), Resources (Pt)	Energy reutilization of biomass recovered from phytoremediation made phytoremediation even more sustainable, compared to conventional methods. Phytoremediation generated less environmental impacts and performed better toward sustainability for the Taichung City farmland and Nan-Hai tannery
Cd contaminated soil[5]	Energy and CO_2 abatement potential of *Salix* spp., *Zea mays* L., and *Brassica napus* L. originating from HMs contaminated land.	1 ha of contaminated land per year	Energy inputs for plowing, planting, herbicide/pesticide application, transportation, seed production, harvesting	Biomass, biofuel, digestate, ashes, rapeseed, silage	GWP	Total energy production post-harvest (MJ), and Net CO_2 avoidance (kg CO_2)	Higher biomass yields for *Salix* spp. make it energetically competitive with *Z. mays* L. and *B. napus*. Further metal concentration in biomass impacts on energy conversion efficiency and rest product use
Nitrogen fertilizer over application[6]	sole maize cultivation, maize + soybean intercropping, and maize + groundnut intercropping	1 ton of dry biomass bioproductivity yield	Energy, resources, and land	Emission to air, water, and soil	Not provided	Abiotic resources depletion (MJ yr^{-1}), Global warming (kg CO_2), Acidification (kg SO_2), Eutrophication (kg PO_4), Human toxicity (1,4-DCB), Water ecotoxicity (1,4-DCB), Terrestrial eco-toxicity (1,4-DCB)	Intercropping maize with suitable plants (groundnut and soybean) reduced the adverse effects of over-application of nitrogen fertilizer on the environment.
Estarreja contaminated soil, contaminants not-specified[7]	The biomass pre-treatment with acid (Sulfuric, Nitric, hydrochloric, or acetic acid)	1 L of bioethanol production	Energy, resources (including acids for pre-treatment), enzymes for fermentation	Emission to air, water, and soil, and bioethanol	ILCD Midpoint 2011	Climate change (kg CO_2), Ozone depletion (kg CFC-11), Photochemical ozone formation (kg NMVOC), Acidification (kg NH$_3$), Eutrophication (kg PO_4), Ecotoxicity (kg 1,4-DCB), Water resource depletion (m³ water), Fossil resource depletion (kg Sb)	Pre-treatment of Sulfuric and hydrochloric acids have a better environmental performance when compared with acetic and nitric acids.

*Studies within orange shade were studied as *Cradle-to-gate* approach, while in blue shade were studied through *gate-to-gate* approach
[1]Vocciante et al. (2019), [2]Vigil et al. (2015), [3]Suer and Andersson-Sköld (2011) [4]Lin et al. (2021), [5]Witters et al. (2012), [6]Nie et al. (2010), [7]Mata et al. (2022)

outputs are in the cycle, with one product being the raw material of other processes (Tian et al., 2021). It is also known as the cradle-to-cradle system. The ISO 14044 standard defines a closed loop strategy as the process of recycling a material without affecting its inherent properties in any way (la Rosa et al., 2021). An example of such close loop strategy was presented by Secchi et al. (2019) for the lignin recovery during pulp and bio-ethanol processes, followed by lignin

utilization as an energy source. However, in most cases, an open-loop strategy is adopted in which multiple flows of input and outputs are possible, but usually, they follow either one of the following systems, including cradle to grave, cradle to gate, and gate to gate system, respectively (Mata et al., 2022; Parisi and Sinicropi, 2021; Vigil et al., 2015; Wu et al., 2021). The open loop strategy is defined as when the inherent qualities of recycled material changes from those of virgin

material, and therefore, the recycled material can only be used in subsequent product applications, usually as a substitute for other materials (Huysman et al., 2015). One such example was the hydrogen production through the indirect popular plant's biomass gasification along the CO_2 biocapture (Susmozas et al., 2016).

The system boundaries determine the unit processes included in the LCA study. A study for life cycle analysis showing a system boundary is illustrated in Fig. 2, adopted from the study of Lin et al. (2021). The boundary for assessment defines the processes included or excluded and the time frame for the inventory flow. Lin et al. (2021) performed the LCA to compare the effectiveness of phytoremediation (using Taiwanese Chenopod and Napier grass) of HMs contaminated soil in tannery and farmland located in Nan-Hai and Taichung, Taiwan, respectively, along with in situ excavation-and-refill. The adopted boundaries for both systems obey the cradle-to-grave cycle concept. The system boundaries are defined to evaluate the environmental performance of phytoextraction and conventional remediation methods. In another study, Vigil et al. (2015) performed the LCA for the remediation of PB-contaminated brownfields in Asturias, Spain. The system boundary scenarios were excavation and landfill, phytoremediation (using *Melilotus alba*) followed by biomass to energy conversation, phytoremediation followed by biomass disposal, and not action. The system boundaries were maintained to examine the contribution of the distance between the site and the biomass management point. This was done to examine its implications for the environmental performance of heavy metal phytoremediation.

