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CUTTING-EDGE TECHNIQUES FOR HEAVY METAL ELIMINATION FROM ECOSYSTEMS

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Abstract

The global population and industrial development surge has triggered a significant influx of heavy metals into ecosystems, posing risks to environmental integrity and human health through food chain contamination. This comprehensive review examines various methodologies to mitigate heavy metal contamination in ecosystems. It meticulously delves into a spectrum of physical and chemical approaches, including mechanical and ultrasonic soil washing, ex situ electrokinetic removal, and the utilization of chelating materials and soil amendments. Furthermore, it scrutinizes biological interventions employing microorganisms, algae, and natural organic products alongside innovative techniques such as phytoextraction and phytoremediation. The latter encompasses multifaceted strategies like rhizofiltration, phytostabilization, phytodegradation, phytoextraction, and phytovolatilization, emphasizing environmentally sustainable solutions to heavy metal pollution. Additionally, the paper evaluates biotechnological methods leveraging genetically modified plants and nanotechnological approaches utilizing nanoparticles for metal remediation, highlighting their potential contributions to remediation endeavors. The review underscores the importance of integrating multiple techniques to foster synergistic approaches for more effective heavy metal removal. Each method is assessed based on its treatment efficacy, advantages, and drawbacks, drawing insights from pertinent studies in the field. This comprehensive analysis offers a nuanced understanding of cutting-edge techniques for heavy metal elimination from ecosystems, elucidating their potential contributions and challenges in environmental remediation efforts. It explores the burgeoning role of artificial intelligence in heavy metal remediation processes, aiming to illuminate advancements and challenges within this rapidly evolving field.

Keywords: Heavy Metal, Cutting-edge Techniques, Elimination, Phytoextraction, Phytoremediation, Artifical Intelligence.

1. INTRODUCTION

Heavy metal pollution in ecosystems represents a critical environmental concern, posing substantial threats to biodiversity and human well-being. Heavy metals infiltrate the environment through natural processes and human activities, such as industrial operations, mining, and agricultural practices, significantly contributing to their presence (Hama Aziz et al. 2023; Tovar-Sánchez et al. 2018). The rapid increase in population coupled with industrial advancements has led to a substantial influx of heavy metals into ecosystems, ultimately integrating into the food chain and consequently impacting human health (Gall, Boyd, and Rajakaruna 2015). Notably, industrial activities are notorious for discharging heavy metal-contaminated wastewater into the environment, exacerbating water pollution (Hama Aziz et al. 2023; Tovar-Sánchez et al. 2018). The ramifications of heavy metal presence in the environment are profound, affecting diverse ecosystems and human health adversely, with chronic exposure potentially resulting in teratogenic and carcinogenic outcomes. Hence, it is imperative to pinpoint the primary sources of heavy metal contamination and devise effective strategies and policies to manage and mitigate their adverse effects (Das et al. 2023; Kumari and Mishra 2021; Norvell and Welch 1984; Tchounwou et al. 2012).

Heavy metals are compounds with a molecular mass exceeding 5.0 g/cm³ (Hodson 2004), ubiquitously present in soils. However, there exists a normal range for their concentration; for instance, copper (Cu), zinc (Zn), lead (Pb), chromium (Cr), nickel (Ni), and cadmium (Cd) typically range from 0.0001% to 0.065%. In comparison, iron (Fe) and manganese (Mn) can reach concentrations of 10.0% and 0.002%, respectively (Ernst 2006). Excluding iron, heavy metals exhibit toxicity to plants above a concentration threshold of 0.1% (Sieghardt 1990). Lead (Pb), cadmium (Cd), arsenic (As), and mercury (Hg) are particularly noteworthy for their toxicity levels, with rankings of first, sixth, third, and second, respectively, according to the US Agency for Toxic Substances and Disease Registry (ATSDR). The contamination of heavy metals represents a burgeoning issue on local, regional, and global scales, with elevated concentrations in aquatic and terrestrial ecosystems acting as ecological hazards (Nazemi 2012; Veschasit, Meksumpun, and Meksumpun 2012). While certain heavy metals such as manganese (Mn), iron (Fe), copper (Cu), zinc (Zn), molybdenum (Mo), and cobalt (Co) are essential for organismal growth within normal ranges (Ernst 2006), excessive amounts can severely impact human health (Gavrilescu 2004).

Certain heavy metals such as cadmium (Cd), uranium (U), lead (Pb), mercury (Hg), thallium (Tl), silver (Ag), and chromium (Cr) consistently exhibit toxicity to organisms. Non-heavy metals like arsenic (As) and selenium (Se) are categorized as “metalloids” (Ernst 2006). Additionally, less common metallic contaminants, including aluminum (Al), cesium (Cs), cobalt (Co), manganese (Mn), molybdenum (Mo), strontium (Sr), and uranium (U), contribute to environmental contamination (Reena Singh et al. 2011). Among these toxic heavy metals, mercury (Hg) uniquely exists in liquid form and adversely affects vegetation (Iv and Susana 2015). Its liquid state facilitates easy dissolution in water, leading to contamination. To combat this, aquatic plants like Lemna minor or Salvinia species absorb mercury, thereby purifying water (Sitarska, Traczewska, and Filyarovskaya 2016). Conversely, terrestrial plants seem less affected by mercury and its compounds (Boening 2000), suggesting the absence of a specialized “Hg-flora” (Bothe and Słomka 2017).

Contamination by toxic heavy metals, radionuclides, metalloids, and organic pollutants, exacerbated by improper industrial waste disposal, escalates pollution levels in ecosystems and risks human health (Gadd 2009). Industries (e.g., electroplating and mining) discharge aqueous effluents that contain significant concentrations of heavy metals, like uranium, mercury, cadmium, and copper, which harm the environment when untreated (Gavrilescu 2004). Biological methods alongside physical and chemical techniques are utilized for sewage and water purification, employing microbial activities to modify inorganic toxins and degrade organic pollutants (Gadd 2009). While conventional technologies like ion exchange and chemical precipitation are used, they are often inefficient and costly (Gavrilescu 2004).

