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Mechanisms and Environmental Applications of Biochar for Heavy Metal Remediation in Contaminated Soils

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Abstract. Soil contamination by heavy metals poses significant threats to ecosystems and human health. Biochar, a carbon-rich material produced from biomass pyrolysis, has emerged as a promising and cost-effective amendment for immobilizing heavy metals in polluted soils. This paper provides a critical review of the key mechanisms governing the immobilization of heavy metals (e.g., Pb, Cd, Cu, Zn) by biochar, including electrostatic attraction, ion exchange, surface complexation, and precipitation. Furthermore, this study evaluates the primary factors influencing remediation efficiency, such as pyrolysis temperature, feedstock type, and soil conditions. The results synthesized from existing literature indicate that biochar application can effectively reduce metal bioavailability and leachability, while also improving soil physicochemical properties. In summary, understanding the mechanism-property relationship of biochar is essential for optimizing its field application. This review therefore provides a theoretical basis and practical guidance for using biochar in sustainable soil remediation.

Keywords: Biochar, Heavy metal contamination, Soil remediation, Immobilization mechanisms, Environmental application

1. Introduction

Rapid industrialization and agricultural intensification have led to the widespread accumulation of toxic heavy metals such as lead (Pb), cadmium (Cd), and copper (Cu) in soils. These pollutants pose persistent risks to food security, groundwater quality, and human health due to their non-biodegradable nature and high toxicity. Conventional remediation approaches, including soil washing and excavation, are often costly and environmentally disruptive. Consequently, there is a growing demand for sustainable, cost-effective, and in-situ remediation technologies. Recently, biochar has gained significant attention as a green functional material for soil amendment. However, a systematic understanding of the physico-chemical mechanisms by which biochar sequesters different heavy metals remains fragmented. Therefore, the primary research questions of this paper are: 1. What are the dominant immobilization mechanisms between biochar and various heavy metals? 2. How do biochar production conditions affect its remediation performance? Recent studies have begun to address these gaps [1-3], yet a integrated review linking mechanisms to practical applications is still lacking [4]. This review adopts a qualitative synthesis method, analyzing

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findings from peer-reviewed studies. This paper is significant as it clarifies the mechanism-property relationships of biochar, offering valuable guidance for engineers to design targeted remediation strategies, thereby contributing to sustainable agricultural and environmental management [5].

2. Primary mechanisms of heavy metal immobilization by biochar

Biochar immobilizes heavy metals through multiple concurrent mechanisms. Physical adsorption and electrostatic attraction occur due to biochar's porous structure and negatively charged surface [2]. Ion exchange involves the replacement of surface cations (e.g., Ca^{2+}, Mg^{2+}) with metal ions [4]. Surface complexation is driven by oxygen-containing functional groups (-COOH, -OH) forming stable metal complexes [3]. Precipitation is induced by increased soil pH and release of anions (CO_3^{2-}, PO_4^{3-}), leading to insoluble metal compounds [6]. These mechanisms often work synergistically depending on biochar properties and metal species. Notably, the dominant immobilization pathway varies distinctly among heavy metals. Pb^{2+} immobilization is primarily governed by precipitation, especially with phosphate or carbonate anions released from biochar, forming highly insoluble minerals such as $Pb_5(PO_4)_3OH$. In contrast, Cd^{2+} shows a stronger dependence on surface complexation with oxygen-containing functional groups (-COOH, -OH), as Cd has limited precipitation affinity under common soil pH ranges. Cu^{2+} tends to be immobilized via ion exchange, readily displacing exchangeable Ca^{2+} or Mg^{2+} on biochar surfaces due to its higher electronegativity and hydration energy. Zn^{2+}, however, is often retained through electrostatic attraction to negatively charged surfaces, particularly under alkaline conditions where its cationic form predominates. These mechanisms are not independent but exhibit synergistic or antagonistic interactions. For instance, phosphate-induced precipitation of Pb can locally elevate pH and create nucleation sites, promoting co-precipitation of coexisting Cd and Cu—a synergistic effect. Conversely, at high metal concentrations, competitive sorption occurs: abundant Pb^{2+} may occupy most reactive sites, suppressing Cd complexation and Zn electrostatic adsorption. Moreover, excessive metal loading can saturate functional groups, block micropores, or alter surface charge polarity, leading to mechanism saturation or even failure, where immobilization efficiency drops sharply and remobilization risk increases.

