environments

MDPI

Review

Phytoextraction of Heavy Metals from Fly-Ash-Contaminated Soils: A Review

Santosh Rajbanshi [1,*], Maheteme Gebremedhin [1], James C. Hower [2,3], George Fouad Antonious [1], Jacob Brown [1] and Ife Familusi [1]

[1] College of Agriculture, Health, and Natural Resources, Kentucky State University, 400 E Main St., Frankfort, KY 40601, USA; maheteme.gebremedhin@kysu.edu (M.G.); george.antonious@kysu.edu (G.F.A.); jacob.brown1@kysu.edu (J.B.); ife.familusi@kysu.edu (I.F.)
[2] Center for Applied Energy Research, University of Kentucky, Lexington, KY 40511, USA; james.hower@uky.edu
[3] Department of Earth & Environmental Sciences, University of Kentucky, Lexington, KY 40506, USA
* Correspondence: santosh.rajbanshi@kysu.edu

Abstract

Fly ash (FA) is a coal combustion product with variable mineral composition, high alkalinity, and elevated enrichment of heavy metals (HMs) such as As, Se, Mo, Cd, and Pb. Fly ash greatly influences soil dynamics by altering soil pH, nutrient mobility, microbial activity, soil structure, and texture. This review evaluates phytoextraction as a sustainable and eco-friendly strategy for remediating FA-contaminated soils. It explores the physicochemical properties of FA, the impact of FA and associated heavy metals (HMs) on soil, the mechanisms of HM hyperaccumulation in plants, and the effectiveness of phytoextraction based on the bioaccumulation factor (BAF) and translocation factor (TF). Case studies from various regions demonstrate the great potential of hyperaccumulator species to extract toxic HMs from FA-impacted soils. However, challenges such as low metal bioavailability, limited field validation, and inadequate management of contaminated biomass hinder large-scale application. Future research should focus on optimizing biomass utilization, developing comprehensive hyperaccumulator databases, and advancing genetic and policy frameworks to enhance the scalability and effectiveness of phytoextraction.

Keywords: hyperaccumulators; indicators; phytoremediation; bioaccumulation; coal combustion products

Check for updates

Academic Editor: Frank Gobas

Received: 20 March 2026
Revised: 26 April 2026
Accepted: 29 April 2026
Published: 3 May 2026

Copyright: © 2026 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license.

1. Introduction

Industrialization is a major contributor to air, water, and soil pollution and is one of the leading causes of growing environmental degradation, reduced crop productivity, and land deterioration [1,2]. Among the various industrial activities, coal combustion is one of the leading sources of land degradation, producing large quantities of coal combustion products (CCPs), including fly ash (FA), bottom ash, boiler slag, and flue gas desulfurization (FGD) materials [3]. Fly ash accounts for approximately 64% of CCPs [4] and is produced in massive quantities globally. The global production of FA is estimated to reach 1 billion tons in 2031 [5,6]. After its production, a fraction of FA is utilized for multiple purposes—for example, as a supplementary cementitious material in the cement and concrete industry; as bricks, blocks, and construction materials; and for road bases, embankments, and structural fills [7]. The leading countries in FA utilization are Japan and the Netherlands, with a 100% utilization rate, followed by Italy, Denmark, the USA,

China, and France, with 92%, 90%, 78%, 76%, and 60% utilization rates, respectively [6,8]. However, the unutilized portion of FA is disposed of in surface impoundments (ponds) and landfills, where it remains exposed to environmental conditions, increasing the risk of pollutant migration into groundwater or nearby water sources [9]. Due to its complex chemical composition, FA poses a considerable environmental concern. It severely impacts soil's physical and chemical properties, soil microorganisms, plant growth, and aquatic life and can persist in soils for an extended period of time [10]. Moreover, the presence of toxic heavy metals (HMs) in FA disrupts soil microbial activity and nutrient cycling, potentially leaching into nearby water sources, thereby affecting aquatic ecosystems, and entering the food chain, where it can lead to ecological imbalance affecting humans and other living organisms [11–14]. (The term "heavy metals" (HMs) is common in the phytoremediation and environmental contamination literature. In this review, "HMs" refers broadly to potentially toxic metal(loid)s and trace elements associated with FA contamination. However, IUPAC has criticized this term as imprecise, as it lacks a consistent definition. It is one of the highly debated terms in the scientific literature. Dr. J.H. Duffus, in an IUPAC technical report, has noted that the term "heavy metals" is both meaningless and misleading and lacks any chemical or toxicological basis for its definition. More information can be obtained from the the references [15,16]. However, the chemical composition of FA and the bioavailability of HM in FA-contaminated soils vary. They depend on the parent coal's geological origin and coal combustion conditions [17]. Given the severe negative impacts of FA contamination in soil, which can disrupt ecological balance, addressing this issue remains imperative.

For immediate soil remediation, physicochemical approaches such as soil washing, excavation, electrokinesis, and chemical stabilization are used; however, these processes are not cost-effective, not suitable for large-scale remediation, and can potentially cause secondary pollution [18–21]. Therefore, a sustainable, cost-effective, and eco-friendly alternative to these remediation strategies is required to address these limitations. Phytoremediation, where plants are utilized for the extraction or stabilization of toxic HMs from contaminated sites, is among the best alternatives in solving this issue [22,23]. There are several types of phytoremediation techniques, viz., phytofiltration, phytoextraction, phytostimulation (plant-assisted bioremediation), phytovolatilization, phytodegradation, and phytostabilization. One of the most common techniques in phytoremediation is phytoextraction, in which plants are used to extract HMs from the contaminated sites through their accumulation in the plant biomasses [21,24]. Certain species of plants have the potential to accumulate unusually high concentrations of HMs in their biomass without showing toxicity symptoms; these plants are known as hyperaccumulators [25].

These plants differ from non-hyperaccumulators in their ability to translocate toxic HMs from roots to shoots, detoxifying and sequestering them in the leaf cell vacuoles [26]. In contrast, normal plants lack such detoxification mechanisms, making them vulnerable to HM toxicity. Under experimental conditions—such as exposure to extremely high concentrations of HMs in greenhouse or hydroponic studies—normal plants may also develop a mechanism called pseudo-hyperaccumulation [27]. However, these plants remain susceptible to metal-induced toxicity, which eventually leads to their death. In contrast, true hyperaccumulators are tolerant of high HM concentrations and exhibit no significant biomass reduction [27].

How do hyperaccumulating plants tolerate and accumulate such high concentrations of HMs without exhibiting any toxicity symptoms? What are the differences between hyperaccumulating and non-hyperaccumulating plant species in terms of their physiological and biochemical mechanisms for sequestering HMs in their biomass? How do the physicochemical properties of FA affect soil systems and metal bioavailability? At present, how successful is the phytoextraction mechanism in remediating FA-contaminated

soils, based on existing research findings? What are the major challenges and limitations associated with the phytoextraction of heavy metals from FA-contaminated soils? Finally, where should future research on this topic focus based on the existing literature? These overarching questions form the fundamental basis for understanding, advancing, and implementing phytoextraction as a viable and effective tool for site restoration.

This review (i) characterizes the physicochemical properties of FA and assesses how these properties influence the bioavailability of HMs in soil that influence the phytoextraction efficiency, (ii) evaluates the mechanisms of hyperaccumulation, (iii) analyzes global case studies of successful phytoextraction in FA-contaminated soils using the bioaccumulation factor (BAF) as an assessment metric, (iv) identifies and discusses the limitations of phytoextraction technology, and (v) proposes future research directions.

2. Materials and Methods

This study followed a structured narrative literature review approach [28], integrating both forward and backward citation chaining to synthesize current knowledge on FA properties; its effects on soil, humans, and the environment; approaches undertaken for the remediation of sites contaminated with FA; phytoextraction; and its efficiency in soil reclamation. In addition, this approach ensured transparency, comprehensiveness, and relevance to the selected literature while also allowing flexibility to incorporate seminal and emerging studies in this research domain. First, a scoping search was conducted using Google to identify key studies and determine relevant keywords for this review. This preliminary assessment was then followed by a structured literature search in Google Scholar and Scopus using keywords such as “fly ash”, “coal combustion products”, “heavy metals”, “phytoremediation”, “phytoextraction”, “hyperaccumulators”, and “hyperaccumulation mechanisms”. In addition, Boolean operators (AND, OR) were used to refine the search results.

The search prioritized recent and relevant peer-reviewed articles (2015–2024). A total of 50 papers were initially selected for review, and screening was performed for their direct pertinence to this study. The following criteria were selected to identify the papers for their relevance to this study:

(a) Focused on the characterization of FA and its impact on the environment, humans, and soils;
(b) Investigated the impacts of HMs on soil physical, chemical, and biological properties;
(c) Evaluated soil–FA interactions affecting the bioavailability and mobility of HMs in soils;
(d) Analyzed the efficiency of the phytoextraction approach in soil reclamation in FA-contaminated soils;
(e) Examined mechanisms of hyperaccumulation in plants including metal uptake, translocation, or tolerance;
(f) Explored the hyperaccumulator species or candidate plants suitable for phytoextraction of HMs.

Among these papers, ten core articles were selected for their direct relevance to our study objectives. These studies served as anchor references for further expansion of the literature. Subsequently, a backward citation chaining approach was employed, in which the references cited in the core articles were systematically screened to identify additional relevant studies. Additionally, forward citation chaining was employed via Google Scholar’s “cited by” function to identify further directly relevant papers. With these approaches, we were able to integrate highly relevant and influential papers that might not have been captured through keyword-based searches alone.

This review paper did not follow a fully systematic protocol for the literature search, such as Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA). Hence, although efforts were made to ensure comprehensive coverage of the literature through forward and backward citation chaining, some relevant studies may still be missed. However, the combined use of keyword-based retrieval and reference tracking enhanced the robustness and depth of the literature coverage.

3. Fly Ash: Properties and Classification

Fly ash refers to very fine and lightweight particles that are carried out of the high-temperature combustion zone, along with the flue gases [29]. It is then subsequently collected using Particulate Collection Devices (PCDs), which prevent its release into the atmosphere. Commonly used PCDs include mechanical collectors, electrostatic precipitators, and fabric filters [30]. In contrast, bottom ash consists of heavier particles than FA particles, which are too heavy to get carried with FA and are left behind at the bottom of the furnace in the combustion zone. Boiler slag comprises black, glassy, and coarse particles formed by quenching of molten ash left behind at the bottom of the furnace [31]. Flue gas desulfurization (FGD) materials are the residuals of the SO_2 removal process. There are two main types of FGD, (i) wet FGD, in which SO_2 reacts with a slurry of pulverized limestone to form gypsum as a byproduct, and (ii) dry FGD, in which the fly ash is used as an inert bed producing either a mixture of Ca sulfate and fly ash or Ca sulfite, depending on the process [29]. FA consists of 64% of the total CCPs, followed by bottom ash at 16%, FGD materials at 13%, and boiler slag at 3% of total CCPs [4].

Fly ash particles, which are usually spherical, can be either solid or hollow, with a predominantly amorphous structure. FA typically has a lower specific gravity ranging from 1.47 to 2.78, with an average of around 2.01 [32]. This variation in specific gravity is primarily a function of its chemical composition, particle-size distribution, and particle shape [32]. Similarly, FA has a low bulk density due to its fine, lightweight nature and high surface area, which enhances its reactivity in various applications such as cement production [33]. The color of fly ash can range from tan to gray to black, with variations influenced by the concentration of unburned carbon and iron within its composition [29,34,35]. Table 1 summarizes the typical physical characteristics of fly ash.

Table 1. Ranges of physical properties of fly ash [32,35].

Property	Range
Specific gravity	1.47–2.78
Bulk density (compacted), kg/m^3	1041.2–1762.03
Hydraulic conductivity, cm/s	10^{-4}–10^{-6}
Porosity	0.40–0.50
Angle of internal friction, degrees	25–40

According to ASTM C618 common standards, FA is broadly divided into two classes: Class C and Class F, based on the amounts of SiO_2, Al_2O_3, and Fe_2O_3. The SiO_2, Al_2O_3, and Fe_2O_3 contents in Classes C and F are >50% and >70%, respectively [36,37]. Class F FA contains a lower lime percentage by mass, is pozzolanic, and requires the addition of Portland cement or hydrated lime to produce cementitious compounds. However, Class C fly ash, with a higher lime percentage, is both pozzolanic and hydraulic, and readily forms cementitious hydrates when water is added [37]. In another classification, FA with a CaO content <20% is classified as Class F, but those with higher CaO content, i.e., >20%, are categorized as Class C [38]. However, the Canadian Standard Classification of fly ash

(CSA A3001) uses three classes: (i) Class F with <8% CaO content by mass, (ii) Class CI with 8–20% CaO content by mass, and (iii) Class CH with >20% CaO by mass [37,39].

Fly ash is composed of three main types of constituents: (i) inorganic components (both in amorphous and crystalline phases); (ii) organic component, i.e., unburned carbon particles originating from the incomplete coal combustion; and (iii) fluid constituents such as moisture, gases, and gas–liquid inclusions associated with both inorganic and organic components [40,41]. The unburned carbon particles in the FA are derived from the coal macerals, such as vitrinite and inertinite [42]. The carbon content in the FA is influenced by a number of factors, including the type of maceral present in the coal, the coal rank, inadequate pulverization of the feed coal, sub-optimal combustion conditions, and the use of unsuitable coal for the boiler [37].

Based on their formation times, FA constituents can be categorized into three phases: primary, secondary, and tertiary. The primary phase consists of minerals that have not undergone transformation during coal combustion. These include stable phosphates, silicates, carbonates, oxides, and other minerals with high decomposition and melting temperatures. The secondary phase consists of minerals formed during coal combustion, including oxides, carbonates, silicates, sulfides, glass, and char. The tertiary phase includes minerals that are formed during the transport and storage of the fly ash, which include portlandite, brucite, gypsum, dolomite, and Al and Fe hydroxides [41].

The inorganic constituents of FA consist of both amorphous and crystalline phases. The amorphous phase, also known as glass or glassy material, is formed during the rapid cooling of molten mineral precursors in the boiler flame [43]. The Ca content in the parent coal plays a key role in determining the type of glass formed during this process—a low Ca level leads to the formation of aluminosilicate glass composed primarily of SiO_2 and Al_2O_3. On the other hand, higher Ca content forms Ca aluminosilicate glass. The latter phase is more reactive and contributes to the higher reactivity of Class C FA compared to Class F FA, and is also the source of FA's pozzolanic activity [44].

The crystalline phase forms during the slow cooling of the FA minerals, allowing more time for crystallization [45]. The FA particle size plays a crucial role in the formation of the crystalline phase due to its effects on the cooling rate: the larger the particle size, the lower the surface-area-to-volume ratio, resulting in a lower cooling rate and a higher percentage of crystalline phase formation [45]. There are at least 10 crystalline phases in FA—(i) anhydrite ($CaSO_4$), (ii) C_3A (tricalcium aluminate), (iii) periclase (MgO), (iv) lime (CaO), (v) mullite ($3Al_2O_3{\cdot}2SiO_2$), (vi) quartz (SiO_2), (vii) magnetite (Fe_3O_4), (viii) hematite (Fe_2O_3), (ix) melilite ($(Ca,Na)_2(Al,Mg,Fe^{2+})[(Al,Si)SiO_7]$), and (x) merwinite ($Ca_3Mg(SiO_4)_2$). Mullite and quartz are less reactive, making them more chemically inert in most conditions, while those in Class C ashes, including lime, periclase, anhydrite, and C_3A, are highly reactive, contributing to hydration or sulfate reactions [43]. Microscopic images of glassy and crystalline phases of fly ash are shown in Figure 1.

Fly ash, depending primarily on the type of parent coal characteristics and place of production, has varying HM concentrations. The range of heavy metals and rare earth elements present in U.S. fly ash samples is summarized in Table 2.

