





Review

Review and Prospects of Phytoremediation: Harnessing Biofuel-Producing Plants for Environmental Remediation

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Abstract: Heavy metal (HM) pollution has become a major environmental concern due to increased anthropogenic activities. The persistence and toxicity of HMs pose significant risks to ecosystems, biodiversity, and human health. This review highlights the pressing issue of HM contamination, its impact on ecosystems, and the potential risks of bio-magnification. Addressing these issues requires sustainable and cost-effective solutions. Among various remediation strategies, phytoremediation stands out as a promising green technology for mitigating environmental damage by using plants to extract or detoxify contaminants. A key challenge in phytoremediation, however, is the management of large volumes of contaminated biomass. This study explores the integration of phytoremediation with biofuel production, which not only addresses biomass management but also offers a sustainable solution within the framework of the circular economy. The dual role of specific plant species in both phytoremediation and biofuel production is evaluated, providing reduced environmental waste, lowering remediation costs, and promoting energy security. Future advancements in plant engineering, biotechnology, and process optimization hold the potential to enhance phytoremediation efficiency and biofuel yields. Expanding research into metal-tolerant, high-biomass crops can further improve scalability and economic feasibility. The review also critically assesses challenges such as the safe handling of contaminated biomass, sustainability concerns, and existing research gaps. By merging environmental remediation with bioenergy production, this interdisciplinary approach presents a viable pathway toward sustainable development.

Keywords: phytoremediation; biomass; biofuel; HMs



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1. Introduction

A significant increase in environmental pollution has been observed worldwide over the last few decades due to industrialization and urbanization. The environmental pollution created by HMs is conspicuous due to anthropogenic reasons. It is postulated that HMs from human-made causes are higher than natural emissions [1]. The industrial revolution has led to an unprecedented dissemination of toxic substances in the environment.

Exposure to these pollutants, primarily through the dietary intake of plant-derived food and drinking water or air, can cause long-term affect human health conditions [2]. Many industries use toxic compounds, including HMs, as raw materials and release them to the environment as waste and byproducts. The petroleum, pharmaceutical, printing and reproduction of recorded media, chemical, chemical product, rubber and plastic product, tannery, and pesticide industries are a few industries working with hazardous materials. The probable sources of pollutants are waste incinerators, untreated industrial wastewater, car exhaust, urban traffic, residues from mining and military activities, smelting industries, metallurgic industry, agricultural amendments, municipal solid waste, etc. [3–6].

Further, when focusing on HMs, contaminants with anthropogenic origins are more mobile than natural origins; thus, bioaccumulation is a noticeable risk. Therefore, it is essential to understand the present status of HM contamination, its temporal and spatial distribution, future contamination and prediction, identification of potential sources, and possible remediation technologies [7]. To mitigate the risk associated with HM pollution numerous in situ methods, such as cover volatilization via air venting, leaching with a surfactant, vitrification, isolation, and containment with physical barriers, and ex situ remediation methods, such as excavation followed by thermal treatment, chemical extraction, and encapsulation before disposal in a landfill, have been utilized, focusing on physical and chemical processes. However, these remediation strategies are often very costly and need technical advancements and substantial maintenance costs depending on the type and extent of contamination and the remediation strategy employed [7,8].

The alternative and sustainable technique of phytoremediation can be effectively used for addressing those drawbacks of conventional remediation techniques. Phytoremediation is an economically and environmentally friendly technique, as it utilizes green plants to contain, sequester, or detoxify contaminants from contaminated soil and water. It utilizes several mechanisms, which include degradation (rhizo-degradation, phytodegradation), accumulation (phytoextraction, rhizofiltration), volatilization (phytovolatilization), and immobilization (hydraulic control and phytostabilization) to degrade, remove, or immobilize the contaminants. Depending upon the extent and the type of the contaminants, plants utilize one or more of these mechanisms to reduce their concentrations from soil and water. For instance, plants uptake and accumulate HMs in their tissues and degrade organic pollutants, reducing their toxicity from soil and water sources [9]. The plants used for phytoremediation generally handle the contaminants selectively without affecting topsoil, thus conserving their utility and fertility while improving soil fertility with organic matter inputs [10]. Further, it has been well noted that HM uptake and accumulation vary significantly among different cultivars of a crop, as well as among different species. Accordingly, an alternative and practical approach, phytoexclusion, has been developed, which has gradually received increasing attention. This strategy involves the selection and use of low-HM accumulation crop cultivars (especially in their harvestable parts) to minimize the health risks in HM-polluted areas [11].

However, the advancements in these technologies are considered a must for amalgamation with other sectors, such as sustainable energy production. Integrating phytoremediation technology into bio-energy production could be beneficial for removing the economic restraints of phytoremediation, decreasing the remobilization of metals, and supplementing energy sources more sustainably. As biofuels are generally focused on offering many benefits, such as reduction of greenhouse gas (GHG) emissions, regional development, social structure, agriculture development, and security of supply [12,13], such applications would lead to a more significant achievement in sustainable development. Moreover, the phytoremediation approach to bioenergy is more economically feasible because lands unutilized for food production can be used for cultivating bioenergy crops

with phytoremediation potential and can achieve an economic gain in terms of bioenergy. Further, this approach provides low-cost and low-impact treatment of contaminated sites and their restoration [14].

Furthermore, this review study narrates the effects of coupling phytoremediation with bioenergy production at the meeting Agenda 2030. This review study articulates the impact of this amalgamation, highlighting the importance of meeting Sustainable Development Goals (SDGs) 07 and 11, affordable and clean energy and sustainable cities and communities. Furthermore, investing in low-carbon energy sources and promoting the effective use of natural resources were intensely discussed. These are the key factors in SDGs 13 and 15, climate action and life on land [15]. Moreover, this comprehensive study is an overview of biofuel-producing plants as a likely technology in phytoremediation that could be used in pollutant extraction at contaminated sites. Moreover, this information could be a resource for further studies on improving the phytoremediation performance of biofuel-producing plants and enhancing their efficiency.

