






Lignocellulosic biochars as a strategy to mitigate cadmium levels in agricultural soils

Biocarbonos de origen lignocelulósico como estrategia para mitigar los niveles de cadmio en suelos agrícolas

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Abstract

Introduction: Cadmium (Cd) is a highly toxic heavy metal that deteriorates soil and crop quality and also poses a risk to human health due to its accumulation in food, seriously compromising agricultural productivity and public health.

Objective: The objective of this review was to analyze the use of biochars obtained from lignocellulosic waste as a strategy for Cd mitigation in agricultural soils, as well as their impact on the physicochemical properties of the soil.

Methods: A systematic review was performed using StArt v.3.0.3 software. The searches were conducted in Scopus, Science Direct, Springer Link, and Google Scholar. Based on this, articles of interest were selected by applying inclusion and exclusion criteria.

Results: The most frequently cited precursors in the literature were identified as agricultural residues, such as rice husks and straw, corn and wheat, due to their mass production, low cost and high carbon content. The effectiveness of biochar in Cd remediation was found to depend on its properties, such as porosity, specific surface area, and pH. Furthermore, biochar was found to significantly improve the physicochemical properties of the soil, optimizing nutrient retention and the immobilization of heavy metals. However, it was shown that the effectiveness of biochar decreases over time, due to the gradual release of trapped Cd and the decomposition of its alkaline components.

Conclusions: In conclusion, biochars are an efficient and sustainable strategy for the remediation of Cd-contaminated soils, with environmental and economic benefits associated with the responsible management of agricultural waste, although their implementation requires careful planning to maximize their effectiveness in different agricultural contexts.

Keywords: Sustainability, heavy metals, amendment, agriculture, soils.

Resumen

Introducción: El cadmio (Cd) es un metal pesado de alta toxicidad que deteriora la calidad del suelo y los cultivos, además de representar un riesgo para la salud humana, debido a su acumulación en los alimentos, lo que compromete seriamente la productividad agrícola y la salud pública.

Objetivo: El objetivo de esta revisión fue analizar el uso de biocarbonos obtenidos a partir de residuos lignocelulósicos como estrategia para la mitigación del Cd en suelos agrícolas, así como su impacto en las propiedades fisicoquímicas del suelo.

Métodos: Se realizó una revisión sistemática con el software StArt v.3.0.3. Las búsquedas se realizaron en Scopus, Science Direct, Springer Link y Google Académico. A partir de esto se seleccionaron los artículos de interés aplicando criterios de inclusión y exclusión.

Resultados: Se encontró que la efectividad del biocarbono en la remediación del Cd depende de sus propiedades, tal como la porosidad, superficie específica y pH. Además, se encontró que el biocarbono mejora significativamente las propiedades fisicoquímicas del suelo, optimizando la retención de nutrientes y la inmovilización de metales pesados. Sin embargo, se evidenció que la efectividad del biocarbono disminuye con el tiempo, debido a la liberación gradual de Cd atrapado y a la descomposición de sus componentes alcalinos.

Conclusiones: En conclusión, los biocarbonos son una estrategia eficiente y sostenible para la remediación de suelos contaminados con Cd, con beneficios ambientales y económicos, asociados al manejo responsable de residuos agrícolas, aunque su implementación requiere una planificación cuidadosa para maximizar su efectividad en distintos contextos agrícolas.

Palabras clave: Sostenibilidad, metales pesados, enmienda, agricultura, suelos.

How to cite?

Agudelo-González H, García-Rosero H, Caro-Caro CI, Briceño-Gamba N. Lignocellulosic biochars as a strategy to mitigate cadmium levels in agricultural soils. *Ingeniería y Competitividad*, 2026, 28(1)e-30115034

<https://doi.org/10.25100/iyc.v28i1.15034>

Received: 18/06/25

Reviewed: 12/09/25

Accepted: 21/01/26

Online: 30/03/26

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Spanish version



Why was this study conducted?

This study was conducted in response to growing concerns about cadmium contamination in agricultural soils and its effects on crop quality, food safety, and human health. While various remediation strategies have been proposed, biochars derived from lignocellulosic waste have garnered attention due to their potential to reduce Cd bioavailability while simultaneously improving soil properties. However, the existing evidence is fragmented, with studies using different raw materials and under varying production conditions. Therefore, this review aimed to analyze the use of lignocellulosic biochars as a strategy for Cd mitigation in agricultural soils and to assess their effects on soil physicochemical properties.

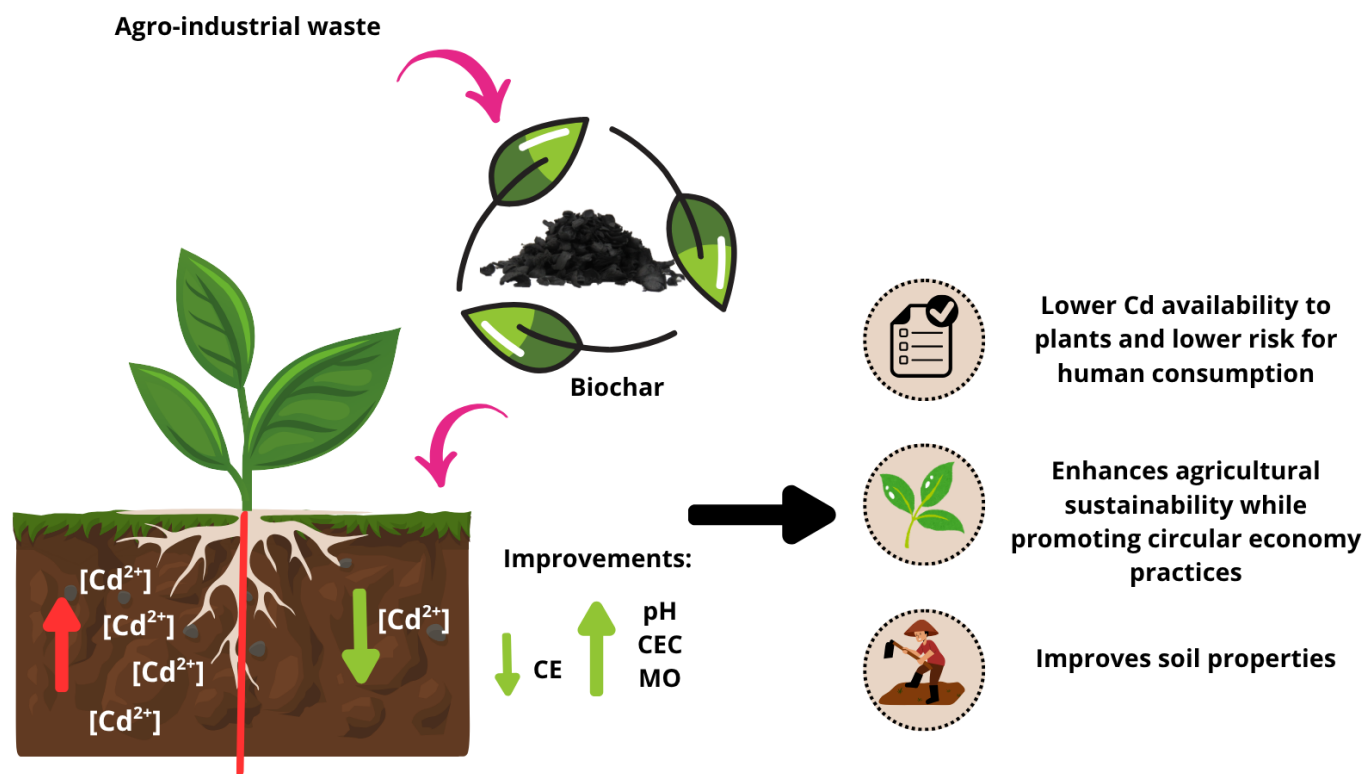
What were the most relevant findings?

