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A REVIEW OF HEAVY METALS ACCUMULATION AND CONTROL IN ACTIVE AGRICULTURAL SOIL

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ABSTRACT

Agricultural soil is contaminated with dangerous heavy metals (HMs) from anthropogenic activities and natural processes. These HMs are passed to humans through the consumption of crops produced in the contaminated soil. Crop production in a contaminated field and irrigation with raw untreated sewage and industrial effluents exposed food crops to HMs contaminations. Consumption of foods contaminated with HMs can be dangerous due to their persistent nature and tendency to accumulate in human tissues. HMs contamination in humans can lead to serious health problems and, in severe cases, can cause death. This review article aimed to compile soil treatment methods reported to be effective in reducing HMs uptake by food crops in active agricultural fields, outline research gaps and suggest areas for future research. Soil treatment with biochar is the most effective control method reported, was found to mitigate the uptake of Cd, Cr, Pb, Zn, and Cu in different crops. Other control measures are the application of inorganic sorbents, chelating agents, and nanomaterials to soil and hydroponic water; the use of microorganisms and their products; gene modification of the food crop; and soil washing and filtration. The control methods reported in soil and the hydroponic solution were found to significantly lower Cd, Pb, Ni, Zn, Cu, Co, Cr, Mn, Hg, and Fe uptake in cereal grains and different types of vegetable and tuber crops.

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1. Introduction

The excessive use of HMs in chemical processing, agrochemicals, healthcare, cosmetics, and other domestic appliances continues to contaminate the environment (Paithankar et al., 2021). Contamination of agricultural soil and water with toxic HMs and metalloids from anthropogenic activities and natural processes is negatively affecting food safety and human health (Liu et al., 2018; Bhagwat, 2019; Wang et al., 2019; Edogbo et al., 2020; Khan et al., 2020a; Qadir et al., 2020; Zhang et al., 2020). Irrigation with raw wastewater poses a serious threat to environmental safety and public health (Rezapour et al., 2019). Food crops are prone to HMs contamination due to the exponential growth of environmental pollution (Afonne and Ifediba, 2020). Contamination of food crops by HMs is becoming a global challenge (Rai et al., 2019). The results of a meta-analysis conducted by Kumar et al. (2019b) showed that water bodies are highly contaminated with HMs and the global average concentrations of Cr, Mn, Co, Ni, As and Cd in the surface water exceed permissible limits approved by WHO. Food is the major pathway for human HMs contamination (Rehman et al., 2018b; Kumar et al., 2019a; Zhang et al., 2019; Huang et al., 2020b) and account for more than 99% of human contamination (Yu et al., 2019). Food contamination commonly occurs through contaminated water, soil, and air, and in very rare cases through leaching of utensils (Fung et al., 2018). HMs are very ubiquitous and inhibiting them completely from foods is nearly impossible (Bragotto, 2019).

Remediation of HMs contaminated soil can mitigate the transfer of HMs into the food chain (Rai et al., 2019). There is an urgent and necessary need for the removal of heavy metals from the environment, it is also crucial to stop the rampant discharge of these toxic metals into the environment (Ahmad et al., 2020). Remediation of contaminated agricultural fields through modification of soil conditions was reported to be effective in lowering HMs uptake in food crops. Most of the approaches reported lower the bioavailability of the HMs and make them inaccessible to the crops.

2. HMs Control Methods in Active Agricultural Fields

Rai et al. (2019) recommended the use of remediation techniques that are cost-effective and friendly to the environment. Phytoremediation is the cheapest remediation technique (Chen and Li, 2018; Dhaliwal et al., 2020), but has little applicability in active agricultural land (Table 1). Soil decontamination before cropping, policy measures, research, public awareness, and health risk assessments are the major control measures reported by Gupta et al. (2019). Low-cost adsorbents from agricultural waste, terrestrial and aquatic biomass, and soil and mineral deposits were also recommended by Joseph et al. (2019). There is an urgent need for the development of economically feasible and environment-friendly methods since conventional remediation techniques are associated with higher operational and maintenance costs, the production of secondary wastes, and soil degradation (Sharma et al., 2018; Vardhan et al., 2019; Varghese et al., 2019; Xu et al., 2019b). Combining techniques provides fruitful results, physiobiological and physiochemical methods improve removal efficiency at an economic cost (Sharma et al., 2018).