3.2. Life cycle inventory analysis

These system boundaries are set between the Technosphere, i.e., the technological system, and the Ecosphere, i.e., the environment. It helps in setting the definition of functional units— which aids in defining the upstream and downstream processes at a specified time. A functional unit can be some amount of resource production or recovery, or it can be the goal/operation to achieve remediation in a specific area. Through these units, LCA compares the impacts of alternative methods with the capacity to achieve similar outcomes. In this analysis, all inputs and outputs of any products and processes are quantified. It quantifies the use of raw material at each step, the condition of the process, and finally, the product itself, but this also helps quantify waste and by-products generated having the capacity to cause pollution. It is a data-driven process used to track flows incurred throughout the product, process, or activity life cycle. These flows are related to raw resources, materials, energy consumption, water usage, emissions due to transportation, and the release of waste into the air, water, or soil. Such data related to exchanged flows are collected either during the study (the system foreground) or through existing Life Cycle Inventory (LCI) databases such as EcoInvent (the system background). These flow models show the process flow and give insights into the technical system boundary (Fig. 2). As a result of this checklist, the database construction was

consistent, and the processes were comparable between the various treatments or scenarios.

Lin et al. (2021) maintained the inventory data for the site excavation and refill using the extraction area, total transportation for the excavation and refill process, and refilling of clean soil in the contaminated site. For the phytoremediation process, petroleum (diesel and petrol) was used for cultivation, as well as the total amount of fertilizer applied (ammonium nitrate, phosphate fertilizer, and potassium sulfate). For the comparison of the processes, the functional units were defined as one-time operations (24–49 days, depending on the contaminated site) for excavation and refill and one year for phytoremediation.

Mata et al. (2022) performed the LCA using the gate-to-gate approach for bioethanol production from heavy metal contaminated corn stover from HMs polluted soil phytoremediation. They compared the performance with different acids pre-treatments of the lignocellulosic biomass. The selected functional unit was the production of 1 L of bioethanol. Inventory was maintained for electricity usage, amount of corn stover, acid treatment(s), water usage, diesel usage, enzyme usage (*Accellerase* enzyme and *Ultraflo* enzyme), *Saccharomyces cerevisiae*, in respective processes of grinding, pre-treatment, enzymatic hydrolysis, fermentation filtration, and distillation.

3.3. Impact assessment

It is possible to identify impacts using LCA theoretically (Nie et al., 2010). However, appropriate impact selection for any given assessment depends on the environmental problems linked with the desired remediation goals, the independence of indicators from each other to avoid duplication, and the validity of the model (van der Ent et al., 2015). The databases for LCA contain processes related to two different types of flow: Intermediate flows, which are the ones that allow connecting processes, and elementary flows, which are the ones that contribute to the impacts. The impact assessment method can be problem-oriented, based on midpoint impact, and damage-oriented, which focuses on endpoints, and methods covering the full scope of impacts. Examples of problem-oriented methods are ILCD Midpoint 2011 (International Reference Life Cycle Data System Midpoint 2011), CML2002, EDIP (Engineering & Development of Industrial Projects), TRACI (Tool for Reduction and Assessment of Chemicals and Other Environmental Impacts), LUCAS (LCIA method Used for a CAnadian-Specific context) and Environmental Footprint (EF) method (European Commission Recommendation (2013/179/EU) on the use of common methods to measure and communicate the life cycle environmental performance of products and organizations). It is mainly used in the EU because it is recommended by the European Commission, and it is also a development of the ILCD 2011. In comparison, damage-oriented methods are Eco-Indicator 99, EPS2000 (Environmental Priority Strategies, 2000), and LIME (LCIA Method based on Endpoint modeling), while Impact 2002+, ReCiPe, and Swiss Ecoscarcity 2013, harmonize midpoints and
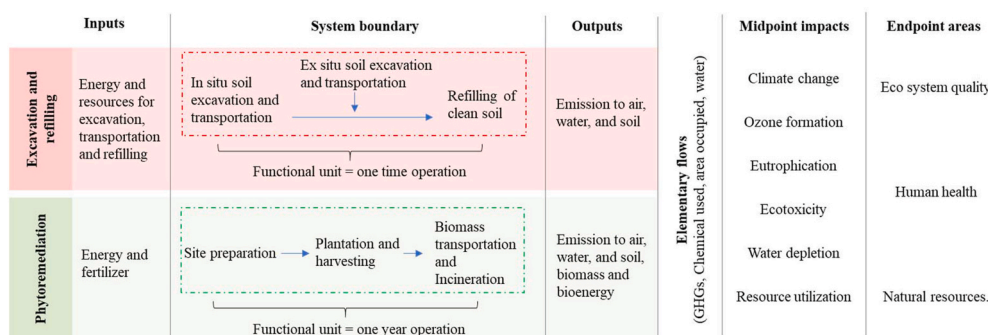
Fig. 2. LCA of phytoremediation and soil excavation pactices for heavy metal contaminated sites (Lin et al., 2021).

endpoints (Jia et al., 2022; Lin et al., 2021; Mata et al., 2022; van der Ent et al., 2015; Vigil et al., 2015).