2. Technologies for Effective Contaminated Site Cleaning

The fundamental purpose of contaminant remediation is to minimize the risk of releasing or introducing contaminants into the ecosystem. Selecting an appropriate remediation method depends on the site characteristics, the extent of the contamination, regulatory limits of the pollutant, available technologies, and the economic status of the project [16]. Several challenges associated with the remediation of polluted soils have been overcome by using several techniques such as soil amendments, thermal desorption, soil washing, electro-kinetic remediation, and bioremediation techniques, which can be carried out ex situ or in situ [17]. Ex situ remediation includes excavation and soil washing, thermal cleansing, and biological treatments, which are very efficient, easy to implement, fast, and capable of adapting to sites highly contaminated with fuel hydrocarbons, halogenated and non-halogenated organic compounds, various pesticides, etc. It is also easy to monitor and achieve more uniformity [18]. However, particular remediation techniques might produce a massive amount of toxic waste, demanding a safer place for disposal. Furthermore, soil treated thermally may not be suitable for agricultural activity, since it severely impacts soil properties [19]. In situ remediation takes place on the site with or without soil excavation [20]. However, the in situ techniques are less efficient than ex situ remedial methods, showing the downside of in situ techniques [21]. Despite these factors, in situ remediation techniques such as adopting phytoremediation and enhanced bioremediation are becoming more popular, considering less demand in terms of technical know-how and the cost of the initiation and management. Biological remedies are important as in situ pollutant treatment strategies, which are environmentally friendly and cost-effective. Among these techniques, phytoremediation plays a significant role in contaminant remediation [22].

3. Phytoremediation as a Promising Technology for Site Remediation

Phytoremediation is not a novel method in toxicity reduction; however, it can be used extensively in contaminated site cleaning as an in situ remediation approach. Phytoremediation is an environmentally friendly, cost-effective potential technology to be implemented in low-income countries due to its ease of application and lower resource requirements in management. It is accessible for soil, water, and air cleaning when the selected plants are grown in the contaminated sites and allow plants to immobilize or convert toxic compounds into degradation products while conditioning the soil for their physical, chemical, and biological properties [19,23]. Nevertheless, phytoremediation offers potential economic benefits through effective ecosystem functioning and improved ecological balance. Selling the produced biomass for anaerobic digestion and for the production of renewable energy

is potentially important to enhance economic feasibility. Some of the reclaimed metals, including Se, Mn, Pb, Zn, Cd, U, Cu, Ni, Co, and Au, can generate huge revenues through phytomining. Many mining companies generate profit through the recovery and utilization of metals from biomass and by producing energy from biomass. As well, ash is a good source of minerals, and a considerable profit can be obtained by selling carbon credits. Extracted Ni from contaminated soils is used as an important substitute for Ni fertilizers and is helpful to save on fertilizer costs [24].

In addition, several factors are considered when selecting suitable plants for phytoremediation, such as toxicity tolerance, rapid growth rate, the magnitude of pollutant extractability, daughter products and their toxicity, and the likelihood of directing contaminants to the food chain [21,25]. Phytoremediation is best applied at sites with low contamination by organic, nutrient, or metal pollutants that are amenable to one of the five mechanisms; phytoextraction (transfer of contaminants from the soil to the shoot of hyperaccumulating plants), phytostabilization (contaminants are immobilized, and thus their bioavailability is reduced), phytodegradation (contaminants are degraded by proteins or enzymes produced by plants and associated microbes), phytovolatilization (volatilization of contaminants by plants extracted from soils into the atmosphere) and rhizofiltration (contaminants are absorbed by plant roots) [26]. The appropriate type of plant should be selected considering the contaminant type and the contaminant concentration at the field, as high concentrations of contaminants have toxic effects on the plants while inhibiting plant growth and the phytoremediation process. Moreover, some plants show tolerance mechanisms with HM concentrations. For instance, hemp, flax, and castor are excellent options for the phytoremediation of Cd and Zn from contaminated soils as they are more tolerant to both metals. *Ricinus communis* has high tolerance for As [14]. Another study revealed that *Koeleria paniculata* is a highly Pb-tolerant woody plant. The main strategy of Pb resistance in *K. paniculata* is the fixation and sequestration of Pb by the cell wall and vesicles of root cells [27].

Additionally, both native and invasive plants are used to alleviate HM toxicity via phytoremediation. Invasive plants have some characteristics that are necessary for effective phytoremediation. In practice, invasive plants show the desirable properties associated with hyperaccumulators: increased tolerance to pollutants, resistance to drought, and allelopathic abilities. They play a role in the uptake of contaminants from the soil via the rhizosphere by immobilizing these metals and significantly reducing their concentrations in the soil. Therefore, the effective use of invasive plants has become an important concern and a focus of phytoremediation [28]. Invasive plants such as *Calotropis gigantea*, *Sida cardifolia*, *R. communis*, *Spartina alterniflora*, *Alternanthera philoxeroides*, and *Eichhornia crassipes* can effectively be used in phytoremediation [29]. Another study showed that *Reynoutria japonica* has a high tolerance for Cd, Cr, Pb and Zn [30]. Moreover, the hyperaccumulation efficiency of invasive plant species depends on their rapid growth, extensive root systems, and increased uptake activities compared to native plant species. These attributes are highly effective in mitigating pollutants, including HMs, from soil and water. *Wedelia trilobata*, a plant species native to southwest America and belonging to the Asteraceae family, is considered an invasive plant in China due to its vigorous spread across various provinces. *W. trilobata* exhibits a strong adaptability to N, enabling it to regulate the toxicity of HMs despite its invasive nature. Further, N is a required macronutrient for plant growth and can enhance Cd tolerance by maintaining the biochemical and physiological characteristics of invasive plant species. The biomass of *W. trilobata* can increase due to N supplementation while possibly alleviating Cd toxicity due to *W. trilobata* having a strong ability to take up Cd from the soil through passive or active diffusion and storing it in aboveground biomass via phytoextraction. It exhibits a higher capacity to accumulate more

Cd in roots and translocate it to shoots. The plant can then mitigate Cd toxicity through various processes including metal chelation, compartmentalization, and sequestration. This exceptional Cd tolerance and accumulation ability indicates that *W. trilobata* may have the potential through phytoremediation to alleviate Cd contamination in wetlands [31–34].

