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Review

Molecular Basis of Energy Crops Functioning in Bioremediation of Heavy Metal Pollution

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Abstract: Heavy metal pollution is a gradually growing environmental issue that hinders the growth and development of plants, and also destabilizes soil. Consequently, eco-friendly phytoremediation methods have gained traction, with energy crops emerging as a particularly effective solution. Energy crops not only provide high-quality plant materials for detoxification and remediation of heavy metal pollution, but also possess energy properties conducive to biofuel production. Therefore, this paper delves into the tolerance mechanism of energy crops towards heavy metal toxicity, elucidating processes such as root complex-mediated inhibition of metal migration and response to reactive oxygen species (ROS) through heavy metal-related proteins, enzyme systems, reactive nitrogen species (RNS), and hormones. Moreover, it summarizes the heavy metals remediation mechanisms of energy crops, including uptake, translocation, chelation, immobilization, and sequestration. This paper explores applications of energy crops in heavy metal pollution remediation, emphasizing the methods for efficient biochar remediation and biofuel generation. Furthermore, potential challenges in using energy crops for heavy metal pollution remediation are outlined. By systematically examining the function mechanisms and prospective applications of energy crops in heavy metal pollution bioremediation, this paper serves as a valuable reference for both research and practical implementation in this field.

Keywords: heavy metal pollution; energy crops; bioremediation; heavy metal toxicity; applications; biofuels

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1. Introduction

The problems of heavy metal pollution have become more serious due to factors such as ore extraction and the over-use of metal products, as well as effluents and emissions [1]. Heavy metals typically include Cd (Cadmium), Zn (Zinc), Cu (Copper), Cr (Chromium), Pb (Lead), Ni (Nickel), and Hg (Mercury), as well as other metals and their compounds with a density greater than 5 g/cm^3, they are characterized by high concealability, long persistence, continuous toxicity, and incomplete remediation. In addition, some of the semi-heavy metals also exhibit similar characteristics, such as As (Arsenic) [2]. Heavy metals are widely distributed in soil, the atmosphere, and water, inhibit seed germination and plant growth, destroy their internal structure, affect cellular physiological and biochemical activities [3], and reduce their bio-functions. Moreover, they directly or indirectly enter the food chain, causing adverse cascade effects [4]. Therefore, timely and efficient heavy metal pollution remediation has become an urgent issue.

In recent years, physical, chemical, and bioremediation methods have been explored to address heavy metal pollution. Physical remediation is a simple and effective method for solving large-scale mild and local heavy metal pollution, but it can damage soil organic matter and structure, require significant human and material resources, and is not a complete solution for heavy metal pollution [5]. Chemical remediation is a low-cost, wide-ranging, and high-efficiency method, but it cannot completely remove heavy metals and is prone to secondary contamination and soil degradation [6]. In comparison to these two methods, bioremediation is the most promising method for heavy metal remediating and soil effectiveness restoration, as it not only protects the soil structure but also is less costly and environmentally friendly [7].

Bioremediation involves phytoremediation, animal remediation, and microbial remediation. Among these, microbial remediation is the most time-consuming and has the lowest survival rate, and if microorganisms that have remediated heavy metal contamination are not treated in time, the heavy metals in these organisms will be released back into the soil upon their death [8]. In addition, lower animals poorly adapt to the environment, and the heavy metals they uptake and enrich can be easily transferred to higher animals through the food chain, resulting in the secondary contamination of the entire food chain [7]. Differently, phytoremediation is a technology that can uptake heavy metals in the soil through plant roots, complete the accumulation and degradation process by plants themselves, and achieve effective soil purification and remediation [9]. Among them, energy crops are particularly advantageous as excellent materials for heavy metal remediation.

Energy crops refer to herbaceous and woody plants that are used as a source of energy and do not compete for land or resources with food crops. From a broad perspective, any plant material with energy production characteristics or potential, such as sunflowers (*Helianthus annuus* L.) [10], sugar beet (*Beta vulgaris* L.) [11], sugarcane (*Saccharum officinarum*) [12], miscanthus sinensis (*Miscanthus*) [13], willow (*Salix babylonica* L.) [14], *Salix integra* (*Salix integra* Thunb.) [15], pennycress (*Thlaspi arvense* L.) [16], poplar (*Populus przewalskii* Maxim.) [17], vetiver (*Chrysopogon zizanioides* (L.) Roberty) [18], cotton (*Gossypium hirsutum* L.) [19], camelina (*Camelina sativa* (L.) Crantz) [20], cardoon (*Cynara cardunculus* L.) [21], ecliptae herba (*Eclipta prostrata* (L.) L.) [22], mustard (*Brassica campestris* L.) [23], rubber tree (*Hevea brasiliensis* (Willd. ex A. Juss.) Muell. Arg.) [24], reed (*Phragmites australis* (Cav.) Trin. ex Steud.) [3], castor bean (*Ricinuscommunis* L.) [25], wheat (*Triticum aestivum* L.) [26], sweet sorghum (*Sorghum dochna* L.) [27], potato (*Solanum tuberosum* L.) [28], maize (*Zea mays* L.) [29], yam (*Dioscorea esculenta* (Lour.) Burkill) [30], and cassava (*Manihot esculenta* Crantz) [31], can be considered an energy crop. Energy crops are known for their environmental adaptability, high photosynthetic rate, and stress tolerance, making them ideal for the remediation of heavy metal pollution [9]. Furthermore, energy crops, mostly oilseed crops, generally have a large biomass and can replace some fossil fuels, making them a crucial source of biofuels [32]. Similarly to most plants, low levels of heavy metals play a positive role in the growth and metabolic processes of energy crops in the environment; however, when exposed to excessive heavy metals, the life processes of many plants are inhibited by toxicity to varying degrees; energy crops exhibit advantages in not only tolerating severe heavy metals toxicity but also remediating the environment's heavy metal pollution to some extent [33].

