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Review

Biochar in the Bioremediation of Metal-Contaminated Soils

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Abstract: Biochar is produced from a wide variety of feedstocks (algal biomass, forest, agricultural and food residues, organic fraction of municipal waste, sewage sludge, manure) by thermochemical conversion. In general, it is a dark, porous material with a large surface area, low density, high cation exchange capacity, and alkaline pH. By reducing the content of harmful substances in the soil, the application of biochar increases the activity, number, and diversity of microorganisms and improves plant growth in contaminated areas. The aim of the review was to explore the advantages and drawbacks of biochar use in soil bioremediation. General issues such as methods of biochar production, its physical and chemical properties, and various applications are presented. As biochar is an efficient adsorbent of heavy metals, the review focused on its benefits in (I) soil bioremediation, (II) improvement of soil parameters, (III) reduction of metal toxicity and bioaccumulation, (IV) positive interaction with soil microorganisms and soil enzymatic activity, and (V) promotion of plant growth. On the other hand, the potential risks of biochar formulation and utilization were also discussed, mainly related to the presence of heavy metals in biochar, dust hazard, and greenhouse gases emission.

Keywords: biochar-treated soil; metal adsorption; metal bioavailability; soil microbiota; soil enzymes; stress mitigation

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1. Introduction

The word "biochar" comes from the Greek word "bios" meaning "life" and the word "char" meaning "made by biomass carbonization". Biochar is produced from residual organic materials (feedstock, raw material) at high temperatures and in the absence of oxygen or with a limited oxygen supply [1–6]. The production and use of biochar has recently become a widely analyzed topic. The large amount of organic waste produced is a problem, but processing it into biochar provides a final valuable product, as well as providing other benefits, such as green energy production, soil character improvement, or even systematic reduction of greenhouse gas concentrations, including carbon dioxide in the atmosphere [5]. Carbonization of organic raw materials makes it possible to obtain a solid fuel with better combustion properties than conventional fuels. Biochar is much more environmentally friendly than hard coal because it contains less pollutants (e.g., Hg) and ash residues (about 8% and 40%, respectively), but it has more carbon (about 70%) and a higher calorific value (about 30 and 16 MJ kg^{-1}, respectively). From a sustainable development perspective, it should be noted that the amount of CO_2 emitted into the atmosphere during combustion is equal to the amount of CO_2 absorbed from the atmosphere by the plants from which it originates [7,8].

Due to its stability, biochar can be used as an adsorbent. It has a high porosity, a large specific surface area with an abundance of functional groups, and can be used to remove pollutants from water and wastewater [9], as well as for the remediation of contaminated soils [10,11]. The effective binding of contaminants by biochar is achieved through several mechanisms, including complexation, ion exchange, electrostatic attraction, reduction, and precipitation. This significantly reduces the mobility, bioavailability, and toxicity of the contaminants to soil organisms. It also improves the physical, chemical, and biological properties of the soil (e.g., increases pH, regulates air-water relations, increases soil organic matter content), which indirectly influences the process of bioremediation and improves plant production. In addition, biochar can act as a carrier for specific microorganisms or enzymes, which can also accelerate the bioremediation process when applied to the soil [12,13]. Biochar has been shown to effectively bind pharmaceuticals [14,15], pesticides [16], nutrients [17], metals [18,19], and hydrocarbons [20]. To enhance the efficacy of biochar in bioremediation, different strategies of its modification are used. These include the functionalization of the surface functional groups through oxidation, sulfonation, amination, metal doping by impregnation with Cu, Fe, Ca, Mg, Mn, magnetization, steam activation, and biological modification [16,19,21,22]. In addition to these post-pyrolysis modifications, the in situ method can be used, where the modifying reagent is pyrolyzed together with the raw material [21].