Further, native plants can be used effectively and efficiently for phytoremediation purposes. A study (to assess the levels of Cd) carried out on Hayat Abad Industrial Estate located in Peshawar showed that, based on concentration of Cd, the most efficient plants for phytoextraction were *Cnicus benedictus*, *Parthenium hysterophorus*, *Verbesina encelioides*, *Conyza canadensis*, and *Xanthium strumarium*, whereas *Cerastium dichotomum* and *Chenopodium murale* were reported to be effective in phytostabilizing Cd [35]. Some researchers have suggested that the diffusion of invasive plants is not usually affected by HM contamination, as invasive species are highly resistant and competitive in relation to other species which avoid higher concentrations of HMs, especially toxic ones. For example, native plant diversity was decreased by between 33% and 50%, resulting from increased HM pollution. However, no evidence was detected in invasive species populations. The stronger tolerance to HMs may further facilitate the spreading of invasive plants and establishment in their new habitats [36]. For an instant, to evaluate its tolerance, the invasive weed *Solidago canadensis* was grown alongside the native plant *Kummerowia striata* in a Pb-contaminated environment. The results revealed that *S. canadensis* has a higher accumulation of Pb and effectively binds it in its aboveground tissues when compared with *K. striata*. This showed that the invasive plant has more capability to alleviate HM toxicity via phytoremediation [33].

Furthermore, attention should be given to the soil type and quality, the viability of the plants and planting system, and meteorological factors, including climate, elevation, and precipitation. Thus, an early site inspection is essential before selecting a suitable plant type for remediation [9]. The phytoremediation mechanism should be identified using comprehensive studies. Plants with a deep, extended root system and rapid plant growth rate expedite continuously removing contaminants from the contaminated site. However, some contaminants might be released into the atmosphere via phytovolatilization; however, the lower contaminant concentrations are monitored in the atmosphere near remediation sites [37]. Poplar trees can remove volatile compounds from fields. The chlorinated compounds are effectively removed by the bark and leaves of the poplar tree via phytovolatilization [38]. Further, many countries have treated persistent organic pollutants (POPs); a mixture of toxic organic compounds commonly found in urban areas and agricultural lands, through phytoremediation technologies [39]. The phytoremediation process also works well in mitigating the soil and groundwater pollution risk caused by HMs. Some fern species can hyper-accumulate As; the extended root system usually goes 10–12 inches in the soil leading to efficient absorbance of As [40]. The same study found that the fern species, such as *Pteris vittata* and *Pityrogramma calomelanos*, hyper accumulate As from the soil. It is about 2% of removal from the total biomass production. Safe recovery of this bio accumulated As can be done through the fluid extraction mechanism and later may use for industrial applications [40].

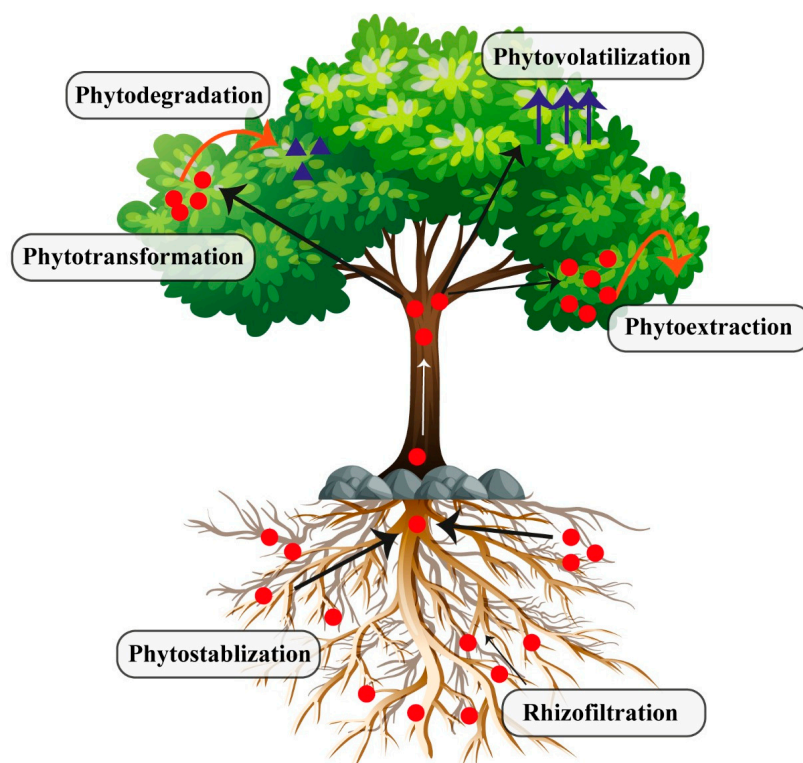
Nevertheless, the ornamental plants can be used in phytoremediation process, including treating dyes, HMs, and organic contaminants. The ornamental plants mediated HM remediation can simultaneously remove contaminants and bring recreational or aesthetic value to the site. For instant, Cd can be effectively removed by *Cosmos bipinnatus*, *Microsorium pteropus*, *Petunia hybrida*, *Nicotiana alata* and *Eichhornia crassipes* whereas Cr can be effectively removed from *Tagetes erecta*, *Euphorbia milli*, *Petunia hybrida*, *Nicotiana alata* and *Hibiscus sabdarifa* [41]. Moreover, a case study conducted in the Gorgan wastewater treatment plant in northern Iran regarding the effects of phytoremediation on treated urban wastewa-