Heavy metal exposure can induce DNA damage, oxidative stress, and cell death, elevating the risk of cancer and related diseases. Antioxidative phytochemical compounds and phytochelatin molecules are employed to counter heavy metal-induced cancer (Kim, Kim, and Seo 2015). The toxicity levels of heavy metals such as nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd), mercury (Hg), lead (Pb), and arsenic (As) are assessed by WHO (World Health Organization) and EPA (United States Environmental Protection Agency) standards (Kumar et al. 2017). These metals exhibit various adverse effects on human health; for instance, zinc affects reproductive system activity, protects against cadmium-induced liver damage, and induces DNA damage and cancer. Copper induces metallothionein (MT) production and conjugation to metallothionein-like proteins (MTLP), while cadmium causes placental abnormalities, testicular apoptosis, and MT induction. Mercury induces embryotoxic and teratogenic effects, disrupts homeostasis, leads to behavioral abnormalities and learning disabilities, and mimics estrogen. Lead decreases sperm count and motility and can lead to brain tumors and alterations in MT isoform gene expression (Kumar et al. 2017).

The review comprehensively examines methodologies to mitigate heavy metal contamination in ecosystems. It explores various physical methods, including mechanical and ultrasonic soil washing, ex-situ electrokinetic removal, chelating materials, and soil amendments. Additionally, the paper explores biological strategies involving microorganisms, algae, and natural organic products alongside innovative techniques such as phytoextraction and phytoremediation, emphasizing environmentally friendly solutions to heavy metal pollution. The review also discusses biotechnological and nanotechnological approaches, highlighting their potential contributions to remediation efforts. Moreover, it investigates integrating multiple techniques to foster synergistic approaches for more efficient heavy metal removal. Lastly, the study explores the emerging role of artificial intelligence in heavy metal remediation processes, aiming to provide insights into the advancements and challenges within this rapidly evolving field.

2. SOURCES OF HEAVY METALS IN CONTAMINATED SOILS

The origins of heavy metals in contaminated soils are multifaceted, stemming from natural processes and human activities. Natural sources encompass geological phenomena such as sedimentary rocks, volcanic eruptions, soil formation, and the weathering of rocks. Conversely, anthropogenic sources arise from industrial operations, mining activities, agricultural practices, and domestic waste discharges. Human endeavors, particularly in industry, agriculture, and mining, play a significant role in introducing heavy metals like lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni) into soil environments. These metals accumulate in soils due to disruptions to nature's geochemical cycles caused by human interference, posing risks to human health, plant and animal life, ecosystems, and various environmental components. Heavy metals can enter soil through multiple pathways, including emissions from industrial zones, discharge from mining activities such as mine tailings, improper disposal of metallic wastes, utilization of fertilizers and pesticides containing heavy metal residues, application of sewage sludge, and atmospheric deposition (Alengebawy et al. 2021; Wuana and Okieimen 2011; Zwolak et al. 2019). A comprehensive understanding of the diverse sources of heavy metals in contaminated soils is paramount for developing effective remediation and management strategies. By grasping the intricacies of heavy metal contamination, stakeholders can implement targeted measures to mitigate associated risks to ecosystems and human health, safeguarding environmental quality and promoting sustainable land use practices.

3. HEAVY METALS IN ECOSYSTEM/ FOOD CHAIN

Heavy metals infiltrate ecosystems and food chains through various sources stemming from human activities and natural occurrences. Anthropogenic sources, such as industrial operations, mining activities, irrigation of crop fields with industrial water, and agricultural practices, are significant contributors to heavy metal pollution. Conversely, natural sources include processes like wind erosion of soil, forest fires, volcanic eruptions, weathering of rocks, biogenic processes, and wildfires, all of which introduce heavy metals into the environment (Gall et al. 2015; Hama Aziz et al. 2023). Soil and common vegetables in daily consumption, including parsley, coriander, cress, beet leaf, amaranth, bitter leaf, garden egg leaf, and fluted pumpkin, often exhibit high levels of heavy metals such as Pb, Zn, Cr, As, and Cd. Among these, Cd stands out as particularly mobile and readily absorbed by crops from the soil, while arsenic tends to accumulate at high concentrations in soil (Jan et al. 2011; Karimi, Ghaderian, and Schat 2013; Nazemi 2012). Research by Jan et al. (2011) indicates higher concentrations of Zn, Mn, and Cu in older individuals' blood than in younger people, suggesting the accumulation of heavy metals over time (Jan et al. 2011).

Heavy metals traverse the food chain via multiple pathways, including ingestion, inhalation, dermal contact, and dietary intake of crops grown in contaminated soils (C.R. et al. 2022; Hama Aziz et al. 2023; Liu, Li, and He 2022). Industrial activities, notorious for releasing heavy metal-contaminated wastewater, contribute to severe water pollution, contaminating aquatic ecosystems and the food chain. Non-point source pollution from agricultural and industrial activities significantly contributes to heavy metal presence, affecting environmental elements like cadmium, nickel, lead, zinc, arsenic, and mercury. Additionally, heavy metals can originate from natural sources like atmospheric deposits and be transported to the earth's surface through precipitation (Briffa, Sinagra, and Blundell 2020). Heavy metal contamination in soil, particularly in agricultural settings, poses significant environmental and health concerns. Excessive accumulation of heavy metals in agricultural soils leads to elevated uptake by food crops, posing potential health risks to humans. Consumption of heavy metal-contaminated food crops represents a significant pathway for human exposure (Nyiramigisha, Komariah, and Sajidan 2021; Rashid et al. 2023). Thus, it is imperative to identify primary contributors to heavy metal contamination and devise effective strategies and policies to manage and mitigate their adverse effects.