The review showed that biochars produced from lignocellulosic waste, particularly agricultural residues such as rice hulls, rice straw, wheat straw, and maize residues, are among the most studied and effective materials for reducing cadmium bioavailability in soils. Their effectiveness depends on physicochemical properties such as porosity, specific surface area, functional groups, and alkaline pH, which promote adsorption, complexation, and immobilization processes. Furthermore, biochar application was consistently associated with improvements in soil properties, including pH, cation exchange capacity, and organic matter content. However, their effectiveness can decrease over time due to surface saturation and the gradual release of previously immobilized cadmium.

What do these findings contribute?

These findings offer a comprehensive perspective on the use of lignocellulosic biochars as a strategy to mitigate cadmium contamination in agricultural soils. This study compiles recent evidence on raw material selection, production conditions, and the mechanisms involved in cadmium immobilization, also addressing its effects on soil properties. Furthermore, it identifies both the potential and limitations of biochar application, offering useful insights to guide future research and its implementation in different agricultural contexts. Overall, this review contributes to linking soil remediation strategies with the sustainable management of agricultural waste.

Graphical Abstract



Introduction

Cadmium (Cd) is a heavy metal that even at low concentrations can be highly toxic to living organisms (1–3). In the soil, this metal is characterized by its high mobility compared to others and by remaining active for extended periods of time, with an estimated average lifespan between 310 and 1500 years (4,5). In agricultural soils, Cd levels tend to be high, due to the intensive use of phosphate fertilizers, which contain this metal as an impurity, contributing significantly to its release and accumulation in the environment (6,7). This situation not only represents a problem for agricultural productivity, but also for crop quality and food security (2,8).

Cd directly affects the physiological processes of plants by interfering with the absorption, transport and incorporation of essential elements such as calcium (Ca), magnesium (Mg), phosphorus (P) and potassium (K), due to its ionic similarity with these elements (8–10). This ionic alteration negatively impacts key processes such as germination, growth, water balance, photosynthesis, stomatal opening and genetic transcription in plants (9,11). Because it is easily absorbed by the roots and accumulates in edible tissues, Cd represents a threat to human health (5,6). Consuming food contaminated with this metal increases the risk of chronic diseases, highlighting the importance of implementing strategies to mitigate its presence in agricultural systems and ensure food safety (4,12).

In response to the problem of Cd contamination in agricultural soils, various strategies have been developed, such as the use of organic, inorganic, chemical and biological amendments (13–15). Among these are those derived from agro-industrial waste, which stand out for their ability to reduce the mobility and bioavailability of Cd in the soil; in addition to improving its physical and chemical properties (5,13,16). One particularly promising amendment is biochar, known to decrease the bioavailability of heavy metals thanks to its adsorption capacity (5,17).

Among the main benefits of implementing biochar, it is highlighted that it promotes microbial activity and contributes to carbon retention, mitigation of greenhouse gases and soil improvement, since it has a large specific surface area and porosity, cation exchange capacity and alkaline pH, which together increase crop productivity and strengthen food security (14,17,18). This review analyzes the implementation of biochars from lignocellulosic waste as an amendment for the mitigation of soils contaminated by Cd. Likewise, the selection of raw materials for the production of biochars, their effect on soil properties and their ability to reduce the levels of Cd present in it are addressed.

Methods

The systematic review was performed using the free software StArt (State of the Art through Systematic Review) v.3.0.3 Beta; inclusion and exclusion criteria were defined to determine what information would be considered or discarded during the analysis (Table 1). The searches were carried out in the Scopus, Science Direct, Springer Link and Google Scholar databases, covering publications made between the 2019–2024 period. The following search equation was used in each database: *(biochar AND cadmium OR cd) AND (vegetable) AND NOT (microbial OR fungal OR bacteria)*.

Based on the search performed, the data were exported in BIBTEX or RIS format for incorporation into the StArt software. In total, 479 items were imported into the program, of which 299 (62%) were eliminated based on inclusion and exclusion criteria, 44 (9%) were identified as duplicates, and 136 (28%) were accepted during the selection stage. Subsequently, we moved to the extraction stage, in which only the 136 documents that had initially been accepted were analyzed. Of these, a detailed analysis was carried out and 53 (38.97%) were eliminated, leaving 83 (61.03%) that made up the final set of studies included in the research.

Table 1. Inclusion and exclusion criteria. **Source:** Authors

| Inclusion |
|---|
| (I) Use of a lignocellulosic biochar source for Cd remediation in agricultural soils. |
| (I) Articles aligned with the objective of the review. |
| Exclusion |
| (E) Articles that are NOT aligned with the objective of the review. |
| (E) No use of a lignocellulosic-type precursor for obtaining biochars. |
| (E) Grey literature. |
| (E) Articles that are written in a language other than English or Spanish. |

Results and discussion

The databases from which the greatest availability of documents related to the topic of interest of the initial search was obtained, in ascending order, are: Scopus (15.45%), Science Direct (23.17%), Google Scholar (29.02%) and Springer Link (32.36%) for a total of 479 articles (Fig. 1).