Bioremediation is an environmentally friendly technology that is in line with the goals of sustainable development. Bioremediation is defined as actions aimed at removing or reducing the toxicity of pollutants introduced into the environment as a result of human activities. The aim of bioremediation is to restore soils and waters to their former utility values using biological processes catalyzed by bacteria, fungi, and plants [23–26]. Bioremediation techniques for contaminated soils are divided into two groups: ex situ or in situ. Though ex situ bioremediation involves additional costs due to the removal and transport of the contaminated soil to the treatment place (e.g., bioreactors, biopiles), it is a rapid process that can be easily monitored. The bioremediation of the metal-contaminated soil using this method is primarily based on microbiological leaching of contaminants [27,28]. On the other hand, in situ bioremediation is generally less expensive than ex situ bioremediation and is applied to large, contaminated areas. This technique focuses on stimulating microbial activity through bioventing and nutrient putting, bioaugmentation, or phytoremediation [23,25,26,28]. In situ bioremediation can also be supported by the use of mineral (e.g., clays, zeolites, lime) or organic (e.g., compost, manure, biochar) amendments [29]. The combination of biochar and microorganisms is proving to be a very promising solution for the bioremediation of metal-contaminated soils. Biochar and microorganisms stimulate mechanisms that modify the toxicity, mobility and bioavailability of metals in the soil, such as surface adsorption, complexation, and precipitation [26,30,31]. Furthermore, live and metabolically active microorganisms can also accumulate metals intracellularly [28]. Both biochar and microorganisms have positive effects on plant growth, so they can support phytoremediation and restoration of plant cover in degraded areas [30,31].

The purpose of the review was to explore the positive and negative aspects of biochar use in the industry. General concerns such as methods of biochar production, its physical and chemical properties, and its various applications were discussed. As biochar is an efficient adsorbent of heavy metals, the review focused on its benefits in (I) soil bioremediation, (II) improvement of soil parameters, (III) reduction of metal toxicity (by decreasing their mobility and bioavailability) and bioaccumulation, (IV) positive interaction with soil microorganisms (through soil enzymatic activity), and finally (V) promotion of plant growth and development (by reducing stress levels). The risks of biochar are also presented, which are mainly related to the potential presence of heavy metals in biochar, dust hazards, and greenhouse gases emissions.

2. Production, General Characteristics and Potential Applications of Biochar

Several thermochemical conversion technologies are used to produce biochar (Table 1). The choice of technology depends on the dominant product to be obtained (biochar, bio-oil, or syngas). The quality and subsequent application of biochar is influenced by the degree of biomass fragmentation and the initial carbon and moisture content. In general, biomass to be subjected to pyrolysis, gasification, or flash carbonization needs to be dried at about 70 °C for a few hours to achieve moisture < 10%, while hydrothermal carbonization can be used for high-moisture biological materials. Pyrolysis is the basic method for production of biochar. It is carried out at high temperatures in the absence of O_2 or with minimal O_2 supply and at atmospheric or elevated pressure, even up to 10 MPa [1,3,5,6]. The modification of the retention time and temperature of the pyrolysis leads to an increase in the final product parameters, including pH, specific surface area, cation sorption capacity, porosity, and calorific value, thus elevating its potential for future applications [8,10–12,32–38].

Table 1. Technologies, reaction conditions, and main products of the thermochemical conversion of organic feedstocks.

Technology	Conditions	Products
Slow pyrolysis	Slow burning process in absence of O_2 or under a limited O_2 supply at 300–700 °C for about 5–6 h at a heating rate of less than 30 °C min^{-1}; the feedstock must be heated [2–6]	biochar—35% bio-oil—30% syngas—35%
Intermediate pyrolysis	Moderate burning process at 300–500 °C for about 1–15 min at a 1–10 °C s^{-1} heating rate in the O_2 free atmosphere [3,6,21]	biochar—20% bio-oil—50% syngas—30%
Fast pyrolysis	Fast burning process in absence of oxygen at 600–1000 °C for about 1–2 s at a 600–1000 °C s^{-1} heating rate in inert atmosphere (N_2); the feedstock with low moisture content (<10%) [2,3,5,6,21]	biochar—12% bio-oil—75% syngas—13%
Torrefaction	Mild pyrolysis at 200–300 °C for 10–180 min at a heating rate of less than 50 °C min^{-1} under atmospheric pressure in inert atmosphere (N_2) [3,6]	charcoal—70% syngas—30%
Microwave pyrolysis	Burning process at 350–650 °C for 1–60 min at a 25–50 °C min^{-1} heating rate; microwaves radiation penetrates the entire volume of the feedstock and generates a rapid and homogeneous temperature increase throughout the reactor [6,21]	biochar—15–80% bio-oil—8–70% syngas—12–60%
Gasification	Short burning process at 600–1500 °C for about 10–20 s at a 50–100 °C s^{-1} heating rate and oxygen-limited conditions; includes 5 steps: drying, pyrolysis, oxidation, reduction and cracking [2,3,21]	biochar—10% bio-oil—5% syngas—85%
Flash carbonization	Partial burning process at 300–600 °C for less than 30 min at a very fast heating rate in a pressurized reactor (1–2 MPa) under air supply [6,21]	charcoal—50% syngas—50%
Hydrothermal carbonization	Conversion of feedstock with high moisture content at 100–300 °C for 1–16 h at a 5–10 °C min^{-1} heating rate and elevated pressure (2–10 MPa) [2,3,21]	biochar—75% bio-oil—20% syngas—5%