ter on the discharge of surface and subsurface drippers using vetiver and pampas plants revealed that pampas grass had more significant phytoremediation effects in drip irrigation systems (reducing the drippers' clogging) compared to vetiver when using wastewater. Therefore, this plant can be practically and effectively used in a complementary treatment unit of wastewater treatment plants and the filtration units of irrigation systems to reduce operating costs [42]. In addition, there are some current trends and future advancements in the phytoremediation sector. Microbially assisted phytoremediation of air pollutants is gaining huge attention as an emerging trend which represents the degradation of air pollutants by plant–microorganism association. As examples, polycyclic aromatic hydrocarbon pollutants can be effectively phytoremediated by microorganisms of *Bradyrhizobium japonicum*, *Pseudomonas* spp., *Alcaligenes faecalis* BDB4, *Stenotrophomonas* sp., *Pseudomonas* sp. with *Jatropha curcas*, *Leptochloa fusca*, *Conyza canadensis*, and *Trifolium pretense* plants with 99% degradation of pheanthrene. Further, the pollutant phenol can be remediated by microorganisms of *Pseudomonas* sp., *Acinetobacter lwoffii* ACRH76, *Acinetobacter calcoaceticus* P23, *Bacillus cereus* with bean and maize, *Phragmites australis*, and *Lemna aoukikosa* plants, which have a phenol accumulation 10 times higher in microbial assistance, showing a 96% removal of phenol in 15 days. Genetic engineering and molecular biology have a huge potential to transform or modify plants and microbes in terms of phytoremediation. Several studies have been successfully carried out on the genetic modification of plants for phytoremediation of several pollutants. Genetic engineering can regulate or overexpress the genes associated with microbial associations, resistance to pollutants, and enhanced biomass of host plants. Genetically modified plants like *P. angustifolia*, *N. tabacum*, and *S. cucubalis* have been shown to accumulate more HMs [43]. Plant growth-promoting bacteria in the phytoremediation of metal-polluted soils are a current trend in phytoremediation. For instance, the plant growth-promoting rhizospheric bacterium *Variovorax paradoxus* has worked well with *Bornmuellera tymphaea*, *Noccaea tymphaea*, and *Alyssum murale* plants, and the plant growth-promoting endophytic bacterium *Jeotgalicoccus huakuii* has worked well with *Cynodon dactylon* and *Eleusine indica* plants for phytoremediation of metal-polluted soils [44].

While phytoremediation offers several advantages, it is important to consider its potential drawbacks. The key drawbacks are as follows: (1) It is a considerably slow process that requires notable time to achieve significant reductions in contaminant levels. To fully remediate a contaminated site, it may take several years or even decades. Therefore, this prolonged timeline may not be suitable for sites requiring immediate remediation. (2) The need for appropriate plant species is crucial to the success of phytoremediation. However, the availability and suitability of specific plant species may be limited, especially for specific contaminants or challenging site conditions making phytoremediation less feasible. (3) The harvested biomass from phytoremediation may contain high concentrations of contaminants. Improper handling of this biomass may result in secondary pollution. Therefore, proper management and disposal of this biomass are crucial to preventing secondary contamination. The costs and logistics associated with biomass management are a significant challenge. (4) Phytoremediation is generally suitable for smaller-scale or localized contamination. Implementing it on a large scale may require extensive land availability, significant resources, and long-term monitoring and maintenance, which may prove unfeasible for larger contaminated sites. (5) Phytoremediation success is influenced by some site-specific factors including soil type, pH, moisture content, and climate conditions. Certain sites may not be suitable for phytoremediation due to extreme conditions that inhibit plant growth or limit contaminant uptake [45]. Table 1 summarizes a few potential plants for contaminated site cleaning. Figure 1 shows the mechanisms of phytoremediation.

Table 1. Potential plants in contaminated site cleaning.

Common Name	Scientific Name	Type of Contaminant	References
Tumu merah	<i>Bruguiera gymnorhiza</i>	Pb Cr Hg	[46]
Sunflower	<i>Helianthus annuus</i>	Pd Cd	[47]
Indian rhododendron	<i>M. melastoma</i>	Ni	[48]
Knob weed	<i>Hyptis capitata</i>	Ni	[49]
Gandapana	<i>Lantana camara</i> L.	Zn Pb Cd	[50,51]
Smooth cord grass	<i>Spartina altiniflora</i>	Zn Pb Ni Cu	[52,53]

**Figure 1.** Mechanisms of phytoremediation.

4. Recent Advances in the Biofuel Industry

Most developed and developing countries' energy systems are based on fossil fuels. However, there are some problems associated with fossil fuels, including the environmental impacts (global warming and air pollution), scarcity of supply, risk of supply, and price and market instability, which put fossil fuels at the center of the shift toward low-carbon economies [54]. Some forecasts postulate that energy consumption will increase by more than 50% over the next 30 years [54]. At current consumption rates, it has been proven that fossil fuels are depleting fast due to increased population, and this may change with

new discoveries, technological advancements, and shifts in energy demand. Focusing on the replacement of fossil fuels with renewable energy sources is considered to be the most practical single pathway to climate stabilization when physical, financial, political, and environmental factors are all examined. Moreover, in 2020, fossil fuels, renewable sources, and nuclear power accounted for about 83.1%, 12.6%, and 4.3% of world energy use, respectively [55].