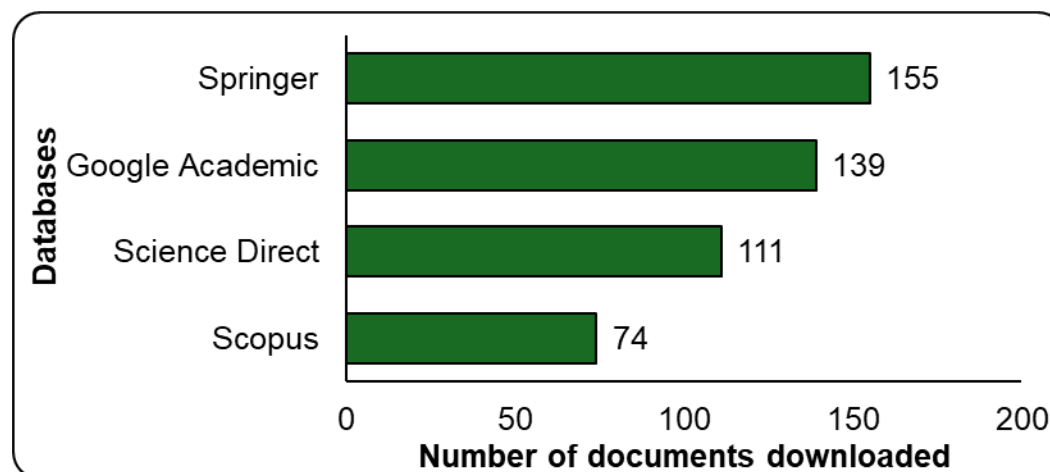


Figure 1. Number of documents downloaded per database used in the study. **Source:** Authors

Based on the documents reviewed after the extraction stage, it was found that, in terms of the generation of knowledge on the use of biochars as organic amendments to mitigate Cd content in

soil, China was the country with the most registered publications, followed by Pakistan and India (Fig. 2b). In terms of frequency of publications related to the topic, it was found that the year with the most activity was 2022, followed by 2020, 2023, 2019 and 2024 (Fig. 2a).

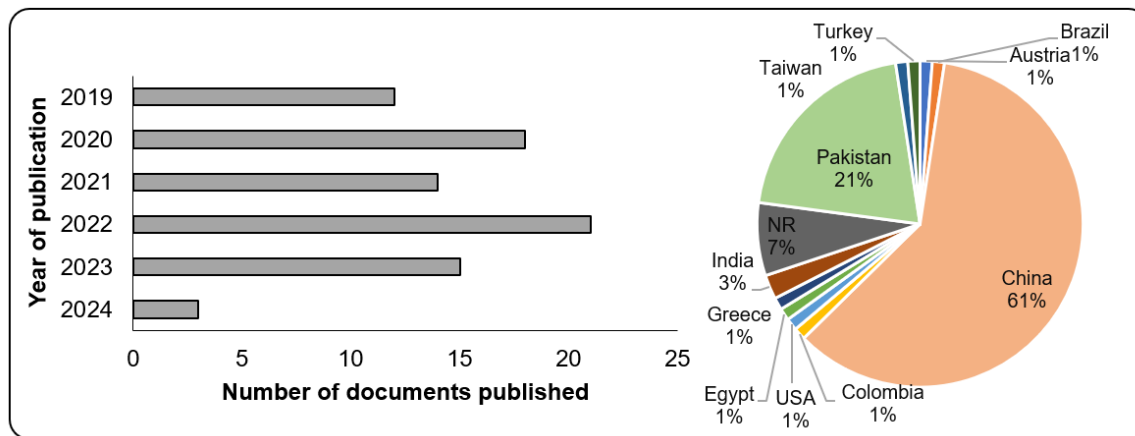


Figure 2. a. Number of articles published per year on the use of biochar as a Cd amendment, b. Main countries of origin of documents related to the use of biochar as a Cd amendment in soils.

Source: Authors

Cd is a heavy metal widely distributed in the environment, presenting serious risks, due to its both natural and anthropogenic origin (9,19). Its presence in soil, water and air, as well as its high bioavailability, makes it a priority contaminant that affects ecosystems and human health (12,14,20). Industrial and agricultural activities are the main sources of environmental pollution by this heavy metal, although natural processes also contribute, to a lesser extent, to its release into the environment (6,10). Faced with this challenge, research has focused its attention on innovative mitigation strategies, such as the use of biochars and other organic amendments, which stand out for their ability to immobilize Cd, reduce its bioavailability and improve the physicochemical properties of the soil (10,17,21). Analysis of the materials used for biochar production and their impact on the remediation of contaminated soils highlights the importance of properly selecting precursors and production conditions (22,23). Through the analysis of these aspects, this review addresses the use of biochars obtained from the utilization of lignocellulosic waste, as a sustainable strategy to mitigate Cd pollution in agricultural soils.

Cadmium and environmental implications

Cd occurs naturally in the Earth's crust generally associated with zinc (Zn), copper (Cu) and lead (Pb) minerals, such as sphalerite, chalcopyrite, galena, tetrahedrite, anglesite, smithsonite and pyromorphite, from where it can be gradually released into the environment by weathering and erosion processes (4,6,20). Cd concentrations generally tend to be higher in sedimentary rocks (0.01 to 2.6 mg/kg) than in igneous (0.07 to 0.25 mg/kg) and metamorphic (0.11 to 1.0 mg/kg) rocks (6,7). Other natural sources of emission of this metal include volcanic eruptions and forest fires, which mobilize the Cd contained in vegetation and organic matter to the atmosphere and soil (1,7).

Cd emissions from anthropogenic sources contribute about 90% of the Cd present in the environment (10). These emissions are the product of industrial activities such as metal smelting and refining, production of non-metallic minerals, battery manufacturing, mining and textile operations, combustion of fossil fuels, sewage sludge from industrial wastewater, use of phosphate fertilizers and urban and agricultural runoff (1,2,8,24,25). Of these, the mining, metallurgical and textile industries are the ones that produce the largest amount of Cd (9,12).

Cd released by natural and anthropogenic sources can take different routes that distribute it in the air, soil and water (1,6). At the atmospheric level, Cd is found in a gaseous phase, as particulate matter or in aerosol form, so it is transported by air for deposition on terrestrial or aquatic surfaces, from where it can be carried to water sources and soil by meteorological phenomena, such as rain and runoff processes (6,7,9,20). Atmospheric deposition, along with industrial drainage and agricultural runoff, leads Cd to water bodies where the metal can remain as suspended particles, attached to sediments or bioaccumulated in tissues of aquatic organisms (6,7,10). In the soil, Cd can be deposited by atmospheric action or by the use of fertilizers and sewage sludge; there, it mainly binds to organic matter and clay minerals, and under specific conditions it can filter into groundwater (1,6,7). Cd discharges gradually enter the soil, where they are easily mobilized to their weakest bond between soil exchange sites, which favors their bioavailability to plants (9,10).