4. PHYSICAL METHODS

Mechanical and ultrasonic soil washing

Mechanical and ultrasonic soil washing represent two physical methods to remove heavy metals from soil. A comparative study to determine optimal operating conditions for full-scale soil washing processes at heavy metal-contaminated sites observed that mechanical and ultrasonic soil washing processes generally met stringent regulatory standards regarding final heavy metal concentrations. However, the removal efficiencies of heavy metals were notably higher in ultrasonic/mechanical soil washing compared to mechanical soil washing alone. For instance, the removal efficiency of copper (Cu) through mechanical soil washing was recorded at 39.4%. In contrast, combining ultrasonic and mechanical soil washing yielded a significantly enhanced removal efficiency of 66.8% for Cu. This enhancement suggests that ultrasound application could substantially improve the removal efficiencies of heavy metals, particularly under less favorable conditions for mechanical processes. Additionally, the quantity of washing liquid utilized also influenced the removal efficiencies of heavy metals in soil when employing these physical methods (Park and Son 2017).

Ex situ electrokinetic removal of heavy metals

Electrokinetic removal is a promising technology for addressing heavy metal contamination in soils, offering an economical and highly effective approach to remediation (Lee et al. 2021). This method can target various pollutants in low-permeability soil, mud, sludge, and marine dredging. The process involves the application of electric fields to mobilize charged contaminants, including heavy metals, towards electrodes embedded in the soil. By periodically reversing the polarity of these electrodes, the direction of contaminants is alternated, facilitating their movement through treatment zones. Electrokinetic remediation has demonstrated efficacy in situating contaminated soils with organic species (USEPA 2018).

Several strategies have been explored to augment the effectiveness of electrokinetic removal of heavy metals. Integration with bioleaching presents a promising avenue, as it addresses limitations inherent in individual methods. Through this integration, bacteria can convert insoluble metal sulfides to sulfates, enhancing their solubility and subsequent transport via electromigration (Narenkumar et al. 2023). Acidification through the addition of acidic electrolytes such as lactic acid and acetic acid, along with the use of complexing agents like EDTA and citric acid, has proven effective in increasing desorption, solubility, mobility, and ultimately, the removal efficiency of heavy metals. Careful selection of desorption and mobility enhancement reagents based on soil characteristics and heavy metal species is crucial. Additionally, modifications such as implementing ion exchange membranes (IEM) and electrode polarity exchange have been adopted to prevent the diffusion of hydroxide ions from the cathode, thereby improving heavy metal removal efficiency (Cai et al. 2022).

Overall, electrokinetic removal of heavy metals represents a promising technology for remediating polluted soils and sediments. Its efficacy can be further enhanced through various methods, including integration with bioleaching, using acidic electrolytes and complexing agents, and adopting ion exchange membranes and electrode polarity exchange techniques.

5. CHEMICAL METHOD

By using chelating materials

Chelating agents can desorb toxic metals from soil solid phases by forming robust water-soluble complexes. Once these complexes are formed, plants can remove them from the soil through enhanced phytoextraction or washing techniques. In phytoextraction facilitated by chelants, the chelant is initially applied to the soil, where it desorbs metals from the soil matrix. The mobilized metals then migrate to the rhizosphere, where they are taken up by plant roots (Tahmasbian and Safari Sinegani 2014). The concentrations of bio-available metals in the soil solution are predominantly influenced by the properties of the soil and the chelant applied (Luo, Shen, and Li 2005; Tandy et al. 2004). It is crucial to carefully select the chelant, determine its quantity, and devise appropriate application processes to minimize its impact on soil microorganisms and prevent discharge into groundwater (Evangelou, Ebel, and Schaeffer 2007; Luo, Shen, and Li 2007).

Ethylene Diamine Tetra Acetic acid (EDTA) emerges as one of the most potent and commonly utilized chelating agents, capable of forming complexes with numerous metal contaminants in the natural environment. Studies have shown that the application of EDTA enhances the efficiency of emergent wetland plant species such as Typha sp. and floating wetland macrophytes like Pistia sp., Azolla sp., Lemna sp., Salvinia sp., and Eichhornia sp. in the phytoremediation of Pb and copper (Dipu, Kumar, and Thanga 2012). However, conventional complexing agents exhibit undesired traits such as persistence or slow environmental transformation and the potential remobilization of toxic metal ions and radionuclides from sediments and soils. Therefore, these agents must be replaced with chelating agents with improved biodegradability (Reinecke et al. 2000).

Most amino polycarboxylic acids, such as EDTA, IDA, and DTPA, resist conventional biological and physicochemical methods. EDTA, for example, is more efficient than ethylenediamine disuccinic acid (S, S)-EDDS in extracting Pb and Cd, while (S, S)-EDDS is more effective in extracting Cu and Zn. Combining EDTA with (S, S)-EDDS has been shown to produce higher extraction efficiency (i.e., a synergy effect) in the phytoextraction of Cu, Pb, Zn, and Cd compared to the application of either chelant alone (Luo et al. 2005).

Studies by Gupta and Sinha (2006) demonstrated varying metal extraction efficiencies among different metal extractants from tannery sludge amendment, with EDTA exhibiting the highest efficiency, followed by DTPA, NH4NO3, NaNO3, and CaCl2 (Gupta and Sinha 2006). Furthermore, Dede et al. (2012) conducted a pot experiment to investigate the influence of elemental sulfur, gypsum, and EDTA on the uptake of heavy metals by Brassica juncea from sewage sludge. The addition of sulfur resulted in acidification of the sludge, leading to a decrease in pH, and applications of EDTA and sulfur notably increased copper and Pb concentrations in the plant. Overall, elemental sulfur was a more effective amendment for phytoextraction of heavy metals from sewage sludge (Dede, Ozdemir, and Hulusi Dede 2012).

Soil Amendments

Various organic and inorganic compounds have been identified for their ability to immobilize heavy metals, preventing their uptake by plants and subsequent entry into the food chain (Walker et al. 2003). Table 1 displays different soil amendments, their sources, and metals that become immobilized.