GHGs play an essential role in maintaining warmth on the planet. The natural temperature would be $-18\text{ }^{\circ}\text{C}$, instead of $15\text{ }^{\circ}\text{C}$, without GHGs, particularly water vapor. GHGs such as carbon dioxide, methane, ozone, nitrous oxide, and chlorofluorocarbons result in temperature increases not only at Earth's surface but also in the troposphere, causing global warming [56]. In particular, burning of fossil fuels is the key contributor for releasing GHGs to the atmosphere (77%), especially carbon dioxide with the most fluctuating concentration. The other sources are agriculture (10%), industry (8%), and waste (3%) [57]. According to statistics, total carbon dioxide emissions were 22.7 billion tons in 1990 and 36.44 billion tons in 2019, representing a nearly 60% increase. Fossil fuels (coal, oil, and gas) caused a 57.5% rise in carbon dioxide emissions from 21.8 billion tons in 1990 to 34.33 billion tons in 2019 [58]. Global waste generation is expected to continue to grow due to economic development and population growth. Pollutants, GHGs, and plastics are the main three constituents of the waste triangle. Waste conversion to energy is the way forward for long-term sustainability. At present, waste-to-energy technology converts waste biomass into biofuel instead of burning fossil fuels, which reduces GHG emissions [57].

The term biofuel is referred to as liquid or gaseous fuels for the transportation sector, predominantly produced from plant biomass. In developed countries, there is a growing interest in employing modern technologies and efficient bio-energy conversion using a range of biofuels, which are becoming cost-effective and competitive with fossil fuels. Biomass appears to be an attractive feedstock for many reasons, including that it is a renewable resource that could be sustainably developed in the future with no net releases of carbon dioxide and very low sulfur content, and its significant economic potential [59]. Over the past nine years, biofuel has been considered an alternative fuel worldwide.

The United States remains one of the largest producers of biofuels, producing approximately 16 billion gallons in 2022, primarily from ethanol and biodiesel. Brazil also plays a significant role in global bioethanol production. The EU has been focusing on the impact of bioenergy development on the environment since the 1990s. The roadmap released by the EU sets general targets for a competitive low-carbon economy: the amount of greenhouse gas emissions in the EU should be reduced by 40% by 2030, 60% by 2040, and 80% by 2050 compared to 1990 by strengthening the R&D of low-carbon technologies and implementing an energy efficiency plan [60].

Biofuel production has evolved from first to fourth generations based on different parameters, such as the type of processing technology, type of feedstock, and their level of development, including different types, such as bioethanol, biodiesel, and their gaseous forms like biogas [61]. In the first generation, biofuel is made mainly from agricultural commodities such as maize, wheat, soybean, sugar, beets, corn, etc. In contrast, second-generation biofuels are designated as those biofuels, including bioethanol and biodiesel, produced from nonfood materials such as feedstocks [58,59]. Third-generation biofuels are mainly derived from microalgae and cyanobacteria biomass, which can be used to naturally generate alcohols and lipids to transform into biodiesel or any other high-energy fuel product, which has been thought to have huge potential to meet future biofuel demands without compromising arable land and food sources [60,61]. The latest biofuel generation, fourth-generation biofuels, encompasses the use of genetic engineering to increase the desired traits of organisms used in biofuel production [62].

Apart from the above production technologies, the operational concept of the bio-refinery is an integrated facility that produces a range of biofuel products based on the given feedstock. On top of diversification and high valuation of products, the enhancement of mass and energy integration in bio-refinery has also been focused by researchers. Technological and economic advances in bio-refinery are being continuously assessed and improved [63]. Modern biofuels (third- and fourth-generation biofuel) are more sustainable than traditional biofuels (first-generation) and can eliminate environmental pollution by reducing carbon emissions [64]. Nevertheless, advanced renewable energy sources that can be produced from agricultural and woodland lignocellulosic biomass and algal feedstock are recent advancements [65].

5. Potential of Biofuel-Producing Plants in Phytoremediation

The biomass produced in phytoremediation could be economically significant in the form of bioenergy, including forms such as biogas, biofuels, and combustion for energy production and heating [66,67]. The management of metal-polluted biomass after the phytoremediation process has been addressed by many authors, who have demonstrated various potentials in incorporating phytoremediation biomass into bioenergy production based on thermal, thermochemical, or biochemical processes [46–48]. Several plants, including the giant reed (*Arundo donax*), Chinese mustard (*Brassica juncea*), jatropha (*J. curcas*), *Miscanthus* species, the castor oil plant (*R. communis*), and *Salix* species with HM accumulating capacity, have been used for cleaning polluted land [68]. Bioenergy crop production on contaminated land could be an additional economic incentive for the phytoremediation of these sites. Thus, using bioenergy plants with abiotic stress tolerance potential has the dual advantage of phytoremediation and a good economic return in producing bioenergy [14]. The new method of joining phytoremediation with bioenergy crop production has been implemented and practiced in recent times to achieve the low-cost decontamination of soil and the production of biofuels [46,47]. For this purpose, the appropriate selection of energy crops that can tolerate various contaminants, especially HMs, is crucial. Additionally, these lands do not compete with lands for food production [69]. However, to increase value, the incorporation of biomass from phytoremediation has gained popularity, and some studies have been carried out; for example, the plant *Cannabis sativa* L. has been reported as a multi-use crop for phytoremediation of soils polluted with toxic metals and also as a potential feedstock for bioenergy production. Phytoremediation by *C. sativa* L. coupled with bioenergy processes has been recently investigated to include concept designs considering biodiesel production, bioethanol, biogas and combined heat, and power [70].