The concentration of bioavailable Cd is the amount that can be absorbed and accumulated in plants, which differs from the total concentration of Cd in the soil (8,9). According to its bioavailability, the amount of free Cd in the soil is classified into total pool, reactive pool and directly bioavailable pool (9). The total pool is composed of reactive Cd, which is immediately available, and non-reactive Cd, which is not available and is unlikely to be reactivated over long periods of time (6,9). The reactive pool is composed of Cd²⁺ ions, short-range hydrated metal oxides, and clay particles adhering to active surfaces of soil organic matter, which are eventually available to the plant (6,9). Finally, the directly bioavailable reserve is composed of free Cd²⁺ ions completely dissolved in the soil solution, available to the plant (6,9). The absorption of the metal in solution by the plant is favored by the acidification of the soil resulting from the presence of inorganic acids or by organic acids released by the roots of the plants (18). Likewise, other soil factors that condition the bioavailability of Cd for the plant are cation exchange capacity, carbonate content, amount of phosphorus and the presence of organic matter (8,9).

Cd enters plants through the root system from where it is translocated directly through the xylem via apoplastic and symplastic pathways, until it reaches the grains, or through the phloem by passing through the culm, rachis, flag leaves, and outer parts of the panicles until it reaches the seeds and grains (Fig. 3) (9,10,26,27). Since the movement of metal ions can vary in tissues, the concentration of Cd is usually higher in the root; however, the amount of the metal that is translocated is dependent on the plant species (6,9,27). Regarding the concentration of Cd in wheat and barley grains, a positive correlation has been found with the total Cd content in the soil (10). In soils with high levels of Cd, plants have higher amounts of this metal, which increases the risk of contamination in products derived from these plant species intended for human consumption, due to the accumulation of this metal in edible tissues (9,10); for example, given the high capacity of rice to accumulate Cd, it has been found that in soils with high concentrations of this metal, the grains

of this cereal can exceed the limits established by food safety regulations, such as regulation (EU) 2023/915, reaching values that exceed 0.15 mg/kg (28).

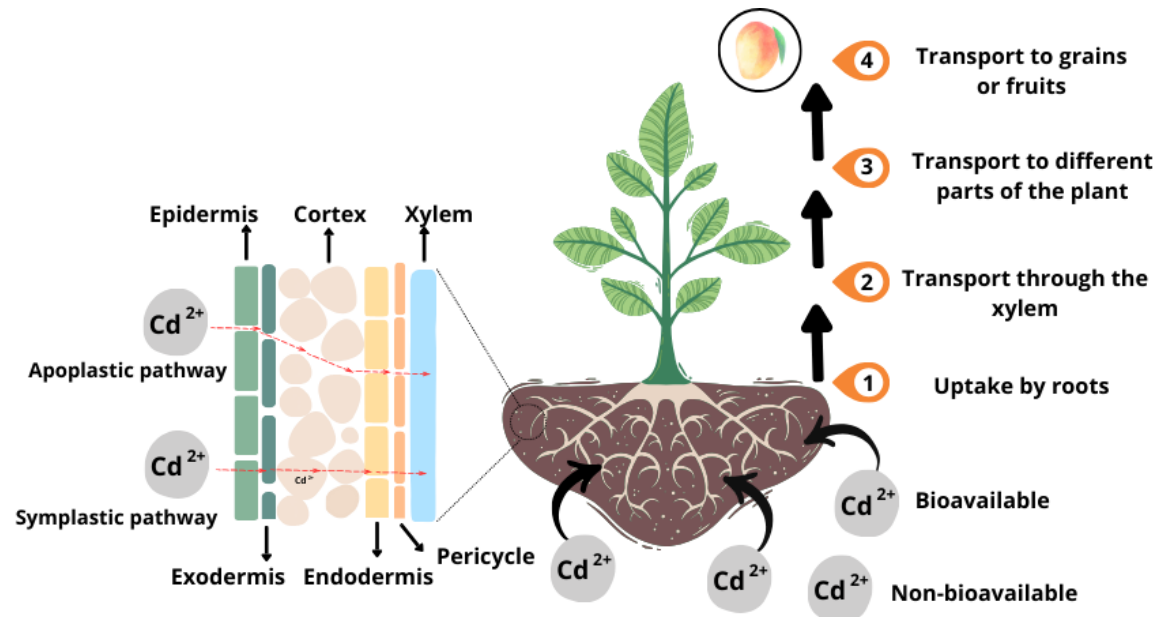


Figure 3. General diagram of the process of Cd absorption and translocation by plants. **Source:** Authors

In food chains, Cd has been found to biodilute or biomagnify, depending on the species that make up the trophic structure and the physicochemical characteristics of the environment (1,29,30). In humans, Cd is incorporated into the body through respiration and the ingestion of food containing this metal, and can bioaccumulate in different organs such as the kidneys, liver and intestines, where it has a half-life of 25 to 30 years (2,4,20). Due to its chemical behavior, Cd can compete with Ca and other elements in the human body, leading to different pathologies that alter the functioning of the organs (1,24). Likewise, exposure to Cd has been found to cause chronic lung diseases, high blood pressure, leukemia, kidney and liver dysfunction, osteomalacia, osteoporosis, genetic toxicity and different types of cancer such as breast, pancreatic, prostate and lung cancer, among others (4,10,12,20).

In this context, the importance of developing amendments to reduce the presence of Cd in crops lies in the need to protect public health and agricultural sustainability (25,28,31). Therefore, the implementation of strategies such as organic amendments that immobilize Cd in the soil or reduce its bioavailability is fundamental to mitigating these risks and ensuring a balance between agricultural productivity and environmental protection.

Organic amendments for the mitigation of Cd in the soil

Organic amendments are materials of biological origin (such as manure, compost, crop residues, sewage sludge, among others) that are incorporated into the soil matrix in order to improve its properties and promote crop performance (13). Organic amendments play an important role in mitigating the negative effects of Cd pollution on crops and the environment (6,32). Its application improves the development of plants exposed to Cd and contributes significantly to the retention and stabilization of Cd in the soil, reducing its mobility and bioavailability (32,33). Among the most

sustainable organic amendment options with positive effects on soil and plant productivity, activated carbon, compost or organic fertilizer and biochars stand out [\(32–34\)](#).