Based on the remediation properties of energy crops, this study explores their tolerance mechanisms and remediation strategies for heavy metals, as well as the application of energy crops in remediating heavy metal pollution, including tolerance, uptake, translocation, chelation, immobilization, and sequestration processes to different heavy metals, as well as biofuels and biochar after metal-accumulating, and the possible challenges in the present and the future.

2. Mechanisms of Heavy Metal Tolerance in Energy Crops

Studies have shown that energy crops can activate their own tolerance networks when exposed to heavy metals, through a well-developed root system that secretes amino acids and organic acids [34]. These substances combine with heavy metals, forming soluble complexes that reduce ion migration into the soil [34]. Organics secreted by roots can adsorb or coprecipitate heavy metals in the soil, preventing further migration and absorption by organisms [35]. For example, proline (Pro), produced by the roots and extensively distributed in the rhizosphere environment, is capable of chelating heavy metals, thereby preventing the migration of soluble complexes [35]. However, root system immobilization alone may not be sufficient in environments with high heavy metal content, and parts of heavy metals may still enter the energy crops.

Heavy metals that enter organisms can cause oxidative stress in energy crops, resulting in the generation of large amounts of reactive oxygen species (ROS) [4]. Additionally, heavy metals, especially Cd, can combine with sulfhydryl groups and cause protein denaturation, rendering the relevant proteins unable to perform their functions, leading to cellular damage and an imbalance in the internal environment [36]. Correspondingly, energy crops engage in heavy metal detoxification by utilizing heavy metal-related proteins, enzyme systems, reactive nitrogen substances (RNS), and hormones to reduce the damage caused by ROS. For instance, sunflowers regulate ROS homeostasis and respond to the stress of Ni through the natural resistance-associated macrophage protein 1 (NRAMP1) and NRAMP3 [10]. Sugar beet glutathione S-transferase U9 (BvGSTU9) acts as a dimer in the cytoplasm and converts toxic ROS into weakly toxic H_2O_2, which is then broken down into nontoxic H_2O and CO_2 and excretes [37]. The detoxification process of ROS in energy crops involves not only heavy metal-related proteins but also enzyme systems. In the case of heavy metal stress, heavy metal-related proteins and enzyme systems of energy crops work together to reduce ROS accumulation, including protective enzymes such as superoxide dismutase (SOD), peroxidase (POD), and catalase (CAT) [38], as well as non-protective enzymes such as amylase (AMS), alcohol dehydrogenase (ADH), and nitrate reductase (NR) [32]. Furthermore, RNS can also participate in the heavy metal detoxification process. RNS is the second most significant messenger after ROS, and its component nitric oxide (NO) is a momentous endogenous molecule of signal that can scavenge ROS directly or induce the antioxidant defense system to scavenge ROS in vivo [39]. Under heavy metal stress, the donor of NO is a single nucleotide polymorphism marker (SNP), which significantly increases the activity of antioxidant enzymes such as SOD, CAT, ascorbate peroxidase (APX), and GST [40], and enhances the content of indole-3-acetic acid (IAA) and gibberellin (GA), resulting in the reduction in ROS production and heavy metal toxicity [41]. Figure 1 shows the mechanisms of heavy metal tolerance in energy crops.

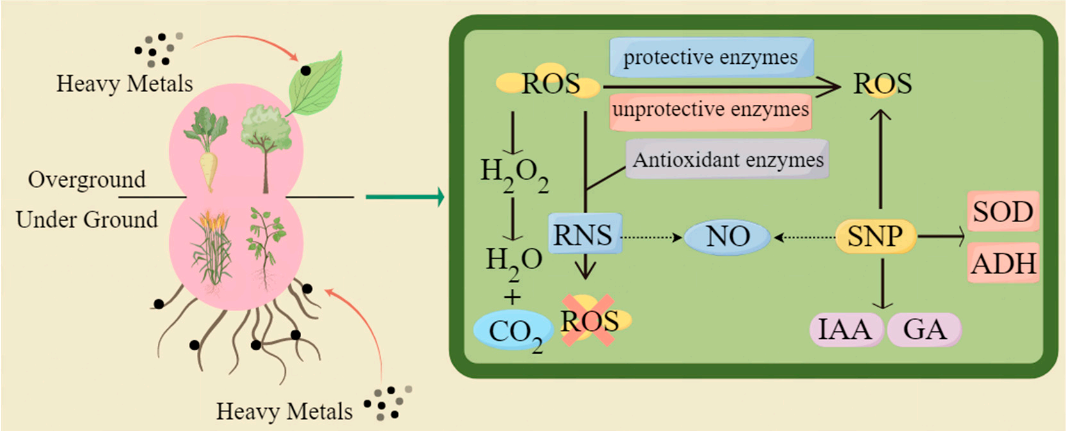

Figure 1. The mechanisms of heavy metal tolerance in energy crops. (ROS: reactive oxygen species, RNS: reactive nitrogen substances, SNP: single nucleotide polymorphism marker, SOD: superoxide dismutase, ADH: alcohol dehydrogenase, IAA: indole-3-acetic acid, GA: gibberellin).