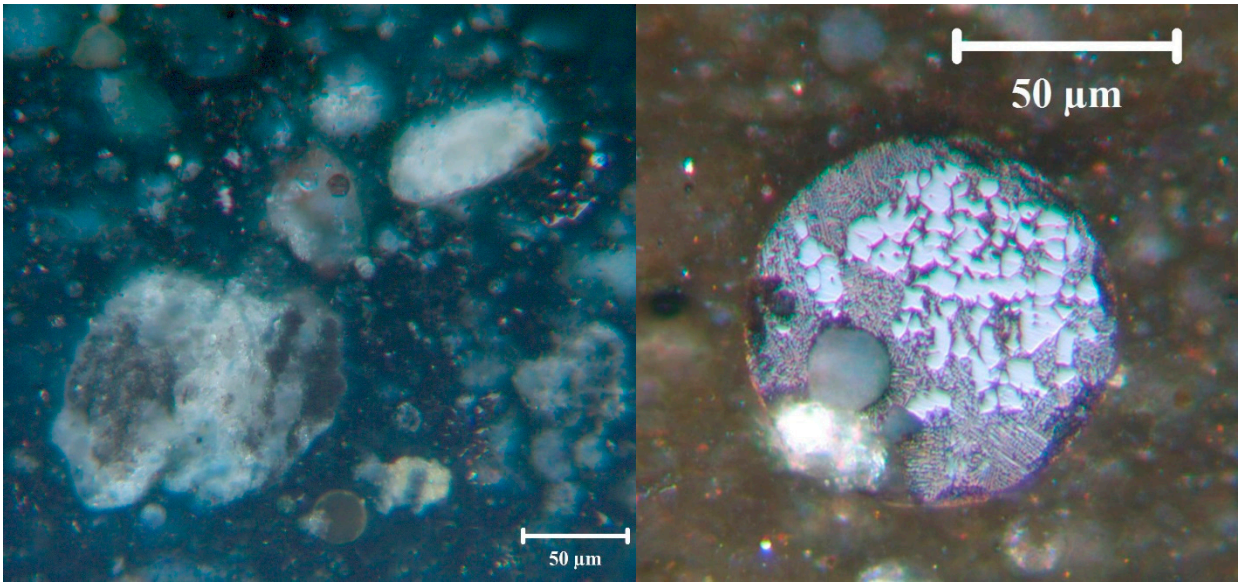

Figure 1. Optical microscopy images of fly ash particles from Kentucky power plants. (**Left**) Glassy FA showing irregular and amorphous particles, variable particle sizes, and fine mineral inclusions within the FA matrix; (**right**) spinel (magnetite) aggregate. Scale bar = 50 µm. Images courtesy of James C. Hower.

Table 2. Range of HM concentrations in FA samples in the U.S. (Source: James C. Hower, personal communication).

Metal/Metalloid	Range in mg/kg	Metal/Metalloid[2]	Range in mg/kg[2]
Aluminum	31,281.63–169,376.00	Lead	17.00–536.00
Iron	34,620.30–386,278.62	Manganese	47.00–439.00
Silicon	102,968.22–270,110.46	Mercury	BDL–3.68
Magnesium	2291.40–28,702.80	Molybdenum	BDL–268.00
Potassium	5478.66–28,555.44	Nickel	BDL–286.00
Sodium	964.47–18,844.26	Selenium	BDL–163.52
Sulfur	80.10–83,544.30	Strontium	BDL–4573.00
Titanium	2158.20–10,371.35	Vanadium	BDL–787.00
Antimony	BDL–20.00	Zinc	9.00–890.00
Arsenic	22.00–1266.00	Calcium	7004.06–306,391.89
Barium	100.00–7886.00	Cobalt	1.00–142.00
Cadmium	1.00–2.00	Phosphorus	349.12–3578.48
Chromium	24.00–252.00	Rubidium	BDL–241.00
Copper	BDL–687.00	Zirconium	BDL–245.00

3.1. Fly Ash Production and Use in the United States

Although fly ash production and utilization vary across regions, the United States is often used as a reference point because of the availability of reliable, consistently reported data on coal combustion residuals. Organizations such as the American Coal Ash Association and the United States Environmental Protection Agency publish detailed reports that provide clear information on FA production, utilization, and disposal practices. This makes it easier to understand long-term trends and management strategies. In addition, the United States shows a wide range of fly ash management practices, from its use in construction materials to its disposal in landfills and surface impoundments. For this reason, U.S. data are used here as an example of fly ash production, while also acknowledging that conditions and practices vary across different countries.

Every year, the United States generates a substantial amount of FA. Approximately 16.2% of the country's electricity is produced through coal combustion (Figure 2). Electricity generation involves the burning of a significant quantity of coal every year, producing proportionate amounts of coal combustion products, including FA [46]. For example, in 2024 alone, the total FA production surpassed 24 Mt, as shown in Table 3 [8]. Over the past two decades (2000–2024), the highest FA production was recorded in 2002, reaching an estimated 77 Mt. This peak coincided with a period of high dependence on coal-fired electric power plants for energy production. During this time, coal was the primary source of energy production in many regions, and regulations on emissions were less strict, allowing for greater coal consumption, which led to increased FA production [47].

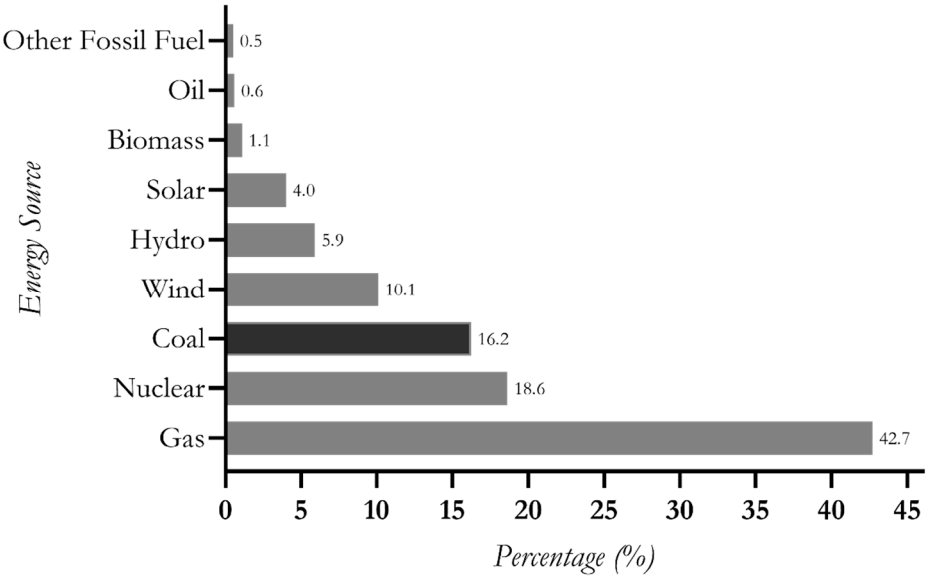

Figure 2. Percentage share of coal in electricity production in the United States [46] (The dark gray bars represent the electricity production through coal combustion, while light gray bars indicate electricity generation from other sources).

Table 3. CCP production and use in 2024 in the United States [8].

CCP Categories	Production in 2024 (Short Tons)
Fly Ash	24,718,600
Bottom Ash	7,666,800
Boiler Slag	1,580,936
FGD Materials Wet Scrubbers/Gypsum	21,982,415
FGD Materials Dry Scrubbers	1,687,795

In recent years, FA production in the US has plummeted due to several factors, including transition to natural gas for electricity production; stricter environmental laws, rules, and regulations along with the depletion of coal reserves; and a shift in focus towards renewable energy production [47–49]. On the other hand, the utilization of fly ash across various sectors increased from around 35% in 2000 to about 78% in 2024 [8]. There are at least two reasons for this increase: (a) a push to increase the utilization of ash, and (b) an overall declining trend in production as more and more fly ash is being utilized despite a similar yearly production rate that has remained the same. Figure 3 shows the trend of fly ash production in the US from 2000 to 2024.

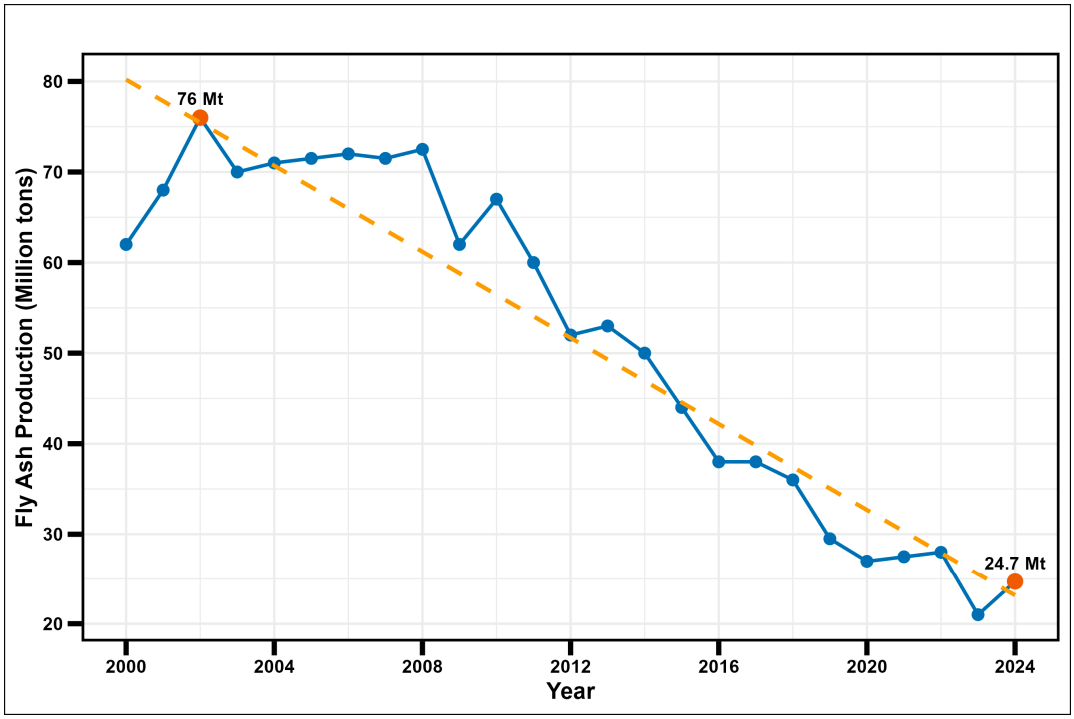

Figure 3. Fly ash production and use trend in the United States from 2000 to 2024 [8] (The blue solid line with circular markers indicates annual fly ash generation values in the United States, whereas the orange dotted line is a linear trendline across the years 2000–2024).

3.2. Impacts of Fly Ash on the Environment, Human, and Soil Health

Fly ash contaminates the environment and contributes to air, water, and soil pollution, affecting all species that live in it. In December 2008, due to the failure of the coal ash impoundment site at the Tennessee Valley Authority's Kingston Fossil Plant in Harriman, Tennessee, an estimated 4.1 million m^3 of coal ash was released into streams and rivers (Tennessee Valley Authority's Kingston Fossil Plant in Harriman, Tennessee) [50–54]. The incident resulted in extensive soil and water contamination, threatening humans, vegetation, and aquatic life [55]. Several other coal ash spills reported in the U.S., including major incidents at Plant Bowen (2002), Martin's Creek (2005), and Eagle Valley (2007–2008), released toxic waste into rivers, exceeding safety limits and causing prolonged contamination [56–59]. Data from 2010 revealed 137 documented cases of drinking water contamination by coal ash in the United States, but this number likely underestimates the true extent of the problem, as numerous incidents remain unreported [60].

Several studies have reported FA contamination in lakes, rivers, and residential and recreational soils near coal power plants in the United States. Cowan et al. (2024) [61] stated that the FA contamination in the United States occurs as localized soil deposition near power plants and persistent sediment contamination in aquatic environments influenced by spills and storage pond releases. For instance, approximately 26% of the total Pb accumulation in five lake water sediments in North Carolina, in the United States, is contributed by FA contamination during the last 40–70 years [62]. A study reported the presence of FA contamination in recreational and residential soils near coal-fired power plants in NC and TN, with FA contents as high as 16.5% in those soils [63].

FA, upon inhalation, poses severe health hazards to exposed humans through the absorption of genotoxic compounds from the lungs and interference with immunological mechanisms in the body [64]. It increases the risks of cancer, organ failure, and nervous system damage in humans, especially children [12].

In soils, the physical, chemical, and biological properties of soil are altered by FA contamination. The physical characteristics of soil include soil aggregation, structure, texture, porosity, bulk density, water retention, and hydraulic conductivity [65]. For instance, FA addition can change the soil texture from sandy and clayey soils to loamy soils [66]. Additionally, Gagnon et al. (2001) [67] reported that fly ash increases soil water holding capacity by increasing the number of micropores.

In terms of chemical properties, FA increases the electrical and hydraulic conductivity but reduces cation exchange capacity [17]. Similarly, pH, organic matter and nitrogen content are also impacted by FA contamination [10,68].

Biologically, FA negatively impacts microbial activity, which is essential for the mineralization of organic compounds in the soil for subsequent root uptake [69]. HMs present in FA inhibit soil enzyme activity by disrupting the spatial structure of the active sites within the enzymes, hindering soil microbial growth and reproduction, further impairing the synthesis and metabolism of microbial enzymes [70].

4. Impacts of Heavy Metals on Soil

The contamination of soil with HMs entails alteration of the soil's physical, chemical, and biological properties. Fly ash contains a diverse range of HMs that differ in their chemical speciation, mobility, and bioavailability, leading to variable impacts on soil properties and ecological functions [9,71]. A high concentration of HMs such as Cd, Pb, and Hg inhibits the growth and development of microorganisms and disrupts microbial cell structures, ultimately leading to a dysfunctional microbial population [72]. Low microbial density slows down various biogeochemical processes like nitrification, denitrification, mineralization, and the nitrogen cycle, which in turn reduces nutrient availability for plants. Additionally, HM toxicity interferes with the enzymatic activities in the soil, disrupting crucial metabolic processes [72]. Further, these contaminants can severely impede symbiotic relationships among plants, microbes, and associated mycorrhizae, impair nutrient uptake by the plant and limit overall plant growth and development [73].

As noted earlier, HM contamination in the soil can significantly alter soil pH. For example, high Al, Pb, and Cd concentrations in the soil reduce soil pH, which negatively affects the viability and functioning of soil microorganisms and earthworms [11,74–76]. Conversely, higher concentrations of Cu and Zn increase soil pH, which is also harmful to the soil microbial ecosystem [13].

In addition to soil microorganisms, heavy metals directly alter the soil's physical and chemical properties. First, they hinder soil aggregate formation and stability, ultimately disrupting the soil structure. For instance, HMs such as Cd, Pb, and Cu compact soil and reduce soil porosity and water infiltration by destabilizing soil aggregates [22]. Further, heavy metals alter soil texture by affecting the particle size distribution, leading to changes in the proportions of sand, silt, and clay, which can degrade soil quality [77]. Additionally, metals like Cr and Cd clog soil pores, reducing water percolation and transport of nutrients in the soil. This results in a lower water-holding capacity and increased surface runoff, further diminishing soil productivity and accelerating soil erosion [78–80]. Chemically, these HMs alter soil pH, with some metals, like Cd, increasing acidity and others, such as Ni, contributing to alkalinity. These changes in pH directly influence the nutrient availability, microbial activity, and overall health of the soil [11,13,81,82]. Moreover, redox reactions involving metals such as Mn and Fe alter the oxidation and reduction states of soil, further affecting nutrient mobility and transformation [22]. In addition, HMs undergo adsorption and desorption processes that influence their bioavailability. Metals such as Pb and Cd often bind strongly to the soil particles, making them less accessible to plants, ultimately contributing to the long-term contamination of the soil [77]. Finally, high concentrations

of heavy metals in the soil from FA can cause physiological disorders in plants, reduce crop yield, and contaminate agricultural products, posing risks to human and animal health and disrupting the food chain [22]. These physical and chemical alterations in the soil compromise soil fertility, productivity, and health, and require urgent attention to remediation strategies.

5. Fly Ash Specificity

Soil contamination by FA significantly differs from other sources of contamination, such as mining waste. There are fundamental differences in the origin, composition, and characteristics of FA and mining waste. Fly ash originates from high-temperature coal combustion, whereas mining waste, including tailings and waste rock, originates from extraction and processing of mineral ores. Similarly, during coal combustion, the high temperature volatilizes and melts the inorganic mineral matter present in the coal, followed by rapid flue gas cooling [43]. These processes provide FA particles with a glassy and amorphous structure, often occurring as hollow spheres called cenospheres. Volatile elements such as As, Se, B, Hg, and Cd get vaporized during combustion and subsequently condense and settle on the outer surface of FA particles during cooling. This leads to weaker bindings of these elements, making them relatively more mobile and susceptible to leaching under favorable environmental conditions [9]. However, less volatile elements such as Mn, Cr, V, Fe, and Al are largely incorporated within the matrix, where they become structurally bound and exhibit comparatively lower immediate mobility [9]. In contrast, mining waste has a crystalline mineral matrix that is produced through geological processes [83]. Metals in these systems are typically incorporated within crystalline lattices and are released primarily through mineral dissolution [84]. Nevertheless, reactive phases, particularly sulfide minerals such as framboidal pyrite, can generate localized zones of intense geochemical reactivity and promote metal mobility [85].