Plant-based activated carbon is a microporous carbonaceous material obtained from biomass, through pyrolysis and activation by physical or chemical processes [\(35,36\)](#). This material has a large specific surface area and high porosity, which creates numerous active adsorption sites, giving it a high capacity to retain ions [\(11,36\)](#). Heavy metal ions, possessing an electrical charge and a relatively small size, readily bind to the surface of activated carbon through electrostatic attraction, as well as through other interaction mechanisms that favor their adsorption and retention in the material [\(20,35\)](#). Regarding Cd, it has been reported that the effectiveness of activated carbon for its retention reaches up to 99.5% effectiveness, so it has been used successfully in the treatment of wastewater and contaminated soils [\(1,11,34,35\)](#).

Another type of amendment is organic fertilizer, which is produced from the biological decomposition of organic waste through an aerobic process [\(33\)](#). The materials present in compost not only raise the pH of the soil and improve Cd sorption sites, but also improve soil fertility by adding carbon and act as an important source of nutrients for plant development [\(15\)](#); however, significant amounts of compost are required to achieve an effective amendment [\(16\)](#). Among the benefits of combining compost with other inputs such as lime, it is reported that it significantly reduces the Cd content in the soil, up to 11 times compared to untreated soils [\(16\)](#); and combined with biochar it reduces Cd stress in plants [\(33\)](#).

Biochar is a solid material with a high carbon content, obtained in oxygen-limited environments from biomass subjected to various thermochemical conversion methods such as hydrothermal carbonization, gasification, pyrolysis and torrefaction, with pyrolysis being the most common technique for obtaining it [\(37–39\)](#). Biochar production can be carried out from different types of organic matter including agro-industrial, agricultural and forestry waste, manure, microalgae and sewage sludge among others, [\(38,39\)](#), its application is low cost and environmentally sustainable, improving the physicochemical and biological properties of the soil [\(5,11,17,21,31,40\)](#). Among the most relevant properties of biochar are its porous structure and its large specific surface area, which provide numerous active sites for the adsorption of heavy metals [\(41–43\)](#); in addition, it has a surface rich in oxygenated functional groups and a negative surface charge, which favors cation exchange between the material and heavy metals [\(31,41,44,45\)](#).

Biochar acts through various mechanisms that favor the retention and immobilization of heavy metals, among which physical adsorption, ion exchange, electrostatic interactions, complexation and precipitation stand out [\(41,45–48\)](#). Physical adsorption consists in the weak retention of metal ions on the surface of biochar, through Van der Waals forces [\(41,49,50\)](#). Ion exchange occurs when positively charged metal ions replace other cations attached to negatively charged functional groups on the surface of biochar [\(41\)](#). Electrostatic interactions occur due to the attraction between the negative charges of the biochar and the positive charges of the metal ions, which favors their attraction. Furthermore, complexation involves the formation of stable complex-type structures, through specific bonds between metal ions and functional groups (ligands) present in the material [\(41,51,52\)](#). Finally, precipitation refers to the formation of solid and insoluble compounds, as a result of chemical reactions between heavy metals and components of the solution or the biochar matrix, which contributes to their immobilization [\(41,52,53\)](#).

Precursors to obtain biochar

The efficiency of biochar as an amendment in soils contaminated with heavy metals is closely related to the physicochemical properties conferred by the raw material of origin (39,54). In this sense, the selection of the precursors used in their production is crucial, since it greatly influences their performance in immobilizing contaminants. The results of this review show the predominant use of agro-industrial waste as the main precursors in biochar production. Among the most common are rice husk, rice straw, wheat straw, corn straw and coconut husk (Fig. 4). These materials stand out for their availability and low cost, as well as their high fixed carbon content, which makes them sustainable and relatively inexpensive resources for biochar production.

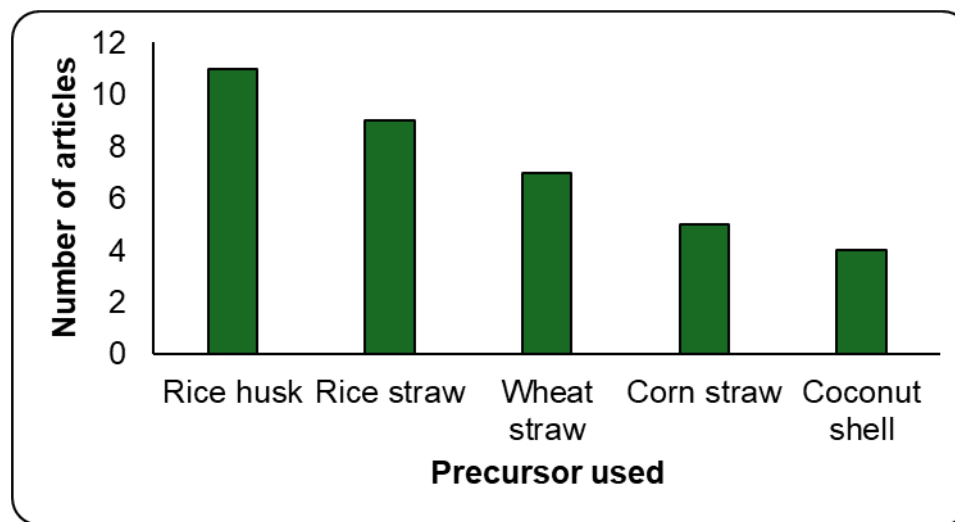


Figure 4. Frequency chart of mention of the different types of biochar precursors used. **Source:** Authors

A biochar that is effective in the adsorption and immobilization of heavy metals must have specific properties that are largely determined by the temperature used during the pyrolysis process, which directly influences the porosity and surface area of the resulting material (40). According to the consulted literature, pyrolysis conditions for obtaining biochars from the use of agro-industrial waste were reported, with temperatures ranging between 350 and 600 °C (Table 2).

Table 2. Use of agro-industrial waste for obtaining biochars implemented as Cd amendments and synthesis temperature conditions. NR: not reported.

| References | Precursor (Biomass used as the source of the biochar) | Temperature (°C) | Residence time | Heating rate |
|------------|---|---------------------------|----------------|--------------|
| (26) | Coconut shell | 800 °C | NR | NR |
| (55) | | 650 °C | NR | NR |
| (56) | Rice straw | 500 °C | NR | NR |
| (45) | | 550 °C | 2h | NR |
| (18) | | 600 °C | NR | NR |
| (57) | | 500 °C | 5h | NR |
| (23) | | 400 °C | 4h | NR |
| (58) | | 500 °C | 2h | NR |
| (59) | Rice husk | 500 °C | NR | NR |
| (60) | | 450 °C | 2h | NR |
| (61) | Corn straw | 400 °C | 2h | NR |
| (61) | | 400 °C | 2h | NR |
| (62) | Peanut shells | 500 °C | 6h | NR |
| (63) | Peanut straw | 400 °C | 3h | NR |
| (64) | Corn straw | 400 °C | 5h | NR |
| (22) | | 500 °C | 2h | 5 °C/min |
| (65) | | 500 °C | NR | NR |
| (44) | | 350–450 ° | 2h | NR |
| (61) | | 400 °C | 2h | NR |
| (19) | Orange peel | 600 °C | 6h | NR |
| (5) | Tobacco biochar | 500 °C | NR | NR |
| (66) | Tobacco straw | 500 °C | 2h | NR |
| | Mixed wood | | | |
| (67) | | 550–600 °C | 1h | NR |
| (68) | Wheat straw | 450 °C | NR | NR |
| (69) | | 450 °C | NR | NR |
| (42) | | 350 °C, 450 °C y 550°C | 2h | 3 °C/min |