Despite the fact that biochar is produced from a wide variety of organic feedstocks (e.g., algal biomass, forest, agricultural and food residues, organic fraction of municipal waste, sewage sludge, manure), it is generally a dark, porous material (pore volume 0.01–0.19 cm^3 g^{-1}) with a large surface area (1–1331 m^2 g^{-1}), a high cation exchange capacity (15–386 cmol(+) kg^{-1}), a large number of different functional groups (e.g., –OH, –COOH, –CH_2– and aromatic C=C), and an alkaline pH (7.3–12.5) [3,5,6,10–12,18,19,32,35,37,39–42]. The choice of feedstock and biochar production technology not only influence the final properties of the biochar, but also determine its potential applications (Figure 1). For example, biochar containing heavy metals (e.g., Hg, Pb, Cd) cannot be used in the production of biofertilizers (e.g., as a carrier material for microorganisms) or soil conditioners, while biochar with a high ash content and a high specific surface area should be used as sorbents in the decontamination and neutralization of pollutants, rather than for combustion and energy production [8,10–12,32–38].

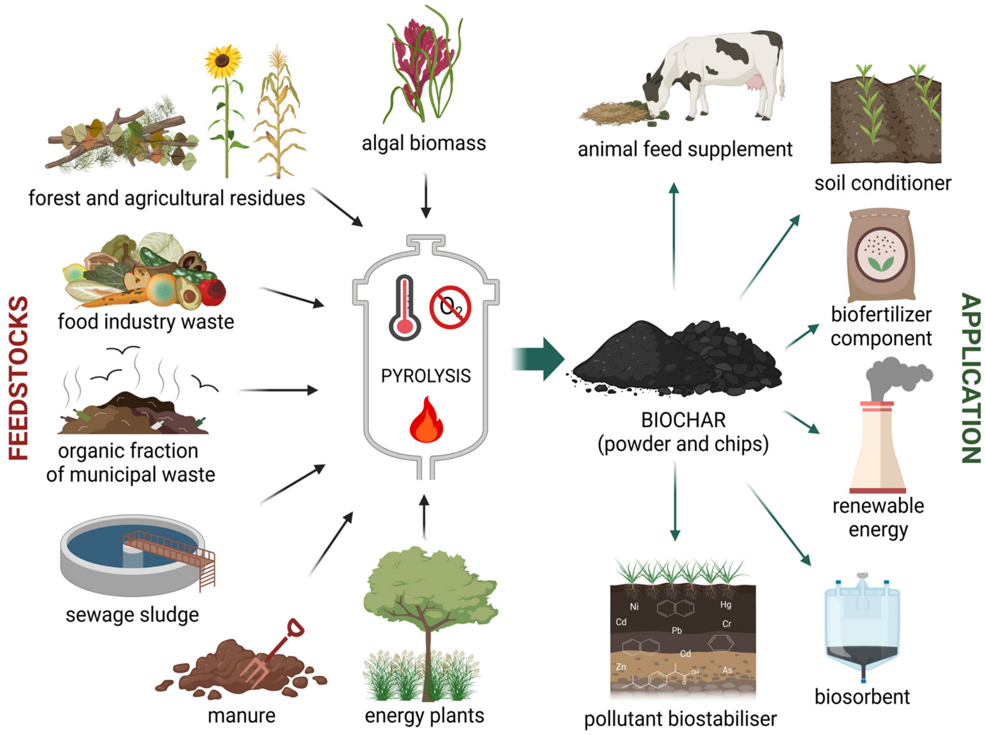

Figure 1. Feedstocks used to produce biochar and its potential applications [8,10–12,32–38]. Created in https://BioRender.com (accessed on 15 January 2025).