3. Remediation Mechanisms of Heavy Metals by Energy Crops

Energy crops can remediate heavy metal pollution by immobilizing heavy metals in specific parts of the organism, mainly through uptake, translocation, chelation, immobilization, and sequestration (Figure 2).

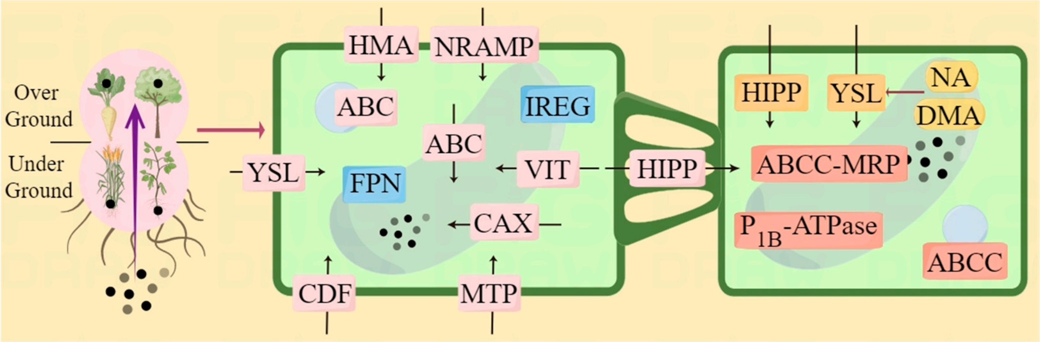

Figure 2. The mechanisms of heavy metal remediation in energy crops. (HMA: heavy metal transporter ATPase, NRAMP: natural macrophage protein, ABC: adenosine triphosphate-binding cassette transporter, IREG: iron-regulated protein, YSL: yellow streak protein, FPN: ferroportin, VIT: vacuolar iron translocation protein, CAX: Ca^{2+}/H^{+} anti-transporter, CDF: cation diffusion facilitator protein, MTP: heavy metal tolerance protein, HIPP: heavy metal isoprenylated plant protein, NA: nicotianamine, DMA: deoxymugineic acid, ABCC-MRP: ATP-binding cassette multidrug resistance-associated protein, P_{1B}-ATPase: P_{1B}-type ATPase, ABCC: subfamily C of ATP-binding cassette transporter).

3.1. Uptake

The uptake of heavy metals by energy crops mainly occurs in their roots, and heavy metals enter the body together with water and nutrients in the soil, while a small number of energy crops also uptake heavy metals through the leaves [9]. Research has demonstrated that sugarcane accumulates more heavy metals in the below ground than in the above ground in contaminated soils. The bioaccumulation factor (BAF) of roots is greater than one, but that of stems is less than one, indicating that heavy metals are mainly absorbed through the root system and are stored mainly in the below ground, and are hardly involved in the transport process [12]. Mangroves also can be used as an excellent energy crop for absorbing heavy metals, exhibiting the capability to uptake Cd, Zn, Cr, Pb, and Cu. Among these, mangroves can achieve a high uptake of up to 57% Cd [13].

Certain energy crops participate in the uptake and accumulation of heavy metals in the below ground through various heavy metal-associated proteins, which prevent their migration to the above ground [42]. The yellow streak protein (YSL) is an essential protein for the uptake of heavy metals from the external environment in energy crops; it belongs to the same family as oligopeptide transporter proteins (OPT) [43], which use nicotianamine (NA) or deoxymugineic acids (DMAs) as a substrate to uptake iron (Fe), Zn, Cd, manganese (Mn), and Cu in the soil [44]. When YSL down-regulates, the Cd uptake of wheat is significantly reduced [26]. Sugar beet BvHIPPs are heavy metal isoprenylated plant proteins that participate in the uptake and translocation of heavy metals. Through the analysis of sugar beet under Cd stress, it has been observed that the expression of HIPP33 (BVRB_4g081750), a family member, is significantly up-regulated in the below ground and down-regulated in the above ground, indicating the importance of HIPP33 in heavy metal uptake rather than translocation [45]. Additionally, certain energy crops, such as willow, are capable of uptaking heavy metals in the environment through their leaves [14]. The heavy metal uptake by energy crops is influenced by various factors, including the concentration of heavy metals, root morphology and structure, and soil pH. Furthermore, energy crops themselves regulate the uptake rate of heavy metals, thereby controlling the amount of heavy metal intake [46].

3.2. Translocation

Some energy crops immobilize heavy metals in their roots after uptake, while others just immobilize certain mineral elements in the roots and translocate most of the heavy metals to other parts of the organism [47]. The movement of heavy metals in energy crops occurs mainly through the xylem, from roots to stems and shoots, and then to nutrient organs such as leaves [48].

Transporter proteins work together to prevent the free movement of heavy metal ions from damaging energy crop cells by translocating them to non-hazardous or sub-hazardous locations [49]. Adenosine triphosphate-binding cassette transporters (ABC) are present in peroxisomes, mitochondria, chloroplasts, and vesicle membranes, and function in the translocation of heavy metals in various energy crops [50]. In bitter willow, ABC participates in the Cd translocation [15]. HIPP, a transporter protein unique to vascular energy crops, participates in the heavy metal translocation of Cd, Cu, and Mn, through both intercellular linkage and intracellular transport functions in wheat and sugar beet [51–54]. In addition to ABC and HIPP, membrane proteins such as heavy metal transporter ATPase (HMA) and NRAMP are involved in the translocation of Cd and Mn in sweet sorghum [54,55]. The translocation of heavy metals is closely related to the endomembrane system in the intracellular environment. The cation diffusion facilitator protein (CDF) and heavy metal tolerance protein (MTP) translocate heavy metal ions such as Mn^{2+}, Cd^{2+}, cobalt (Co^{2+}), Fe^{2+}, and Zn^{2+}, from the cytoplasm to the extracellular space or translocation in subcellular structures [56]. In pennycress, TcYSL3 is a transporter protein involved in their endocytosis for Fe and Ni and maintains the internal homeostasis of heavy metals [16].