The common HMs control methods reported in food crop is the treatment of soil with biochar (Table 1) produced by subjecting the biomass to pyrolysis or gasification treatment (Huang et al., 2021); a process that generates product rich in organic carbon (Yaashikaa et al., 2020), with good porosity, significant surface area, and excellent water holding capacity (Godlewska et al., 2021). Biochars can be produced from all forms of wastes generated along the food supply chain (O'Connor et al., 2021). The use of biochar in horticulture was demonstrated at different levels and its suitability for large-scale agriculture was studied (Hu et al., 2020). Plant biochars are cheaper, more readily available, and less effective than animal-derived biochar (Nie et al., 2021). The properties of biochar depend on the feedstock composition, heating methods, and temperature (Yaashikaa et al., 2020; Ahmad et al., 2021). The effectiveness of biochar can be improved by modifying its physical and chemical properties through acid or alkaline treatment, oxidation, nitrogenation, sulfuration, composting, or physical treatments such as heating (Huang et al., 2021). Modification of biochar can improve grain qualities and lower their toxic accumulation capacity (Gao et al., 2021). Nie et al. (2021) reported that treating the soil with aged biochar enhances the oxygen-containing functional group of the biochar, improves soil organic carbon content and pH, and lowers Cd^{2+} and Zn^{2+} bioavailability.

The use of biochar in the amendment of HM-contaminated soil was reported by many researchers in the last three years at the application rate ranges between 0.75% to 7%. At this application rate, the uptake of Cd, Cr, Pb, Zn, Cu, Co, Ni, Mn, and Hg was successfully mitigated in spinach, maize, potato, lettuce, wheat, eggplant, cilantro, kale, tomato, and cabbage (Table 1). Biochar was also reported to lower Cd uptake from hydroponic water. Biochars from different plant materials were used to minimize metal uptake in food crops, their application modifies the biological and physicochemical properties of soil. Biochar minimizes plant metal uptake by increasing soil pH, surface area (Khan, et al., 2020a), complexation, adsorption, or co-precipitation (Wang et al., 2018). The modification reduces HMs mobility and their phytoavailability and also increases crop yield (Palansooriya et al., 2019) by improving soil fertility (Zhi et al., 2020), and the activities of soil enzymes (Naeem et al., 2021). A results compilation by (Chen et al., 2018) showed that biochar can reduce Cd, Pb, Cu, and Zn accumulation in a plant by 38, 39, 25, and 17% respectively. The effectiveness of biochar in mitigating HMs uptake depends on the type of biochar, the soil condition, the properties of the crop, and the nature of the HMs (Chen et al., 2018; Palansooriya et al., 2019).

Microorganisms, including endophytic bacteria, and their products reported to mitigate HMs uptake in food crops in both soil and hydroponic production (Table 1). Soil amendment with biochar and organic fertilizer increases soil microbial diversity (Zhaoxiang et al., 2020). Microorganisms accumulate HMs and reduce their bioavailability in soil. Xia et al. (2021) reviewed the HMs resistance mechanisms of microorganisms and their capability in the amendment of Cd and Cr contaminated soil. The effects of soil amendment on the activities of microorganisms depend on soil nutrients (Wu et al., 2021). Proteobacteria, Acidobacteria, and Chloroflexi showed strong resistance to HMs stress (Wang et al., 2019). *Streptomyces rimosus* biomass is an active bio-absorbent of Cd and Ni from wastewater (Yous et al., 2018). *Pseudomonas aeruginosa* demonstrates higher resistance to Cd with excellent bioaccumulation and bio-absorption capacity (Chellaiah, 2018). Engineered baker's yeast is an excellent As, Cr, and Cd accumulator (Sun et al., 2019). Ureolytic bacteria, *Stenotrophomonas rhizophila* (A323), and *Variovorax boronicumulans* (C113) demonstrate high affinity to Pb, Cd, and Zn and efficiently convert them into insoluble carbonate minerals in an in vitro experiment (Jalilvand et al., 2020). Li et al. (2021) reported the potential of *Weissella viridescens* ZY-6 in removing Cd from an aqueous solution. Qi et al. (2021) demonstrate the efficiency of mixed bacteria-loaded biochar in enhancing uranium and Cd immobilization in soil.