Moreover, FA is neutral to alkaline in nature. Its pH depends on the concentrations of basic oxides such as MgO, CaO, and Na_2O (particularly CaO). In FAs with a high CaO content, pH values can reach 12, making them highly alkaline [86]. In the case of FAs with low concentrations of these oxides, the pH is neutral to slightly alkaline. On the other hand, mining waste, particularly sulfide-bearing tailings, gets oxidized when exposed to water and the atmosphere, generating acid mine drainage, with a pH as low as 2.23 [87]. The pH plays an important role in metal mobilization and bioaccumulation in plants, which are crucial for the success of a phytoextraction project. For instance, oxyanion-forming elements such as arsenic, Mo, Se, V, and Cr are highly bioavailable at neutral-to-alkaline pH, whereas cationic elements such as Cu, Zn, REEs, Pb, Cd, and Mn are more bioavailable at lower pH [9]. Additionally, leaching studies in fly ash have reported two key mechanisms of releasing HMs: sorption control and solubility control [88]. Sorption control depends on the affinity of HMs on the surfaces, such as oxides and oxyhydroxides, whereas solubility control depends on the dissolution of oxides such as Al_2O_3, FeO, and ZnO. These processes are highly pH-dependent [88]. Finally, pH affects the surface charge on Fe/Al oxides and clays, precipitation/dissolution (carbonates and hydroxides), and complexation in soil solution [89]. Thus, it directly regulates the concentration and composition of elements in the soil solution—the fraction readily available for plant uptake. The HMs that are highly bioavailable in FA include elements that form oxyanions under alkaline conditions, including As, Se, Mo, B, and V, instead of classical Pb-Zn-Cd domination from ore/smelting [89].

6. Remediation Strategies for the Fly-Ash/Heavy-Metal-Contaminated Soils

To maintain the fertility, productivity, and health of the soil, removal of pollutants and HMs from the soil or immobilizing and detoxifying them is imperative. The reclamation techniques for FA-contaminated sites include physicochemical and biological approaches [22]. Included in physicochemical approaches are (1) burying soil at a hazardous/dumping site and then immobilization of the HMs through chemical processing, followed by their leaching using acid solutions [90], (2) soil washing [91,92], (3) electrokinesis [90], (4) solidification and stabilization [93], and (5) vitrification [94], among others. One of the widely applied traditional approaches for HM remediation is stabilization/solidification. Shen et al. (2019) [95], performed a meta-analysis of research publications in the Web of Science (WoS) in 2019 and found 80 papers discussing HM stabilization treatments worldwide that used biochar as a stabilizing agent. However, stabilization of these elements in this study can be attributed to an increase in pH, since their mobility decreases markedly at higher pH levels. In addition, FA contains a wide range of HMs that are mobile across variable pH values. Hence, stabilizing one HM can increase the susceptibility of another HM to leaching in FA-contaminated sites. Additionally, the physicochemical approaches are expensive and have many side effects, such as (a) soil structure degradation, (b) secondary pollution, and (c) irreversible changes in the soil ecosystem and soil physical and chemical properties [19,21,71,96,97]. Biological approaches include use of microorganisms to eliminate the harmful effects of HMs on soil and plants, and use of some plants that can accumulate, degrade, or transform heavy metals in their biomass into non-toxic forms [22,96]. Phytoremediation, the technique of reclaiming soils using plants, is eco-friendly, cost-effective, applicable at a large scale, able to maintain and improve soil health, simple to manage due to its autotrophic nature, and able to stabilize HMs and reduce metal leaching [98,99]. There are several types of phytoremediation techniques, including phytofiltration, phytoextraction, phytostimulation (plant-assisted bioremediation), phytodegradation, and phytostabilization. Among various phytoremediation techniques, phytodegradation, rhizodegradation, and phytostimulation are employed to degrade organic pollutants [100,101]. Phytodegradation involves using plants and their associated microorganisms to break down or transform organic contaminants into less toxic compounds. Rhizodegradation leverages the rhizosphere, the region of soil influenced by plant roots, for the degradation of organic pollutants. Similarly, phytostimulation uses plants to activate rhizospheric microbes to degrade organic compounds in soils [102]. Phytofiltration (using plants to filter HMs from contaminated aqueous medium) and phytostabilization (utilizing plants to immobilize and stabilize HMs in soil) do not remove HMs from the soil. This review delves into the mechanisms by which plants can be used in HM removal from soils through phytoextraction.

7. Phytoextraction

Phytoextraction is an approach in which certain plant species are used at contaminated sites to absorb and accumulate heavy metals in their aboveground biomass. Those plant biomasses are then harvested and safely disposed of [21,103]. Phytoextraction has been employed on sites contaminated with HMs, metalloids, and non-metals, on sludges containing organic pollutants, radionuclides, and on sediments [103–106]. In this technique, the translocation of HMs from roots to shoots is a critical process because roots are left unharvested [107]. The translocation process depends on factors such as the physical and chemical properties of the soil, the bioavailability of HMs in the soil and the nature of the HM being accumulated by the plant [21]. Plant species used in this technique exhibit unique characteristics that make them suitable for phytoextraction. These include a rapid growth

rate, elevated tolerance level to metal accumulation and toxicity, presence of extensive root branching for efficient metal uptake from soil, a high translocation factor, adaptation to unfavorable environmental conditions, resistance to pests and pathogens, ease of cultivation and harvesting, and natural repellence to herbivores, inhibiting contaminants from entering the food chain [97,108–112]. For the determination of the capacity of the plants for phytoextraction, two factors are critical—shoot metal concentration and shoot biomass [113]. In this technique, two approaches have been tested: (i) use of hyperaccumulator species having low biomass and high HM concentration [114] and (ii) use of non-hyperaccumulator species with high biomass and low HM concentration, compensating for the lower rate of metal accumulation [115,116]. As these studies have shown, hyperaccumulators produce compact, metal-rich biomass, facilitating economical and manageable metal recovery and safer disposal. Conversely, non-accumulators yield voluminous, metal-poor biomass, making the HM recovery process uneconomical and safe disposal costly [117].

The efficiency of phytoextraction ultimately depends on the bioavailability fraction of the polluting HMs [118]. This is because the total metal concentration in the soil does not always reflect metal bioavailability [119]. When HMs are not readily available for plant root absorption, chelate-induced phytoextraction can be performed, wherein different chelating or acidifying chemicals are applied to contaminated soils to make HMs bioavailable to the plants. Such practices can enable even non-hyperaccumulator species to accumulate greater quantities of HMs in their biomass than would otherwise be attainable under natural soil conditions. Some common soil chelating agents used in chelate-induced phytoextraction include ethylenediaminetetraacetic acid (EDTA), ethylene diamine disuccinate (EDDS), low-molecular-weight organic acids (LMWOAs), nitrilotriacetic acid (NTAA) [118], elemental sulfur, citric acid, and ammonium sulfate [120–123]. Among them, a widely used chelating agent is EDTA [124]. However, it should be noted that the natural degradation rate of EDTA in soil is very low; i.e., this compound remains in the soil for an extended period without degradation [125–128], causing secondary soil and water pollution. EDTA destroys the outer membranes of some soil bacteria [129], has cytotoxic and slightly genotoxic properties [130,131], and can cause reproductive problems in humans and animals when water contaminated with this chemical is consumed [132]. Therefore, recent studies are more directed towards the use of more biodegradable chelating agents such as EDDS (ethylenediamine-N,N′-disuccinic acid, one of the naturally occurring isomers of EDTA), GLDA (glutamic acid diacetic acid), MGDA (methylglycinediacetic acid), and others [118,133]. Using these biodegradable chelating agents offers several other benefits over non-biodegradable chelators. First, they can easily be degraded by microbes into non-toxic compounds, reducing their effects on plants and the environment [134]. Second, they promote mineralization in soils, accelerating nutrient availability to plants from organic matter decomposition [135]. Third, biodegradable chelating agents, such as [S,S]-ethylenediamine-N,N′-disuccinic acid ([S,S]-EDDS), can mobilize HMs such as Pb while being less aggressive toward essential nutrients [136]. Fourth, increasing environmental regulations discourage the use of persistent chelators like EDTA. Biodegradable alternatives offer a compliant and safer option for remediation efforts [126]. Finally, biodegradable chelating agents enhance the bioavailability of HMs for plant uptake while decomposing after their role is fulfilled, preventing residual environmental harm [133].

7.1. Hyperaccumulators

Different plant species behave differently in soils contaminated with heavy metals. Those plants are categorized into four classes, namely excluders, indicators, accumulators, and hyperaccumulators [137–140]. Excluders are plants that inhibit the translocation of metals to aerial parts, maintaining low concentrations in shoots. These include the

members of the Poaceae family, e.g., fescue, bromegrass, sorghum, sudangrass, etc., and are widely recognized for their insensitivity to the HM concentrations in the soil [139]. Similarly, the indicators are plants in which metal concentrations proportionally reflect soil concentrations. Examples include food crops such as wheat, corn, and soybeans. Elevated metal concentrations in the soil lead to increased metal accumulation in plant leaves, resulting in visible toxicity symptoms in these indicator plant species when grown in HM-contaminated soils [141]. On the other hand, accumulators consist of the species of plants that accumulate higher concentrations of metals in their tissues compared to that of soil. Finally, the hyperaccumulator plant species are plants with capacities to accumulate at least 10 times higher metal concentrations than that of soils.

Hyperaccumulators are capable of absorbing and sequestering exceptionally high concentrations of specific metals and metalloids in their aboveground tissues, i.e., 10- to 100-times higher than that of the usual concentrations [25]. This unique physiological adaptation is often defined by threshold values in their natural habitat or natural soil (but not applied to plants in soil amended with heavy metals). For example, a plant is considered to be a hyperaccumulator of Cd, Tl, or Se if it accumulates over 100 μg/g in its dry leaf tissue. Similarly, to be considered a hyperaccumulator of Ni, As, or REE, a plant should accumulate at least 1000 μg/g of dry leaf tissue [137,142–144]. For Zn and Mn, it should exceed 3000 μg/g and 10,000 μg/g of the dry leaf tissue, respectively, showing the substantial capability of these plants to concentrate metals that would otherwise be toxic [145,146]. However, a precise definition of hyperaccumulation on the basis of molecular mechanisms does not exist [27]. Efforts have been made to define the hyperaccumulation phenomenon in operational terms. A recent study was done to statistically verify the historically established threshold values [143]. The results largely supported those values and revealed a non-linear relationship between the accumulation of the HM in question and hypertolerance of that metal by the plant. But this relationship and the core mechanisms involved in hyperaccumulation differ greatly between HMs and among plant species [147].

The term "hyperaccumulator" was initially proposed by Jaffré et al. (1976) [148] to describe species that accumulate unusually high amounts of Ni, such as *Homalium guillainii*, *Hybanthus austrocaledo-nicus*, *Psycho-tria douarrei*, and *Sebertia acuminata* (now *Pycnandra acuminata*) [149]. According to Reeves et al. (2017) [142], a total of 756 species have been identified and recorded as hyperaccumulators (523 of Ni, 53 of Cu, 42 of Mn, 42 of Co, 41 of Se, 20 of Zn, 8 of Pb, 7 of Cd, 5 of As, 2 of Tl, 2 of REE, and one of Cr), especially in metal-rich soils such as serpentine and ultramafic substrates, where they exhibit unique ecological resilience [138,142]. These plants possess a unique evolutionary advantage of reduced herbivory due to their ability to thrive in soils enriched with potentially toxic elements, as many herbivores avoid plants with high metal content [137,150].

There are two main classes of hyperaccumulators based on their distribution, viz., obligate and facultative hyperaccumulators. Obligate hyperaccumulators are the plant species that always exhibit hyperaccumulation above the defined threshold and are limited in their distribution to the metalliferous soils [137,142,151]. On the other hand, facultative hyperaccumulators are plant species whose individuals or populations hyperaccumulate only under certain environmental conditions. Specifically, these are the plant populations that, when grown in metalliferous soils, hyperaccumulate, while on normal soils, they do not [137]. Facultative hyperaccumulation is the result of differences in metal ion availability in the soil, genetic variability within the species, factors such as soil pH, metal speciation and other soil characteristics that influence metal bioavailability [137,151].

Table 4 shows the number of hyperaccumulator species along with their target metals and concentrations.

Table 4. Hyperaccumulator species data from the global database [120].

Element	Threshold ($\mu g\ g^{-1}$)	Families (Main)	Genera (Main)	Species	Highest Records
Cadmium (Cd)	>100	6 (Crassulaceae, Brassicaceae)	7 (*Sedum*, *Noccaea*)	7	*Arabidopsis haller* (0.36%) [152]
Selenium (Se)	>100	7 (Fabaceae)	15 (*Stanleya*, *Astragalus*)	41	*Astragalus bisulcatus* (1.5%) [153]
Thallium (Tl)	>100	1 (Brassicaceae)	2 (*Biscutella*, *Iberies*)	2	*Biscutella laevigata* (1.9%) [154]
Copper (Cu)	>300	20 (Lamiaceae, Fabaceae, Linderniaceae, Commelinaceae, Asteraceae, Polygonaceae, Orobanchaceae)	43 (*Crepidorhopalon*, *Anisopappus*, *Haumaniastrum*, *Commelina*)	53	*Aeolanthus biformifolius* (1.4%) [155]
Cobalt (Co)	>300	18 (Orobanchaceae, Lamiaceae, Linderniaceae, Asteraceae, Phyllanthaceae)	34 (*Phyllanthus*, *Glochidion*, *Persicaria*, *Anisopappus*, *Crepidorhopalon*)	42	*Haumaniastrum roberti* (1%) [156]
Arsenic (As)	>1000	1 (Pteridaceae)	2 (*Pityrogramma*, *Pteris*)	5	*Pteris vittata* (2.3%) [157]
Nickel (Ni)	>1000	52 (Brassicaceae, Buxaceae, Asteraceae, Phyllanthaceae, Cunoniaceae, Salicaceae, Violaceae)	130 (*Geissois*, *Homalium*, *Hybanthus*, *Alyssum*, *Buxus*, *Berkheya*, *Glochidion*, *Xylosma*, *Leucocroton*, *Senecio*, *Phyllanthus*)	532	*Berkheya coddii* (7.6%) [158]
Lead (Pb)	>1000	6 (Brassicaceae)	8 (*Noccaea*)	8	*Noccaea rotondifolia* subsp. *Cepaeifolia* (0.8%) [159]
Rare Earth Elements (REEs)	>1000	2 (Gleicheniaceae)	2 (*Dicranopteris*)	2	*Dicranopteris linearis* (0.7%) [160]
Zinc (Zn)	>3000	9 (Brassicaceae, Crassulaceae)	12 (*Arabidopsis*, *Noccaea*, *Sedum*)	20	*Noccaea caerulescens* (5.4%) [161]
Manganese (Mn)	>10,000	16 (Celastraceae, Proteaceae, Myrtaceae)	24 (*Virotia*, *Gossia*, *Denhamia*)	42	*Virotia neurophylla* (5.5%) [142]

7.2. Mechanisms of Hyperaccumulation

Hyperaccumulators have unique physiological abilities to transport HMs from roots to aboveground biomass. They first detoxify toxic metals into non-toxic metal complexes using metal ligands and then transport them to the aboveground plant biomass. In contrast, non-hyperaccumulators sequester HMs in their root vacuoles as metal complexes as a detoxification strategy but do not transport them to their shoots and ultimately show toxicity symptoms [162]. The uptake and transport of these HMs in hyperaccumulators is facilitated by the overexpression of the transporter genes [163]. Several biological processes, mediated by specific genes and pathways, are involved in hyperaccumulation, including uptake, transport, storage, and detoxification. Below, we provide in-depth information about the biological processes and genetic factors responsible for hyperaccumulation, as shown in Figure 4.