The translocation of heavy metals in energy crops also involves anti-transporters. CAXs (Ca^{2+}/H^{+} anti-transporters) are transmembrane proteins that are located on vacuoles that maintain ionic homeostasis at the cellular level by exchanging cations with protons [57]. Research has demonstrated that CAXs participate in translocating Cd in poplar and potato plants [17,28]. Additionally, VIT, a vacuolar iron translocation protein that is linked to the Ca^{2+} pathway, acts as an anti-transporter for H^{+} and Fe^{2+} and translocates heavy metal ions by folding into a dimeric ion-transport channel consisting of methionine (Met) and carboxylic acid residues [58]. In the analysis of the transcriptome of dwarf polish wheat and bread wheat, VITs have been proven to mediate heavy metal translocation [59,60].

The translocation processes of heavy metals have demonstrated that some heavy metals, particularly Cd and Zn, can promote the translocation of other heavy metals. In the study of sugar beet, the exogenous application of different concentrations (1–50 μM) of Cd resulted in an 8-fold increase in Zn content in the roots, a 2-fold increase in Mn content, and a 1-fold increase in Cu and Fe content; the stems showed a 9-fold increase in Zn content, a 1-fold increase in molybdenum (Mo) content, and a 1-fold increase in Fe content. Additionally, the leaves exhibited a 2-fold increase in boron (B) content and a 1-fold increase in Cu, Mn, and Mo content. These results indicate that sugar beet is capable of translocating various heavy metals and the efficiency of the translocation depends on the other heavy metal concentrations in the environment [61].

3.3. Chelation

Energy crops primarily use phytochelatins (PCs) and metallothioneins (MTs) to chelate heavy metals, together with chelating proteins such as glutamate synthase (GOGAT) and plant ferritin (FER) [62,63]. PCs are ion-binding peptides rich in cysteine (Cys), which are catalyzed by PCases using glutathione (GSH) as a substrate and can chelate metals such as Fe, magnesium (Mg), calcium (Ca), Cu, and Zn [64]. In poplar, PCs have been found to chelate Cd in roots, bark, wood, and leaves, with the highest Cd chelation efficiency in roots, and most Cd presents in the form of a PCs-Cd complex [65]. In wheat, PCs are most efficient at chelating Cd, followed by Zn [66]. In the unfamiliar energy crops pennycress and vetiver, PCs can chelate Cd and Cr, respectively [18,67]. Meanwhile, willow leaves efficiently chelate Cd by PCs, and the content of PC-associated proteins significantly increases when the heavy metal content elevates [68]. However, although PCs are involved in the chelation, they do not participate in the heavy metals' accumulation [69]. During the heavy metal chelation by PCs, chelating proteins are also involved. The ATP-binding cassette multidrug resistance-associated protein (ABCC-MRP) is a subfamily of the ABC located in the vesicular membrane, which participates in the heavy metal chelation in many energy crops [70]. It chelates Cd in wheat and synthesizes intermediates of the PC chelation using adenine (A) [70]. The ABCC in cotton is capable of phosphorus (P) chelation and anthocyanin translocation [19]. The ABCC protein in maize has the ability to chelate heavy metals in vesicles and regulate hormonal homeostasis [29]. In arsenic-tolerant castor, the content of ABCC protein is significantly higher than that in control plants [25].

MTs are genetically encoded polypeptides that contain high levels of Cys and chelate heavy metals through thiol binding or related gene expression [71]. In sweet potato and pennycress, MTs maintain internal homeostasis by chelating Cu^{2+} [30,72]. The special energy crop camelina chelates Pb and Zn in the above ground through the MT-mediated process, and regulates the ratio and content of saturated and unsaturated fatty acids [20,73]. The protein associated with the MT process is P_{1B}-ATPase, the only protein subfamily of vacuolar proton pump p-type ATPase (P-ATPase), which functions in heavy metal homeostasis and functions as a transporter and chelator of heavy metals because of its multiple Cys residues [74]. HMA, another member of the P-ATPase family, participates in the uptake and translocation of heavy metals. The synthesis of PCs and MTs has shown that these proteins contain the structural domain of Cys, a physiologically active amino acid containing sulfur, and the only amino acid known to contain a sulfhydryl group on the branched chain to bind heavy metals [75]. Energy crops also use citric acid (CA) and malic acid (Mal) as heavy metal-binding ligands to chelate heavy metals, especially Cd [76].