Sobik-Szołtysek et al. [37] produced biochar from poultry manure by pyrolysis in a nitrogen atmosphere at different temperatures (425 and 725 °C) and with a resident time of 60 min. The elevation of temperature increase resulted in a reduction in biochar yield from 53% to 40%, but it had no effect on the carbon content of the obtained product (average 37% C). The reduction in biochar yield resulting from the accelerated release of gaseous volatiles is also observed when the heating rate is increased [6]. On the other hand, a significant positive relationship was found between the increase in temperature (from 425 to 725 °C) and the enhancement in pH (from 10.4 to 12.4), the specific surface area (from 12 to 19 m^2 g^{-1}), and exchangeable cation capacity (increased up to 10 times) [37]. In addition to temperature, the resident time also had a significant effect on biochar properties. Saletnik et al. [8] demonstrated that a simultaneous increase in temperature by 100 °C and an increase in thermal processing time from 5 to 15 min resulted in a significant increase in carbon content and calorific value of biochar. The amount of potential ash produced after combustion is also an important characteristic of biochar, which depends significantly on the type of biological material employed. A comparison of biochar produced from wood wastes such as pine, willow, and miscanthus biomass [32], as well as apple, cherry, and pear branches [8], showed that they had a markedly lower ash content (from 4.9% to 9.4%) than biochar produced from poultry manure, which contained 52.07% to 78.38% of ash [37].

Man et al. [38] described the benefits of incorporating biochar to the diets of ruminants, pigs, poultry, and fish. They found that biochar plays an important role in animal farming, as it supports the functioning of the digestive system, immunity, absorption, and neutralization of toxins of intestinal pathogens. Additionally, it has been demonstrated to reduce methane production by ruminants. It should be emphasized that for this purpose, biochar must be produced from high-quality organic feedstock, such as natural and untreated wood, leaves, roots, bark, and branches. The raw material cannot contain any organic or non-organic pollutants, and production must follow appropriate standards and sustainable forest management practices [38].

3. Biochar as the Adsorbent of Metals

One of the many properties of biochar is its ability to adsorb a range of ions and molecules with varying degrees of efficiency, which is dependent on the total sorption capacity and the energy of the adsorption sites [43]. Adsorption is a surface phenomenon that is created by electrostatic interactions, van der Waals forces, and chemical reactions. Therefore, there are generally four types of adsorption: ion exchange and physical, chemical, and mechanical (pore filling) adsorption (Table 2). In the Langmuir model of adsorption, the adsorbent can be covered with only one layer of adsorbate, and the adsorption sites with the highest energy are the first to be saturated, with no interactions between the adsorbed molecules. For example, the Cd adsorption on iron and manganese oxide-coated biochar can be represented by this model [44]. In contrast, the Freundlich model assumes a multilayer model, where each molecule of the first layer becomes an adsorption site for the next one, but the layer density decreases with increasing distance from the adsorbent surface. The adsorption of Cd on the iron oxide-containing magnetic biochar was exactly in accordance with this model [45]. As a porous material, biochar exhibits a very large specific surface area, with values ranging from 1–2 $m^2\ g^{-1}$ [10] to 1331 $m^2\ g^{-1}$ [42] depending on the feedstock [32] and the pyrolysis conditions [37]. Li et al. [42] observed that the internal pore surface area of biochar particles was significantly larger (932 $m^2\ g^{-1}$) than their external surface area (427 $m^2\ g^{-1}$). It can contain both pyrolyzed and unpyrolyzed material, which can also increase its adsorption capacity [18]. This diversity allows for metal immobilization through non-specific or specific metal sorption at the physical and chemical levels. It is important to note that all four types of adsorption can occur simultaneously.

Biochar is currently being studied as an adsorbent material due to its high specific surface area, stability, potential for easy regeneration, and capacity for permanent capture of CO_2 bound by plant biomass [9,18,19]. Biochar can bind metals through its abundant surface oxygen-containing functional groups. The negatively charged surface of the biochar allows for the rapid adsorption of the positively charged metal ions, and electrostatic interactions can be inferred as one of the mechanisms of metal adsorption [9,19,46]. Oxygen-containing groups (e.g., –OH and –COOH) also attract cations that are effectively immobilized by complexation or proton exchange [18,19]. For example, the adsorption of Cu [47] and Cd [45] was predominantly facilitated by the dissociated carboxyl and phenolic hydroxyl groups. Manori et al. [11] indicated that in addition to carboxyl and hydroxyl groups, $–CH_2–$ groups are also involved in Cd adsorption. Metal complexation can occur through specific interaction with other organic and inorganic ligands derived from unpyrolyzed organic matter [18]. In addition, π-π interactions may also occur in the sorption process. The presence of aromatic C=C in biochar can provide an electron

π donor, thereby enabling metal-π interactions [44]. Furthermore, Li et al. [19] observed coordination between Cd and the electrons provided by the aromatic structure. However, this mechanism was found to be less important than the observed complexation and ion exchange on the magnetic biochar surface.