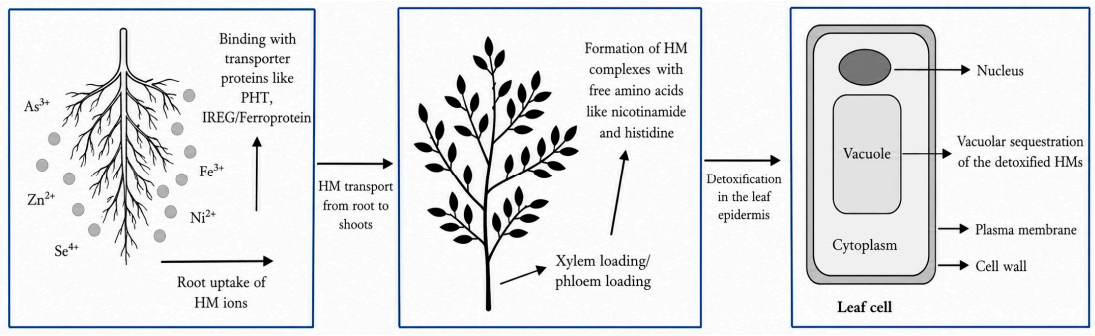

Figure 4. Key mechanisms of hyperaccumulation.

7.2.1. HM Uptake

HM uptake in hyperaccumulation occurs through root transporters, specialized protein molecules in the root system that facilitate the influx of metal ions into the root system along with other essential nutrients and minerals [162]. It is the first step in metal hyperaccumulation. Specific transporter proteins facilitate the uptake of HMs in hyperaccumulator plants. For example, PHT (Phosphate Transporter) facilitates the uptake of As in the form of arsenate from the soil into the roots of *Pteris vittata*, an arsenic hyperaccumulator [164]. In the case of Ni hyperaccumulators, such as *Leucocroton havanensis*, IREG/Ferroportin transporters are used for Ni uptake [165]. These transporter genes are constitutive in nature, meaning that they are always expressed in the hyperaccumulator plants, even in the absence of metal stress, which differentiates the hyperaccumulator plants from the non-hyperaccumulating plants [163,166]. A study conducted to compare the uptake of Zn into the roots of the Zn hyperaccumulators *T. caerulescens* and *A. helleri* with non-hyperaccumulators of the same genus revealed that the enhanced uptake of Zn in these hyperaccumulators is due to the constitutive expression of genes of the Zn-Fe regulated proteins (ZIP) [167]. In the case of Se hyperaccumulators like *Astragalus bisulcatus* and *Stanleya pinnata*, one or more sulfate transporters that gain Se-specificity play a role in the Se hyperaccumulation [153]. This process is largely absent in non-hyperaccumulator plants, which tend to sequester HMs in the roots through chelation in the cytoplasm and subsequent compartmentalization within root cell vacuoles [162]. In hyperaccumulators, however, HMs are translocated to the aerial parts of the plant via xylem loading, in which metals are actively transferred from root cells into the xylem sap and subsequently transported to the shoots through the transpiration stream.

7.2.2. HM Transport from Root to Shoot

The transport of HMs from roots to shoots is the second step in the hyperaccumulation mechanism. This process is largely absent in the non-hyperaccumulator plants; instead, these plants store HMs in the roots by chelation in the cytoplasm and locking them inside the root cell vacuoles [162]. In hyperaccumulators, however, HMs are transported from roots to shoots via xylem loading. In this process, HMs are transported from root cells into the xylem sap and subsequently transferred to shoots/leaves through transpirational pull.

This rate of HM translocation from roots to shoots is significantly higher in hyperaccumulators than in non-hyperaccumulators. For example, the efflux of Zn from the root cell vacuoles of hyperaccumulators like *T. caerulescens* [168] and *S. alfredii* [169] is twice that of the non-hyperaccumulator relatives of these species. Conversely, the non-hyperaccumulators have two- to three-times more HM accumulation in the root cell vacuoles than in the hyperaccumulators, possibly due to some specific characteristics of the root tonoplast of the hyperaccumulators [168]. Similarly, in comparative studies of hyperaccumulator species of *Pteris* with their non-hyperaccumulating counterpart species, it was

found that As translocation was enhanced by hyperaccumulators, accompanied by lower As sequestration in root vacuoles than in non-hyperaccumulators [170]. In some hyperaccumulators, phloem transport is also observed alongside xylem transport, redistributing metals to the growing tissues of the plants. For instance, in the case of Ni hyperaccumulators like *Noccaea cearulescens*, phloem transport is seen to deliver Ni to the young leaves and reproductive tissues of the plants [171].

In the metal transport process, ligands play an essential role in the xylem loading and in the prevention of metal entrapment in root cell vacuoles [172,173]. For example, free amino acids such as nicotinamine and histidine (His) act as ligands to form stable complexes with bivalent cations, facilitating xylem loading [174]. In nickel hyperaccumulators such as *Alyssum lesbiacum*, His forms a stable Ni–His complex with Ni during root-to-shoot transport via the xylem loading process [175]. Increased level of His concentrations in the xylem sap prevents Ni entrapment in root cell vacuoles, allowing more efficient translocation of Ni into the shoots [171]. In addition to the free amino acids, organic acids such as malate and citrate also contribute to the chelation of the metals during their transport via xylem and phloem [176]; however, their role is controversial since they have low affinity towards metals at the neutral pH value of the cytosols and are considered effective only under acidic vacuolar pH [177].

7.2.3. Storage/Detoxification

HMs, after their absorption in the roots and translocation to the aboveground biomass, are sequestered in the leaves of the hyperaccumulators [163]. HM sequestration and detoxification occur in the leaf epidermis, trichomes, and cuticles [178], where photosynthesis does not occur and the stomatal guard cells are prevented from the phytotoxic effects of HMs [162]. After the HMs reach leaves for storage, they are detoxified and moved from the metabolically active cytoplasm to inactive cellular compartments, such as vacuoles or cell walls [163]. Tonoplast transporters that mediate this sequestration of HMs in the vacuoles and cell walls, e.g., TIP (Tonoplast Intrinsic Protein) and *ACR3* in *Pteris vittata*, are responsible for the vacuolar compartmentalization of As in the form of non-toxic arsenite [164]. In Ni hyperaccumulators like *Leucocroton havanensis*, IREG/Ferroportin transporters are involved in vacuolar sequestration [165]. Detoxification of HMs is achieved by forming complexes using small ligands, such as organic acids. For instance, citrate is the primary ligand to form the Ni–citrate complex in the leaves of *T. geosingense*, a Ni hyperaccumulator [162]. In the case of *Solanum nigrum*, a Cd hyperaccumulator, citrate and acetate detoxify and bind Cd in the leaves [179]. Hyperaccumulators, unlike non-hyperaccumulators, do not depend on the heavy molecules of ligands like phytochelatins [180], since this costs the plants a lot of energy [181]; instead they depend on the overexpression of genes related to antioxidation [182] and production of glutathione (GSH) [183], which also helps them in coping with Reactive Oxygen Species (ROS) that increase during the HM stress in the plants [163].

8. Phytoextraction in FA-Contaminated Soils

Field and controlled-environment studies conducted worldwide have investigated the phytoextraction potential of various plant species for heavy metals in fly-ash-contaminated soils. The studies cited in this section are not based on the hyperaccumulation thresholds of HMs in the selected plant species; instead, they rely on indices such as the bioaccumulation factor (BAF)/bioconcentration factor (BCF) and translocation factor (TF). Here, the BAF represents the ratio of HM accumulation in plant biomass to the amount of HM left in the soil. In contrast, TF represents the ratio of HM concentration in shoots to that remaining in the roots. Non-accumulators have BAF and TF values < 1. Plant species with BAF > 1 in the roots and TF < 1 are considered best for phytostabilization, whereas plants with BAF > 1 in

the roots or shoots and TF > 1 are considered best for phytoextraction [184–186]. These plants effectively translocate and accumulate HMs in their aboveground biomass.

Banerjee et al. (2020) [184], using *Saccharum spontaneum* and *Saccharum ninja* in a pot-based experiment, found high BAF > 1 in roots and TF > 1 for Zn, Cd, Pb, Cu, and As in roots, indicating their great potential for phytoextraction and phytostabilization in FA-contaminated soils. In another study conducted in a fly ash pond at Unchahar Thermal Power Station, Raebareli District, Uttar Pradesh, India, using *Eichhornia crassipes*, Pandey (2016) [187] found that this plant species has great potential in the phytoextraction of Cu, Cr, and Cd based on his findings on BAF, TF, and their ability to thrive in FA-contaminated soils. A great potential of phytoextraction was also shown by *Helichrysum splendidum* in a study conducted in South Africa, where Munyengabe et al. (2024) [188] were able to extract 18–56% of the HMs, including As, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn, with the highest numbers being for Zn and Cu. Similarly, *Erigeron canadensis* exhibited effectiveness for Cd and Zn; *Tamarix tetrandra* for Cu, Mg, and Se; *Populus alba* for B, Ni, and Zn; and *Robinia pseudoacacia* for As and B, in phytoextraction in a study at an FA disposal site in Serbia [189]. In addition, *Scirpus littoralis* exhibited effective uptake of Mn, Zn, Ni, Cu, and Pb in the order of Mn > Zn > Ni > Cu > Pb from 25% FA-amended soil in a greenhouse experiment [190]. In addition to these examples, many other studies have demonstrated the phytoextraction potential of various plant species in FA-contaminated soils. Pandey (2016) [187] demonstrated the vigorous growth of these plant species in FA-contaminated sites, suggesting the potential for large-scale phytoextraction to remediate these sites. Table 5 summarizes examples of studies demonstrating the potential of different plant species for HM removal from FA-contaminated sites.

Table 5. Reported examples of phytoextraction of heavy metals from FA-amended soils.

Plant Species	Metals Extracted	Type of Experiment	BAF	Region/ Country	Citation
Saccharum spontaneum and *Saccharum munja*	Zn, Pb, Cu, Ni, Cd, and As	Pot-based	Zn—8.01, Pb—1.40, Cu—3.02, Ni—0.92, Cd—1.66 and As—1.47 for *S. spontaneum* Zn—8.54, Pb—1.66, Cu—3.24, Ni—0.76, Cd—1.63 and As—1.41 for *S. munja*	India	Banerjee et al. (2020) [184]
Eichhornia crassipes	Cr, Cu, and Cd	Field-based (on FA ponds)	Cr—3.75, Cu—3.62, and Cd—1.05	India	Pandey (2016) [187]
Helichrysum splendidum	As, Cr, and Zn	Pot-based	As—1.22, Cu—1.19, Zn—1.03	South Africa	Munyengabe et al. (2024) [188]
Erigeron canadensis	Cd and Zn	Field-based (on FA landfill)	Cd—1.21, Zn—1.34	Serbia	Krgović et al. (2015) [186]
Tamarix tetrandra	Cu, Mn, and Se	Field-based (on an FA disposal site)	Cu—>5, Mn—>5, Se—>60	Serbia	Kostić et al. (2022) [186]
Populus alba	B, Ni, and Zn	Field-based (on an FA disposal site)	B—>13, Ni—>2, Zn—>30	Serbia	Kostić et al. (2022) [186]

Table 5. *Cont.*

Plant Species	Metals Extracted	Type of Experiment	BAF	Region/ Country	Citation
Robinia pseudoacacia	As and B	Field-based (on an FA disposal site)	As—>9, B—>5	Serbia	Kostić et al. (2022) [186]
Brassica juncea	Fe, Mn, Zn, Cu, and Ni	Pot-based	Fe—68.31, Mn—24, Zn—16.43, Cu—6.53, Ni—1.20	South Africa	Mashau et al. (2018) [185]

Note: BAF = bioaccumulation factor; FA = fly ash. The studies summarized in this table are based on available FA-specific phytoextraction reports and do not represent all major FA-producing countries. Plant performance depends on FA chemistry, soil properties, metal bioavailability, plant species, climate, and experimental design; hence, the transferability of these findings should be interpreted cautiously.

The phytoextraction efficiencies of plant species for different elements vary in FA-contaminated soils because of four main reasons. First, HMs are correlated in their accumulation patterns across plant species in various ways. For example, Ca and Ba/Sr are inversely related to each other in plant bioaccumulation since they belong to the same group in the periodic table and compete as bivalent cations for uptake pathways such as Ca transporters and binding sites in roots [105,191]. Therefore, a higher BAF value for Ca will likely follow a lower BAF value of Ba/Sr. On the other hand, Cd and Zn are strongly and positively correlated and driven by their chemical similarities, such as shared ionic charge and radius, which allow Cd to utilize ZIP-family metal transporters and to co-accumulate in shoots [192]. Second, differences in BAF values across species can be attributed to transport mechanisms and species-specific HM specificity. For example, monocots, typically grasses, accumulate higher concentrations of Si than dicots because of a higher density of Si-transporters in their roots [193]. Legumes have higher pectin density in their root cells, which provides binding sites for Ca retention [194]. Hence, grass species have higher BAF values for Si, whereas legumes have higher BAF values for Ca. Third, FA is a heterogeneous material, and HMs within it are not evenly distributed. Mineral phases in FA undergo multiple transformations during coal combustion and flue-gas cooling, including volatilization–condensation cycles, fusion reactions, and particle agglomeration [195]. Some volatile elements, such as Hg, As, Se, and S, are enriched on FA particle surfaces, where they are more soluble and readily leached. In contrast, HMs such as Ba, Pb, Cr, Mn, Ni, and Co are more uniformly distributed within the aluminosilicate matrix and are released more slowly through diffusion-controlled processes [9]. This difference in surface enrichment and leachability influences metal bioavailability and contributes to variability in BAF values among elements. Finally, phytoextraction efficiency is dependent on the pH of the substrate. The most direct and quantitatively dominant effect of pH on phytoextraction is through its control of HM speciation and solubility in the soil solution. It is the immediate source of available HMs for root uptake. It has already been discussed in earlier sections that lower pH increases the bioavailability of cation-forming HMs. Hence, the phytoextraction of cationic HMs is more efficient at a low pH and that of oxyanion-forming HMs at a higher pH. In addition to this, pH is related to root uptake mechanisms. pH can influence root metal uptake indirectly by modifying the rhizosphere microenvironment surrounding the AHA2–FRO2–IRT1 uptake system, particularly through effects on proton-mediated Fe solubilization and Fe redox transformation [196]. Similarly, the pH and ionic composition of the outer solution determine the cation exchange capacity of apoplasts and the HM accumulation in root tissues [197].

9. Limitations

Over the years, significant advancements have been seen in the field of phytoextraction, and there is ample literature documenting the success of this technology in real-world applications. However, there are several challenges that hinder the widespread adoption of this technology for FA-contaminated site remediation. For example, the efficiency of phytoextraction heavily depends on the bioavailability of HMs in soil. Due to its high pH, FA often decreases the metal bioavailability, thereby limiting their availability for plant uptake [198–201]. Additionally, HMs are found in complex forms in FA, such as metal silicates or carbonates, which further complicates their extraction by the plants [202].

At present, there is a critical shortage of a comprehensive database that records the list of hyperaccumulator plants along with the elements that each species accumulates. Several efforts to develop a global database of hyperaccumulator plant species have been made in the past. Notable examples include the PHYTOREM database of Environment Canada and the METALS database from Environmental Consultancy at the University of Sheffield, UK, which together form a global database of hyperaccumulators. But these database catalogs categorized plants based on their metal tolerance capacities rather than their hyperaccumulating capabilities in the field [142]. In 2015, the Center for Mined Land Rehabilitation at The University of Queensland in Australia launched a global database for hyperaccumulator plant species (www.hyperaccumulators.org); however, the link and the redirection to (https://hyperaccumulators.smi.uq.edu.au/collection/) remain inactive (as of 24 February 2026). Due to the lack of a comprehensive database, the choice of species for phytoextraction projects is limited. Many studies have misclassified non-hyperaccumulator species as hyperaccumulators due to artificial experimental conditions, such as hydroponics with excessively high metal concentrations. These conditions often lead to pseudo-hyperaccumulation, in which plants exhibit uptake capacities that are unrepresentative of their natural behavior. There also exists insufficient field validations to prove or disprove the replicability of studies in a controlled environment, due to the in-field variability and complexity [27].