Land remediation using HMs phytoremediation, or any other remediation method involves many environmental issues such as volatile organic compounds emission, ecotoxicity, greenhouse gas emissions, eutrophication, urban land occupation, agricultural land occupation, natural land transformation, particulate matter formation, fossil depletion, climate change, and acidification. The selection of an appropriate impact assessment methodology is vital for LCA, as the results are dependent on assumption and model (Table 1). For instance, in the study conducted by Mata et al. (2022), climate change (kg CO_2 eq/FU), ozone depletion (kg CFC-11 eq/FU), photochemical ozone formation (kg NMVOC eq/FU), acidification potential (kg NH_3 eq/FU), eutrophication potential (kg PO eq/FU), ecotoxicity (kg 1,4 DB eq/FU), Water resource depletion (m^3 water/FU), and fossil resource depletion (kg Sb eq/FU) were used for impact assessment, while Vigil et al. (2015) focused on urban land occupation (m^2 yr eq/FU), agricultural land occupation (m^2 yr eq/FU), natural land transformation (m^2 yr eq/FU), particulate matter formation (kg PM 2.5 eq/FU), fossil resource depletion (kg Sb eq/FU), and climate change (kg CO_2 eq/FU).

3.4. Interpretation

The LCA helps identify the processes and steps that result in the most to a given impact. Further, the degree of uncertainty can also be analyzed and evaluated. Vigil et al. (2015) interpreted the sustainability of phytoremediation without biomass valorization by comparing land-filling vs. anaerobic co-digestion. It was concluded that biomass management for sustainability of phytoremediation is needed, as even with intensive cultivation, there was no net carbon capture, and there were negative impacts from landfilling. Vigil et al. (2015) further proposed that plants in their study have a metal concentration within the acceptable range for an inert landfill. However, if biomass has higher metal accumulation, special considerations like landfilling in hazardous material would be needed. Vigil et al. (2015) suggested that biomass transportation for the anaerobic co-digestion process to digesters located more than 300 km from phytoremediation sites should be avoided for the sustainability. Therefore, such facilities should be established in close proximity to the remediation site. In another study, Mata et al. (2022) reported that sulfuric and hydrochloric acid pre-treatment was more effective at producing bioethanol from heavy metals contaminated corn stover than acetic and nitric acids. authors also concluded that pre-treatment and enzymatic hydrolysis contributed to the most significant environmental impacts.

4. Life Cycle Costing and economic window in phytoremediation

The economic evaluation is crucial to determine the viability of implementing different techniques for phytoremediation. In combination with LCA, Life Cycle Costing can be used as a decision support tool in terms of estimating costs considering the whole life cycle of a system. This can be done by analyzing the financial implications for the implementation of different phytoremediation techniques.

The methodology to perform an LCC assessment is not standardized as in the case of LCA. The closest approach to standardization is ISO 15686–5:2017 for buildings and constructed assets, providing the steps and requirements for the performance of LCC (ISO, 2017). Hunkeler et al. (2008) developed guidelines to complete an LCC assessment and combine the methodology with LCA. In this line, Swarr et al. (2011) described a code of practice to integrate environmental and economic assessments following the steps to perform an LCA established in ISO 14040:2006. This approach to economic assessment can include the externalities resulting from LCA considering the same boundaries and functional unit, developing an integrated model providing results in monetary units (Gluch and Baumann, 2004).

5. Strategies to manage HMs contaminated biomass

The previous section centered on evaluating the sustainability of phytoremediation compared with other remediation methods. It also centered on finding an effective way to execute these green technologies by identifying critical process hotspots. Undoubtedly, using green technologies like phytoremediation has added advantages. Phytoremediation can assist in soil carbon sequestering, which is a process of removing CO_2 from the atmosphere and storing it in soil carbon pool, as humus, root exudates, soil fauna, and microorganism (Thomas et al., 2022). Further, phytoremediation also helps in the soil stabilization by removing the contaminants, improving the soil quality, and preventing the soil erosion (Aftab et al., 2021; Afzal et al., 2019). However, despite being sustainable and friendly to the environment, the sustainable application of these phyto-technologies is highly dependent on the efficient post-phytoremediation strategies related to the produced HMs-contaminated biomass (Khan et al., 2021). Many researchers have no data on the fate of pollutants containing biomass harvested after phytoremediation (Abhilash and Yunus, 2011; Song and Park, 2017; Vigil et al., 2015). While many published studies only focus on phytoremediation, research and management strategies for biomass-produced post-remediation are limited (Khan et al., 2021; Song et al., 2016; Song and Park, 2017). Due consideration regarding the contaminants present in the biomass is essential.