Table 2. Types of adsorption on porous materials.

Ion exchange adsorption	The ions of the adsorbate concentrate on the active sites on the external surface of the adsorbent and/or in its pores (internal surface). The cations present in this site are exchanged for adsorbate cations in equivalent amounts [43,44,46,48–51].
Chemisorption	The ions of the adsorbate form the bonds with the functional groups of the surface adsorbent. It is an irreversible or hardly reversible process. It involves the formation of insoluble salts on the adsorbent or surface complexation [43,44,46,48–51].
Physisorption	It is the result of nonspecific Van der Waals' forces without transfer of electrons between ions. It is an easily reversible process. Only molecules that have not dissociated are subject to this sorption [43,44,46,48–51].
Mechanical (sieve) adsorption	It depends on the degree of porosity and the ability to trap molecules in the pores (pore filling). The porous material acts like a sieve, retaining larger molecules and allowing smaller ones to pass through [18,51,52].

The phenomenon of precipitation describes the formation of insoluble salts on the biochar surface. These can be attributed to the reaction of metal cations with carbonate and phosphate anions present in biochar [18], as well as the co-precipitation of metals during redox reactions and conversion of soluble Fe and Mn to insoluble oxides and hydroxides [44]. Fe and Mn added to the biochar at the time of modification are mainly oxidized, thus diversifying the adsorption mechanisms. The sorption of toxic metals by biochar modified by the addition of various salt solutions and increased the importance of the exchange of e.g., Mg, K, Ca for toxic metal [44]. It cannot be excluded that cations of some metals are exchanged for others. It should be recognized that metal adsorption by biochar is a complex process that is controlled by chemical, physical, and ion exchange adsorption. Sometimes, as in the case of magnetic biochar, diffusion into pores may be less important due to the presence of Fe and Mn oxide particles on the surface [19]. The adsorption equilibrium is reached within a relatively short time, with the maximum effect being achieved after approximately 30–60 min [44]. Therefore, biochar has the potential to enhance the efficacy of current methods for the removal of metallic contaminants from water and wastewater while simultaneously reducing their costs.

4. Biochar in Soil Bioremediation

Soil contamination with metals (e.g., Zn, Mn, Pb, Hg, Cu, Ni, Sr, Ba, Cd, Co, Mo) is a serious environmental problem due to the prolonged persistence of these elements in the soil [53–55]. Metals can be found in different forms in the soil environment due to their high capacity to develop sparingly soluble oxides or salts, to adsorb on the surface of mineral components, and to bind to organic acids and humic substances [56]. Regardless of their form in the soil, heavy metals cause soil degradation and lead to changes in soil pH and biochemical properties. They disrupt the metabolism of microorganisms, thereby inhibiting their growth and development. In turn, limitation of the activity of rhizosphere microorganisms is an important factor that inhibits plant development and reduces their resistance to pathogens [54,57]. In plant cells, Cd binds to sulfhydryl groups of enzymes, reducing the synthesis of anthocyanins and chlorophyll [11]. This metal has been observed to cause damage to roots and leaves, resulting in chlorosis and browning of leaf margins [53]. The reduction of the phytoavailability of toxic metals and all processes leading to the removal of the excess of these elements from the environment are very important for limitation of their concentration in agricultural crops and the production of healthy food. In such cases, bioremediation supported by physicochemical stabilization is considered to be a relatively inexpensive and quite effective method of cleaning the metal-contaminated soils [58]. Bioremediation is a promising "green technology", the effectiveness of which is determined by interactions between soil, pollutants, microorganisms, and plants [59]. This environmentally friendly technology has been divided into two main branches due to the type of processes involved: (1) metal extraction, based on metals mobilization and leaching from the soil, and (2) metal stabilization, transforming metals into an insoluble form and excluding them from the soil solution [25].