3.4. Immobilization and Sequestration

The immobilization and sequestration of heavy metals can be understood as occurring at two levels: the xylem, from a plant structural point of view; and endomembrane systems such as vacuoles, from a spatial structural point of view. Certain energy crops immobilize heavy metals in the roots to reduce their retention in the stems and prevent their flow to the fruits [77,78]. During the hydroponic trials with willow, the roots have uptake and immobilized Cd in the roots, preventing heavy metal contamination of the above ground [79]. The rare prickly thistle is able to extract Cd from the environment and maintain the stability of the enriched soils of As [21]. The study of sunflowers has revealed that the As-PCs complex is a crucial indicator for detecting heavy metal translocation in high-As-concentration environments, and the As-PCs complex does not participate in the translocation of As, indicating the ability of sunflowers to immobilize and sequester metal ions in its roots [80]. In the study of energy crops, various proteins have been identified to participate in heavy metal immobilization and sequestration. Specifically, P_{1B}-ATPase, which is involved in chelation, also acts on the Cd accumulation, immobilization, and sequestration in roots [81]. Energy crops are known for their ability to accumulate heavy metals, and in addition to immobilizing heavy metals in roots, some energy crops also sequestrate heavy metals in other parts, such as leaves and stems. An analysis of sweet sorghum grown near a mine has shown that the bioaccumulation coefficient (BCF = heavy metal concentration in the plant part/heavy metal concentration in the soil) of Cd in stems is greater than one, and the translocation factor (TF) is also greater than one, and the total biomass of sweet sorghum stems and roots is greater than 87% [82]. Sorghum can efficiently participate in the immobilizing and sequestrating of heavy metals in the non-fruiting parts of the plant [82]. The sugar beet field experimentation has revealed that sugar beets grow normally in soil with 3.02 mg/kg Cd, with the concentration of Cd in the above ground reaching 19.23–20.10 mg/kg. The BCF of roots and leaves exceeds one, and is even greater than two at specific positions. These findings indicate that sugar beet is an excellent crop for the immobilization of heavy metals and serves as a high-quality material for heavy metal pollution remediation [83]. Although the xylem has the capacity to immobilize and sequester certain heavy metals, it cannot guarantee the stationary retention of all heavy metals. Some heavy metals may still be translocated to the cell along with water and nutrients. These immobilization and sequestration processes take place within the endomembrane system [1]. The endomembrane system plays a vital role in heavy metal accumulation, such as the endoplasmic reticulum, Golgi apparatus, lysosomes, vacuoles, and vesicles; among them, vacuoles are the most effective location for heavy metal sequestration, followed by vesicles [75]. During heavy metal immobilization and sequestration in energy crops, relative proteins translocate and sequestrate the heavy metals to vesicles, maintaining the homeostasis of the internal environment [84,85]. The immobilization and sequestration involve several proteins, including ABC, CAX, VIT, ABCC-MRP, MTP, CDF, the iron-regulated protein (IREG), and ferroportin (FPN). IREG and FPN are located in vesicle membranes and have highly conservative structural domains that can immobilize and sequester heavy metals [86,87]. In Populus, PgIREG is tolerant to Ni and accumulates Ni [88]. Along with the immobilization and sequestration of heavy metals, energy crops release quantitatively essential metals from the endomembrane system like vacuoles for their own use, such as Zn, Cu, and Ni [89].

4. The Application of Post-Harvest Energy Crop Biomass Which Remediated Heavy Metals

There are four main strategies for the application of remediating heavy metals through energy crops after harvesting: direct landfilling, composting, biochar (BC) remediation, and biofuel generation (Figure 3).

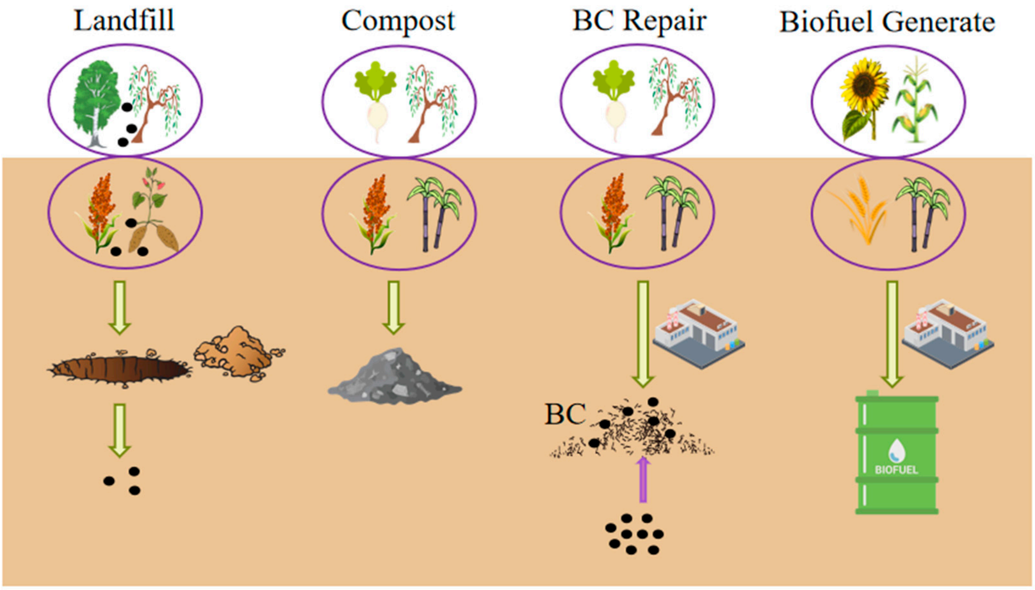

Figure 3. The application of post-harvest energy crop biomass after heavy metal remediation. (BC: biochar).

The direct landfill method, in which energy crops remediated with heavy metals are directly landfilled into the soil of a specific area, is currently the least recommended approach [90]. The research on the heavy metal contamination remediation in willow has revealed that direct landfilling reintroduces approximately 50% of the heavy metals back into the soil, thereby significantly weakening the remediation efficiency [91]. Energy crops have high biomass and heavy metal uptake efficiency, therefore direct landfilling will lead to secondary soil contamination.