5.1. Natural mineralization using composting and compost leachate stabilization

The improper disposal of fresh biomass for phytoremediation can cause changes in the soil microbial composition. This is because due to the degradation of organic matter, the bound HMs can become bioavailable. Using composting, a stable product, i.e., compost, can be achieved through biological transformation, which releases nutrients and metals slowly (Khan et al., 2020). Fig. 3 shows the sketch for the compositing of HMs containing biomass. The process of composting results in the production of leachate. The metal-containing phytoremediation biomass should be collected and compacted into the composts and other available organic matter that can be dehydrated (Muthusaravanan et al., 2020). Thus, the compost produced will have a high level of nutrients and metals. Selenium, iron, and zinc are essential for food biofortification, as they play a vital role in tackling nutrient deficiency (Pandey and Souza-Alonso, 2019). Hence, the use of compost produced by a plant capable of hyperaccumulating such micronutrients can be considered a potential application.

5.2. Metal recovery from HMs contaminated phytoremediation biomass

Agromining and phytomining rely on growing the metal accumulators and hyperaccumulator plants on the matrices (soil or water) contaminated with HMs, then harvesting the biomass, drying, ashing, and processing for the recovery of the target metal (Simonnot et al., 2018; Tisserand et al., 2021). The economic perspective of this technique depends on numerous factors. Among these are the plants' accumulation characteristics, the type of metal to be recovered, and the cost and understanding of methods related to metal recovery (Bani et al., 2015a,b; Dube et al., 2021; Nkrumah et al., 2019). Fig. 4 shows the general flow of processing needed to recover metal (in the present case Ni). The processes include three different types of extraction, pyrometallurgical (i.e., drying, ashing, and melting), hydrometallurgical (i.e., drying, leaching, and precipitation or electrowinning), and pyro-hydrometallurgical metal recovery (Dang and Li, 2021). The flow defined in Fig. 4 can help recover not only heavy metals but precious metals as well. These include gold (Au) using *Nicotiana tabacum* (Krisnayanti et al., 2016), and rare earth metals including Cerium (Ce), Neodymium (Nd), Praseodymium (Pr), Gadolinium (Gd), Samarium (Sm), and Yttrium (Y) from the biomass of *Dicranopteris linearis* (Chour
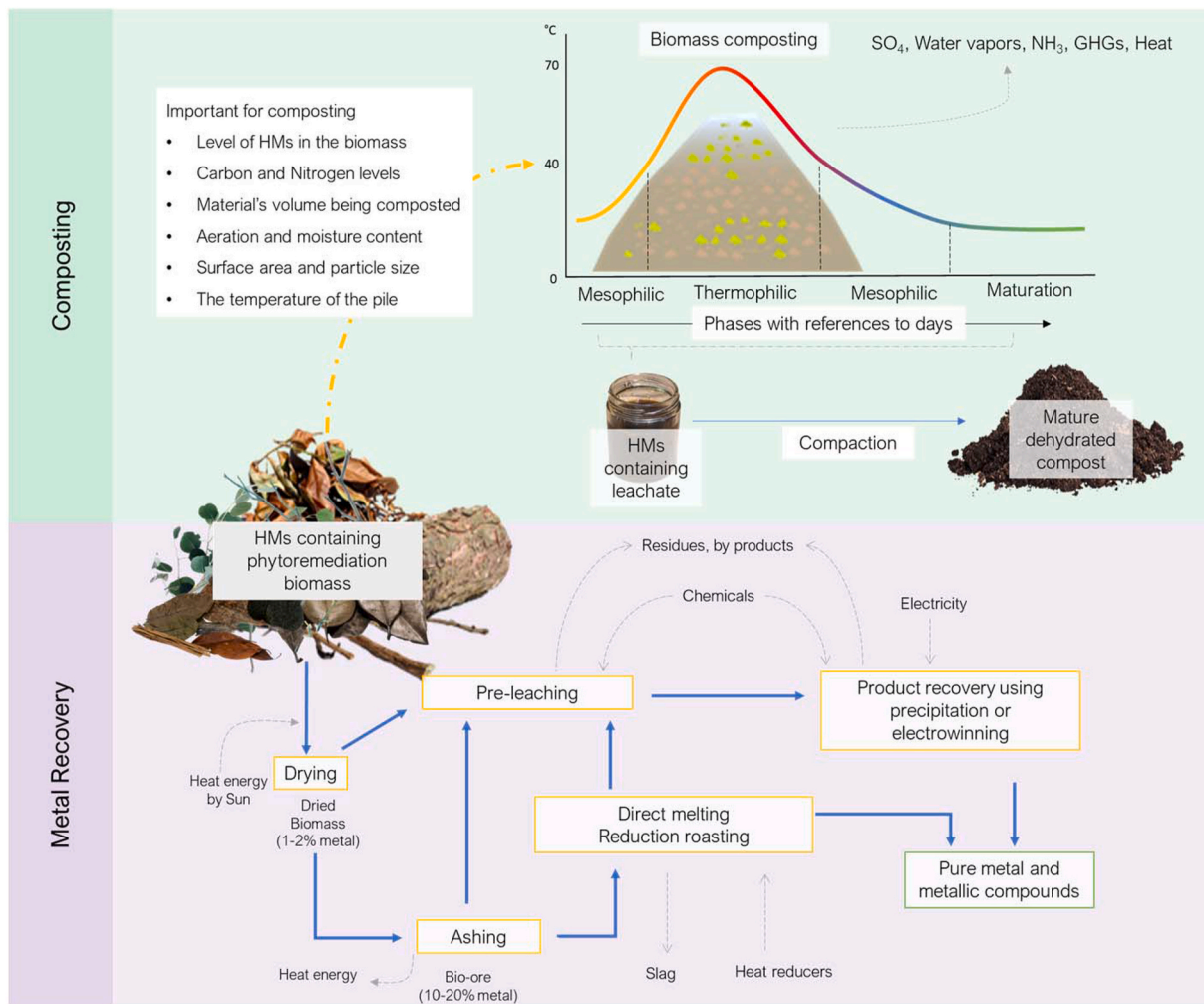
Fig. 3. Composting and metal recovery using phytomining of metals using biomass of HMs accumulators and hyperaccumulator of HMs containing phytoremediation biomass (Muthusaravanan et al., 2020; van der Ent et al., 2015). GHGs = Greenhouse gases, Soild lines with arrows represent the flow of processing, while broken line arrow represents the major inputs, intermediates, and wastes.
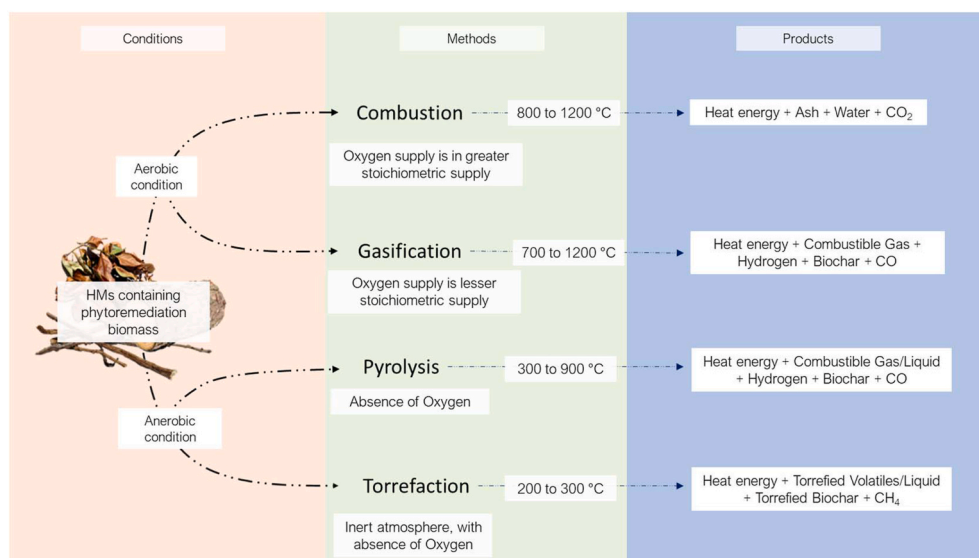