Source: Authors

Among the agro-industrial residues used for the synthesis of biochars, rice husk was identified as the most frequently used precursor in the reviewed studies (Fig. 4); this agro-industrial residue proved to be particularly effective, due to its high silicon (Si) content, an element that facilitated the immobilization of Cd by forming insoluble complexes with this metal. Furthermore, the presence of Si in biochar increased the negative charge of its surface, improving the adsorption capacity (24,32,70–72); which decreases both Cd contamination and its bioaccumulation in the edible parts of plants (73). In this sense, Wang et al., (74), proposed the term “Sichar” to refer to biochars modified with Si.

Rice straw was the second most used precursor in the synthesis of biochars; this residue is generated in large quantities due to the extensive cultivation of rice worldwide, of which a world production for 2024 and 2025 was estimated at 543 million tons (75), making it an ideal raw material for the production of biochar (76). Studies have shown that precursors derived from the straw of certain crops can be especially effective in reducing the presence of divalent metals such as Cd²⁺, through processes such as ion exchange and complex formation (63). Its macroporous structure favors the retention of Cd, while the functional groups present on its surface, such as hydroxyls, carboxyls, phenols and aromatic compounds, play an important role in the chemical interactions that facilitate the immobilization of the metal (45).

The ability of biochar to reduce Cd mobility depends largely on the type of biomass used, so it is important to consider the potential risks associated with its selection (5,40). In particular, the source of the raw material can become a problematic factor, as some sources contain high levels of heavy metals, increasing their concentration instead of offering a mitigation alternative (40). Therefore, although biochar has great potential as a soil amendment, a rigorous evaluation of the raw material to be used is essential to ensure that its application is safe and effective in soil remediation.

Effect of biochar on the physicochemical properties of the soil

It has been shown that the application of biochar can modify soil properties such as pH, cation exchange capacity, electrical conductivity and the amount of organic matter (17,19,77,78), important properties in the recovery processes of degraded and contaminated soils (14,21,43).

Effect on soil pH

Soil pH tends to rise after application of biochar (Fig. 5); however, this variation depends on the alkalinity of the biochar and its application rate (25,78,79). In this regard, Awad et al., (17) evaluated the effectiveness of bamboo biochar, Paulownia and garden waste on the same type of soil, finding that the pH of the soil increased significantly when the concentration of biochar was raised, showing a greater variation after the application of biochar from garden waste. Likewise, Ibrahim et al., (62), determined the effects of biochar derived from rice husks, corn cobs and peanut shells, finding increases in soil pH up to 1.61 units, with corn cob biochar being the one that raised the pH the most. Similarly, it has been shown that the application of tobacco biochar along with other alkaline amendments such as Ca-bentonite, limestone and zeolite can significantly increase the pH of the soil (5).

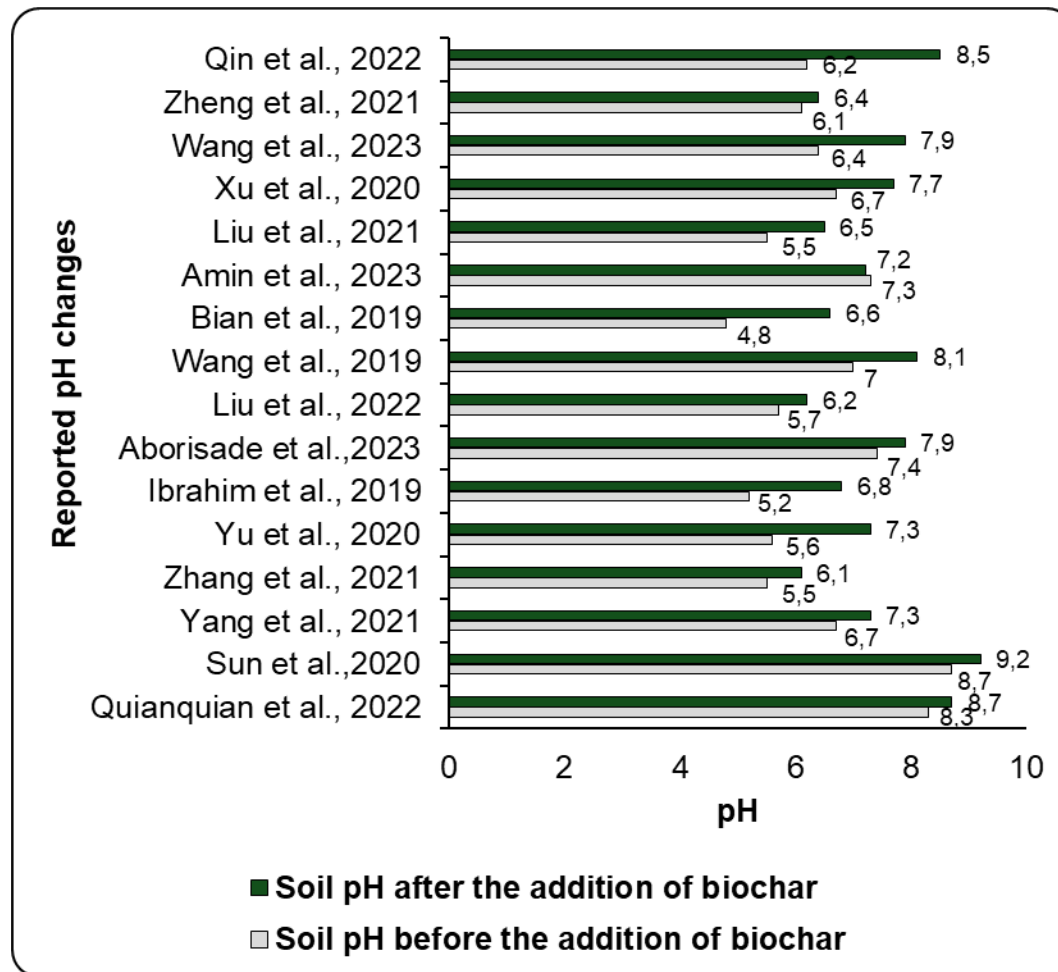


Figure 5 Effect of the use of biochars on the modification of soil pH. **Source:** Authors

It has been reported that when Brassica napus straw residue biochar is modified with manganese, soil pH values tend to be higher than when pristine biochar is applied (80). In contrast, Aborisade et al., (26) noted that pristine biochar produced from coconut shells had a more alkaline pH than biochar modified with zero-valent nanoscale iron. However, when considering the interaction of the soil with the modified material, it has been observed that the addition of zero-valent nano-iron can significantly increase the pH compared to a control soil. This effect is explained by the synergy between the intrinsic alkalinity of biochar and the generation of hydroxyl ions (OH⁻) during the oxidation of metallic iron, which leads to a higher concentration of basic species (26).