The second treatment method is composting, where remediated energy crops of heavy metals are mixed and fermented with the help of auxiliaries and microorganisms to create fertilizer for vegetation that needs nutrients [92]. Remediated energy crops can be used as fertilizers after composting; however, it is unclear whether vegetation can absorb them and the rate of uptake cannot be measured [93]. Additionally, this process requires auxiliary reagents to be jointly used, but it is unclear whether the auxiliary reagents impact the vegetation and soil; it is also uncertain whether the cost of inputting reagents is positively correlated with the fertility of the fertilizer [94].

Biochar remediation is using energy crops that have already remediated heavy metals to create carbon-rich materials, and then they are used to remediate heavy metals again through biochar technology, including slow pyrolytic charring and wet pyrolytic charring (i.e., hydrothermal charring) [95]. Biochar has three main roles: inhibiting the heavy metals migration, adsorbing and complexing heavy metals, and reducing the toxicity of heavy metals. (i) BC is typically alkaline and can regulate environmental pH, promoting the combination of heavy metals with BC surface groups to form insoluble substances, thus inhibiting heavy metal mobility [96]. For instance, Cd exists in the pattern of $CdCO_3$, $Cd(PO_4)_2$, $Cd(OH)_2$, Cd_3P_2, and K_4CdCl_6 under the regulation of BC, thereby reducing the fluidity of Cd [97]. BC also reduces free heavy metal mobility by coprecipitation, effectively encapsulating free heavy metals in stable compounds [98]. In a rice pot experiment, the application of energy crop BC and Fe^{2+} reduced the content of active Cd and As in the soil [99]. (ii) The surface of BC contains numerous negatively charged functional groups that attract heavy metal ions such as sodium (Na), Ca, potassium (K), and Mg through physical interactions such as van der Waals forces, electrostatic adsorption, and hydrogen bonding [100]. Studies have shown that using the BC of energy crops in rice fields can effectively adsorb Cd, consequently reducing the Cd content in rice [101]. Furthermore, the surface of BC contains a significant number of oxygen-containing functional groups that can bind heavy metals in the soil and form stable complexes, thereby preventing vegetation from damage by heavy metals [102]. BC is capable of effectively complexing heavy metals such as Zn, Pb, and As through its oxygen-containing functional groups, which can complex with heavy metals without undergoing cation exchange; furthermore, the pH made BC rich in cations and complex with anions, and the cation exchange capacity (CEC) and metals-related dissolved organic matter (DOM) can combine with the negative charges of the metals through electrostatic interactions [102–104]. Notably, it exhibits high efficiency in binding Cd and Pb [105,106]. In addition to oxygen-containing functional groups, BC also complexes with Cu through amino functional groups to form non-toxic five-membered chelate rings, thus remediating heavy metal pollution [107]. (iii) BC has a redox effect that can reduce heavy metal toxicity by altering the valence of heavy metals [108]. For instance, BC can decrease the toxicity of Cr and As by converting the more toxic Cr^{6+} and As^{3+} into the less toxic Cr^{3+} and As^{5+} [109,110]. However, in the study of willow trees, it is found that although charred plants can deposit 80% of Pb and over 90% of Zn and Cu in the ash after remediation for easy disposal, the heavy metals in the ash are less significant for recycling and could not be used as production materials, and 60% of the Cd in the form of submicron particles have deposited in the flue gas or volatilized in the incineration system, which could not be collected and disposed of, resulting in pollution from the incineration system [111]. Fortunately, modified BCs such as manganese-modified bagasse biochar (MBC) and iron- and manganese-modified bagasse biochar (FMBC) are commonly used today to improve the heavy metal (Cd or Pb) stabilization efficiency compared to conventional BC [112].

The last application of energy crops after remediating heavy metals and harvesting is biofuel generation. Biofuels are fuels derived from energy crops and can be in the form of solids, liquids, or gases, including bioethanol, biobutanol, vegetable oil, biodiesel, biohydrogen, bio-methanol, and pyrolysis oil [113,114]. Among them, bioethanol is a biofuel produced through the microbial fermentation of biomass, which consists mostly of energy crops and biological waste residues that remediate heavy metals [115], and it can replace all or part of petrol to make ethanol gasoline, thereby reducing the use of fossil fuels. Furthermore, bioethanol is considered a high-quality renewable energy source due to its low toxicity, high density, and weak permeability [116]. Ethanol from germination-damaged grains is comparable to robust grains, and even moldy maize and sweet sorghum can produce bioethanol, providing a potential application for moldy energy crops [117].