Fig. 4. Thermochemical conversion HMs containing phytoremediation biomass (Senthil and Lee, 2021; Wang et al., 2020).

Table 2
Recent studies for metal recovery from biomass produced from phytomining.

Plant	Metal targeted	Plant type[j]	Environmental matric	Metal concentration in contaminated media	Percentage of metal in plant dried biomass	Metal production capacity/recovery yield
Alyssum murale[a]	Ni	Ni-HYA	Soil	2.06–3.30 g kg^{-1}	1.10–0.71	103 kg ha^{-1} with 4 plant per m^{-2}
Dicranopteris linearis[b]	Al, Ca. Ce, Gd, K, La, Mg, Mn, Nd, Pr, Sm, and Y	REE and Al-HYA	Soil	REE and metals range from 300 to 700 mg kg^{-1} of dry soil	La 0.128, Ce 0.113, Nd 0.088, Pr 0.027, Sm 0.014, Y 0.012, Gd 0.007 and K 0.254, Al 0.205, Ca 0.174, Mn 0.051, and Mg 0.048	70% and higher for all REEs and metals with H$_2$SO$_4$ extraction
Phyllanthus rufuschaneyi[c]	Ca, Co, Fe, K, Mg, Mn, Ni, and Zn	Ni-HYA	Soil	>2 g kg^{-1}	2.64–0.69 (depending on the plant compartment)	not studied
Nicotiana sp.[d]	Au, Ag, and Cu	ACC	Mine cyanidation tailings	Au 1.03, Ag 18.2, and Cu 53.6 mg kg^{-1}, respectively	Au 1.20×10^{-4}, Ag 5.43×10^{-3}, and Cu 3.97×10^{-3}, respectively	0.023% of Au, 0.024% of Ag, and 0.63% of Cu with smelting using borax and silver as collector metal
Manihot esculenta[e]	Ru	ACC	Soil	0.869 g kg^{-1}	1.89–29.5 (depending on the plant compartment)	not studied
Alyssum serpyllifolium (AS), *Sedum plumbizincicola* (SP), *Brassica napus* (BN), *B. juncea* (BJ), and *Nicotiana tabacum* (NT)[f]	Ni, and Zn	AS and SP-HYA, and BN, BJ, and NT-ACC	Waste incineration bottom ash	Cu 0.34, Ni 0.005, and Zn 0.12 g kg^{-1}, respectively	Ni 0.025 in *A. serpyllifolium* and Zn 0.169 in *S. plumbizincicola*, respectively	not studied
Odontarrhena chalcidica[g]	Ni	ACC	Industrial galvanic sludge	0.85 to 1.50 in different sludges	2.02–2.68	not studied
Manihot esculenta[h]	Pd and Pt	ACC	Soil	Pd 0.356, and Pt 2.408 g kg^{-1}, respectively	for Pd 22 and for Pt 68.4, respectively	not studied
Brassica Juncea[i]	Au	Au-HYA	Waihi and Tui gold ore, disseminated gold in sand (DGS), and gold fine powder	22.6% in Tui ore, 1.8% in Waihi ore, 9.2% in DGS	5.732×10^{-3} to 7.00×10^{-6}	not studied

[a] Bani et al. (2015b).
[b] Chour et al. (2020).
[c] Nkrumah et al. (2019).
[d] Krisnayanti et al. (2016).
[e] Dube et al. (2021).
[f] Rosenkranz et al. (2017).
[g] Tognacchini et al. (2020).
[h] Akinbile et al. (2021).
[i] Anderson et al. (1998).
[j] HYA = Hyperaccumulator and ACC = Accumulator.

et al., 2020). Table 2 summarizes some of the studies on agromining and metal recovery using the plant as bio-ores. It is worth mentioning that at present, the proof of concept for metal recovery is well established for Ni; however, for other metals, it is either not thoroughly investigated or not economically feasible (Akinbile et al., 2021; Rosenkranz et al., 2017; Tognacchini et al., 2020).

5.3. Combustion, gasification, pyrolysis, and torrefaction

Though contaminated biomass can present problems, they are an indirect solar energy source. It is renewable and carbon-neutral, as the CO$_2$ amount produced during the processing for management through a thermochemical process is equivalent to the CO$_2$ amount absorbed during the lifetime of biomass production (Nugroho et al., 2021). Fig. 4 shows an exact scheme for the thermochemical conversion of biomass. By drying and burning biomass in controlled conditions, the stored chemical energy can be released by complete oxidation. Ash, heat, water, and CO$_2$ are among the products released. This ash can be used as a bio-ore to recover metals (van der Ent et al., 2015). Section 5.2 covers phytomining and the metal recovery process from biomass.

Compared to combustion, gasification and pyrolysis offer efficient production of multiple value-added products (VAPs), including gaseous, liquid, or solid products. Biochar is one of these VAPs. It serves as energy carriers or intermediate platforms for valuable chemicals (Ali et al., 2017; Senthil and Lee, 2021). One reason for the preference for biomass

gasification and pyrolysis processes over combustion is that it reduces fly ash levels (Wang et al., 2020). The gasification process occurs when the incomplete combustion of biomass takes place, usually at 700–1200 °C. The unique products of this process are syngas, hydrogen, and biochar. The quality of biochar produced through gasification is highly related to the carbon content of the feedstock, which is affected heavily by the equivalence ratio (ER). The ER is the ratio between the air amount supplied and the air needed for stoichiometric combustion. A common consensus is that by increasing ER, the gasification temperature also increases, affecting the biochar quality.

Pyrolysis is a thermal conversion method used to convert biomass into liquid, solid, and gaseous fractions by heating the biomass without air or oxygen (Senthil and Lee, 2021). Whichever pyrolysis method is used, the premium product produced is biochar. While hydrogen-rich gas production can also occur, it makes the process inefficient. The removal of the volatile fractions as gaseous by-products happens due to pyrolysis. It acts as the porogenic agent leading to micro and meso-porous biochar surface (Wang et al., 2020). The quality and quality of biochar production are dependent on many factors, including slow or fast pyrolysis heating rate, temperature, feedstock composition, and carbon ratio. Consequently, the biochar produced from the HMs-contaminated biomass can be further used for removing HMs, and this used material can be utilized for metal recovery. It is well established that biochar can be used for the treatment of heavy metals and other contaminants (Hussain et al., 2021; Khan et al., 2019b; Yousaf

et al., 2022).