Table 1: Different soil amendments, their sources, and metals that become immobilized (Guo, Zhou, and Ma 2006)

Material	Soil Amendments	Source	Immobilizing Heavy metals
Organic	Xylogen	Paper Mill Wastewater	Zn, Hg, Pb
	Cattle Manure	Cattle farm	Cd
	Poultry Manure	Poultry farm	Cd, Zn, Pb, Cu
	Bagasse	Sugar Cane	Pb
Inorganic	Phosphate salt	Fertilizer Plant	Cd, Zn, Pb, Cu
	Hydroxyapatite	Phosphorite	Cd, Zn, Pb, Cu
	Slag	Thermal Power Plant	Cd, Zn, Pb, Cr
	Fly ash	Thermal Power Plant	Cd, Zn, Pb, Cu, Cr.
	Lime	Lime Factory	Cd, Cu, Ni, Pb, Zn

6. BIOLOGICAL METHODS

Biosorption encompasses several mechanisms, including ion exchange, chelation, adsorption, and diffusion through cell walls and membranes. These mechanisms vary depending on the species employed, the biomass’s source and treatment, and the solution’s chemistry. Bioremediation, derived from “bio” (living) and “remediation” (to fix or cure), is a subset of biotechnology that harnesses bacteria and other microorganisms to mitigate pollution (Gavrilescu 2004).

By using microorganisms

Bioremediation, employing microorganisms, has emerged as an environmentally friendly, cost-effective, and efficient approach to restoring contaminated environments (Hrynkiewicz and Baum 2014). Microorganisms play an indirect yet crucial role in supporting the growth of phytoaccumulation plants, thereby aiding in the remediation of heavy metals (Jing, He, and Yang 2007; Zhuang et al. 2007). Specifically, plant growth-promoting rhizobacteria (PGPR), closely associated with plant roots, have garnered attention for their ability to enhance plant growth and development in heavy metal-contaminated soils.

PGPR encompasses a diverse group of soil bacteria capable of ameliorating the toxic effects of heavy metals on plants and promoting their growth and nutrition. These bacteria facilitate plant growth through nitrogen fixation, production of phytohormones and siderophores, and transformation of nutrient elements (Koo and Cho 2009). In areas such as mine tailings contaminated with heavy metals, PGPR is introduced to plant seeds during sowing to bolster plant growth (Grandlic, Palmer, and Maier 2009). Studies have shown that PGPR application not only enhances plant growth and yield but also mitigates metal toxicity in crops such as Cicer arietinum, Vigna radiata, and Pisum sativum (Gupta et al. 2004; Wani, Khan, and Zaidi 2008).

Furthermore, PGPR plays a pivotal role in enhancing phytoremediation efficiency, particularly in the presence of metals like cadmium. Certain bacteria can reduce Chromium (VI) enzymatically, aiding in chromium reduction (Kanmani, Aravind, and Preston 2012). Untreated wastewater contaminated with heavy metals released into aquatic systems can accumulate metals in soil and water bodies, adversely affecting aquatic organisms and potentially posing health risks to humans (Davies and Uyi 2006; Fatoki, Lujiza, and Ogunfowokan 2002). However, the biosorption process, wherein nonliving biomass passively binds heavy metals from aqueous solutions, offers a promising avenue for metal removal (Kumar JI 2012).

Compared to conventional separation techniques, using microorganisms for metal contamination reduction offers biomaterial reusability, low operating costs, improved selectivity for specific metals, and shorter operation times (Srinath et al. 2002). As a novel technology, the biosorption process holds promise for refining treatment in shallow water bodies (Kumar, Soni, and Kumar 2006).

By Using Algae

Algae play a significant role in removing heavy metals from aquatic systems through various mechanisms such as sedimentation, flocculation, absorption, ion exchange, complexation, precipitation, oxidation/reduction, microbiological activity, and uptake. Microalgae, in particular, employ two primary mechanisms for heavy metal removal: metabolism-dependent uptake into their cells at low concentrations and non-active adsorption through biosorption (Mitra et al. 2012). Algae possess several characteristics that render them ideal candidates for selective removal and concentration of heavy metals. These include high tolerance to heavy metals, the ability to grow autotrophically and heterotrophically, large surface area/volume ratios, phototaxy, expression of phytochelatins, and potential for genetic manipulation.

Macroalgae have also been extensively utilized as biomonitors of metal availability in marine systems due to their capacity to accumulate metals within their tissues. Chlorophyta and Cyanophyta, in particular, exhibit hyper-absorbent and hyperaccumulating properties for elements like arsenic and boron, effectively reducing water pollutant levels (Ben Chekroun and Baghour 2013). Certain algal species have been observed to convert mercuric or phenylmercuric ions into metallic mercury, which is then volatilized out of the cell and the solution. For instance, the blue-green algae Phormidium demonstrates remarkable hyperaccumulation capabilities for heavy metals such as cadmium, zinc, lead, nickel, and copper (Ben Chekroun and Baghour 2013). Table 2 displays microorganisms that absorb heavy metals.

Table 2: Microorganisms that absorb the heavy metals

Organism	Species	Metal Ion	References
Bacteria	*Arthrobacter sp.*	Copper Cu(II)	(Hasan and Srivastava 2009)
	Enterobacter sp. J1	Copper Cu(II)	(Parungao 2007)
	Pseudomonas fluorescence	Chromium Cr(VI)	(Uzel and Ozdemir 2009)
	Pseudomonas sp	Chromium Cr(VI)	(Ziagova et al. 2007)
	Pseudomonas putida	Zinc (Zn)	(Green-Ruiz, Rodriguez-Tirado, and Gomez-Gil 2008)
	Bacillus jeotgali	Zinc (Zn)	(Green-Ruiz et al. 2008)
	E. coli	Nickel Ni(II)	(Quintelas et al. 2009)
	Pseudomonas fluorescence	Nickel Ni(II)	(Uzel and Ozdemir 2009)
	Enterobacter sp. J1	Cadmium Cd(II)	(Quintelas et al. 2009)
Algae	*Ulva lactuca sp.*	Cadmium Cd(II)	(Bulgariu et al. 2013)
	Sargassum sp.	Cadmium Cd(II)	(Bulgariu et al. 2013)
	Spirulina platensis	Copper Cu(II)	(Bulgariu et al. 2013)
	Spirogyra sp.	Lead (Pb)	(Gupta and Rastogi 2008)
	Sargassum muticum	Zinc (Zn)	(Çelekli, Yavuzatmaca, and Bozkurt 2010)
Fungi	*Penicillium chrysogenum*	Nickel (Ni)	(64)
		Copper (Cu)	(Infante J, De Arco R, and Angulo M 2014)
	Penicillium purpurogenum	Chromium (Cr)	(Katsumata et al. 2003; Safarikova, Maderova, and Safarik 2009)
	Aspergillus niger	Lead (Pb)	(Zeng et al. 2015)

By using natural and organic products

Replacing conventional adsorbents with natural sorbents has gained considerable attention as an alternative due to their availability in the environment and economic feasibility (Babel and Kurniawan 2003). Materials such as farmyard manure (FYM), sawdust, rice husk, and other agricultural or industrial by-products have emerged as potential low-cost sorbents.