The increase in pH favors the formation of insoluble complexes with heavy metals such as Cd²⁺ and increases the number of available binding sites in the soil, which decreases the amount of bioavailable Cd (25,57,61,62,78,81). This effect is related to the ability of biochar to provide protons and negative charges that neutralize soil acidity, in addition to the presence of functional groups on its surface that retain metallic cations (17,82). Furthermore, increased pH can induce the precipitation and complexation of Cd, forming less mobile compounds such as CdCO₃ and Cd(OH)₂ (45,56,83). pH-facilitated hydrolysis of Cd²⁺ ions also contributes to the formation of less reactive phosphates, carbonates, and hydroxides (26).

Despite the known effects of biochar to increase pH levels in the soil, it has been reported that this variable can decrease over time, due to the depletion of the alkaline components provided by the biochar (56). Furthermore, surface saturation and decomposition of biochar reduces its capacity to retain heavy metals, while oxidation of its functional groups can decrease its alkalinity and even increase the availability of metals under certain conditions (5,79,84,85).

Predicting the decomposition period of biochar is complex due to the interaction of multiple variables that condition its loss rate (86). Its decrease in the soil may be related to the carbon content of the material, to leaching processes and to migration to deeper layers, as well as to decomposition mediated by the soil microbiota (87, 88,89,90,91). In this regard, it has been found that the carbon in biochar can be lost by about 2% through leaching, while the losses associated with vertical and horizontal transport range from 9–19% and 20–53%, respectively (92). It has also been reported that approximately 0.5% of the carbon derived from biochar is degraded annually by microbial action and that around 2.2% of the total biochar is degraded during the first two years after its incorporation into the soil (92). These losses are compounded by the effects of climatic factors that can accelerate their degradation, affecting both their yield and the recommended application rates in crops (87, 93).

Although it was initially estimated that its natural degradation occurred on a scale of 10^2 to 10^7 years, which supported its use as a long-term remediation strategy in contaminated soils (88,91), recent studies indicate that, five years after its application, the amount of biochar present in the surface layers of the soil can be reduced by up to 40% (89,91). Likewise, other studies have shown that the average residence time of biochar carbon in the soil is longer than that of other carbon sources and it has been found that about 3% of labile carbon degrades during the first year, while approximately 97% of recalcitrant carbon has an average residence time of 556 years (94).

In addition, it has been reported that the effectiveness of biochar on crop yield tends to decrease around the third growing season (96). In some cases, a reduction in the adsorption capacity of biochars obtained from rice husk has been observed, going from 5.56 mg g^{-1} to 3.68 mg g^{-1} , under controlled conditions (86). However, the use of biochars is considered effective for periods of 2 to 3 years and even longer, so it continues to be an effective strategy (88). Furthermore, it has been noted that its effectiveness can be maintained or even increased when additional doses are applied periodically (90,95).

Effect on cation exchange capacity of the soil

Biochar has been widely studied as an effective amendment that significantly increases cation exchange capacity of the soil (31,78). This increase provides more anchoring sites for cations, optimizing soil fertility by avoiding the leaching of essential nutrients, and reducing the mobility and toxicity of heavy metals through their sorption and retention in the soil matrix (82). In this regard, research conducted on soils irrigated with wastewater, treated with biochar from banana peels, reported a 58% increase in cation exchange capacity at depths below 0.1 m (81). Likewise, Almaroai and Eissa (31) found that corn stem biochar significantly increases cation exchange capacity compared to the control soil, observing a direct relationship between cation exchange capacity and the amount of biochar applied to the soil. These results are consistent with other

research showing that biochar induces improvements in cation exchange capacity compared to traditional organic amendments (96).

Effect on the electrical conductivity of the soil

Another relevant parameter in the evaluation of the impact of biochar on the modification of the physicochemical properties of the soil is electrical conductivity, which is related to the concentration of salts in the soil matrix (26,97). Low electrical conductivity in the soil can contribute to the availability of nutrients and reduce the osmotic potential, which favors plant growth (98). In general, it has been noted that the application of biochar reduces the levels of electrical conductivity in the soil, which is beneficial, since high levels of this parameter are associated with greater mobility and concentration of heavy metals (26). The reduction in soil electrical conductivity after the application of biochar is related to its negatively charged surface and its strong sorption capacity, particularly in soils with pH greater than 6 (99).

Liu et al., (22), evaluated biochar from different plant sources such as rice hulls, corn straw and *Pinus massoniana* wood chips, and observed that in all cases the electrical conductivity of the soil was reduced, with the lowest value in the biochar from wood chips. Awad et al., (72) found similar results in the application of biochar with rice husk and showed an inverse correlation between electrical conductivity and the dose of biochar applied to the soil. However, some studies have reported that the use of biochar from raw materials such as bamboo and garden waste can increase the electrical conductivity of the soil (17).

Effect on soil organic matter levels

Biochar can increase the organic matter content of the soil, by promoting the formation of stable structures and improving essential properties such as water and nutrient retention (5,17,68), not only because of its high carbon content, but also because its porous structure provides a suitable habitat for the growth of microorganisms that promote humus formation (17). Humus is mainly composed of humic and fulvic acids which are related to the bioavailability of heavy metals in the soil, since their extraction allows the evaluation of possible interactions between these metals and organic matter, which function as indicators of the presence of heavy metals (100). For example, mercury (Hg) is often found associated with both humic and fulvic acids; however, it is the latter that shows a greater tendency to release the metal, which favors its bioaccumulation in the soil (100). Additionally, opposite effects can occur in the dynamics of organic matter, since during its decomposition, organic acids are released that can cause a temporary decrease in soil pH (23) in parallel, the formation of humus as a product of the decomposition of organic compounds can also induce a decrease in pH levels (23).