Identifying the most suitable plant species before the potential biomass production in a particular region is essential. This also depends on the degree of climatic adaptation by those plant species [71]. Generally, biofuel-producing plants should have higher oil content, a high conversion rate to biofuel, local availability, and cost-effectiveness. Also, it is vital to understand the responses of bioenergy plants to HM stress so that plants can be generated with suitable agronomic traits for HM tolerance [72]. Bioenergy plants should have the potential to adapt well to polluted lands and have the capacity to produce higher biomass along with increased energy potential; this is also highly important [14]. For an instance, jatropha (*J. curcas*) is a drought-tolerant, biofuel-producing plant, and plant performance varies depending on the host country's climate, management, and varieties. The plant's productivity depends on the vegetative and generative characteristics of the plant. The number of fruits per plant, leaf width, primary and secondary branches, and fruit bunches show high predictive and high heritability values [53,54,68]. Figure 2 and Table 2 show examples of bioenergy-producing plants with phytoremediation potential.

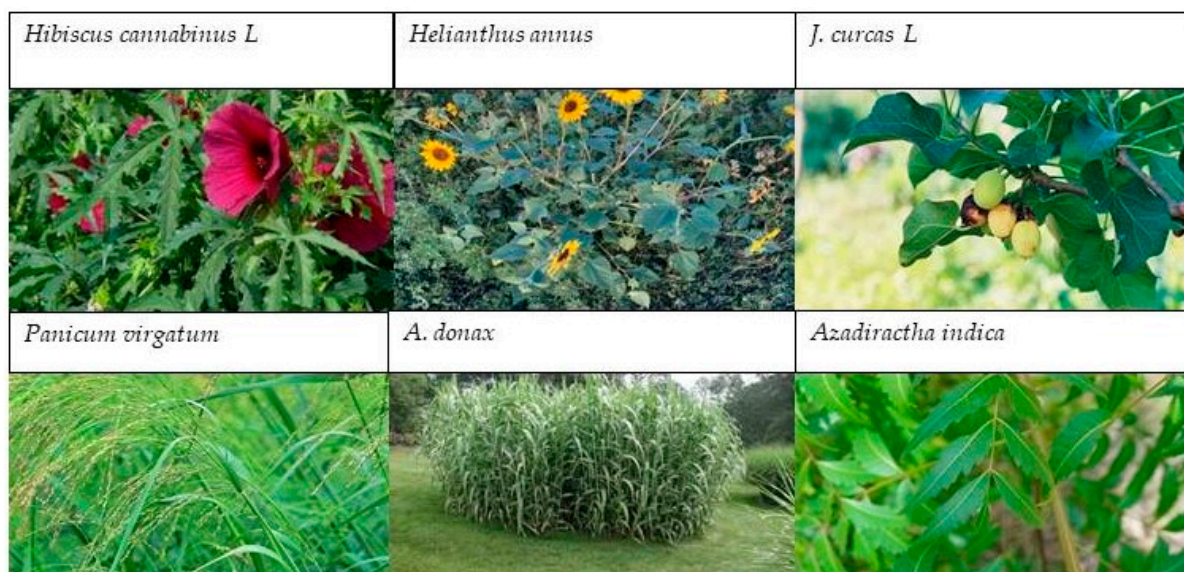


Figure 2. Examples of bioenergy-producing plants with phytoremediation potential.

Table 2. Examples of bioenergy-producing plants with phytoremediation potential.

Plant Type	Contaminant Type	Plant Part	Possibility of Use in Biofuel Production	References
<i>Hibiscus cannabinus</i> L.	Cd, Zn, Pb, Cr, Ni	Shoots and roots	Bioethanol Biodiesel	[73,74]
<i>Helianthus annuus</i>	Pd, Cd, Cu, As, Zn	Biomass and seeds	Bioethanol Biodiesel	[75]
<i>J. curcas</i> L.	Zn, Cd, Al, Cr, Pd, Mn, Cu	Shoots and roots	Bioethanol Biodiesel	[59–61,76]
<i>Panicum virgatum</i>	Cd, Pb, Cr, Ni, Ba, Cu	Biomass	Bioethanol	[62,64,77]
<i>A. donax</i>	Zn, Hg, Pb, Ni, As, Cd, Cu	Roots	Bioethanol Biogas	[63,78]
<i>Azadiractha indica</i>	Zn, Pb, Cd, Cu	Leaves and Stems	Biodiesel Bioethanol	[65,66,79]

6. Challenges of Coupling Phytoremediation with Bioenergy Production

The concept of coupling phytoremediation and biofuel production is a potential and promising pathway toward sustainable use of polluted biomass as metal-free biofuels and by-products while allowing for the recovery of HMs. Besides the benefits of producing bioenergy from polluted biomass, the generation of potentially toxic streams must be minimized, which has spurred the investigation of sorbents, demineralization, and leaching techniques to remove or immobilize HMs [80]. Depending on the type of contaminant and fate of the plant, the bioenergy production process should be carefully selected, since contaminants could be released into the environment. Therefore, this aspect represents the first barrier to facilitating the incorporation of phytoremediation biomass into bioenergy production; some safety and regulatory aspects are still under revision [79].

6.1. Residual Contaminants in Biomass

Contaminant transfer from biomass to biofuel is a possible complication in this mechanism. Contamination of the crop can cause severe problems in subsequent stages of the biofuel production process, and the decision regarding whether crop capture of HMs

should be stimulated should be made on a case-by-case basis [81]. Moreover, it is crucial to know the destination of pollutants in plants to make decisions about the fate of metals in downstream processing, which would be incorporated into bioenergy production. Nevertheless, understanding the pollutants' fate in plants allows us to estimate the possible transfer of metals in some by-products or residues during biofuel production. Furthermore, the safety of phytoproducts (bioenergy obtained from biomass used for phytoremediation) should be taken into consideration, as these phytoproducts are easily contaminated by HMs, causing human health issues. The use of edible plants during phytoremediation is an additional risk. Therefore, using non-edible crops must be encouraged in bioremediation technologies [79]. Coupling a site-specific SWOT analysis with a detailed cost–benefit analysis and social impact, an assessment must be applied to ensure the sustainability of bioenergy production from polluted lands. These initiatives are essential for the success of bioenergy production from contaminated lands [80]. The level of site cleaning needs to account for how to safely process and dispose of contaminated biomass without causing secondary pollution.