These materials, often disposed of at the end of their lifecycle, can be repurposed for heavy metal remediation purposes, given their abundance and availability. The organic substances present in soil significantly influence the absorption and translocation of heavy metals, leading to their accumulation in organic horizons and peat (Kabata-Pendias 2001).

Studies have shown that compost or vermicompost amendments in soil can decrease the concentration of heavy metals like lead and copper in plants such as potato peel and tubers (Angelova et al. 2010). Metal removal and stabilization can also be achieved through compost, biosolids, recycled paper waste, and agricultural mineral amendments (Jones and Healey 2010; Paulose et al. 2007). These amendments reduce the risk of metal exposure to humans and biota and mitigate metal availability in soil, water, or air (O’Day and Vlassopoulos 2010).

Natural products like sawdust and rice husk act as binding agents, reducing the uptake of heavy metals from contaminated sites (Wan Ngah and Hanafiah 2008). Sawdust and rice husk have been demonstrated to act as biosorbents in hydroponic systems, reducing the availability of metals like cadmium (Subhan 2011).

The reduction in metal availability is attributed to the basic nature of complex compounds present in sawdust and rice husk, such as cellulose, hemicellulose, lignin, mineral ash, and tannins, which actively participate in ion exchange processes (Rafatullah et al. 2009).

Additionally, the application of fly ash in contaminated soil has been found to significantly reduce the availability of heavy metals by modifying their chemical speciation into less available forms.

Experiments involving the growth of corn in soil amended with fly ash stabilized sludge demonstrated a decrease in the availability of metals like copper, zinc, nickel, and cadmium, along with an increase in corn biomass. This chemical modification of metal speciation renders them less available for plant uptake, thereby reducing potential risks associated with heavy metal contamination (Su and Wong 2004).

7. PHYTOEXTRACTION AND PHYTOREMEDIATION: GREEN SOLUTIONS FOR HEAVY METAL CONTAMINATION

Naturally grown hyperaccumulator plants can mitigate metal contamination in agricultural land systems. These plants can accumulate, transfer, and stabilize heavy metals from contaminated soils (Garbisu et al. 2002; Jadia and Fulekar 2009).

Phytoaccumulator plants accumulate metals in their shoots and exhibit high tolerance to heavy metals (Sarma 2011). However, many hyperaccumulator plants are slow-growing and produce low biomass. Phytoremediation involves using specific types of plants to decontaminate soil or water by either immobilizing metals in the rhizosphere or translocating them into their aerial parts.

Various plant families, including Asteraceae, Brassicaceae, Caryophyllaceae, Cyperaceae, Cunouniaceae, Fabaceae, Flacourtiaceae, Lamiaceae, Poaceae, Violaceae, and Euphorbiaceae, have demonstrated remediation properties (Sarma 2011).

For instance, *Myriophyllum spicatum* and *Ceratophyllum demersum* effectively remove lead, zinc, and copper. Batch studies have shown that these plants conform well to the Langmuir Model, achieving maximum adsorption capacities (qmax) for each metal. M. spicatum exhibited maximum adsorption capacities of 10.37 mg/g for Cu^2+, 15.59 mg/g for Zn^2+, and 46.49 mg/g for Pb^2+, while *C. demersum* showed capacities of 6.17 mg/g for Cu^2+, 13.98 mg/g for Zn^2+, and 44.8 mg/g for Pb^2+. M. spicatum demonstrated a better adsorption capacity than *C. demersum* for each metal tested (Keskinkan et al. 2007). Table 3 presents a list of Phytoaccumulator plants and their respective absorbed metals.

Table 3: List of Phytoaccumulator plants and their respective absorbed metals

Phytoaccumulator Plant	Metal Absorb	References
Myriophyllum spicatum	Pb, zinc, and copper	(Keskinkan et al. 2007)
Ceratophyllum demersum	Pb, zinc, and copper	(Keskinkan et al. 2007)
Cancapapaya Wood	Hg(II)	(Uslu and Tanyol 2006)
Oryza sativa husk	Pb(II)	(Mapolelo, Torto, and Prior 2005)
Sawdust(Acacia arabica)	Pb(II), Hg(II), Cr(IV)	(Sousa, Cebolla, and de Lorenzo 1996)

Rhizofiltration

Rhizofiltration involves using terrestrial and aquatic plants to absorb, concentrate, and precipitate contaminants from polluted aqueous sources with low contaminant concentrations in their roots. This method can be employed to partially treat industrial discharge, agricultural runoff, or acid mine drainage, and it is effective for pollutants such as lead, cadmium, copper, nickel, zinc, and chromium, primarily retained within the roots (Chaudhry et al., 1998; Environmental Protection Agency, 2000).

One of the advantages of rhizofiltration is its versatility, as it can be applied in situ and ex-situ, and a wide range of plant species, not just hyperaccumulators, can be utilized. Various plants, including sunflower, Indian mustard, tobacco, rye, spinach, and corn, have been studied for their ability to remove lead from effluent, with sunflowers showing exceptionally high efficiency. Indian mustard has also effectively removed lead over a wide concentration range (4 – 500 mg/l) (Raskin and Ensley 1999).