According to Yu et al., (101), the increase in soil organic matter content is proportional to the amount of biochar used (derived from coffee grounds); however, in the same study, for *Wedelia trilobata* biochar, lower application rates showed more significant increases in soil organic matter. This phenomenon could be related to the release of carbon from biochar or to its more efficient use by microorganisms present in the soil (101). Therefore, higher amounts of biochar do not always guarantee a proportional increase in organic matter content (17,101).

Effect of biochar use on Cd levels in soil

Biochar is a highly effective amendment for reducing Cd levels in the soil, which is closely linked to its physicochemical properties; its porous structure, characterized by the abundance of micro and mesopores, provides a large specific surface with numerous adsorption sites for Cd²⁺ ions (97). The presence of oxygenated functional groups, such as carboxyls and phenols on the surface of biochar, allows the formation of stable complexes with Cd, reducing its mobility in the soil (64,82). The bioavailability of Cd in the soil is influenced by factors such as cation exchange capacity, organic matter content, pH, the presence of oxygenated functional groups and the composition of microbial communities (23,64).

The efficiency of biochar in the remediation of soils contaminated with Cd has been demonstrated in several studies. For example, Zhou et al., (57) reported that, after 28 days of treatment with biochar obtained from chestnut husk, the bioavailable fraction of Cd in a soil that was contaminated with 30 mg kg⁻¹, was reduced between 34.8% and 39.2%. Similarly, Chen et al., (77) observed decreases of up to 26.8% in the concentration of extractable Cd in soils dedicated to vegetable cultivation, with an initial concentration of 1 mg kg⁻¹, after a controlled contamination process. Furthermore, Rehman et al., (32) highlighted that, in soils intended for rice and wheat cultivation, contaminated in a controlled manner to reach an initial concentration of 50 mg kg⁻¹ of Cd, biochars made from rice husk reduced bioavailability by up to 69.01%, while those obtained from wheat straw and cotton stem reached decreases of 53.31% and 50.36%, respectively. These results surpassed the effectiveness of other organic amendments produced from the waste generated by pressing sugar cane (46.85%), farm manure (42.56%) and poultry manure (22.43%) (32). Aborisade et al., (26) reported that, in soils with an initial concentration of 2.43 ± 0.3 mg kg⁻¹ of Cd, the higher doses of biochar were more effective than the lower ones, achieving reductions of up to 56% in the bioavailable fraction. This effect is attributed to the increase of negatively charged ions on the surface of biochar, which facilitates electrostatic interactions and surface precipitation or complexation processes (26).

However, cadmium immobilization using biochars can vary significantly depending on soil pH, as this parameter regulates both the chemical form of the metal and the processes that determine its mobility (102). In acidic soils (pH <6.0), biochar usually increases the pH and thereby generates an increase in negative charges in minerals, hydrated oxides and organic matter, which favors the adsorption of Cd²⁺ and explains the marked decrease in the exchangeable fraction observed after the application of biochars (42, 62, 103). With increasing pH, Cd²⁺ can be hydrolyzed and form hydroxylated species with greater affinity for soil adsorption sites (25, 61, 103). Furthermore, a higher pH (>7.5) favors the precipitation of cadmium with anions such as OH⁻ and CO₃²⁻ in the form of poorly soluble hydroxides and carbonates, including CdO, CdCO₃ and Cd(OH)₂, which decreases its mobility and bioavailability (45, 83, 104). These physicochemical reactions make the immobilization of Cd more effective in acidic soils, while in slightly alkaline pH ranges the response is still positive, although less marked (102,103,104,105).

The ability of biochar to remediate Cd-contaminated soils can be optimized through chemical modifications; for example, biochar treated with cystamine has been shown to be up to six times more effective in adsorbing Cd than its unmodified form, since cystamine allows the formation

of a large number of disulfide bonds, amino groups and hydroxyls, which through complexation processes and electrostatic interactions can provide multiple binding sites for heavy metals on the surface of the biochar (24). The combination of biochar with compounds such as FeCl_3 or rock phosphate enhances its effectiveness, achieving significant reductions in the concentration of Cd in contaminated soils (78). In soils with an initial concentration of 1.28 mg kg^{-1} of Cd, the use of biochar derived from wheat straw combined with FeCl_3 in different weight proportions achieved reductions of 43.9%, 56.1% and up to 73.2%. This improvement is due to the fact that biochar favors the formation of amorphous iron compounds, such as oxides and hydroxides, which can bind to Cd through bonds with iron and manganese oxides, immobilizing it in the soil (78). Furthermore, in soils with initial concentrations of 8.3 ± 0.6 and $11.4 \pm 1.5 \text{ mg kg}^{-1}$ of Cd, the application of phosphate-rock-modified biochar achieved reductions of up to 73.8% when using material derived from poultry manure, and 68.7% when using biochar obtained from plant waste. These decreases are attributed to the increase in organic matter and the precipitation of metallic phosphates, which fix Cd and reduce its bioavailability (14). In this sense, the modifications applied to biochars increase the amount of active functional groups and raise their pH, which enhances their adsorption capacity and the stabilization of heavy metals (25).

Despite the advantages reported with the incorporation of biochars into the soil, it has been observed that their effectiveness decreases over time (56). The ability of biochar to retain Cd can be reduced by protonation of its surface, which favors desorption of the metal (18). As a result, previously immobilized Cd may be released gradually, compromising the effectiveness of the treatment and potentially turning biochar into a secondary source of pollution (56,106).

Conclusion

Cadmium is a highly toxic heavy metal whose accumulation in ecosystems, largely derived from anthropogenic sources, poses serious implications for environmental sustainability and human health. In this context, the development and application of mitigation strategies for the presence of this metal, based on the use of agro-industrial waste such as biochar, represent significant advances in reducing its levels in soils with agricultural potential. Biochar, obtained from organic waste, has proven to be effective in immobilizing Cd, reducing its bioavailability, and improving the physicochemical properties of the soil. Additionally, the selection of appropriate raw materials and the design of chemical modifications are important elements to optimize its performance in the remediation of contaminated soils. On the other hand, it is important to consider that the benefits of biochar can decrease over time due to the depletion of its alkaline components, the saturation of its surface and the oxidation of its functional groups, processes that can reduce its ability to retain Cd and even increase its mobility under specific conditions. Thus, although biochar is a valuable tool within the circular economy to mitigate Cd pollution, it is advisable to complement its application with assessments that allow ensuring and maintaining its performance under different conditions.

Credit authorship contribution statement

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Ethical implications: The authors have no ethical implications that should be declared in the writing and publication of this article.

Conflicts of Interest: The authors do not declare.

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