The identification of metal accumulators and hyperaccumulators is a crucial first step in phytoextraction, but it is only part of a much larger challenge. Transitioning from controlled experiments to large-scale field application depends on several practical factors. These include selecting suitable genotypes, ensuring that plants can adapt to local soil and climate conditions, and developing appropriate agronomic cultivation and management practices for contaminated sites [203]. In addition, hyperaccumulators are specific to metals, which is one of the major limitations in soils contaminated by multiple HMs. Their performance might decline in multiple-metal-contaminated soils. To overcome this limitation the use of multiple plant species with diverse metal specificity is required [203]. However, this can increase the complexity of field operations and management. The competition between different hyperaccumulators for growth and resources in such cases might decrease the total biomass of plants. This ultimately reduces the overall phytoextraction efficiency. Hence, a major limitation in this field is the lack of enough studies focused on agronomic management practices and use of multiple consortia of hyperaccumulators in multi-metal-contaminated sites, such as those with FA.

Moreover, there are many studies and much research focused on HM hyperaccumulation by plants, but there are too few studies that discuss the fate of heavy-metal-contaminated biomass [106]. The disposal of that toxic biomass is as critical as the hyperaccumulation process. If not managed properly, those toxic biomasses can cause secondary pollution. In addition, these biomasses are not economically valuable due to the presence of HMs. Phytomining, a technique that has gained significant attention in recent years, offers a solution for recovering valuable metals such as Ni and Co from plant biomass. However,

this method is economically viable only for high-value elements and is less applicable for more toxic, low-value metals or metalloids such as Cd, Zn, and As. Simultaneously, there is a risk of heavy metals entering the food chain through herbivory, which can disrupt ecological balance and amplify the dangers of metal contamination by introducing toxins into higher trophic levels.

Finally, phytoextraction technology is a slow process and often takes years or decades to achieve a meaningful reduction in contamination levels. The accumulation rates of HMs are limited by plant growth cycles and biomass limitations.

For example, consider a soil with a bulk density of 1.2 g/cm^3 and a Ni concentration of 1000 mg/kg. For a 1 ha area and a 15 cm soil depth, the total soil mass is:

$$10{,}000\ \text{m}^2 \times 0.15\ \text{m} \times 1200\ \text{kg/m}^3 = 1{,}800{,}000\ \text{kg}$$

The total Ni mass in this soil layer is:

$$1000\ \text{mg/kg} \times 1.8 \times 10^6\ \text{kg} = 1.8 \times 10^9\ \text{mg}$$

If a hyperaccumulator plant species produces 10,000 kg/ha shoot biomass and accumulates 10,000 mg/kg Ni in shoots, then the amount of Ni removed per cropping cycle is:

$$10{,}000\ \text{mg/kg} \times 10{,}000\ \text{kg} = 1.0 \times 10^9\ \text{mg}$$

Therefore, the estimated number of cropping cycles required is:

$$\frac{1.8 \times 10^9}{1.0 \times 10^8} = 18$$

Thus, approximately 18 cropping cycles would be required under this simplified scenario. However, assuming uniform contamination, constant biomass production, constant shoot metal concentration, and complete removal of harvested biomass, this example scenario shows that approximately 18 years will be required for an annual plant species and 36 years for a biennial plant species for these idealized conditions. This slow pace makes phytoextraction unsuitable for urgent remediation needs or sites with high economic pressure for rapid redevelopment.

10. Future Research Directions

Future research efforts in phytoremediation should prioritize comprehensive field-based studies over controlled pot or hydroponic experiments, with a focus on accurately, reliably, and effectively identifying, characterizing, and validating targeted remediation strategies for true hyperaccumulator species. This approach will enhance the selection of reliable hyperaccumulators and fast-track field deployment. Additionally, establishing an extensive and systematically organized database cataloging hyperaccumulator species, including their taxonomic classification, botanical characteristics, and specific metal accumulation profiles, is crucial for advancing targeted remediation strategies. Investigating the synergistic potential of multiple hyperaccumulator species co-cultivated at multi-metal-contaminated sites can address the complexity of heterogeneous pollution and improve remediation efficacy. Concurrently, genetic and breeding programs should focus on enhancing metal uptake efficiency, increasing biomass production, accelerating accumulation rates, and shortening the life cycle of hyperaccumulator species to optimize phytoremediation performance. To address the major issue of HM-contaminated plant biomass disposal, future studies should focus on developing hyperaccumulators whose biomass can be used for biofuel production. Research must also emphasize developing best management prac-

tices that integrate appropriate soil amendments and agronomic techniques to maximize plant growth and metal extraction. Moreover, there should be extensive research into novel hyperaccumulators across diverse ecological regions to expand the range of species available for site remediation projects. Economic feasibility analyses should be integral to future studies to assess the cost-effectiveness and scalability of phytoremediation technologies. Lastly, policy development and public engagement must be strengthened to promote phytoremediation as a sustainable environmental management strategy, ensuring regulatory support and societal acceptance for widespread implementation.

Fly ash is typically alkaline, and at elevated pH, the solubility and bioavailability of many cationic HMs such as Cd, Pb, Fe, Hg, and Cr decline, thereby limiting their bioaccumulation in plant tissues [204]. Conversely, alkaline conditions tend to increase the mobility and plant availability of oxyanion-forming elements such as As, Mo, V, and Se [9]. This contrasting pH-dependent behavior poses a fundamental challenge in FA-contaminated soils, where different HM groups exhibit opposing mobility trends across the pH spectrum. Therefore, addressing the variable mobility of heavy metals under fluctuating acidity–alkalinity conditions may require the strategic use of microbial consortia in combination with hyperaccumulator plant species [205]. A critical research question emerges: can we develop a specific plant–microbe combination that improves the uptake of both cation- and oxyanion-forming metals in FA-contaminated soils by effectively regulating rhizosphere pH and chemistry?

Finally, future research can also focus on the use of contaminated hyperaccumulator plant biomass in developing fertilizers for soils. In phytoextraction systems using hyperaccumulator species, target metals are concentrated in plant biomass along with normal plant nutrients. For example, a Zn-hyperaccumulator accumulates high levels of Zn while still containing essential macro- and micronutrients. This raises an important question: can Zn-rich biomass be recycled as an organic amendment in Zn-deficient agricultural soils? Instead of relying solely on synthetic Zn fertilizers, farmers could potentially apply chopped or composted hyperaccumulator biomass. Such organic amendments would release nutrients gradually, improve soil organic matter, reduce deficiency problems, and may contribute to crop biofortification. Moreover, hyperaccumulators typically concentrate specific elements rather than a broad range of metals, which may reduce the risk of excessive accumulation of unintended elements. Hence, based on this rationale, the authors hypothesize that essential micronutrients from FA-contaminated soils can be extracted using hyperaccumulators, and these biomasses can be directly used in agricultural fields as biofertilizers.

11. Conclusions

In conclusion, this review synthesizes existing knowledge on fly ash properties, heavy metal behavior, plant hyperaccumulation mechanisms, and field and controlled case studies assessed using bioaccumulation and translocation indices, and critically examines phytoextraction as a viable remediation strategy in FA-contaminated soils. Fly ash is heterogeneous in composition, alkaline in nature, has dominant amorphous aluminosilicate phases, and has surface enrichment of volatile trace elements, creating a metal-availability pattern that fundamentally differs from other HM-contaminated soils. These properties tend to limit the mobility of many cationic metals while maintaining or enhancing the mobility of certain oxyanion-forming elements, ultimately posing strong chemical selectivity on phytoextraction performance.

Similarly, phytoextraction depends on rhizosphere mobilization of HMs, root absorption, xylem loading, shoot translocation, sequestration, and tolerance. These mechanisms explain why metal accumulation differs substantially among plant species and among

elements within the same substrate. Moreover, physiological tolerance and translocation capacity are as important as root uptake alone, particularly in FA-contaminated sites, where the unfavorable growth environment can limit plant establishment and biomass production. Furthermore, the case studies reported in this review indicate that the phytoextraction potential of plant species in FA-contaminated soils is highly plant-species- and element-specific. These studies suggest that consistent success across a broad range of contaminants remains limited. Hence, BAF- and TF-based interpretation is useful for identification of candidate hyperaccumulator species, along with biomass production and field adaptability.

Despite encouraging global case studies, phytoextraction faces limitations, including slow remediation rates, limited biomass production, and the absence of comprehensive hyperaccumulator databases. Addressing these challenges requires future research focused on genetic enhancement of plant traits, the development of economically viable biomass utilization strategies, such as phytomining and biofuel production, and robust field-based validations. Similarly, heterogenous nature of FA, variable mobility and bioavailability of HMs at different pH levels pose a serious challenge in efficient remediation. Hence, a consortium of multiple hyperaccumulator species and microbes needs to be studied to enable efficient phytoremediation of FA sites. Moreover, the use of contaminated biomass of hyperaccumulators of essential elements as biofertilizers should also be studied. Finally, strengthening policy frameworks and public engagement will be essential to scale up phytoextraction as a viable tool for ecological restoration.

Author Contributions: Conceptualization, S.R. and M.G.; investigation, S.R.; resources, S.R., M.G. and J.C.H.; writing—original draft preparation, S.R.; writing—review and editing, S.R., M.G., J.C.H., G.F.A., J.B. and I.F.; supervision, M.G. and J.C.H.; project administration, M.G.; funding acquisition, M.G. All authors have read and agreed to the published version of the manuscript.

Funding: The APC of this review paper was funded by the National Energy Technology Laboratory (NETL) under the Department of Energy (DOE). Award number: DE-FE0032197.

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Karthika, V.; Sekaran, U.; Jainullabudeen, G.B.; Nagarathinam, A. Chapter 9—Advances in bioremediation of industrial wastewater containing metal pollutants. In *Biological Approaches to Controlling Pollutants*; Kumar, S., Hashmi, M.Z., Eds.; Advances in Pollution Research; Woodhead Publishing: Cambridge, UK, 2022; pp. 163–177. [CrossRef]
2. Emeka, C.I.; Nsima, A.A.; Kelvin, C.I.; Awajiiroijana, U.O.; Peter, I.E.; Justina, N.O.; Samuel, E.A. Environmental and Toxicological Risk Assessment of Heavy Metals in Eleme Agricultural Soils. *Asian J. Agric. Hortic. Res.* **2026**, *13*, 67–81. [CrossRef]
3. Heidrich, C.; Feuerborn, H.; Weir, A. Coal Combustion Products: A Global Perspective. In Proceedings of the 2013 World of Coal Ash (WOCA) Conference, Lexington, KY, USA, 22–25 April 2013. Available online: https://www.mcilvainecompany.com/Decision_Tree/subscriber/Tree/DescriptionTextLinks/International%20flyash%20perspective.pdf (accessed on 20 April 2026).
4. ACAA; USGS. Coal Combustion Products. 2001. Available online: https://pubs.usgs.gov/fs/fs076-01/fs076-01.pdf (accessed on 20 April 2026).
5. Ram, A.K.; Mohanty, S. State of the art review on physiochemical and engineering characteristics of fly ash and its applications. *Int. J. Coal Sci. Technol.* **2022**, *9*, 9. [CrossRef]
6. Wang, D.; Islam, M.A.; Mischo, H. The Utilization of Fly Ash in the Mining Sector. In *Integrative Approaches in Urban Sustainability—Architectural Design, Technological Innovations and Social Dynamics in Global Contexts*; Almusaed, A., Almssad, A., Yitmen, I., Wallhagen, M., Yang, Y.-F., Eds.; IntechOpen: London, UK, 2024; Chapter 11. [CrossRef]
7. Dhadse, S.; Kumari, P.; Bhagia, L.J. Fly ash characterization, utilization and government initiatives in India—A review. *J. Sci. Ind. Res.* **2008**, *67*, 11–18.

8. ACAA. Coal Combustion Products (CCP) Production and Use Charts. American Coal Ash Association. Available online: https://acaa-usa.org/wp-content/uploads/2023/12/2022-Production-and-Use-Charts.pdf (accessed on 23 June 2025).
9. Izquierdo, M.; Querol, X. Leaching behaviour of elements from coal combustion fly ash: An overview. *Int. J. Coal Geol.* **2012**, *94*, 54–66. [CrossRef]
10. Sheoran, H.S.; Duhan, B.S.; Kumar, A. Effect of Fly Ash Application on Soil Properties: A Review. *J. Agroecol. Nat. Resour. Manag.* **2014**, *1*, 98–103.
11. Collin, S.; Baskar, A.; Geevarghese, D.M.; Ali, M.N.V.S.; Bahubali, P.; Choudhary, R.; Lvov, V.; Tovar, G.I.; Senatov, F.; Koppala, S.; et al. Bioaccumulation of lead (Pb) and its effects in plants: A review. *J. Hazard. Mater. Lett.* **2022**, *3*, 100064. [CrossRef]
12. Office of Solid Waste and Emergency Response and Office of Resource Conservation and Recovery. Human and Ecological Risk Assessment of Coal Combustion Wastes. 2014. Available online: https://downloads.regulations.gov/EPA-HQ-OLEM-2019-0173-0008/content.pdf (accessed on 20 April 2026).
13. Sazykin, I.; Khmelevtsova, L.; Azhogina, T.; Sazykina, M. Heavy Metals Influence on the Bacterial Community of Soils: A Review. *Agriculture* **2023**, *13*, 653. [CrossRef]
14. Banda, M.F.; Matabane, D.L.; Munyengabe, A. A phytoremediation approach for the restoration of coal fly ash polluted sites: A review. *Heliyon* **2024**, *10*, e40741. [CrossRef] [PubMed]
15. Ali, H.; Khan, E. What are heavy metals? Long-standing controversy over the scientific use of the term 'heavy metals'–proposal of a comprehensive definition. *Toxicol. Environ. Chem.* **2018**, *100*, 6–19. [CrossRef]
16. Duffus, J.H. 'Heavy metals'—A meaningless term? (IUPAC technical report). *Pure Appl. Chem.* **2002**, *74*, 793–807. [CrossRef]
17. Adriano, D.C.; Page, A.L.; Elseewi, A.L.; Chang, A.C.; Straughan, I. Utilization and disposal of fly ash and other coal residues in terrestrial ecosystems: A review. *J. Environ. Qual.* **1980**, *9*, 333–344. [CrossRef]
18. McGrath, S.P.; Zhao, F.J.; Lombi, E. Plant and rhizosphere processes involved in phytoremediation of metal-contaminated soils. In *Interactions in the Root Environment: An Integrated Approach*; Springer: Dordrecht, The Netherlands, 2002; pp. 207–214. [CrossRef]
19. Wei, S.; da Silva, J.A.T.; Zhou, Q. Agro-improving method of phytoextracting heavy metal contaminated soil. *J. Hazard. Mater.* **2008**, *150*, 662–668. [CrossRef]
20. DalCorso, G.; Fasani, E.; Manara, A.; Visioli, G.; Furini, A. Heavy metal pollutions: State of the art and innovation in phytoremediation. *Int. J. Mol. Sci.* **2019**, *20*, 3412. [CrossRef]
21. Ali, H.; Khan, E.; Sajad, M.A. Phytoremediation of heavy metals-Concepts and applications. *Chemosphere* **2013**, *91*, 869–881. [CrossRef] [PubMed]
22. Alloway, B.J. Heavy Metals in Soil: Trace Metals and Metalloids in Soils and their Bioavailability. In *Environmental Pollution*, 3rd ed.; Springer: Dordrecht, The Netherlands, 2013.
23. Qi, M.; Ye, C.; Li, R.; Cao, J.; Li, X.; Qing, J.; Zhang, Z.; Xu, R.; Wang, X.; Zheng, B. Fly ash and FeSO4 synergistically modified ecological concrete for sustainable remediation of vanadium-titanium magnetite tailings. *J. Build. Eng.* **2026**, *119*, 115306. [CrossRef]
24. Nepal, A.; Antonious, G.F.; Bebe, F.N.; Webster, T.C.; Gyawali, B.R.; Neupane, B. Heavy Metal Accumulation in Three Varieties of Mustard Grown under Five Soil Management Practices. *Environments* **2024**, *11*, 77. [CrossRef]
25. Chaney, R.L.; Li, Y.-M.; Brown, S.L.; Homer, F.A.; Malik, M.; Angle, J.S.; Baker, A.J.M.; Reeves, R.D.; Chin, M. *Improving Metal Hyperaccumulator Wild Plants to Develop Commercial Phytoextraction Systems: Approaches and Progress*; CRC Press: Boca Raton, FL, USA, 2020. [CrossRef]
26. Jeevanantham, S.; Saravanan, A.; Hemavathy, R.V.; Kumar, P.S.; Yaashikaa, P.R.; Yuvaraj, D. Removal of toxic pollutants from water environment by phytoremediation: A survey on application and future prospects. *Environ. Technol. Innov.* **2019**, *13*, 264–276. [CrossRef]
27. van der Ent, A.; Rylott, E.L. Inventing hyperaccumulator plants: Improving practice in phytoextraction research and terminology. *Int. J. Phytoremediat.* **2024**, *26*, 1379–1382. [CrossRef]
28. Theile, C.M.; Beall, A.L. Narrative Reviews of the Literature: An overview. *J. Dent. Hyg.* **2024**, *98*, 78–82.
29. Steier, W.; Li, C.; Sabatini, P.; Lodato, M.; Bardol, M.; Gross, B.; Seymour, J. Coal Combustion Residuals Pond Closure: Guidance for Dewatering and Capping. 2014. Available online: https://restservice.epri.com/publicdownload/000000003002001143/0/Product (accessed on 20 April 2026).
30. National Research Council of the National Academics (NRC). *Managing Coal Combustion Residues in Mines*; National Academies Press: Cambridge, MA, USA, 2006. [CrossRef]
31. Energy Education. Boiler Slag. Energy Education. Available online: https://energyeducation.ca/encyclopedia/Boiler_slag? (accessed on 31 January 2025).
32. Matsimbe, J.; Dinka, M.; Olukanni, D.; Musonda, I. Characterization and valorization of fly ash and phosphogypsum into a binary composite for construction. *Clean. Waste Syst.* **2025**, *12*, 100355. [CrossRef]
33. Ram, L.C.; Masto, R.E. Fly ash for soil amelioration: A review on the influence of ash blending with inorganic and organic amendments. *Earth-Sci. Rev.* **2014**, *128*, 52–74. [CrossRef]