3. Key factors influencing remediation efficiency – pyrolysis temperature and feedstock type

The performance of biochar varies greatly with production conditions. Pyrolysis temperature is a critical factor: low-temperature biochars (e.g., 300°C) retain more functional groups, favoring surface complexation, while high-temperature biochars (e.g., 600°C) exhibit higher pH, surface area, and ash content, enhancing precipitation and physical sorption [1-3]. For example, Pb immobilization is often more effective at high temperatures due to phosphate-induced precipitation, whereas Cd removal may benefit from oxygen-containing groups at moderate temperatures [4]. Feedstock type also matters: manure-based biochars are rich in ash and phosphorus, making them efficient for Pb precipitation; wood-based biochars have higher porosity and carbon content; crop straw-derived biochars offer a balance between functional groups and surface area [2-5]. Therefore, selecting appropriate production parameters for target metals is essential for field success. Beyond pristine biochar, various modification strategies have been developed to enhance its remediation performance. Acid modification (e.g., with HCl, HNO_3, or H_2SO_4) typically increases specific surface area and introduces additional oxygen-containing functional groups (e.g., carboxyl and hydroxyl groups), thereby improving surface complexation capacity for metals like Cd and Cu. However, acid washing may reduce ash content and pH, weakening precipitation-dependent

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immobilization for Pb. Alkaline modification (e.g., with KOH or NaOH) substantially increases surface area and microporosity through chemical activation, while also raising biochar pH and ash content, which favors electrostatic attraction and precipitation of cationic metals. Metal loading (e.g., impregnation with Fe, Mn, or Al oxides) introduces new reactive mineral phases that form inner-sphere complexes with heavy metals or induce coprecipitation, significantly enhancing the sorption of As, Pb, and Zn even under adverse pH conditions. Ball milling is a physical modification technique that reduces particle size, increases external surface area, and exposes fresh reactive edges, often improving cation exchange capacity and functional group accessibility without substantially altering chemical composition. In field applications, modified biochars generally outperform pristine biochars in terms of immobilization efficiency for specific metals, especially in complex multi-metal contaminated soils. However, they also present drawbacks: higher production costs, potential leaching of chemical residues (e.g., residual acids or metal nanoparticles), and uncertain ecological compatibility with soil biota. Pristine biochars, while less targeted, offer a more cost-effective and environmentally benign option for broad-spectrum, low-to-moderate contamination scenarios. The choice between pristine and modified biochar should therefore be guided by site-specific contamination levels, target metal species, economic feasibility, and long-term environmental safety.

4. Key factors influencing remediation efficiency – soil environmental conditions and aging effects

Soil environmental factors significantly modulate biochar's remediation efficiency. Soil pH is the master variable: acidic conditions increase metal solubility and reduce immobilization, while alkaline soils favor precipitation and electrostatic attraction [6]. Organic matter content can compete for sorption sites, potentially reducing biochar's effectiveness. Additionally, the presence of coexisting ions (e.g., Cl^-, SO_4^{2-}) may form soluble metal complexes, hindering immobilization [2]. Biochar aging in soil—through oxidation, fragmentation, or interaction with microorganisms—can alter its surface chemistry and pore structure over time. Some studies show that aging may reduce functional groups but increase oxygen-containing sites, leading to complex long-term effects [3-5]. Understanding these soil-dependent dynamics is crucial for predicting biochar's performance beyond short-term trials. Soil texture also plays a critical role in biochar efficacy. In sandy soils, large macropores and low water-holding capacity result in rapid percolation and limited biochar-soil contact, reducing retention time and immobilization efficiency. Conversely, clay soils with abundant micropores and high specific surface area can trap biochar particles and enhance physical adsorption, though excessive clay may block biochar pores through clogging, diminishing accessibility to reactive sites. Loamy soils offer a balanced pore structure, generally providing optimal conditions for biochar dispersion and metal immobilization.

Furthermore, the synergistic coupling between soil microorganisms and biochar constitutes a vital yet often overlooked mechanism. Biochar's porous architecture provides a stable micro-habitat for indigenous bacteria, fungi, and actinomycetes, protecting them from predation and desiccation. These colonizing microbes can actively contribute to heavy metal passivation through multiple pathways: (1) microbial acidification—via excretion of organic acids (e.g., citric, gluconic acid)—dissolves carbonate-bound metal fractions, which are then re-adsorbed or reprecipitated on biochar surfaces; (2) extracellular polymeric substances (EPS) produced by biofilms bind metal ions through complexation and ion exchange, enhancing overall immobilization; (3) some metal-reducing bacteria (e.g., Shewanella or Geobacter species) can enzymatically reduce redox-sensitive metals, altering their valence state and solubility. This biochar-microbe synergy not only improves short-

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term immobilization but also contributes to long-term stabilization, as microbial activity continuously regenerates binding sites and modifies biochar surface chemistry. However, this beneficial interaction can be hindered by high metal toxicity, which suppresses microbial activity, especially in heavily contaminated sites. Thus, integrating soil texture considerations and microbial ecology into biochar application strategies is essential for maximizing remediation durability and effectiveness across diverse field conditions.