Biobutanol is a biofuel obtained by fermenting hydrolysate from high starch energy crops with enzymes produced by the acetone butanol bacterium. The resulting product is further distilled into biofuel, which can replace fossil fuels [118]. Research has discovered that biobutanol can be produced from bagasse and rice straw [119], and has a higher productivity, less volatility, less corrosiveness, and higher safety than bioethanol [120]; however, the production efficiency is not stable due to the unstable production capacity of the bacterium, the high number of metabolic byproducts, and the inhibition of inter-products [121]. Vegetable oil fuels are derived from energy crops with high oil content and have become promising sustainable energy sources due to their degradability, convenient storage and transport, non-combustibility in an open flame, and low cost [122]. Research has shown that oilseed energy crops, such as sunflowers, are capable of producing vegetable oil [123], which can be reprocessed to obtain biodiesel, and the biodiesel is similar to petrochemical diesel but cleaner [124]. Biohydrogen is produced by anaerobic bacteria decomposing biomass in the presence of hydrogenase enzymes, reducing the amount of environmentally damaging methane produced [125]. The research has found that mixtures of bagasse and rice straw, in the presence of gas-producing *Escherichia coli* and *Clostridium acetobutylicum*, produce, respectively, 3.4 and 1.5 times more biohydrogen than pure cultures, illustrating that energy crop mixtures are an important source of biohydrogen [119]. Despite the abundance of raw materials, high production efficiency, and environmental friendliness of biohydrogen, its instability due to hydrogenase inactivation and the proportion of relatively high by-products remains a challenge [126]. Bio-methanol is a biofuel that is resynthesized from biomass conversion into biohydrogen and CO_2 by microorganisms, is easy to store and transport, and provides a clean energy source [127]. Less-known energy crops like herba ecliptae also have the potential to produce bio-methanol [22]. Research has shown that methane, which is environmentally harmful, can be converted into methanol; however, precise control of the activity of methane monooxygenase, produced by methanotrophic bacteria, is required to ensure the efficiency and stability of the conversion process [128]. Pyrolysis oil is a complex multi-phase mixture that can be obtained by rapidly decomposing biomass at medium temperatures (500–600 °C) and has the advantages of easy transport and high yield [129]. However, it also has some drawbacks, such as low purity, poor stability, and low economic benefits; but it has been found that the stability of pyrolysis oil can be significantly improved by extracting pyrolysis lignin [130]. Energy crops, such as sugar beet, maize, and sugar cane, are more efficient in producing biofuels than other plants, and can effectively reduce the use of fossil fuels.

However, it is also essential to consider the potential impact of heavy metals on biofuels produced using energy crops after remediation and harvest. In these processes, some components such as heavy metals and lignin need to be removed to ensure the purity and safety of the biofuel [131]. During this process, the valence states of the heavy metals are changed. For example, CdO is transformed into soluble Cd and stored in the aqueous solution, which can be extracted by added coagulant [132,133]. Additionally, some heavy metals such as Zn, Pb, and Cd, are fixed in the biochar residue at a high temperature of 160 °C, preventing them from directly entering the purification process of biofuel [134]. It has been proven that the heavy metal content of Cd, Pb, and Zn in biofuel is significantly reduced by the above two methods; therefore, high-quality and cleaner biofuels can be obtained [135]. Nevertheless, a minor amount of heavy metals may still persist in the biofuel, but the contamination of the environment can be significantly reduced due to the change in the valence states of heavy metals during the high-temperature combustion and refining process [135].

5. The Challenges of Remediating Heavy Metal Pollution by Energy Crops

5.1. Limitations of Energy Crops

Remediating heavy metals with energy crops may have some limitations. Typically, an energy crop is only effective in remediating one or a few heavy metals in the environment, while having poor remediation effects on others [136]. For instance, willow, a multipurpose energy crop for remediating heavy metal pollution, has significant effects on Cd and Zn, but weak cumulative effects on other heavy metals [137]. Consequently, energy crop rotation is a crucial strategy for remediating multiple heavy metal pollution, and the rotation methods require further discussion. In addition, the root system of most energy crops is only distributed in the surface layer of soil; only a few energy crops are capable of remediating heavy metals in deep soil, accordingly, limiting their remediating abilities [138]. Therefore, it is essential to investigate or improve energy crops for such a situation. Energy crops, like hyperaccumulators, are limited in the number of well-defined species for remediation; if energy crops propagate in inappropriate geographic areas or are cultivated too long, the adsorption efficiency and accumulation will likely be weakened. Therefore, experimental support is necessary to update energy crops for remediation purposes [139].

5.2. More Environmental Influencing Factors

Compared with physical and chemical methods, energy crop remediations are considered environmentally friendly approaches with low initial costs and simple follow-up treatments [140]. However, the bioremediation of heavy metal pollution by energy crops may face challenges such as longer cycle times and susceptibility to climatic and environmental factors. Additionally, it may be difficult to measure the relationship between the time cost of remediation and the value of ecological remediation, which may result in the difficulties of inaccurate cost and effectiveness estimates [141]. Therefore, more practice is required to evaluate the remediation effect of heavy metals by energy crops.

5.3. Difficulties in Energy Crop Transformation

Numerous proteins function in heavy metal bioremediation, and how to accordingly target the transformation of energy crops is an important issue. Researchers have modified the crambe through agrobacterium-mediated transformation, and the result shows that the modified crambe can improve the content of oil and remediate heavy metal pollution efficiently without affecting plant growth and development [142]. Genetic transformation, molecular markers, and genome sequencing are used to modify some energy crops and enhance their performance in heavy metal-polluted environments [143]. However, the current research on heavy metal response pathways is still unclear, and the modification of energy crops is limited to one or a few proteins. There may be difficulties in the transformation of energy crops into stable materials for heavy metal pollution remediation [144]. Therefore, there are still challenges in the biotechnology of energy crops, and it is crucial to excavate the core proteins involved in heavy metal bioremediation pathways.

5.4. Less Research on Unpopular Energy Crops

Currently, there are over 4000 types of energy crops developed and utilized, and among them, oilseed crops account for a relatively high proportion [143]. However, most of the energy crops used in heavy metal bioremediation are maize, sugarcane, sugar beet, and poplar. There is limited research on other unusual energy crops, and their mechanism of heavy metal pollution remediation is still unclear [145]. Therefore, potential energy crops should be researched and developed for extensive heavy metal bioremediation.