Other control methods reported in Table 1 are the application of inorganic sorbents, chelating agents, and nanomaterials to soil and hydroponic water, gene modification of food crops, and soil filtration. Clay minerals are effective, reliable, affordable, and sustainable soil and water HMs remediation materials (Otunola and Ololade, 2020). Chitosan possesses a high affinity to HMs and can efficiently eliminate HMs from contaminated water and soil (Pal et al., 2021). Nanomaterials have specific surface properties and excellent HMs absorption capacity (Borji et al., 2020) due to their ample active sites that increase the removal rate (Zhang et al., 2021a). They possessed great affinity to Cd and can safely be used in the amendment of Cd contaminated soil (Zhang et al., 2021b). Soil remediation using nanomaterials and the development of food crops with HMs limited uptake capacity through biotechnology can provide an efficient and economically viable solution to HM contamination issues (Kumar et al., 2019a). Carbon nanomaterials are potential candidates for HMs remediation due to their numerous functionality and modification simplicity (Baby et al., 2019). A nanocomposite made from copper iodide nanoparticles and acidophilic bacteria cultures demonstrates excellent decontamination ability for Cr and Zn (Akhtar et al., 2020). Amino-functionalized modified silica gel can efficiently remove Pb, Cu, and Cd from tea polyphenols with little effect on the catechins and antioxidants contents (Huang et al., 2020a). Modified cellulose-based adsorbents have wide application in the treatment of wastewater (Varghese et al., 2019). Soil washing of severely contaminated soil is cost-effective (Chen and Li, 2018) and an active control method when washing conditions are optimized to improve HMs solubility and availability (Yang et al., 2018). Soil washing using a chelating agent and filtration lower Cd content below a safe level (Xu et al., 2019b). Arsenic can be removed from contaminated soil by washing the soil with Na_2EDTA and ascorbic or oxalic acid (Wei et al., 2018). Drinking water treatment residues can be used in the treatment of wastewater polluted soil (Shen et al., 2019), and groundwater (Holmes et al., 2019). Removal of straws can minimize HMs accumulation since they contain much higher concentrations than the grains as reported by (Feng et al., 2020) in rice straw, (Xiang et al., 2020)