4.1. Improvement of Soil Parameters

All organic amendments, including manure, compost, and biochar, improve soil quality by modifying its physical and chemical properties. Biochar application increases pH, soil organic matter content, and cation exchange capacity, enhances nutrient retention, and reduces the toxicity, mobility, and bioavailability of metals, metalloids, and radionuclides [33,59,60].

Due to its alkaline properties (pH from 7.4 to 12.5), biochar significantly elevates soil pH [10,33,36,37,61]. The increase in soil pH depends on the pH of the biochar itself and the amount of biochar added to the soil. Manori et al. [11] found that the application of pine needle biochar with pH of 9.88 in the amount of 200 mg kg^{-1} increased soil pH from 7.67 to 7.90, while 100 mg kg^{-1} increased pH only to 7.79. However, the application of wheat straw biochar (pH 9.86) to the acidic soil (pH 4.87) resulted in an increase of pH by 0.58 units regardless the dose (5% or 10% higher) [34]. In the mildly acidic soil with pH 5.0, the addition of 3% barley straw biochar increased pH by only 0.33 units [35]. The increase in pH following the addition of willow biochar (pH 10.2) was also noticeable in the alkaline soils. The initial soil pH (8.7) was significantly increased by 1.0–1.3 units after the addition of 3% biochar [61]. Increasing pH is particularly important in soils contaminated with metals, as it significantly reduces their solubility, mobility, and bioavailability. It is one of the most important factors in the stabilization of metals in the soil.

As expected, the total organic carbon content was significantly increased following the biochar application to the soil [34,60,62,63]. Howell et al. [59] found an increase in organic carbon content proportional to the dose of 5 and 10% jarrah wood biochar (0.57% and 0.74%, respectively) compared to the control soil (0.31%). Consequently, the total organic carbon content in the soil was more than doubled with the application of 10% biochar. Similarly, the organic carbon content was increased from 0.79% in the control to 1.10% and 1.37% when 1% and 2% biochar were added to the soil, respectively [33]. The application of low levels of biochar (100–200 mg kg^{-1}) did not change the total organic carbon content when compared to the control soil without biochar [11].

Additionally, biochars, due to their composition, can serve as a source of elements such as N, P, K, Ca, Mg, etc., thereby enhancing their abundance in the soil. For example, maize straw biochar containing 0.75% N and 0.45% P significantly increased the levels of these nutrients in the soil. In proportion to the amount of biochar added (1% or 2%), soil P and N contents were increased when compared to soil not supplemented with biochar [33]. Radziemska et al. [61] showed that the application of 3% willow biochar improved soil fertility, resulting in the increase of N, P, Ca, Mg, and K. After application of jarrah wood biochar, the soil P, S, K, and Mn levels were significantly increased [59]. The increased release of cations from biochar into the soil solution is the reason for an increase in soil electrical conductivity [33]. Therefore, this parameter can be used to describe the potential bioavailability of microelements or toxic metals.

The meta-analysis performed by Singh et al. [64] demonstrated that the cation exchange capacity was closely related to the amount of biochar added to the soil regardless the source material. The addition of biochar to the soil has been shown to increase the cation exchange capacity from 19% up to 41% [64]. However, there are reports showing that this soil parameter did not change significantly despite the addition of 2% [60], 5%, or 10% biochar [34].

4.2. Modification of the Metal Mobility and Bioavailability

Generally, soil supplementation with biochar is used to reduce the toxicity of metals by decreasing their mobility and bioavailability. Biochar can increase the sorption capacity of the soil, thereby improving metal immobilization and subsequently slowing metal uptake by plants [9,18,46]. Soil sorption capacity is the maximum amount of ions that can be adsorbed by a specific soil mass. It depends primarily on the quantity and quality of inorganic (e.g., montmorillonite, illite, kaolinite) and organic (e.g., humic and fulvic acids) components of the soil solid phase that have a negatively charged surface. The sorption capacity of the soil is greater when it contains more of these particles [55,65]. For this reason, biochar utilization can be a good natural resource for improving soil adsorption properties. Saleem et al. [33] found that the immobilization of Cd, Cr, and Pb in the soil was significantly increased and their bioavailability significantly reduced when biochar was applied at 1% and 2% concentrations. These observed changes were proportional to the amount of biochar supplemented and greater than after application of the same amount of compost or manure. This phenomenon was explained by the alkaline nature of biochar and its high sorption capacity, which enhanced metal binding and opened the possibility of its use in soil remediation [33].