Field tests of rhizofiltration have demonstrated its effectiveness in treating uranium-contaminated water with concentrations ranging from 21 to 874 ug/l. In a study by Dushenkov et al. (1997), the treated uranium concentration was reported to be < 20 ug/l before discharge into the environment (Dushenkov et al. 1997). This result highlights the potential of rhizofiltration as a practical and efficient method for water remediation.

Phytostabilisation

Phytostabilization is a remediation method primarily used for soil, sediment, and sludges, relying on the roots' ability to limit contaminant mobility and bioavailability in the soil (Itrc 2009). This process can occur through sorption, precipitation, complexation, or metal valence reduction.

The primary goal of phytostabilization is to reduce water percolation through the soil matrix, thereby minimizing the formation of hazardous leachate and preventing soil erosion and the spread of toxic metals to other areas. A dense root system stabilizes the soil and prevents erosion (Raskin and Ensley 1999).

Phytostabilization is highly effective when rapid immobilization of contaminants is necessary to protect groundwater and surface water and when biomass disposal is not required. However, one major drawback is that the contaminants remain in the soil, necessitating regular monitoring.

Phytoextraction

Phytoextraction, or phytoaccumulation, is a practical approach to remove contamination primarily from the soil without damaging its structure and fertility (Environmental Protection Agency, 2000). This method involves plants absorbing, concentrating, and precipitating toxic metals and radionuclides from contaminated soils into their biomass. Phytoextraction is particularly suitable for diffusely polluted areas where pollutants occur at relatively low concentrations and are superficially distributed (Rulkens, Tichy, and Grotenhuis 1998).

Two basic strategies of phytoextraction have been developed: chelate-assisted phytoextraction or induced phytoextraction, where artificial chelates are added to increase metal mobility and uptake, and continuous phytoextraction, where metal removal depends on the natural ability of the plant to remediate, with control over the number of plant growth repetitions (Salt et al. 1995).

The discovery of hyperaccumulator species has further advanced this technology. Yet limitations such as slow growth, shallow root systems, small biomass production, and challenges in final disposal constrain the use of hyperaccumulator species (Brooks et al. 1998; Cunningham and Ow 1996; Ghosh and Singh 2005).

Phytovolatilization

Phytovolatilization involves plants absorbing contaminants from the soil, transforming them into volatile forms, and releasing them into the atmosphere through transpiration (Ghosh and Singh 2005). This method has been primarily used for removing mercury, where the mercuric ion is transformed into less toxic elemental mercury.

However, a disadvantage of phytovolatilization is that the released contaminants may be recycled by precipitation and redeposited into the ecosystem (By and Henry n.d.). Some plants growing in high selenium environments can also produce volatile selenium compounds (Bañuelos, Zambrzuski, and Mackey 2000).

Phytovolatilization has also successfully removed tritium, a radioactive isotope of hydrogen, by decay to stable helium (Dushenkov 2003).

Phytodegradation

Phytodegradation involves the breakdown of organic contaminants taken up by plants through metabolism, leading to their transformation, breakdown, stabilization, or volatilization. Plant enzymes can break down and convert various organic contaminants, such as ammunition wastes, chlorinated solvents, and herbicides, into simpler molecules incorporated into plant tissues.

Rhizodegradation, on the other hand, involves the breakdown of organics in the soil through microbial activity in the root zone (rhizosphere), albeit at a slower rate than phytodegradation. Microorganisms like yeast, fungi, and bacteria break down organic substances like fuels and solvents.

All phytoremediation technologies can be used simultaneously; nevertheless, the effectiveness of metal extraction depends on the soil's bioavailable fraction (Black 1995; Chaudhry et al. 1998; Ghosh and Singh 2005).

8. BIOTECHNOLOGICAL APPROACH

By using biotechnologically modified plants

Biotechnological tools, including genetic engineering, offer promising avenues for enhancing the efficacy of plants in removing metals from the environment. Through genetic engineering, the overall functionality of plants can be modified, augmenting their remediation capabilities. By incorporating new genotypes and phenotypes obtained from metal-hyperaccumulating plants and microbes, the remediation potential of plants can be significantly increased (James and Strand 2009).

Transgenic plants engineered with specific traits may also offer safer options for phytoremediation purposes (Van Aken 2008). Researchers have explored various genetic modifications to enhance plant metal tolerance and accumulation. For instance, transferring the bacterial merAB operon to tobacco chloroplasts rendered the plants more resistant to highly toxic organic mercury (Heaton et al. 2005).

Similarly, integrating metallothionein genes into plant genomes has been shown to confer enhanced tolerance to high metal concentrations. Introduction of the yeast metallothionein CUP1 gene into tobacco plants has increased the uptake of metals like copper and cadmium, thus enhancing phytoextraction capabilities (M. Czako, X. Feng, Y. He, D. Liang, R. Pollock 2006; Peron n.d.).

Genetic engineering also allows transferring specific genes associated with metal binding and detoxification mechanisms. For instance, the partial peptides from the Thlaspi heavy metal ATPase (TcHMA4) protein have been identified for their ability to confer high levels of cadmium tolerance and hyperaccumulation in yeast.

Expression of TcHMA4 in higher plants could potentially enhance their metal tolerance and phytoremediation potential. Moreover, genes encoding enzymes such as merB, which degrade methylmercury to less toxic forms, have been introduced into plants like tobacco, resulting in increased resistance to methylmercury and enhanced mercury accumulation (Nagata et al. 2010).

Additionally, introducing a gene for mercuric reductase into tobacco and Arabidopsis plants enabled the conversion of ionic mercury to less toxic metallic mercury, facilitating its volatilization (Meagher and Bizily 2000).

These biotechnological approaches, along with others such as biomineralization, biosorption, phytostabilization, hyperaccumulation, and rhizoremediation, offer versatile strategies for metal remediation. Their integration and cooperation are essential for advancing environmental cleanup efforts (Mani and Kumar 2014).

9. NANOTECHNOLOGICAL APPROACH

By using nanotechnology

Although primarily associated with animal science and medical research, nanotechnology holds significant potential in plant science and environmental remediation. In plant science research, nanotechnology can aid in analyzing plant genomics and gene function and improving crop species (Monica and Cremonini 2009). Moreover, the application of nanotechnology for contaminant remediation shows promise in purifying air and water resources by utilizing nanoparticles as catalysts and sensing systems (Fulekar, Pathak, and Kale 2014).