5. Practical applications and future perspectives

Current applications of biochar include field trials for reducing Cd uptake in rice and stabilizing heavy metals in mine tailings [6]. Biochar is often applied as a pure amendment or combined with compost, clay minerals, or synthetic fertilizers to enhance performance [1]. However, several limitations remain: long-term field data (>5 years) are scarce, and the ecological impact on non-target soil biota (e.g., earthworms) requires more attention [3]. Future research should focus on: (a) designing engineered biochars (e.g., magnetic or nano-metal oxide modified) for specific metals, (b) developing cost-effective regeneration protocols for spent biochar, and (c) integrating biochar remediation with carbon sequestration accounting [4, 5]. These directions will help transition biochar from a promising research material to a routine environmental practice. Beyond these general perspectives, several practical constraints merit closer examination. Particle size of biochar is a key operational parameter: fine-grained biochars (e.g., <0.5 mm) offer larger specific surface area and more accessible reactive sites, leading to higher immobilization efficiency in short-term applications. However, they are prone to wind erosion, surface runoff loss, and potential inhalation hazards during field application. Coarse biochars are easier to handle and more resistant to physical transport, but their limited contact area with soil and metals often reduces remediation performance. A trade-off thus exists, necessitating site-specific granulation or pelletization strategies. Another significant concern is the use of low-temperature biochars (produced at ≤350°C), which tend to retain substantial amounts of labile dissolved organic carbon (DOC). Upon field application, this DOC can be released into soil solution, acting as a mobile ligand that complexes with heavy metals and increases their solubility and bioavailability—a phenomenon known as "secondary mobilization." This counterproductive effect is particularly problematic for Cu and Zn, which have strong DOC affinity. Conversely, high-temperature biochars (≥600°C) with dominant microporous structures are susceptible to pore clogging by soil colloids, clay minerals, and microbial byproducts over time, leading to a gradual decline in physical adsorption capacity. Long-term aging further raises the risk of remobilization of previously immobilized metals. As biochar surfaces oxidize and functional groups degrade, or as pH and redox conditions fluctuate in field soils, metal-bearing precipitates (e.g., $PbCO_3$, $CdCO_3$) may dissolve, and surface complexes may dissociate, resulting in the gradual release of fixed heavy metals back into the soil solution. This "time-bomb" effect has been observed in some 3–5 year field studies, underscoring the urgent need for extended monitoring. Climatic variations also impose substantial constraints: in humid tropical regions with high rainfall and intense weathering, biochar undergoes rapid physical disintegration and leaching of soluble components, shortening its effective lifespan; in arid or semi-arid zones, low moisture and high evapotranspiration limit biochar-soil interaction and microbial activity, reducing immobilization kinetics. Cold-climate applications face challenges from freeze-thaw cycles that fragment biochar structure and alter surface charge properties. Therefore, future application strategies must adopt a "climate-smart" approach, tailoring biochar production, modification, dosage, and application method to local climatic and edaphic conditions. Additionally, establishing standardized field trial

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protocols, including multi-site, multi-year monitoring networks, will be indispensable for generating robust evidence to guide practical biochar deployment on a global scale.

6. Conclusion

In conclusion, this review has systematically examined the role of biochar as an effective and sustainable amendment for remediating heavy metal-contaminated soils. The primary conclusion is that biochar's efficacy is achieved through a synergy of four key mechanisms: electrostatic attraction, ion exchange, surface complexation, and precipitation. The dominant mechanism depends heavily on biochar properties (controlled by pyrolysis temperature and feedstock type) and the chemical nature of the target heavy metal. This paper confirms that biochar application can not only reduce the bioavailability and leachability of toxic metals like Pb and Cd but also concurrently improve soil functions, including pH buffering, nutrient retention, and water-holding capacity. Despite these promising findings, this review acknowledges limitations such as the predominance of short-term laboratory studies and a lack of standardized methodologies for cross-study comparisons. Future research should prioritize long-term field trials to assess aging effects and the environmental fate of biochar-bound metals, as well as the potential co-release of contaminants from biochar itself. The development of cost-effective, targeted, or engineered biochar composites represents a promising avenue for advancing this technology.

In final summary, biochar offers a viable, multifunctional solution for heavy metal soil remediation, but its sustainable application requires continued mechanistic understanding and field validation.

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