The amount of metal taken up by a definite plant species, i.e., the bioavailable metal, is influenced by the type of metal, its concentration, and its chemical speciation in the soil. Seven operationally defined geochemical fractions of metals are described according to the strength of their binding to the soil constituents: (1) a mobile fraction containing soluble and non-specifically adsorbed metal, as well as organometallic complexes, (2) a readily mobilized fraction containing metal specifically adsorbed to the particle surface and bound to carbonates, (3) occluded in Mn oxides, (4) bound to soil organic matter, (5) occluded in amorphous Fe oxides, (6) occluded in crystalline Fe oxides, and (7) structurally bound in soil minerals [66–68]. However, the European Community Bureau of Reference recommends the four-sequence extraction method (Table 3).

Table 3. European Community Bureau of Reference (BCR) procedure of sequential extraction of soil [34,41,61,66,69,70].

Fractions	Extractants	Conditions
Mobile/Bioavailable exchangeable and acid-soluble	40 mL of 0.11 M CH_3COOH	shaking at room temperature for 16 h
Reducible bound to Fe and Mn oxides	40 mL of 0.5 M $NH_2OH{\cdot}HCl$	shaking at room temperature for 16 h
Oxidizable bound to soil organic matter	step 1: 10 mL of 30% H_2O_2 step 2: 50 mL 1 M CH_3COONH_4 pH 2	step 1: digestion at 85 °C for 1 h step 2: shaking for 16 h
Residual stable fraction	aqua regia: 7.5 mL 37% HCl and 2.5 mL 70% HNO_3	digestion for 2 h

The application of biochar to the contaminated soil significantly altered the chemical speciation of metals, consequently influencing its potential bioavailability. The sequential extraction performed by Liu et al. [42] showed that Cd added to the soil as $Cd(NO_3)_2$ after 90 days of growth of *Brassica chinensis* L. was predominantly present (exceeding 90%) in the most mobile fractions, i.e., exchangeable and carbonate fractions. Following the same period in the wheat straw biochar supplemented soil, Cd was transferred to the fractions with higher stability, i.e., Fe/Mn oxide and organic, as well as to the residual fraction considered to be the most stable. These observations reinforce the hypothesis that the added biochar enriches the solid phase of the soil, increases the sorption capacity of the soil, and thereby controls the mobility and bioavailability of metals [42].

Medyńska-Juraszek et al. [34] proved that the addition of wheat straw biochar caused an alteration in the distribution of metals (Cd, Cr, Cu, Ni, Pb, Zn) in the contaminated soil from the cooper smelter area [34]. The application of this type of organic material significantly decreased the content of Cd and Pb in the bioavailable fraction. The shift of Cd from the bioavailable, reducible, and oxidizable fractions to the residual fraction resulted in its stabilization [34]. Pb was mainly immobilized by organic matter and Fe and Mn oxides. In contrast, the bioavailability of Cu and Zn was enhanced after biochar supplementation. A significant decrease in Cu and Zn contents was observed in the residual and oxidizable fractions. Biochar had no effect on the chemical speciation of Cr and Ni. The distribution of these elements remained consistent regardless of the introduction of biochar into the soil [34]. In the soil phytostabilized by *Lolium perenne* L. and supplemented with willow biochar, the distribution of metals (As, Cr, Cu, Hg, Pb, and Zn) was significantly changed compared to the soil without biochar [61]. In the experiment conducted by Radziemska et al. [61], more than 50% of Cr and Hg and more than 40% of As were stabilized in the residual fraction. Zn and Pb were generally stabilized in the reducible fraction, more than 30% and 50%, respectively. On the other hand, Cu and Zn were stabilized in the residual and reducible fractions. In general, the tendency to reduce the content of Zn, Pb, Cr, and Hg in the bioavailable fraction was observed after the addition of biochar to the soil. Radziemska et al. [61] calculated the stability of the tested metals using the reduced partitioning index. The results indicated that Hg, Cr, Pb, and Zn were more stabilized in the biochar supplemented soil than in the control without biochar. As can be seen from the aforementioned examples, the efficacy of metal stabilization and its chemical speciation in the soil after biochar addition depends on the metal and the age of contamination. The newly introduced Cd in the form of a dissolved salt [42] was stabilized more quickly and easily than metals that entered the soil as industrial contaminants [34,61]. Furthermore, the distribution between the fractions of sequential extraction may be unpredictable in the soils with multimetalic and long-term contaminations.