Table 1. Heavy metals control methods during food crop production

Treatment	Application-level/concentration	Effectiveness	Food Crop	Reference
Rice husk biochar	Addition of 1.0% in soil	Lower Cd bioavailability 74 % Minimized Cd uptake by 62 %	Wheat grains	(Rehman et al., 2018a)
Silver-grass biochar + chitosan	Addition of 0.75% each in wastewater	Reduces Cd, Cr, Co, Ni, and Pb uptake.	Eggplant	(Turan et al., 2018)
Sugarcane bagasse biochar	Addition of 7.0% in soil	Reduces Cr and Pb uptake	Lettuce	(Khan et al., 2020b)
Plantain peel biochar	Addition of 1.0% in soil	Lower Cd and Zn	Potato tubers	(Nzediegwu et al., 2019)
Polyacrylamide super absorbent polymer + plantain peel biochar	Addition of 1.0% in soil	Lower Cd, Cu, Pb, and Zn uptake	Potato tubers	(Dhiman et al., 2020)
Anaerobically digested food waste compost	2812.5 m^3ha^{-1}	Lower Ni and Pb uptake	Maize	(Ulm et al., 2019)
Cassava peel + Mexican sunflower composts	At 2.0 kg m^{-2}	Lower Pb uptake by 37.8	Maize	(Adejumo et al., 2018)
Sulfur application	Addition of 5.28 mM in soil or hydroponic solution	minimize Cd uptake and accumulation	Rice	(Cao et al., 2018)
Sorbent (Alginate, biochar, Sepiolite, Halloysite)	Addition of 2.5% in soil	Lower Zn uptake	Maize	(Strachel et al., 2018)
Plantain peel biochar	Addition of 1.0% in soil	Lower Zn uptake	Spinach	(Nzediegwu et al., 2020)
Corn stover biochar	Addition of 7.0% in soil	Lower Hg bioavailability in the soil	Spinach	(Zhao et al., 2021)
Brewery sludge biochar	Addition of 4.0% to the soil in a pot experiment	Lower conc. of Cd by 93 % in the shoot	Ethiopian kale	(Tsadik et al., 2020)
Rice straw biochar	Addition of 6.0% in the soil	Reduces Pb and Cu in shoot and root by 46 and 36%, and 77 and 58%, respectively	Tomato	(Rizwan et al., 2021)
Modified gangue	Application of 2.0 kgm^{-2}	Lower Cd uptake in shoot and root by 54.9–61.5% and 9.3–13.2% respectively	Lettuce	(Zhao et al., 2020)
Modified Attapulgite clay	50 g/Kg of contaminated soil	lower Cd Cr and Pb uptake	Chinese cabbage	(Xu et al., 2019a)
Zinc oxide	Addition of 100 mgL^{-1} in hydroponic solution	mitigate the uptake Cd and Pb	Spinach, parsley, and cilantro	(Sharifan et al., 2020)
Cerium oxide nanoparticles	Addition of 200 mgL^{-1} into Hoagland solution	Lower Cu, Mn, Zn, and Fe uptake	Sugar pea	(Skiba and Wolf, 2019)
N-acetylcysteine	Addition of 1 mM to a petri dish containing seed	Alleviate Cu, Hg, Cd, and Pb toxicity	Wheat seedlings	(Colak et al., 2019)
Bio-filtration	Cultivation on bio-filters	Significantly reduced Cu, Mn, Ni, Pb, and Zn concentrations	broad beans, kohlrabi, kale, lettuce, mint, mustard, radish, spinach, and sweet corn	(Ng et al., 2018)
Yak manure biochar modified with H_2O_2	1000 mgL^{-1} of HMs stock solution	Bind with Pb^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+} and reduced their bioavailability		(Wang and Liu, 2018)
Cat manure + Spent coffee ground compost (1:3)	Addition of 5.0% to soil	Lower Zn, Cu, Cd, and Pb uptake	spinach	(Keeflee et al., 2020)
Endophytic bacteria, *Stenotrophomonas maltophilia* R5-5	Inoculation with 2^8 $cfumL^{-1}$ in a pot experiment	Significantly reduced Cd content	Rice	(Zhou et al., 2020)
microbial inoculant + garbage enzymes	Addition to the soil in a pot experiment	Minimize Cd uptake	Red sage	(Wei et al., 2020)
Bacillus megaterium N3 and *Serratia liquefaciens* H12	Addition of 60 mL of 10^8 cells mL^{-1} bacterial suspension into a pot	Minimizing Cd and Pb absorption	Chinese cabbage	(Han et al., 2020)
Ectomycorrhizal fungi	Root immersion of the seedling before transplanting into a pot	Lower translocation of Pb, Zn, Mn, As, Cr, Cd, and Cu	Massion's pine	(Yu et al., 2020)
Salicylic acid	Seedlings pre-treatment with 100 µM for 3 days	Reduced Cd accumulation	Tomato	(Jia et al., 2021)
Compost made from olive pomace (82 %) + poultry manure (10 %) + wheat straw (8 %)	50 $kgha^{-1}$	Lower Zn, Cu, Pb, Ni uptake	Organic emmer	(Diacono and Montemurro, 2019)
Hydroxyapatite/calcium silicate hydrate + wood biochar	Addition of 3.0% in soil	Lower Cd bioavailability	Water spinach	(Chen et al., 2020)