Another method that can be used for the management of HMs contaminated biomass is the milder form of pyrolysis that takes place at 200–300 °C, at a low heating rate (usually lower than 50 °C min^{-1}), a relatively long residence time (20–120 min), and atmospheric pressure with oxygen absence (Wang et al., 2020). During this process, extra volatiles and water are released as torrefied volatiles, which lowers the amount of biomass by up to 30%. The final product is the torrefied biochar or bio-coal, which is dry, solid, and dark brown to black material having 90% of initial energy with which 1.3 times energy densification is achieved (Cardona et al., 2019). This process is affected by moisture content, ash content, and heating levels, and moisture content is the most crucial factor.

6. The monetary perspective of proper utilization of HMs contaminated biomass

When evaluating the economic aspects of phytoremediation techniques for HMs treatment, we can consider the various options to generate revenue through the harvesting and commercialization of contaminated biomass. When considering the investment costs needed to implement phytoremediation and the incomes from the exploitation of biomass, the evaluation of the project in a long term can be performed through different stages in the life cycle of the study, identifying the economic hotspots that should be considered.

The calculation of the cashflows, namely the costs minus the incomes during a period, will be used to assess the economic feasibility of the techniques. By analysing the cashflows, the financial viability of phytoremediation techniques can be assessed. It can be evaluated by combining the LCC with LCA results, to confirm if the reduction of environmental impacts derived from a contaminated site produces a win-win situation that will make the investment more sustainable and profitable for different stakeholders. The monetary benefits of phytoremediation and the outflows of this sustainable process can be relatively large, however, the data on this subject is very limited (Pandey and Souza-Alonso, 2019; Song and Park, 2017). It would be interesting to evaluate the cash flow and economic benefits of contaminated biomass utilization, but there is limited information available. Considering the advancements in phytoremediation, it will be imperative to assess the monetary value of value-added products produced from HMs contaminated biomass (Suer and Andersson-Sköld, 2011; Vocciante et al., 2019).

However, seeing the few studies that are available, the future looks very promising. By the end of 2050, the demand for essential oil from aromatic herbs is predicted to surpass 5 trillion US$ (Verma et al., 2014). Hence, the biomass produced by cultivation on landfills, mine dumps, and barren land also has the potential to not only be economically viable but also profitable. In addition to this, the use of HMs contaminated biomass for energy is also promising, as it reduces CO_2 emissions (Pandey and Souza-Alonso, 2019). Witters et al. (2012a) performed LCA and reported *Salix* spp, *Zea mays,* and *Brassica napus* can be used as energy crops with the capacity to perform CO_2 abatement when cultivated on Cd-contaminated agricultural soil. Phytoremediation of a barren HMs contaminated site can offer external benefits of CO_2 abatement ranging from 50 to 500 US$ ha^{-1} (Witters et al., 2012b; Verma et al., 2014). Phytoremediation using hyperaccumulators *Aeolanthus biformifolius* for Cu, and *Haumaniastrum robertii* for Co, can yield biomass containing up to 1% of metal in the total plant's weight can be produced (Lee et al., 2021) Through this a total of 20 kg metal per tonne of the plant dried biomass can be produced, and 100% metal recovery is expected to produce worth 31 and 6.6 thousand US$ per tonne dried biomass, respectively contaminated with Co and Cu. Such a yield can generate revenue of 1.5–6 thousand US$ per hectare. Thus, mine dumps and HMs polluted sites can be treated with phytoremediation, but the produced by-products of phytoremediation can generate significant amounts of revenue, rather than being a liability (van der Ent et al., 2015; Krisnayanti et al., 2016; Lee et al., 2021). Similarly, the economic

return for Ni recovery from contaminated biomass of *Streptanthus polygaloides* can yield up to 1 thousand US$ ha^{-1}, while the same biomass can be used for energy which will be worth 410 US$ ha^{-1}, based on present value (Robinson et al., 1997; Pandey and Souza-Alonso, 2019).