6.2. Low Yield with Contaminated Biomass

This integrated approach (phytoremediation for bioenergy) is challenging because some plants have less tolerance to HMs or show plant toxicity when they grow on contaminated lands, which results in retarded or inhibited growth, either of the whole plant or plant parts, causing a low yield in the end. When concentrations inside plant cells accumulate above threshold levels, it can result in direct toxicity by damaging cell structure due to oxidative stress caused by reactive oxygen species and the inhibition of several cytoplasmic enzymes. Additionally, it can cause indirect toxic effects by replacing essential nutrients at cation exchange sites in plants [82]. For instance, the response of *J. curcas* L. to Pb exposure include a decrease in root elongation and biomass production, accelerated leaf senescence, inhibition of chlorophyll biosynthesis, inhibition of seed germination, and a wide range of adverse effects on the growth and metabolism of plants. Moreover, interfering with nutrient uptake and influencing the net photosynthetic rate and respiration can also be identified as plant toxicity factors [83]. Furthermore, the harvesting frequency required for bioenergy production might conflict with the optimal timeline for effective phytoremediation. However, dedicated energy crops like poplars, willows, elephant grass, and switch grass can accumulate and tolerate high levels of HMs and grow well on contaminated lands [84].

6.3. Level of Site Cleaning

This is an important challenge to be considered when coupling phytoremediation with bioenergy production from HM-contaminated land because it is necessary to fulfill both parameters (phytoremediation plus bioenergy production), not just one. The level of site cleaning presents a significant challenge when coupling phytoremediation with bioenergy production, especially on HM-contaminated land. Achieving an adequate level of decontamination while balancing biomass production for bioenergy introduces several complexities that need careful consideration. However, phytoremediation may not fully remove contaminants, especially in deeply rooted or highly polluted sites. Some HMs might persist in the soil even after multiple cycles of phytoremediation, limiting the effectiveness of the process and prolonging land recovery timelines. Furthermore, contaminants are not evenly distributed across a site. Areas with higher concentrations may need more extensive remediation efforts, making it challenging to determine when the entire site has been sufficiently cleaned for safe use or bioenergy production.

6.4. Phytoremediation Plant Selection

Different plants have different abilities to absorb and tolerate specific contaminants. Choosing the right plants to match the contaminant profile is crucial but challenging, especially in multi-contaminant sites. This may require a combination of plant species or even different phytoremediation techniques over time, complicating the cleaning process. Plants effective in removing contaminants may not always be suitable for bioenergy production due to their low biomass yield or other agronomic limitations. Striking a balance between effective site cleaning and sufficient biomass for energy production can be difficult. Different kinds of plants can be used for phytoremediation purposes along with bioenergy production, including *A. donax* (giant reed), *Arachis hypogea* (peanut), *Brassica rapa* (rapeseed), *C. sativa* (hemp), *J. curcas*, *Glycine max* (soybean), *H. annuus* (sunflower), *Linum usitatissimum* (flax), etc. [14,85]. Poplars represent a potential feedstock for applications in bioenergy, since they are deep-rooted multipurpose hardwood trees known to be an excellent candidate for phytoremediation and reducing environmental pollutants due to their highly efficient potential for photosynthesis [86]. Moreover, *A. donax* is an auspicious energy plant, which can be cultivated in contaminated soils to provide biomass for energy production purposes along with some potential for As, Ni, Cd, and Cr remediation, indicating tolerance against high concentration of Cd, As, Ni, and Cr [87].

7. Research Gaps in Coupling Phytoremediation with Bioenergy Production

There remain significant knowledge gaps regarding the potential toxic emissions and environmental risks associated with using plants in contaminated site cleaning and converting them into bioenergy. One of the key research gaps is the lack of comprehensive studies on the fate of contaminants during conversion processes. For example, during the conversion process, contaminants may volatilize and become airborne, contributing to environmental pollution. Thus, there should be crucial research requirements to respond to such important issues before applying the concept in the field. Moreover, pretreatment methods, including dry, wet, and physicochemical treatments, have not been thoroughly tested for their efficacy and ability to detoxify contaminated biomass before it is processed for energy. These pretreatment techniques are critical for minimizing the risk of releasing harmful contaminants during bioenergy production. However, their performance under different conditions (e.g., varying levels of contamination, types of pollutants) requires more investigation at both the laboratory and field scales.

Another gap lies in understanding how different contaminants, such as HMs, persistent organic pollutants, or emerging contaminants, behave during bioenergy production. The interactions between these contaminants and the bioenergy production process need further exploration to develop safe and effective technologies for converting contaminated biomass into clean energy. Bioenergy production from multiple and heavily contaminated sites is technically challenging, as crop production will be heavily retarded by the toxicity of mixed pollutants. Most areas are polluted with metals and metalloids, persistent organic pollutants, petroleum hydrocarbons, pesticides, herbicides, radionuclides, and other new and emerging contaminants that retard plant growth. For instance, HM content (Cd, Cu and Pb) has been detected in the oil extracted from the seeds of rape plants (*Brassica napus*) which were cultivated in polluted soil [39,69,88]. Therefore, suitable agronomic practices must be optimized to reduce the toxicity of multiple pollutants and maximize the growth and yield of selected bioenergy crops in polluted lands to achieve maximum output. As well, it is crucial to develop a planting model for maximizing the economic returns from such remediation activities [59]. Therefore, the proper involvement of respective stakeholders, including site owners, local people, farmers, technology providers and consultants,

remediation experts, certification bodies, and other voluntary organizations, is essential for the success of the multipurpose clean-up process [88].