in sorghum stover, and (Zhou and Zhu, 2020) in rapeseed straw. The use of rice stubble after harvesting grain in a modified fish-rice system in removing Cd from contaminated paddy fields was reported by (Luo et al., 2021). Soil and hydroponic solution HMs control methods reported in Table 1 significantly lower Cd, Pb, Ni, Zn, Cu, Co, Cr, Mn, Hg, and Fe uptake in cereal grains, different types of vegetable and tuber crops.

3. Conclusion and Future Studies

The major factors that account for food crops HMs contamination are rapid urbanization, vigorous industrial activities, poor environmental policy, reluctance by the government to enforce environmental protection laws, poverty, food scarcity, and to a lesser extent illiteracy. Modifying soil conditions can discourage HMs uptake and accumulation in food crops since their bioavailability is favored by low soil pH and high organic matter content. Soilless farming secure crops from soil HMs contaminations, crops can only be contaminated from the atmospheric deposit when the system is operated in an urban area. The use of clean water, such as properly treated wastewater and clean underground water for irrigation can save soil and underground water from HMs contamination. Various control methods of HMs in food crops recently reported by researchers were discussed. These control methods involve the application of biochar, inorganic sorbents, chelating agent, nanomaterials, microorganisms, and their products to the soil and hydroponic solutions. Soil washing and filtration, and modification of the food crop genes were also reported. The control methods were found to significantly lower Cd, Pb, Ni, Zn, Cu, Cr, Mn, Hg, and Fe uptake in cereal grains, different types of vegetable and tuber crops. The article identified the following research gaps:

- Researchers pay more attention to the HM uptake mitigation effects of the various soil amendment techniques and show no interest in the aftermath of the soil alteration. The effects of the amendment on the soil chemical, physical and biological properties and the effects on the plant physiology, genetics, and chemical composition other than the metal content should be given due consideration in the future. Godlewska et al. (2021) reported that biochars are toxic to soil microorganisms at higher concentrations or when used without soil.
- Most of the soil amendment studies reported in recent years were conducted in a laboratory and greenhouse in a pot experiment. The effects of these techniques should be studied in large scale agriculture.
- Some researchers studied the effectiveness of the amends using artificial contamination where healthy soil is contaminated with the required dosage of metal contaminant. The effectiveness of these treatments will only be justified when studied in an active contaminated agricultural field.
- The residual effects of biochar application can be minimized by modifying the biochar, hence, researches should be conducted on the efficiency of modified biochars in different crops under different soil conditions.
- Amendment methods reported to be effective in a hydroponic system should be studied in soil agriculture.
- Little data was reported on preventing HMs uptake in fruits and nuts, these classes of foods are staple in some communities and deserve similar attention given to vegetables due to their similar nutritional functions.
- Development of HMs resistant varieties will certainly minimize HM consumption by both humans and animals.
- Understanding the properties of feedstock for biochar production and how burning conditions determine the qualities and properties of the biochar will assist in choosing the right stock and processing conditions that will produce biochar with the desired characteristics.

Compliance with Ethical Standards

Conflict of Interest

As the author of article declare that there are no conflicts of interest with respect to the research, authorship, and/or publication of this article.

Authors' Contributions

Nura ABDULLAHİ: Conceptualization, literature search, original draft preparation. **Ernest Chukwusoro IGWE**: Supervision, literature search, writing-reviewing, and editing. **Munir Abba DANDAGO**: Supervision, literature search, writing- review, and editing. **Abdulkadir SANİ**: Supervision, writing- review, and editing. **Nasiru Bilkisu UMAR**: literature search, writing- review and editing.

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We humbly give consent for this article to be published.

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