Researchers have found that nanostructured materials can be effective adsorbents or catalysts to remove toxic substances from wastewater, air, and soil (Monica and Cremonini 2009; Shen et al. 2009). The small particle size of nanoparticles (1–100 nm) enables their effective transport by groundwater flow, making them versatile remediation tools (Masciangioli and Zhang 2003).

Multi-walled carbon nanotubes (CNTs) have been successfully used for the removal of heavy metals such as Copper(II), Lead (II), Cadmium(II), and Zinc(II) from aqueous solutions (Abdel Salam 2013; Yu et al. 2014). Carbon nanoparticles have also demonstrated exceptional adsorption properties, significantly reducing metal contamination from soil and water systems (Rathor, Adhikari, and Chopra 2013).

Additionally, nanoparticles derived from plants like Euphorbia macroclada have shown potential for removing and detoxifying metals, with significant reductions observed in concentrations of metals like Lead, Zinc, Copper, Cadmium, and Nickel (Mohsenzadeh and Rad 2011). Similarly, zero-valent iron nanoparticles have been utilized to remove Chromium from contaminated soil, achieving a remarkable 99% removal rate (Ritu Singh, Misra, and Singh 2011). Nanotechnology offers innovative approaches for environmental remediation, with the potential to address challenges related to pollutant removal and detoxification effectively. Continued research in this field holds promise for developing sustainable solutions to environmental pollution. Table 4 compares the advantages and disadvantages of different methods used for metal remediation.

Table 4: Comparison between the advantages and disadvantages of different methods used for metal remediation

Methods	Treatment	Detail and results	Advantages	Disadvantages	References
Physical	Mechanical soil washing	Reduction in metals and contamination in soil	Significant volume reduction in contaminated soil	External chemicals are used	(Park and Son 2017; Son et al. 2011)
	Ultrasonic soil washing	Reduction in metals and contamination in soil	Significant volume reduction in contaminated soil. Green method and external chemicals are used	Expensive and not applicable for practical use	(Park and Son 2017; Son et al. 2011)
	Ex-situ electrokinetic removal of heavy metals	Reduction in metals and contamination in soil	This method is applicable to different metals	Any heterogeneity of the soil body decreases the effectiveness of the method, and considerable acidification of the remediated soil is a side effect of this method	(Iman Tahmasbian 2012; Kim et al. 2002)
Chemical	Chelating materials	Reduce the mobility of Pb and Cu	Desorption of metals and effective amendment for phytoextraction of heavy metals	Different chemicals are used	(Dipu et al. 2012)
	Soil Amendments	Reduce the mobility of Cd, Cu, Ni, Pb, Zn, Hg, and Cr.	Natural sources are used	Change the physic-chemical properties of soil	(Guo et al. 2006)
Biological Approach	Microorganisms	Removes the metal contaminants as a result of sorption and/or transformation	Removes contaminants as a result of sorption and/or transformation. Soil retains its properties and could be replaced on the reclaimed site	Construction of a special installation is required. Large amounts of waste (solid, liquid) are generated	(Singh and Prasad 2015)
	Algae and fungi	Heavy metal is removed from aquatic systems by sedimentation, flocculation, absorption and cations and anion exchange, complexation, precipitation, oxidation/ reduction, microbiological activity, and uptake	Microalgae remove heavy metals directly from polluted water	May cause disease	(Mitra et al. 2012)

	Natural sorbents	Biosorbent in hydroponic system	More stable economical and reduces the risk of exposure to humans	Not Found	(Kabata-Pendias 2001)
Phytoremediation	Rhizofiltration. Phytostabilization, Phytodegradation, Phytoextraction, and Phytovolatilization	Contaminants are absorbed into roots and precipitated in the roots' area. Contaminants are picked up by the roots of plants and transported to their overground parts, then removed together with the crops. Uptake and transpiration of such elements by plants. The element is taken up by plant roots, transported through the xylem, and is finally released to the atmosphere from cellular tissues (evaporates or vaporizes)	Low-cost method. Practically no side effects. Relatively low costs. The method is environmentally friendly	Contaminants are not removed from the soil but only immobilized. Plants and soil require long-term monitoring	(Ghasemi-fasaei 2012; Jiang et al. 2010)
Biotechnological Approach	Biotechnologically modified plants	Transgenic plants removed up to 6 % Zn and 25 % Cd of the soil metal; Tobacco callus showed more resistance to methylmercury (CH3Hg?) and accumulated more mercury from CH3Hg?- containing medium	Transgenic plants might be able to contribute to the broader and safer application of phytoremediation	It may cause toxins and reduce the nutritional value	(Küpper and Kochian 2010; Nagata et al. 2010)
Nanotechnological Approach	Use of Nanoparticles	The use of nano-ZVI, bimetallic nanoparticles, and emulsified zero-valent nanoparticles reduces the metal contamination from soil and groundwater	It is very efficient for removing metal	It may cause pollution and expensive	(Ashutosh Agarwal and Himanshu Joshi 2010; Xiong et al. 2009)

10. INTEGRATION OF MULTIPLE TECHNIQUES: SYNERGISTIC APPROACHES FOR HEAVY METAL REMOVAL

Synergistic heavy metal removal approaches combine chemical flocculation, electrolysis, reduction, membrane separation, and adsorption to achieve more effective and efficient remediation outcomes (Sun et al. 2020). These integrated processes aim to synergize physical, chemical, and biological methods, addressing challenges like cost and in-situ treatment failures faced by individual methods. They have gained popularity for their reported effectiveness in removing heavy metals from different environmental matrices. However, successful implementation requires a thorough understanding of heavy metal sources, chemistry, and associated environmental and human health risks (Selvi et al. 2019).