34. Ahmaruzzaman, M. A review on the utilization of fly ash. *Prog. Energy Combust. Sci.* **2010**, *36*, 327–363. [CrossRef]
35. Electric Power Research Institute (EPRI). Coal Ash: Characteristics, Management and Environmental Issues. 2009. Available online: http://www.epri.com/abstracts/Pages/ProductAbstract.aspx?ProductId=000000000001019022 (accessed on 20 April 2026).
36. *ASTM C618-15*; Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete. American Society for Testing and Materials (ASTM): West Conshohocken, PA, USA, 2017. Available online: https://www.astm.org/c0618-15.html (accessed on 20 April 2026).
37. Hower, J.; Henke, K.; Dai, S.; Ward, C.; French, D.; Liu, S.; Graham, U. *Generation and Nature of Coal Fly Ash and Bottom Ash*; Woodhead Publishing: Cambridge, UK, 2017. [CrossRef]
38. Bentz, D.P.; Durán-Herrera, A.; Galvez-Moreno, D. Comparison of ASTM C311 strength activity index testing versus testing based on constant volumetric proportions. *J. ASTM Int.* **2011**, *9*, 1–7. [CrossRef]
39. Thomas, M.D.A.; Shehata, M.H.; Shashiprakash, S.G. The Use of Fly Ash in Concrete: Classification by Composition. *Cem. Concr. Aggreg.* **1999**, *21*, 105–110. [CrossRef]
40. *ASTM C1157/C1157M-23*; Standard Performance Specification for Hydraulic Cement. American Society for Testing and Materials (ASTM): West Conshohocken, PA, USA, 2023. Available online: https://standards.iteh.ai/catalog/standards/astm/a4e8efe6-5904-4bd8-a3c3-8e32c3fbae69/astm-c1157-c1157m-23?srsltid=AfmBOooFGGyxiJbQ0cE3FZPHGFSm0c650_WBg57RE3YuUrAadptRYElr (accessed on 26 January 2025).
41. Vassilev, S.V.; Vassileva, C.G. A new approach for the classification of coal fly ashes based on their origin, composition, properties, and behaviour. *Fuel* **2007**, *86*, 1490–1512. [CrossRef]
42. Wojtaszek, M.; Wasielewski, R.; Kalaitzidis, S. Organic petrographical features of fly ashes originating from coal and coal-srf co-combustion. *Minerals* **2021**, *11*, 128. [CrossRef]
43. Alterary, S.S.; Marei, N.H. Fly ash properties, characterization, and applications: A review. *J. King Saud Univ. Sci.* **2021**, *33*, 101536. [CrossRef]
44. Kruse, K.; Jasso, A.; Folliard, K.; Ferron, R.; Juenger, M.; Drimalas, T. *Characterizing Fly Ash. Center for Transportation Research*; The University of Texas at Austin: Austin, TX, USA, 2013; Volume 7, pp. 1–172. Available online: https://library.ctr.utexas.edu/ctr-publications/0-6648-1.pdf (accessed on 20 April 2026).
45. Matsunaga, T.; Kim, J.K.; Hardcastle, S.; Rohatgi, P.K. Crystallinity and selected properties of fly ash particles. *Mater. Sci. Eng. A* **2002**, *325*, 333–343. [CrossRef]
46. EPA. Electric Power Sector Basics. United States Environmental Production Agency. Available online: https://www.epa.gov/power-sector/electric-power-sector-basics (accessed on 26 January 2025).
47. Hower, J.C.; Thomas, G.; Hopps, S. Trends in Coal Utilization and Coal Combustion Product Production in Kentucky: Results of the 2012 Survey of Power Plants. *Coal Combust. Gasif. Prod.* **2014**, *6*, 35–41. [CrossRef]
48. Vu, H.; Frýdl, T.; Bastl, T.; Dvořák, P.; Kristianová, E.; Tomáško, T. Recent Development in Metal Extraction from Coal Fly Ash. In *Clean Coal Technologies: Beneficiation, Utilization, Transport Phenomena and Prospective*; Jyothi, R.K., Parhi, P.K., Eds.; Springer International Publishing: Cham, Switzerland, 2021; pp. 575–603. [CrossRef]
49. Kamara, S.; Foday, E.H., Jr.; Wang, W. A Review on the Utilization and Environmental Concerns of Coal Fly Ash. *Am. J. Chem. Pharm.* **2023**, *2*, 53–65. [CrossRef]
50. Hower, J.C. Book Review. *Int. J. Coal Geol.* **2017**, *181*, 75–77. [CrossRef]
51. Dewan, S. Tennessee ash flood larger than initial estimate. *New York Times*, 26 December 2008.
52. Dewan, S. At Plant in Coal Ash Spill, Toxic Deposits by the Ton. *New York Times*, 29 December 2008. Available online: https://www.nytimes.com/2008/12/30/us/30sludge.html (accessed on 27 January 2025).
53. Dewan, S. Coal Ash Spill Revives Issue of Its Hazards. *New York Times*, 24 December 2008. Available online: https://www.nytimes.com/2008/12/25/us/25sludge.html (accessed on 27 January 2025).
54. Hower, J.C. Valley So Low: One Lawyer's Fight for Justice in the Wake of America's Great Coal Catastrophe, by Jared Sullivan, 2024. Book Review. *Int. J. Coal Geol.* **2014**, *127*, 104672. [CrossRef]
55. Earth Justice. Waste Deep Filling Mines with Coal Ash Is Profit for Industry, But Poison for People. 2009. Available online: https://earthjustice.org/wp-content/uploads/earthjustice_waste_deep.pdf (accessed on 20 April 2026).
56. Bosch, E. Georgia Power Proposes Risky Coal Ash Pond Closure at Plant Bowen. Sierra Club. Available online: https://www.sierraclub.org/press-releases/2021/10/georgia-power-proposes-risky-coal-ash-pond-closure-plant-bowen? (accessed on 26 January 2025).
57. Sturgis, S. Coal's Dirty Secret. Facing South; A Voice for a Changing South. Available online: https://www.facingsouth.org/2010/05/coals-dirty-secret.html (accessed on 26 January 2025).
58. EPA. Drinking Water Arsenic Rule History. United States Environmental Protection Agency. Available online: https://www.epa.gov/dwreginfo/drinking-water-arsenic-rule-history? (accessed on 26 January 2025).

59. Indianapolis Power and Light Company (IPLC). Assessment of Dam Safety of Coal Combustion Surface Impoundments. Martinsville, Indiana, 2010. Available online: https://archive.epa.gov/epawaste/nonhaz/industrial/special/fossil/web/pdf/ipl-lighteagle-final.pdf (accessed on 20 April 2026).
60. Gottlieb, B.; Gilbert, S.G.; Evans, L.G. Coal Ash: The Toxic Threat to Our Health and Environment. 2010. Available online: http://www.psr.org/resources/coal-ash-the-toxic-threat-to-our-health-and-environment.html (accessed on 20 April 2026).
61. Cowan, E.A.; Wang, Z.; Brachfeld, S.A.; Hageman, S.J.; Seramur, K.C.; Pearson, W.F.; Wilson, J.; Karcher, R.; Hill, R.; Vengosh, A. Role of coal ash morphology and composition in delivery and transport of trace metals in the aquatic environment. *Environ. Pollut.* **2024**, *363*, 124982. [CrossRef] [PubMed]
62. Wang, Z.; Dai, S.; Cowan, E.A.; Dietrich, M.; Schlesinger, W.H.; Wu, Q.; Zhou, M.; Seramur, K.C.; Das, D.; Vengosh, A. Isotopic Signatures and Outputs of Lead from Coal Fly Ash Disposal in China, India, and the United States. *Environ. Sci. Technol.* **2023**, *57*, 12259–12269. [CrossRef] [PubMed]
63. Wang, Z.; Coyte, R.M.; Cowan, E.A.; Stapleton, H.M.; Dwyer, G.S.; Vengosh, A. Evaluation and Integration of Geochemical Indicators for Detecting Trace Levels of Coal Fly Ash in Soils. *Environ. Sci. Technol.* **2021**, *55*, 10387–10397. [CrossRef] [PubMed]
64. Borm, P.J.A. Toxicity and occupational health hazards of coal fly ash (CFA). A review of data and comparison to coal mine dust. *Ann. Occup. Hyg.* **1997**, *41*, 659–676. [CrossRef] [PubMed]
65. McBride, M.B. Soil Chemistry. In *Environmental Chemsitry of Soils*; Oxford University Press: Oxford, UK, 1994; p. 406. Available online: https://books.google.com/books/about/Environmental_Chemistry_of_Soils.html?id=jgZhQgAACAAJ (accessed on 20 April 2026).
66. Carlson, C.L.; Adriano, D.C. Environmental Impacts of Coal Combustion Residues. *J. Environ. Qual.* **1993**, *22*, 227–247. [CrossRef]
67. Gagnon, B.; Lalande, R.; Fahmy, S. Organic matter and aggregation in a degraded potato soil as affected by raw and composted pulp residue. *Biol. Fertil. Soils* **2001**, *34*, 441–447. [CrossRef]
68. Biswal, T.; Panda, R.B. Impact of fly ash on soil properties and Productivity. *Int. J. Agric. Environ. Biotechnol.* **2018**, *11*, 275–283. Available online: https://www.researchgate.net/publication/347355971_Impact_of_Fly_Ash_on_Soil_Properties_and_Productivity (accessed on 20 April 2026). [CrossRef]
69. Wong, M.H.; Wong, J.W.C. Effects of fly ash on soil microbial activity. *Environ. Pollut. Ser. A Ecol. Biol.* **1986**, *40*, 127–144. [CrossRef]
70. Chu, D. Effects of heavy metals on soil microbial community. *IOP Conf. Ser. Earth Environ. Sci.* **2018**, *113*, 012009. [CrossRef]
71. Ogunsola, S.S.; Oladele, O.L.; Abdulraheem, T.; Cooke, C.G. Synergizing phytoremediation and geopolymerization: A sustainable waste-to-wealth approach for heavy metal-contaminated soils. *Chemosphere* **2025**, *385*, 144539. [CrossRef]
72. Bortoloti, G.A.; Baron, D. Phytoremediation of toxic heavy metals by Brassica plants: A biochemical and physiological approach. *Environ. Adv.* **2022**, *8*, 100204. [CrossRef]
73. Mustapha, L.S.; Obayomi, O.V.; Obayomi, K.S. A comprehensive review on potential heavy metals in the environment: Persistence, bioaccumulation, ecotoxicology, and agricultural impacts. *Ecol. Front.* **2026**, *46*, 434–449. [CrossRef]
74. Porter, J.R.; Sheridan, R.P. Inhibition of nitrogen fixation in alfalfa by arsenate, heavy metals, fluoride, and simulated Acid rain. *Plant Physiol.* **1981**, *68*, 143–148. [CrossRef]
75. Ukalska-Jaruga, A.; Siebielec, G.; Siebielec, S.; Pecio, M. The Effect of Soil Amendments on Trace Elements' Bioavailability and Toxicity to Earthworms in Contaminated Soils. *Appl. Sci.* **2022**, *12*, 6280. [CrossRef]
76. Mohammad, S.J.; Ling, Y.E.; Halim, K.A.; Sani, B.S.; Abdullahi, N.I. Heavy metal pollution and transformation in soil: A comprehensive review of natural bioremediation strategies. *J. Umm Al-Qura Univ. Appl. Sci.* **2025**, *11*, 528–544. [CrossRef]
77. Gong, C.; Shao, Y.; Luo, M.; Xu, D.; Ma, L. Distribution Characteristics of Heavy Metals in Different Particle Size Fractions of Chinese Paddy Soil Aggregates. *Processes* **2023**, *11*, 1873. [CrossRef]
78. Xie, Z.; Jiang, Y.; Zhang, H.; Wang, D.; Qi, S.; Du, Z.; Zhang, H. Assessing heavy metal contamination and ecological risk in Poyang Lake area, China. *Environ. Earth Sci.* **2016**, *75*, 549. [CrossRef]
79. Imfeld, G.; Meite, F.; Wiegert, C.; Guyot, B.; Masbou, J.; Payraudeau, S. Do rainfall characteristics affect the export of copper, zinc and synthetic pesticides in surface runoff from headwater catchments? *Sci. Total Environ.* **2020**, *741*, 140437. [CrossRef] [PubMed]
80. Adriano, D.C. Biogeochemistry of Trace Metals. In *BiogeochemistryOT*; Available online; CRC Press: Boca Raton, FL, USA, 1992. [CrossRef]
81. Pan, J.; Yu, L. Effects of Cd or/and Pb on Soil Enzyme Activities and Microbial Community Structure. *Ecol. Eng.* **2011**, *37*, 1889–1894. [CrossRef]
82. Liu, H.; Probst, A.; Liao, B. Metal contamination of soils and crops affected by the Chenzhou lead/zinc mine spill (Hunan, China). *Sci. Total Environ.* **2005**, *3*, 153–166. [CrossRef]
83. Li, J.; Hitch, M. Ultra-fine grinding and mechanical activation of mine waste rock using a planetary mill for mineral carbonation. *Int. J. Miner. Process.* **2017**, *158*, 18–26. [CrossRef]
84. Heikkinen, P.M.; Räisänen, M.L. Mineralogical and geochemical alteration of Hitura sulphide mine tailings with emphasis on nickel mobility and retention. *J. Geochem. Explor.* **2008**, *97*, 1–20. [CrossRef]