The biomass produced by phytoremediation of HMs can be utilized for numerous practical purposes (Chen et al., 2019). The high quantities of phytoremediation biomass can be managed effectively, and many value-added products can be derived from contaminated biomass (Table 3). If the plant used for phytoremediation is ornamental, the flower and potted plants can be sold (Khan et al., 2021; Qurban et al., 2021). Thus, not only the environmental matrices (soil, water, and air) are remediated, but the resulting biomass can produce substantial economic opportunities (Khan et al., 2019a; Raza et al., 2019). Fragrant aromatic compounds from plant parts, including flowers and woods, are valuable, as they are used to produce essential oils, attar, perfume, and insect repellents (Chen et al., 2018; Gharib et al., 2020; Husain et al., 2019). The potential for energy generation with dried biomass is another perspective (Bani et al., 2015a; Budzyńska et al., 2021; Lachapelle et al., 2021; Phieler et al., 2015; Ribeiro et al., 2018). Pandey and Souza-Alonso (2019) presented excellent information regarding the capital opportunities of the biomass produced on HMs contaminated sites. They reported the used for pulpwood production (using *Leucaena leucocephala, Dendrocalamus strictus,* and *Populus* spp., respectively), timber wood production (using *Eucalyptus tereticornis, Tectona grandis,* and *Gmelina arborea*, respectively), and essential oils production (using *Lavandula angustifolia, Lavandula vera, Anethum graveolens, Mentha arvensi,* and *Mentha piperita*, respectively). Youssef (2020) concluded that the cultivation of *Ocimum basilicum* L. in Cd and Pb contaminated soils caused undesired changes in morphology, however a positive impact on essential oils yield, composition, and phytoremediation of the soil.

7. Conclusion

The use of phytoremediation is getting much attention due to its green and biophilic appeal. Much of the attention was directed toward the movement of HMs from environmental matrices into the plant, thus making the phytoremediation of HMs more efficient for field application. By reusing the contaminated biomass, the release of HMs back into the environment can be minimized. In this regard, potential methods for phytoremediation biomass management, including composting, leachate compaction, combustion, gasification, pyrolysis, torrefaction, and metal recovery, were presented. To quantify the sustainability of phytoremediation techniques and HM extraction, LCAs and LCCs are vital decision-making and assessment tools. However, examination using LCA and LCC indicates that proper biomass disposal is another challenge, on which not many recently published findings focus. It can be concluded that the biomass produced during the HMs phytoremediation is a valuable bio-product. However, this review also identified the limitation of available data in the domain of LCA related to phytoremediation and need for investigation linked to the efficacy of adopted post-phytoremediation harvest method. It can be converted into a value-added product through processing. The extraction and recovery of metalloids and metals from HMs-contaminated biomass is one of the most attractive uses. Other beneficial products that can be produced include biochar, compost, solid composites, fragrant products, and plant-based fabric and fiber production. However, the risk associated with VAPs produced by HMs-contaminated biomass must nonetheless be quantified.

Credit author statement

Table 3
Value added product recovery from phytoremediation biomass.

Plant	Family	Contaminants	Matrix	Mechanism[k]	Duration	Potential uses of biomass						
						Energy	Solid composite	Essential oil	Pulp and paper	Biofortification	Decorative purposes	Metal recovery
Alyssum murale[a]	Brassicaceae	Ni	Soil	PM	5 years	*	*					*
Eleocharis acutangular Cyperus papyrus Typha domingesis[b]	Liliopsida Typhaceae	Ba	Soil	RE	4 Months	*	*					*
Salix interior Trifolium pratens[c]	Salicaceae Fabaceae	As, Cr, and Cu	Soil	CP with PE	3 Months	*	*		*			*
Sorghum bicolor[d]	Poaceae	Mn	Soil	PE	6 Months	*				*		*
Betula pendula, Pinus sylvestris, Salix viminalis[e]	Betulaceae Salicaceae Pinopsida	Al, As, B, Ba, Ca, Ce, Cu, In, K, Mg, Na, Sr, Ta, Tm, V, and Zn	Soil	PE	8 Years	*	*	*	*			*
Hibiscus cannabinus[f]	Malvaceae	Pb, Zn, Cu, Cd	Soil	RR	3 Month		*	*	*		*	
Petunia hybrida, Nicotiana alata[g]	Solanaceae	Cd, Cr, Cu, Mn, Ni, Pb, and Zn	Contaminated water irrigation	PS	1.5 Months			*			*	
Catharanthus roseus, Celosia argentea[h]	Apocynaceae Amaranthaceae	Ni, Cr, Cd, Pb, and Cu	Contaminated water irrigation	PS	1 Month			*			*	
Cannabis sativa[i]	Cannabaceae	As, Cd, Hg, Ni, and Pb	Soil	PS	<1 Month	*	*	*				
Mentha longifolia[j]	Lamiaceae	Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn	Soil	PS	1 Year			*			*	

[a] Bani et al. (2015a).
[b] Ribeiro et al. (2018).
[c] Lachapelle et al. (2021).
[d] Phieler et al. (2015).
[e] Budzyńska et al. (2021).
[f] Chen et al. (2018).
[g] Khan et al. (2020).
[h] Qurban et al. (2021).
[i] Husain et al. (2019).
[j] Gharib et al. (2020).
[k] PM = Phytomining, PE = Phytoextraction, CP = co-planting, RR = Rhizoremediation, and PS = Phytostabilization.

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Declaration of competing interest

Data availability

No data was used for the research described in the article.

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