Benefits of synergistic approaches include increased efficiency, cost-effectiveness, minimal environmental disturbance, and applicability in various settings. They offer advantages over individual methods in terms of effectiveness, cost, environmental impact, and control over treatment systems (Li et al. 2020; Selvi et al. 2019; Sun et al. 2020; Tovar-Gómez et al. 2015). For example, integrating electrokinetic processes with phytoremediation minimizes environmental disruption while enhancing removal efficiency. Similarly, using acidic electrolytes, complexing agents, ion exchange membranes, and electrode polarity exchange improves heavy metal desorption, solubility, and mobility (Kumar, Dwivedi, and Oh 2022; Selvi et al. 2019).

Moreover, integrating microorganisms and waste molasses provides an efficient and cost-effective method for heavy metal removal. Understanding the underlying mechanisms allows for better control of treatment systems (Cheah, Cheow, and Ting 2022; Yin et al. 2019). These integrated approaches hold promise for in-situ operations in various settings, including developed areas and agricultural regions, contributing to more sustainable and effective remediation strategies for heavy metal pollution.

11. ARTIFICIAL INTELLIGENCE FOR HEAVY METAL REMOVAL

Artificial Intelligence (AI) is crucial in understanding and remedying heavy metal pollution across various environmental settings. AI can assess the most effective methods for treating contaminated soil or water by extracting pertinent information from environmental reports. In water and wastewater treatment, AI and machine learning algorithms detect and remove heavy metals like lead, cadmium, and mercury, which pose risks to human health and the environment (Maurya et al. 2024). Integrating AI with techniques such as electrokinetic processes and phytoremediation enhances heavy metal removal efficiency. For instance, machine learning can identify plastics in water bodies and pinpoint areas with high pollution levels, facilitating targeted cleanup efforts (Anon n.d.). AI also aids in monitoring water output and detecting spills promptly to prevent further contamination (Mal et al. 2018).

In agriculture, machine learning identifies microbes, their mechanisms of action, and suitable environments, predicting the efficacy of microbial remediation and assessing ecological benefits and crop growth post-remediation (Wu and Zhao 2023). Techniques like surface-enhanced Raman spectroscopy (SERS) and convolutional neural networks (CNNs) analyze spectroscopic data to detect heavy metal ions in water and environmental samples (Park et al. 2022; Zhang et al. 2023). AI models trained on SERS measurements accurately identify specific heavy metal ions like Pb(NO3)2, showcasing balanced accuracy in cross-batch testing (Park et al. 2022). CNN-based methods swiftly detect heavy metal ions and their concentrations in water samples (Zhang et al. 2023).

Optical imaging spectroscopy, coupled with machine learning, detects heavy metals in plants, focusing on spectroscopic applications to assess contamination levels (Li et al. 2022). Deep learning algorithms analyze Raman spectra to identify cadmium-phytochelatin2 complexes in plants (Mandal et al. 2022). AI predicts heavy metal interactions with biochar, a promising area for heavy metal removal research (Wei et al. 2024). Moreover, AI selectively removes heavy metals from Lanthanide solutions using previously prepared graphene oxide-citrate (GO-C) composites (Abu Elgoud et al. 2022). These AI-driven advancements promise more effective and sustainable solutions to heavy metal pollution.

12. CHALLENGES AND FUTURE PERSPECTIVES IN HEAVY METAL ELIMINATION FROM ECOSYSTEMS

The challenges and future perspectives in heavy metal elimination from ecosystems underscore the importance of effective, sustainable, and scalable removal methods while mitigating environmental impacts. Leveraging plants and microorganisms for heavy metal removal offers effective, economical, and environmentally friendly solutions. Bioaccumulation, combined with phytostabilization and phytodegradation, enhances heavy metal removal efficiency (Nnaji et al. 2023). Phytoremediation, employing green plants to detoxify and render soil reusable, presents numerous advantages over conventional methods. However, addressing challenges to make it feasible and scalable on a large scale is essential (Thakur et al. 2016). Despite recent advancements in heavy metal removal from wastewater, high costs associated with some methods hinder their widespread adoption. Exploring cost-effective techniques such as physicochemical adsorption with biochar and natural zeolite ion exchangers, along with advanced oxidation processes (AOPs), is crucial (Hama Aziz et al. 2023).

Developing ecohydrological biotechnologies and Nature-Based Solutions (NBS) is vital for addressing global heavy metal contamination in aquatic ecosystems. These methods aim to enhance heavy metal removal while meeting regulatory requirements like the EU Water Framework Directive (Piwowarska, Kiedrzyńska, and Jaszczyszyn 2024). Green technologies, including bioremediation, offer cost-effective and sustainable solutions for heavy metal removal. Bioremediation, employing living entities like bacteria, fungi, and plants to degrade toxic substances, is considered practical, reliable, and environmentally benign (Das et al. 2023). Addressing these challenges and embracing these future perspectives will be crucial for developing effective, sustainable, and environmentally friendly strategies for heavy metal elimination from ecosystems.

13. CONCLUSION

The escalation of unwanted waste generated by modern civilization has led to widespread contamination of our ecosystems. Among the myriad challenges posed by this contamination, heavy metal pollutants are particularly concerning due to their toxic effects on the environment and ability to infiltrate the food chain. In response to this pressing issue, we have examined various techniques that employ diverse approaches, including physical, chemical, and biological methods. These techniques encompass strategies such as immobilization using cost-effective absorbents, the application of chelating agents, and biological interventions such as phytoremediation. Furthermore, advancements in molecular and nanotechnology hold promise for enhancing remediation capabilities, offering novel avenues for removing heavy metals. The development of remediation technologies must remain closely linked to agricultural production, food safety, and land management considerations. While individual approaches have shown promising results, synergistic combinations of technologies, particularly those incorporating cutting-edge nano- and biotechnological methods, have emerged as particularly efficient. Additionally, integrating artificial intelligence can optimize remediation strategies by leveraging pertinent information extracted from environmental reports. As we confront the challenges and contemplate future perspectives in eliminating heavy metals from ecosystems, it becomes evident that prioritizing the development of effective, sustainable, and scalable removal methods is crucial for mitigating environmental impacts and safeguarding ecological integrity.

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