85. Weisener, C.G.; Weber, P.A. Preferential oxidation of pyrite as a function of morphology and relict texture. *N. Z. J. Geol. Geophys.* **2010**, *53*, 167–176. [CrossRef]
86. Catalfamo, P.; Di Pasquale, S.; Corigliano, F.; Mavilia, L. Influence of the calcium content on the coal fly ash features in some innovative applications. *Stud. Environ. Sci.* **1997**, *71*, 599–602. [CrossRef]
87. Nicola, K.; Sayouba, S.; Ousmane, B.; Prosper, Z.; Roza, C. Acid mine drainage and heavy metals contamination of surface water and soil in southwest burkina faso—West africa. *Int. J. Multidiscip. Acad. Res.* **2014**, *2*, 9–19.
88. Komonweeraket, K.; Cetin, B.; Aydilek, A.H.; Benson, C.H.; Edil, T.B. Effects of pH on the leaching mechanisms of elements from fly ash mixed soils. *Fuel* **2015**, *140*, 788–802. [CrossRef]
89. Martínez, C.E.; Motto, H.L. Solubility of lead, zinc and copper added to mineral soils. *Environ. Pollut.* **2000**, *107*, 153–158. [CrossRef] [PubMed]
90. Xu, L.; Zhao, F.; Xing, X.; Peng, J.; Wang, J.; Ji, M.; Li, B.L. A Review on Remediation Technology and the Remediation Evaluation of Heavy Metal-Contaminated Soils. *Toxics* **2024**, *12*, 897. [CrossRef] [PubMed]
91. Liu, H.-M.; Yan, Y.; Shao, D.-J.; Li, D.-L.; Zhang, Y.-L. Remediation of the Contaminated Soils by Washing with an Aqueous Cysteamine Lixiviant. *J. Mater. Sci. Chem. Eng.* **2015**, *3*, 1–4. [CrossRef]
92. Liu, L.; Hu, S.-P.; Chen, Y.-X.; Li, H. Feasibility of washing as a remediation technology for the heavy metals-polluted soils left by chemical plant. *Ying Yong Sheng Tai Xue Bao* **2010**, *21*, 1537–1541. [PubMed]
93. EPA. A Citizen's Guide to Solidification and Stabilization. 2012. Available online: https://www.epa.gov/sites/default/files/2020-06/documents/iss_cg_fs_eng.pdf (accessed on 20 April 2026).
94. Trifunović, V. Vitrification as a method of soil remediation. *Mater. Prot.* **2021**, *62*, 166–179. [CrossRef]
95. Shen, Z.; Jin, F.; O'Connor, D.; Hou, D. Solidification/Stabilization for Soil Remediation: An Old Technology with New Vitality. *Environ. Sci. Technol.* **2019**, *53*, 11615–11617. [CrossRef] [PubMed]
96. Blenis, N.; Hue, N.; Maaz, T.M.C.; Kantar, M. Biochar Production, Modification, and Its Uses in Soil Remediation: A Review. *Sustainability* **2023**, *15*, 3442. [CrossRef]
97. Sharma, S.; Dadhwal, R.; Banerjee, R. Nanoparticle assisted phytoremediation: An eco-friendly approach for removal of heavy metals from the environment. *J. Environ. Sci.* **2026**, *159*, 705–720. [CrossRef]
98. Wuana, R.A.; Okieimen, F.E. Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation. *ISRN Ecol.* **2011**, *2011*, 402647. [CrossRef]
99. Mukherjee, S.; Leri, A.C.; Bandaranayaka, C.; Vázquez-Núñez, E.; Barros, R.; Khan, A.H.A.; Zhou, P.; Zhang, T.; Bernal, M.P.; Clemente, R.; et al. Sustainable management of post-phytoremediation biomass. *Energy Ecol. Environ.* **2025**, *10*, 675–709. [CrossRef]
100. Yan, A.; Wang, Y.; Tan, S.N.; Yusof, M.L.M.; Ghosh, S.; Chen, Z. Phytoremediation: A Promising Approach for Revegetation of Heavy Metal-Polluted Land. *Front. Plant Sci.* **2020**, *11*, 359. [CrossRef] [PubMed]
101. Islam, M.M.; Saxena, N.; Sharma, D. Phytoremediation as a green and sustainable prospective method for heavy metal contamination: A review. *RSC Sustain.* **2024**, *2*, 1269–1288. [CrossRef]
102. Tak, H.I.; Ahmad, F.; Babalola, O.O. Advances in the application of plant growth-promoting rhizobacteria in phytoremediation of heavy metals. *Rev. Environ. Contam. Toxicol.* **2013**, *223*, 33–52. [CrossRef]
103. Nepal, A.; Antonious, G.F.; Gyawali, B.R.; Webster, T.C.; Bebe, F. Assessing the Bioaccumulation of Heavy Metals in Cabbage Grown under Five Soil Amendments. *Pollutants* **2024**, *4*, 58–71. [CrossRef]
104. Balint, R.; Boajă, I.P. Assisted phytoextraction as a nature-based solution for the sustainable remediation of metal(loid)-contaminated soils. *Integr. Environ. Assess. Manag.* **2024**, *20*, 2003–2022. [CrossRef] [PubMed]
105. Rajbanshi, S.; Gebremedhin, M.; Hower, J.C.; Antonious, G.; Upadhaya, S.; Brown, J.; Familusi, I. Effects of biochar amendment on the phytoextraction of twenty potentially toxic elements in fl y ash contaminated soils. *Front. Plant Sci.* **2026**, *17*, 1783879. [CrossRef]
106. Anggraini, Z.; Nurliati, G.; Pratama, H.A.; Sriwahyuni, H.; Sumarbagiono, R.; Shadrina, N.; Mirawaty, M.; Pamungkas, N.S.; Putra, Z.P.; Yusuf, M. A critical review about phytoremediation of heavy metals and radionuclides: From mechanisms to post-remediation strategies. *Chemosphere* **2025**, *381*, 144475. [CrossRef]
107. Zacchini, M.; Pietrini, F.; Mugnozza, G.S.; Iori, V.; Pietrosanti, L.; Massacci, A. Metal tolerance, accumulation and translocation in poplar and willow clones treated with cadmium in hydroponics. *Water. Air. Soil Pollut.* **2009**, *197*, 23–34. [CrossRef]
108. Mejáre, M.; Bülow, L. Metal-binding proteins and peptides in bioremediation and phytoremediation of heavy metals. *Trends Biotechnol.* **2001**, *19*, 67–73. [CrossRef]
109. Tong, Y.; Kneer, R. Vacuolar Compartmentalization: A Second-Generation Approach to Engineering Plants for Phytoremediation. *Trends Plant Sci.* **2004**, *9*, 7–9. [CrossRef] [PubMed]
110. Shabani, N.; Sayadi, M.H. Evaluation of heavy metals accumulation by two emergent macrophytes from the polluted soil: An experimental study. *Environmentalist* **2012**, *32*, 91–98. [CrossRef]

111. Adesodun, J.K.; Atayese, M.O.; Agbaje, T.A.; Osadiaye, B.A.; Mafe, O.F.; Soretire, A.A. Phytoremediation Potentials of Sunflowers (Tithonia diversifolia and Helianthus annuus) for Metals in Soils Contaminated with Zinc and Lead Nitrates. *Water Air Soil Pollut.* **2010**, *207*, 195–201. [CrossRef]
112. Sakakibara, M.; Ohmori, Y.; Ha, N.H.; Sano, S.; Sera, K. Phytoremediation of Heavy Metal-Contaminated Water and Sediment by Eleocharis acicularis. *Clean Soil Air Water* **2011**, *39*, 735–741. [CrossRef]
113. Li, J.T.; Liao, B.; Lan, C.Y.; Ye, Z.H.; Baker, A.J.M.; Shu, W.S. Cadmium Tolerance and Accumulation in Cultivars of a High-Biomass Tropical Tree (*Averrhoa carambola*) and Its Potential for Phytoextraction. *J. Environ. Qual.* **2010**, *39*, 1262–1268. [CrossRef]
114. Okpoghono, J.; Anani, A.O. Phytoremediation for heavy metal recovery. *Bioresour. Technol. Rep.* **2026**, *33*, 102578. [CrossRef]
115. Robinson, B.H.; Leblanc, M.; Petit, D.; Brooks, R.R.; Kirkman, J.H.; Gregg, P.E.H. The Potential of *Thlaspi caerulescens* for Phytoremediation of Contaminated Soils. *Entomol. Exp. Appl.* **1998**, *203*, 47–56. [CrossRef]
116. Tlustoš, P.; Száková, J.; Hrubý, J.; Hartman, I.; Najmanová, J.; Nedělník, J.; Pavlíková, D.; Batysta, M. Removal of As, Cd, Pb, and Zn from contaminated soil by high biomass producing plants. *Plant Soil Environ.* **2006**, *52*, 413–423. [CrossRef]
117. Bhat, B.A.; Rather, M.A.; Bilal, T.; Nazir, R.; Qadir, R.U.; Mir, R.A. Plant hyperaccumulators: A state-of-the-art review on mechanism of heavy metal transport and sequestration. *Front. Plant Sci.* **2025**, *16*, 1631378. [CrossRef]
118. Yogalakshmi, K.N.; Kohli, R.K.; Garg, V.K.; Dhawan, A.; Khosla, B. Environmental Microbiology & Biotechnology: Role of Microbes and Plants in Remediation-Phytoremediation. Available online: https://epgp.inflibnet.ac.in/epgpdata/uploads/epgp_content/S000014ER/P000284/M026110/ET/1515056403paper15_module_13_etext.pdf (accessed on 20 April 2026).
119. Antonious, G.; Kochhar, T.; Coolong, T. Yield, quality, and concentration of seven heavy metals in cabbage and broccoli grown in sewage sludge and chicken manure amended soil. *J. Environ. Sci. Health Part A Toxic Hazard. Subst. Environ. Eng.* **2012**, *47*, 1955–1965. [CrossRef]
120. Elkhatib, E.A.; Thabet, A.G.; Mahdy, A.M. Phytoremediation of cadmium contaminated soils: Role of organic complexing agents in cadmium phytoextraction. *Land Contam. Reclam.* **2001**, *9*, 359–366.
121. Lai, H.; Chen, Z.-S. Effects of EDTA on solubility of cadmium, zinc, and lead and their uptake by rainbow pink and vetiver grass. *Chemosphere* **2004**, *55*, 421–430. [CrossRef]
122. Lone, M.I.; He, Z.L.; Stoffella, P.J.; Yang, X.E. Phytoremediation of heavy metal polluted soils and water: Progresses and perspectives. *J. Zhejiang Univ. Sci. B* **2008**, *9*, 210–220. [CrossRef] [PubMed]
123. Sun, Y.; Sun, G.; Zhou, Q.; Xu, Y.; Wang, L.; Liang, X.; Sun, Y.; Qing, X. Induced-phytoextraction of heavy metals from contaminated soil irrigated by industrial wastewater with Marvel of Peru (*Mirabilis jalapa* L.). *Plant Soil Environ.* **2011**, *57*, 364–371. [CrossRef]
124. Sillanpää, M.; Kurniawan, T.; Lo, W. Degradation of chelating agents in aqueous solution using advanced oxidation process (AOP). *Chemosphere* **2011**, *83*, 1443–1460. [CrossRef]
125. López-Rayo, S.; Nadal, P.; Lucena, J.J. Reactivity and effectiveness of traditional and novel ligands for multi-micronutrient fertilization in a calcareous soil. *Front. Plant Sci.* **2015**, *6*, 752. [CrossRef]
126. Pinto, I.S.S.; Neto, I.F.F.; Soares, H.M.V.M. Biodegradable chelating agents for industrial, domestic, and agricultural applications—A review. *Environ. Sci. Pollut. Res.* **2014**, *21*, 11893–11906. [CrossRef]
127. Allard, A.S.; Renberg, L.; Neilson, A.H. Absence of 14C02 evolution from 14C-labelled EDTA and DTPA and the sediment/water partition ratio. *Chemosphere* **1996**, *33*, 577–583. [CrossRef]
128. Kari, F.G.; Giger, W. Modeling the photochemical degradation of ethylenediaminetetraacetate in the River Glatt. *Environ. Sci. Technol.* **1995**, *29*, 2814–2827. [CrossRef]
129. Oviedo, C.; Rodríguez, J. EDTA: The chelating agent under environmental scrutiny. *Quim. Nova* **2003**, *26*, 901–905. [CrossRef]
130. Lanigan, R.S.; Yamarik, T.A. Final Report on the Safety Assessment of EDTA, Calcium Disodium EDTA, Diammonium EDTA, Dipotassium EDTA, Disodium EDTA, TEA-EDTA, Tetrasodium EDTA, Tripotassium EDTA, Trisodium EDTA, HEDTA, and Trisodium HEDTA. *Int. J. Toxicol.* **2002**, *21*, 142–195. [CrossRef] [PubMed]
131. World Health Organization. Edetic Acid (EDTA) in Drinking-Water. In *Guidelines for Drinking-Water Quality*; WHO: Geneva, Switzerland, 2003; Volume 2, pp. 1–10. Available online: https://www.who.int/teams/environment-climate-change-and-health/water-sanitation-and-health/chemical-hazards-in-drinking-water/edetic-acid-edta (accessed on 20 April 2026).
132. Beltyukova, M.; Kuryntseva, P.; Galitskaya, P.; Selivanovskaya, S.; Brusko, V.; Dimiev, A. Biodegradation Rate of EDTA and IDS and Their Metal Complexes. *Horticulturae* **2023**, *9*, 623. [CrossRef]
133. Yin, F.; Li, J.; Wang, Y.; Yang, Z. Biodegradable chelating agents for enhancing phytoremediation: Mechanisms, market feasibility, and future studies. *Ecotoxicol. Environ. Saf.* **2024**, *272*, 116113. [CrossRef] [PubMed]
134. Srivastava, M.; Srivastava, A.; Yadav, A.; Rawat, V. Source and Control of Hydrocarbon Pollution. In *Hydrocarbon Pollution and Its Effect on the Environment*; Ince, M., Ince, O.K., Eds.; IntechOpen: Rijeka, Croatia, 2019; Chapter 2. [CrossRef]
135. Shao, H.; Zhang, Y. Non-target effects on soil microbial parameters of the synthetic pesticide carbendazim with the biopesticides cantharidin and norcantharidin. *Sci. Rep.* **2017**, *7*, 5521. [CrossRef]
136. López-Rayo, S.; Valverde, S.; Lucena, J.J. [S,S]-EDDS Ligand as a Soil Solubilizer of Fe, Mn, Zn, and Cu to Improve Plant Nutrition in Deficient Soils. *J. Agric. Food Chem.* **2023**, *71*, 9728–9737. [CrossRef]