5.5. Few Sources of Biofuel

One of the advantages of energy crops is that those used for remediating heavy metals can still produce biofuels to replace certain fossil fuels. However, the current known energy crops capable of producing biofuels are the most common species, such as sugar beet, maize, sugar cane, and castor [146]. The effectiveness of biofuel production varies among different energy crops. For instance, sugar beet, maize, and sugar cane are all used to produce biofuels such as bioethanol, biomethane, biobutanol, and biohydrogen; among them, maize and sugar cane have high biofuel yields, while sugar beet has lower yields. However, sugar beet exhibits a better heavy metal remediation effect than others [147]. Therefore, it is crucial to identify energy crops that are efficient in both heavy metal bioremediation and biofuel production.

5.6. Commercialization Difficulties

Heavy metal remediation by energy crops is still in the experimental phase, involving potting and field trials, with potentially insufficient validation, and commercialization may take some time [146]. Hence, further data support, adequate funding, and well-established regulations are indispensable for heavy metal contamination remediation by energy crops [148].

6. Conclusions

Energy crops are known for their high biomass production, strong environmental adaptability, high stress tolerance, and dual-use capabilities. They can remediate heavy metal pollution while also providing energy as biofuels. Energy crops inhibit heavy metal migration in the soil through root complexes, respond to ROS oxidative stress, and utilize uptake, translocation, chelation, immobilization, and sequestration to remediate heavy metals. In these processes, various functional molecules such as heavy metal transporter proteins and chelating proteins rich in Cys, are involved in the effective translocating and binding of ions, maintaining internal environmental homeostasis, and confining heavy metals to the xylem, vacuoles, or vesicles to minimize damage. Despite persistent challenges, energy crops are still the most promising materials in the bioremediation of heavy metal pollution.

7. Future Prospects

The utilization of energy crops for remediating heavy metal pollution presents a cost-effective and innovative environmental protection strategy. Given the increasing global prevalence of heavy metal pollution, this paper advocates for further research efforts to explore novel energy crops, improve existing germplasms, investigate the underlying mechanisms of heavy metal remediation by energy crops, boost biofuel yield from these crops, and modify excellent energy crops capable of efficiently remediating heavy metal pollution while also producing biofuels.

Table A1 supports the content of this paper and summarizes the mechanisms of multiple high-quality energy crops in the remediation of heavy metal pollution.

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Appendix A

Table A1. Mechanisms of remediating heavy metal pollution in quality energy crops.

Energy Crop Types	**Latin Name**	**Introduction**	**Main Mechanism**	**Biomass Application**	**Related Heavy Metals**	**Related Literature**
Sugar beet	*Beta vulgaris* L.	Biennial herbs of the genus Beet in Amaranthaceae	Tolerance, uptake, translocation, immobilization, and sequestration	Biochar, biofuel	Cd, Pb, Zn, Cu, Ni, Fe, Mn	[11,37,45,53,83,146]
Sugarcane	*Saccharum officinarum*	Perennial herbs of the Sugarcane in Gramineae	Uptake, immobilization, and sequestration	Biochar, biofuel	Zn, Cu, Cd, Pb, As	[12,112,119]
Maize	*Zea mays* L.	Annual herbs of the Zea in Gramineae	Uptake, chelation, immobilization, and sequestration	Biofuel	Cu, Cd, Co, Pb, Cr, Zn	[29,146,149,150]
Sweet sorghum	*Sorghum dochna* L.	Annual plants of the Sorghum in Gramineae	Tolerance, uptake, translocation, immobilization, and sequestration	Biochar, biofuel	Pb, Zn, Cd, Cu, As, Cr, Ni	[82,117,151,152]
Wheat	*Triticum aestivum* L.	Annual or perennial herbs of the Wheat in Gramineae	Uptake, translocation, chelation, immobilization, and sequestration	Biofuel	Cd, Zn, Cr, Pb, As, Hg	[26,51,66,153,154]
Yam	*Dioscorea esculenta* (Lour.) Burkill	Twisted herbaceous vine of the Dioscorea in Dioscoreaceae	Uptake, chelation, immobilization, and sequestration	Biochar	Cd, Cu	[30,155,156]
Cassava	*Manihot esculenta* Crantz	Cassava plants of the Euphorbiaceae	Uptake, immobilization, and sequestration	Biochar, biofuel	Zn, Pb, Mn, Cu, Co, Ni, Cd, Cr	[31,157,158]
Mustard	*Brassica campestris* L.	Annual or biennial herbs of the Brassica in Cruciferae	Tolerance, translocation, immobilization, and sequestration	Biofuel	Cd, Cr, Cu, Hg, Ni, Pb, Zn	[23,159,160]
Rubber tree	*Hevea brasiliensis* (Willd. ex A. Juss.) Muell. Arg.	Hevea of the Euphorbiaceae	Uptake, immobilization, and sequestration	Biochar, biofuel	Cd, Na, Ni, Zn	[24,161,162]
Willow	*Salix babylonica* L.	Salix plants of the Chrysopoda in Salicaceae	Tolerance, uptake, translocation, chelation, immobilization, and sequestration	Biochar	Cd, Hg, Zn, Ni, Pb, Cu	[14,68,79,111]
Reed	*Phragmites australis* (Cav.) Trin. ex Steud.	Reed plants of the Gramineae	Uptake, translocation, immobilization, and sequestration	Biochar, biofuel	Cu, Zn, Pb, As, Cd	[3,163–165]
Miscanthus sinensis	*Miscanthus*	Plants of the Miscanthus in Gramineae	Tolerance, uptake, immobilization, and sequestration	Biochar, biofuel	Cd, Cu, Ni, Pb, Zn, Cr	[13,166–168]

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