Additionally, phytoremediation linked with biofuel production has a common concern regarding invasive and exotic plants. There has been a seriously deleterious effect on certain invasive and exotic species' biodiversity, including *Pueraria Montana*, a semi-woody perennial plant belonging to the *Fabaceae* family [89]. Additionally, *A. donax*, a plant that has capacities of both bioenergy production and phytoremediation, altered hydrology and eliminated native species in central Texas [90]. Thus, investigating plant behavioral characteristics in different ecosystems should be carefully examined.

Moreover, extensive studies are needed to determine the level of contaminant removal and bioenergy yield through relevant plants. For instance, corn is extensively used for bioethanol production worldwide, with a yield of approximately 29 kg from 100 kg corn by wet milling and 34 kg from 100 kg corn from dry milling [91]. Therefore, achieving the maximum bioethanol yield from a given extent of contaminated land is possible. Additionally, it is also responsible for the phytoremediation purposes because corn is an effective accumulator plant for phytoremediation of Cd- and Pb-polluted soils [92]. Although corn is used for both phytoremediation and bioenergy production, it is still an edible plant and thus causes bioaccumulation in the food chain, posing a high risk to human health, and its contaminant removal potential is still under debate. Therefore, the level of site cleaning when coupling phytoremediation with bioenergy production still needs to be considered extensively.

Nevertheless, the phytoremediation process may only expect a partial recovery of soil. It is time-consuming to remediate contaminated soil. Contamination concentration, toxicity and bioavailability, plant choice, and stress tolerance are the main reasons for taking more time in the remediation process. Due to low biomass production in some phytoremediators and seasonal effects on plants, several planting and harvesting cycles are required to decontaminate contaminated land, resulting in consuming more time in the remediation process [45]. Thus, selecting suitable plants for the given climatic conditions of the area and investigating the growth habits of the required plants before installing them for the phytoremediation process is crucial and strongly needs to be considered. The plants used for the phytoremediation purpose are contaminant-specific and site-specific. Therefore, it is essential to have a plant selection criterion introduced into different contaminant areas based on contaminant type, climatic conditions, harvesting conditions, and relevant bioenergy type as well. Table 3 refers to the plant selection criteria for different contaminated areas.

Table 3. Potential of plant selection criteria for contaminated areas (relevant to commonly used bioenergy plants for phytoremediation).

Plant	Contaminant Type	Climatic Growing Condition	Harvesting Condition	Biofuel Type	References
Giant reed (<i>A. donax</i>)	Zn, Cr, Pb, Ni, As, Cd, Cu	Subtropical, and semi-arid climates (Hot areas)	Multiple harvests per year for about 10–15 years	Bioethanol Biogas	[87,93–96]
Neem (<i>A. indica</i>)	Zn, Pb, Cd, Cr, Ni, Co	Sub-arid and sub-humid areas with tropical and subtropical climates	Once in year, harvesting can be carried out for about 10–11 years	Biodiesel Bioethanol	[97–100]

Table 3. Cont.

Plant	Contaminant Type	Climatic Growing Condition	Harvesting Condition	Biofuel Type	References
Jatropha (<i>J. curcas</i>)	Fe, Cd, Al, Cr, Pb, Mn	Tropical and subtropical regions	Harvest seeds around 90 days after flowering regions	Bioethanol Biodiesel	[101–106]
Switch grass (<i>P. virgatum</i>)	Cd, Pb, Cr, Ni, As, Fe	Temperate and subtropical zones and tropical climates	Once a year (later in winter or even early spring) for over 10 years	Bioethanol	[107–110]
Sunflower (<i>H. annuus</i>)	Pd, Cd, Ni, Cr, As	Temperate and tropical climates	Harvest seeds 70 to 100 days after planting	Bioethanol Biodiesel	[47,111–113]
Java jute (<i>H. cannabinus</i>)	Cd, Cr, Cu, Ni	Tropics and subtropics where temperatures are greater than 20 °C	Harvesting at 180 days after planting	Bioethanol Biodiesel	[114–116]
Castor (<i>R. communis</i>)	Cr, Ni, Pb, Zn, Cu, Mn	Tropical and subtropical regions with hot and dry climates	Harvest seeds 140–180 days after planting	Biodiesel Bioethanol	[117–120]
Gandapana (<i>L. camera</i>)	Ni, Cr, Cd	Temperate climate and drought conditions	Harvest seeds once a year	Bioethanol	[121–123]
White willow (<i>Salix alba</i>)	Cd, Cu, Hg, Pb, Zn	Temperate climates, tolerate both high and low temperatures	Start harvesting 3 years after establishing	Bioethanol	[124–126]
Silver grass (<i>Miscanthus sinensis</i>)	Cd, Cr, Cu, Ni, Pb, Zn	Temperate and tropical climates	Harvest in the flowering stage	Bioethanol	[67,127–129]

8. Conclusions

The findings of this review demonstrate that bioenergy-producing plants possess the unique ability to uptake and bio-concentrate HMs at elevated levels from the soil. Utilizing HM-contaminated lands for cultivating bioenergy-producing plants with phytoremediation potential offers a viable solution to avoid competition with agricultural lands, thereby supporting sustainable biofuel production. The study also aimed to identify effective methods for removing HMs from contaminated zones, determine suitable plant species for both phytoremediation and biofuel production, and address the challenges associated with integrating phytoremediation and biofuel production. By focusing on the phytoremediation mechanisms of these plants, further advancements can be made to enhance their capability to achieve bioenergy production and phytoremediation of toxic metals simultaneously. The HM remediation potential and biomass production of the non-edible bioenergy plants can be amplified using biotechnological approaches such as generation of transgenic plants. The efficacy of phytoremediation as a suitable approach for decontaminating metal-impacted sites is undeniable, as it reduces pollutants and generates biomass and byproducts that can be utilized for biofuel production. A clear focus on the phytoremediation mechanisms in desired plants will help to further improve the plants to accomplish the dual task of bioenergy production and phytoremediation of toxic metals.

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