137. van der Ent, A.; Baker, A.J.M.; Reeves, R.D.; Pollard, A.J.; Schat, H. Hyperaccumulators of metal and metalloid trace elements: Facts and Fiction. *Plant Soil* **2013**, *362*, 319–334. [CrossRef]
138. Baker, J.M.; Brooks, R.R. Terrestrial higher plants which hyperaccumulate metallic elements—A review of their distribution, ecology and phytochemistry. *Biorecovery* **1989**, *1*, 81–126.
139. Adriano, D.C. Trace Elements in the Terrestrial Environment. *J. Environ. Qual.* **1987**, *16*, 94. [CrossRef]
140. Lam, E.J.; Keith, B.F.; Bech, J.; Alvarez, F.A.; Zetola, V.; Pereira, L.H.; Montofré, Í.L. Characteristic curve modeling of plant species behavior in soils with heavy metals. *Environ. Geochem. Health* **2022**, *45*, 8867–8880. [CrossRef]
141. Baker, A.J.M. Accumulators and Excluders—Strategies in the Response of Plants to Heavy Metals. *J. Plant Nutr.* **1981**, *3*, 643–654. [CrossRef]
142. Reeves, R.D.; Baker, A.J.M.; Jaffré, T.; Erskine, P.D.; Echevarria, G.; van der Ent, A. A global database for plants that hyperaccumulate metal and metalloid trace elements. *New Phytol.* **2017**, *218*, 407–411. [CrossRef] [PubMed]
143. Purwadi, I.; Erskine, P.D.; Casey, L.W.; van der Ent, A. Recognition of trace element hyperaccumulation based on empirical datasets derived from XRF scanning of herbarium specimens. *Plant Soil* **2023**, *492*, 429–438. [CrossRef]
144. Bayuo, J.; Rwiza, M.J.; Choi, J.W.; Njau, K.N.; Mtei, K.M. Recent and sustainable advances in phytoremediation of heavy metals from wastewater using aquatic plant species: Green approach. *J. Environ. Manag.* **2024**, *370*, 122523. [CrossRef]
145. Zhang, X.; Zhang, X.; Huang, K. Phytostabilization of Acidic Soils with Heavy Metal Contamination Using Three Forage Grasses in Combination with Organic and Inorganic Amendments. *Soil Sediment Contam.* **2016**, *25*, 459–475. [CrossRef]
146. Shrestha, P.; Bellitürk, K.; Görres, J.H. Phytoremediation of heavy metal-contaminated soil by switchgrass: A comparative study utilizing different composts and coir fiber on pollution remediation, plant productivity, and nutrient leaching. *Int. J. Environ. Res. Public Health* **2019**, *16*, 1261. [CrossRef] [PubMed]
147. van der Ent, A.; Baker, A.J.M.; Reeves, R.D.; Pollard, A.J.; Schat, H. Commentary: Toward a more physiologically and evolutionarily relevant definition of metal hyperaccumulation in plants. *Front. Plant Sci.* **2015**, *6*, 554. [CrossRef]
148. Jaffré, T.; Brooks, R.R.; Lee, J.; Reeves, R.D. Sebertia acuminata: A Hyperaccumulator of Nickel from New Caledonia. *Science* **1976**, *193*, 579–580. [CrossRef]
149. Swenson, U.; Munzinger, J. Revision of Pycnandra subgenus Sebertia (Sapotaceae) and a generic key to the family in New Caledonia. *Adansonia* **2010**, *32*, 239–249. [CrossRef]
150. Boyd, R.S.; Martens, S.N. The significance of metal hyperaccumulation for biotic interactions. *Chemoecology* **1998**, *8*, 1–7. [CrossRef]
151. Pollard, A.J.; Powell, K.D.; Harper, F.A.; Smith, J.A.C. The genetic basis of metal hyperaccumulation in plants. *CRC Crit. Rev. Plant Sci.* **2002**, *21*, 539–566. [CrossRef]
152. Stein, R.J.; Höreth, S.; de Melo, J.R.F.; Syllwasschy, L.; Lee, G.; Garbin, M.L.; Clemens, S.; Krämer, U. Relationships between soil and leaf mineral composition are element-specific, environment-dependent and geographically structured in the emerging model Arabidopsis halleri. *New Phytol.* **2017**, *213*, 1274–1286. [CrossRef]
153. Galeas, M.; Zhang, L.; Freeman, J.; Wegner, M.; Pilon-Smits, E. Seasonal fluctuations of selenium and sulfur accumulation in selenium hyperaccumulators and related nonaccumulators. *New Phytol.* **2007**, *173*, 517–525. [CrossRef]
154. LaCoste, C.; Robinson, B.; Brooks, R.; Anderson, C.; Chiarucci, A.; Leblanc, M. The phytoremediation potential of thallium-contaminated soils using Iberis and Biscutella species. *Int. J. Phytoremediat.* **1999**, *1*, 327–338. [CrossRef]
155. Malaisse, F.; Gregoire, J.; Brooks, R.R.; Morrison, R.S.; Reeves, R.D. Aeolanthus biformifolius De Wild.: A hyperaccumulator of copper from Zaïre. *Science* **1978**, *199*, 887–888. [CrossRef]
156. Brooks, R.R. Copper and cobalt uptake byHaumaniastrum species. *Plant Soil* **1977**, *48*, 541–544. [CrossRef]
157. Ma, L.Q.; Komar, K.M.; Tu, C.; Zhang, W.; Cai, Y.; Kennelley, E.D. A fern that hyperaccumulates arsenic. *Nature* **2001**, *409*, 579. [CrossRef] [PubMed]
158. Mesjasz-Przybyłowicz, J.; Nakonieczny, M.; Migula, P.; Augustyniak, M.; Tarnawska, M.; Reimold, W.U.; Koeberl, C.; Przybyłowicz, W.; Głowacka, E. Uptake of cadmium, lead, nickel and zinc from soil and water solutions by the nickel hyperaccumulator Berkheya coddii. *Acta Biol. Cracoviensia Ser. Bot.* **2004**, *46*, 75–85.
159. Reeves, R.D.; Brooks, R.R. Hyperaccumulation of lead and zinc by two metallophytes from mining areas of Central Europe. *Environ. Pollut. Ser. A Ecol. Biol.* **1983**, *31*, 277–285. [CrossRef]
160. Shan, X.; Wang, H.; Zhang, S.; Zhou, H.; Zheng, Y.; Yu, H.; Wen, B. Accumulation and uptake of light rare earth elements in a hyperaccumulator Dicropteris dichotoma. *Plant Sci.* **2003**, *165*, 1343–1353. [CrossRef]
161. Reeves, R.D.; Schwartz, C.; Morel, J.L.; Edmondson, J. Distribution and metal-accumulating behavior of *Thlaspi caerulescens* and associated metallophytes in France. *Int. J. Phytoremediat.* **2001**, *3*, 145–172. [CrossRef]
162. Sytar, O.; Ghosh, S.; Malinska, H.; Zivcak, M.; Brestic, M. Physiological and molecular mechanisms of metal accumulation in hyperaccumulator plants. *Physiol. Plant.* **2020**, *173*, 148–166. [CrossRef]
163. Rascio, N.; Navari-Izzo, F. Heavy metal hyperaccumulating plants: How and why do they do it? And what makes them so interesting? *Plant Sci.* **2011**, *180*, 169–181. [CrossRef]

164. Bai, Y.; Wan, X.; Lei, M.; Wang, L.; Chen, T. Research advances in mechanisms of arsenic hyperaccumulation of Pteris vittata: Perspectives from plant physiology, molecular biology, and phylogeny. *J. Hazard. Mater.* **2023**, *460*, 132463. [CrossRef] [PubMed]
165. González, D.A.; de la Torre, V.S.G.; Fernández, R.R.; Barreau, L.; Merlot, S. Divergent roles of IREG/Ferroportin transporters from the nickel hyperaccumulator Leucocroton havanensis. *Physiol. Plant.* **2024**, *176*, e14261. [CrossRef]
166. Gallopin, M.; Drevet, C.; de la Torre, V.S.; Jelassi, S.; Michel, M.; Ducos, C.; Saule, C.; Majorel, C.; Burtet-Sarramegna, V.; Pillon, Y.; et al. Detection of orthologous genes with expression shifts linked to nickel hyperaccumulation across Eudicots. *bioRxiv* **2022**. [CrossRef]
167. Assunção, A.G.L.; Martins, P.D.C.; De Folter, S.; Vooijs, R.; Schat, H.; Aarts, M.G.M. Elevated expression of metal transporter genes in three accessions of the metal hyperaccumulator *Thlaspi caerulescens*. *Plant Cell Environ.* **2001**, *24*, 217–226. [CrossRef]
168. Lasat, M.M.; Pence, N.S.; Garvin, D.F.; Ebbs, S.D.; Kochian, L.V. Molecular physiology of zinc transport in the Zn hyperaccumulator *Thlaspi caerulescens*. *J. Exp. Bot.* **2000**, *51*, 71–79. [CrossRef] [PubMed]
169. Yang, X.; Li, T.; Yang, J.; He, Z.; Lu, L.; Meng, F. Zinc compartmentation in root, transport into xylem, and absorption into leaf cells in the hyperaccumulating species of Sedum alfredii Hance. *Planta* **2006**, *224*, 185–195. [CrossRef]
170. Poynton, C.Y.; Huang, J.W.; Blaylock, M.J.; Kochian, L.V.; Elless, M.P. Mechanisms of arsenic hyperaccumulation in Pteris species: Root As influx and translocation. *Planta* **2004**, *219*, 1080–1088. [CrossRef] [PubMed]
171. Deng, T.-H.; van der Ent, A.; Tang, Y.-T.; Sterckeman, T.; Echevarria, G.; Morel, J.-L.; Qiu, R.-L. Nickel hyperaccumulation mechanisms: A review on the current state of knowledge. *Plant Soil* **2018**, *423*, 1–11. [CrossRef]
172. Fonia, A.; Singh, P.; Singh, V.; Kumar, D.; Tripathi, B.N. Molecular mechanisms of heavy metal hyperaccumulation in plants. In *Phytoremediation of Environmental Pollutants*; CRC Press: Boca Raton, FL, USA, 2017; pp. 99–116. [CrossRef]
173. Richau, K.H.; Kozhevnikova, A.D.; Seregin, I.V.; Vooijs, R.; Koevoets, P.L.M.; Smith, J.A.C.; Ivanov, V.B.; Schat, H. Chelation by histidine inhibits the vacuolar sequestration of nickel in roots of the hyperaccumulator *Thlaspi caerulescens*. *New Phytol.* **2009**, *183*, 106–116. [CrossRef]
174. Callahan, D.L.; Baker, A.J.M.; Kolev, S.D.; Wedd, A.G. Metal ion ligands in hyperaccumulating plants. *J. Biol. Inorg. Chem.* **2006**, *11*, 2–12. [CrossRef] [PubMed]
175. Kerkeb, L.; Krämer, U. The role of free histidine in xylem loading of nickel in Alyssum lesbiacum and Brassica juncea. *Plant Physiol.* **2003**, *131*, 716–724. [CrossRef]
176. Panda, A.; Fatnani, D.; Parida, A.K. Uptake, impact, adaptive mechanisms, and phytoremediation of heavy metals by plants: Role of transporters in heavy metal sequestration. *Plant Physiol. Biochem.* **2025**, *221*, 109578. [CrossRef]
177. Haydon, M.J.; Cobbett, C.S. Transporters of ligands for essential metal ions in plants: Research review. *New Phytol.* **2007**, *174*, 499–506. [CrossRef]
178. Sahito, J.H.; Ma, C.; Zhang, J.; Li, J.; Zhao, J.; Mu, L.; Zhang, Y.; Gishkori, Z.G.N.; Ding, D.; Zhang, X.; et al. Selenium and its mechanisms mitigate cadmium toxicity in plants: Promising role and future potentials. *Ecotoxicol. Environ. Saf.* **2025**, *300*, 118422. [CrossRef]
179. Sun, R.L.; Zhou, Q.X.; Jin, C.X. Cadmium accumulation in relation to organic acids in leaves of *Solanum nigrum* L. as a newly found cadmium hyperaccumulator. *Plant Soil* **2006**, *285*, 125–134. [CrossRef]
180. Schat, H.; Llugany, M.; Vooijs, R.; Hartley-Whitaker, J.; Bleeker, P.M. The role of phytochelatins in constitutive and adaptive heavy metal tolerances in hyperaccumulator and non-hyperaccumulator metallophytes. *J. Exp. Bot.* **2002**, *53*, 2381–2392. [CrossRef]
181. Zhao, F.J.; Dunham, S.J.; McGrath, S.P. Arsenic hyperaccumulation by different fern species. *New Phytol.* **2002**, *156*, 27–31. [CrossRef]
182. Chiang, H.-C.; Lo, J.-C.; Yeh, K.-C. Genes associated with heavy metal tolerance and accumulation in Zn/Cd hyperaccumulator Arabidopsis halleri: A genomic survey with cDNA microarray. *Environ. Sci. Technol.* **2006**, *40*, 6792–6798. [CrossRef] [PubMed]
183. Van De Mortel, J.E.; Schat, H.; Moerland, P.D.; Van Themaat, E.V.L.; Van der Ent, S.; Blankestijn, H.; Ghandilyan, A.; Tsiatsiani, S.; Aarts, M.G. Expression differences for genes involved in lignin, glutathione and sulphate metabolism in response to cadmium in Arabidopsis thaliana and the related Zn/Cd-hyperaccumulator *Thlaspi caerulescens*. *Plant Cell Environ.* **2008**, *31*, 301–324. [CrossRef] [PubMed]
184. Banerjee, R.; Jana, A.; De, A.; Mukherjee, A. Phytoextraction of heavy metals from coal fly ash for restoration of fly ash dumpsites. *Bioremediat. J.* **2020**, *24*, 41–49. [CrossRef]
185. Mashau, A.S.; Gitari, M.W.; Akinyemi, S.A. Evaluation of the bioavailability and translocation of selected heavy metals by brassica juncea and spinacea oleracea l for a south african power utility coal fly ash. *Int. J. Environ. Res. Public Health* **2018**, *15*, 2841. [CrossRef]
186. Krgović, R.; Trifković, J.; Milojković-Opsenica, D.; Manojlović, D.; Marković, M.; Mutić, J. Phytoextraction of metals by *Erigeron canadensis* L. from fly ash landfill of power plant 'Kolubara'. *Environ. Sci. Pollut. Res.* **2015**, *22*, 10506–10515. [CrossRef]
187. Pandey, V.C. Phytoremediation efficiency of Eichhornia crassipes in fly ash pond. *Int. J. Phytoremediat.* **2016**, *18*, 450–452. [CrossRef] [PubMed]

188. Munyengabe, A.; Kamogelo, L.S.; Ngmenzuma, T.Y.; Banda, M.F. The Potential of Helichsryum splendidum (Thunb.) Less. for the Restoration of Sites Polluted with Coal Fly Ash. *Plants* **2024**, *13*, 2551. [CrossRef]
189. Kostić, O.; Gajić, G.; Jarić, S.; Vukov, T.; Matić, M.; Mitrović, M.; Pavlović, P. An assessment of the phytoremediation potential of planted and spontaneously colonized woody plant species on chronosequence fly ash disposal sites in serbia—Case study. *Plants* **2022**, *11*, 110. [CrossRef]
190. Bhattacharya, T.; Chakraborty, S.; Singh, G. Phytoextraction of few metals from fly ash amended soil by Scirpus littoralis. *Recent Res. Sci. Technol.* **2011**, *3*, 9–15.
191. Cooke, J.; Leishman, M.R. Consistent alleviation of abiotic stress with silicon addition: A meta-analysis. *Funct. Ecol.* **2016**, *30*, 1340–1357. [CrossRef]
192. Clemens, S. Toxic metal accumulation, responses to exposure and mechanisms of tolerance in plants. *Biochimie* **2006**, *88*, 1707–1719. [CrossRef]
193. Ma, J.F.; Yamaji, N. Silicon uptake and accumulation in higher plants. *Trends Plant Sci.* **2006**, *11*, 392–397. [CrossRef] [PubMed]
194. White, P.J.; Broadley, M.R. Calcium in plants. *Ann. Bot.* **2003**, *92*, 487–511. [CrossRef] [PubMed]
195. Jones, D.R. The Leaching of Major and Trace Elements from Coal Ash. In *Environmental Aspects of Trace Elements in Coal*; Swaine, D.J., Goodarzi, F., Eds.; Springer: Dordrecht, The Netherlands, 1995; pp. 221–262. [CrossRef]
196. Martín-Barranco, A.; Spielmann, J.; Dubeaux, G.; Vert, G.; Zelazny, E. Dynamic control of the high-affinity iron uptake complex in root epidermal cells. *Plant Physiol.* **2020**, *184*, 1236–1250. [CrossRef]
197. Meychik, N.R.; Yermakov, I.P. Ion exchange properties of plant root cell walls. *Plant Soil* **2001**, *234*, 181–193. [CrossRef]
198. Shaheen, S.M.; Hooda, P.S.; Tsadilas, C.D. Opportunities and challenges in the use of coal fly ash for soil improvements—A review. *J. Environ. Manag.* **2014**, *145*, 249–267. [CrossRef]
199. Zhang, H.; Lv, X.; Yang, Z.; Li, Q.; Wang, P.; Zhang, S.; Xu, Y.; Wang, X.; Ali, E.F.; Hooda, P.S.; et al. A field trial for remediation of multi-metal contaminated soils using the combination of fly ash stabilization and Zanthoxylum bungeanum- Lolium perenne intercropping system. *J. Environ. Manag.* **2024**, *361*, 121231. [CrossRef]
200. Houben, D.; Pircar, J.; Sonnet, P. Heavy metal immobilization by cost-effective amendments in a contaminated soil: Effects on metal leaching and phytoavailability. *J. Geochem. Explor.* **2012**, *123*, 87–94. [CrossRef]
201. Bashir, Z.; Raj, D.; Selvasembian, R. Sustainable phytoremediation technologies for the efficient removal of toxic metals from coal mining contaminated soils with the potential approaches of circular bioeconomy. *Pedosphere* **2026**, *36*, 254–277. [CrossRef]
202. Tsadilas, C.; Samaras, V.; Evangelou, E. Influence of fly ash and sewage sludge application on wheat biomass production, nutrients availability, and soil properties. *Int. J. Coal Sci. Technol.* **2014**, *1*, 221–226. [CrossRef]
203. Wan, X.; Zeng, W.; Cai, W.; Lei, M.; Liao, X.; Chen, T. Progress and future prospects in co-planting with hyperaccumulators: Application to the sustainable use of agricultural soil contaminated by arsenic, cadmium, and nickel. *Crit. Rev. Environ. Sci. Technol.* **2023**, *53*, 2112–2131. [CrossRef]
204. Kabata-Pendias, A. *Trace Elements in Soils and Plants*, 4th ed.; CRC Press: Boca Raton, FL, USA, 2010. [CrossRef]
205. Xu, Z.; Lu, H.; Li, S.; Ma, Y.; Wang, Y.; Li, R.; Yang, X.; Huang, B.; Zhang, H.; Pan, X. Integrating biochar, microbe, and hyperaccumulator for sustainable remediation of soils contaminated with heavy metals. *Environ. Rev.* **2025**, *33*, 1–19. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.