Bioavailability of metals is regulated by physical, chemical, and biological processes occurring within the soil. However, an increase in the total content of metal in the soil does not always correlate with an increase in its availability to plants. If the majority of the metal is present in poorly mobile forms, it can be assumed that the possibility of its leaching or uptake by plants will be limited. Regardless of whether we consider the accumulation of metals in plants as an undesirable phenomenon (entry into the food chain) or as a desirable phytoremediation, bioavailability and plant uptake capacity may be the most important and least understood factors. The concentration of bioavailable metals in the soil solution is the result of a continuous process of adsorption and desorption, which in turn is controlled by the size of the soil sorption surface.

4.3. Modification of the Metal Bioaccumulation

Metal concentration in the plant biomass increases with the increase of this metal concentration in the growth medium [68] within the tolerance range of the plant and is usually higher in the root than in the shoot for phytostabilizing plants; this situation is reversed for phytoextracting plants [29]. By using different types of extractants, it is possible to determine the potential bioavailability of the metal, but the actual bioavailability can only be determined by analyzing the metal accumulated in the plant. Bioaccumulation can be expressed directly as the amount of metal per mass unit of the plant (e.g., roots, stems, leaves, seeds) or indirectly as the bioaccumulation (BAF) and translocation (TRL) factors [34,68,71,72]. BAF (Equation (1)) describes metal uptake as a function of the amount of metal present in the soil, and its value decreases with increasing metal concentration in the soil. On the other hand, TRL (Equation (2)) is an indicator of metal transfer from the roots to shoots or, more precisely, to individual plant organs [63,72]. The BAF and TRL factors have been developed to estimate the progress of phytoremediation, e.g., the efficiency of metal accumulation efficiency in above-ground plant parts or the effectiveness of metal accumulation in edible plant organs, as values useful in predicting health risks (Table 4).

$$\mathrm{BAF} = \frac{\text{plant metal concentration } [\mathrm{mg \cdot kg^{-1}}]}{\text{soil metal concentration } [\mathrm{mg \cdot kg^{-1}}]} \tag{1}$$

$$\mathrm{TRL} = \frac{\text{metal in shoots } [\mathrm{mg \cdot kg^{-1}}]}{\text{metal in roots } [\mathrm{mg \cdot kg^{-1}}]} \tag{2}$$

Table 4. Type of biochar, its properties, and its effect on the Cd bioaccumulation factor (BAF) in plant shoots. SSA—specific surface area; CEC—cation exchange capacity; EC—electrical conductivity; TPV—total pore volume; – no data.

Feedstock	Pyrolysis	Biochar Properties		Cd in Soil	Plant	Biochar in Soil	BAF	Ref.
Wheat straw	550 °C, 30 s	pH SSA CEC	9.86 239 m^2 g^{-1} 63 cmol(+) kg^{-1}	6.2 mg kg^{-1}	*Raphanus sativum* L.	0 5% 10%	0.80 0.38 0.17	[34]
Wheat straw	550 °C, 30 s	pH SSA CEC	9.86 239 m^2 g^{-1} 63 cmol(+) kg^{-1}	6.2 mg kg^{-1}	*Spinacia oleracea* L.	0 5% 10%	0.62 0.37 0.35	[34]
Wheat straw	550 °C, 30 s	pH SSA CEC	9.86 239 m^2 g^{-1} 63 cmol(+) kg^{-1}	6.2 mg kg^{-1}	*Lactuca sativa* L.	0 5% 10%	0.73 0.91 0.81	[34]
Pine needles	500 °C, 3 h	pH SSA EC	9.88 124 m^2 g^{-1} 5.82 µS cm^{-1}	20 mg kg^{-1}	*Bidens pilosa* L.	0 0.01% 0.02%	3.46 5.14 4.72	[11]
Rice straw	600 °C, 1 h	pH SSA CEC TPV	10.2 82 m^2 g^{-1} 45 cmol(+) kg^{-1} 0.08 cm^3 g^{-1}	50 mg kg^{-1}	*Brassica chinensis* L.	0 0.5% 1.0% 2.5% 5.0%	0.83 0.83 0.63 0.59 0.49	[40]
Bamboo chips	600 °C, 1 h	pH SSA CEC TPV	9.80 190 m^2 g^{-1} 15 cmol(+) kg^{-1} 0.17 cm^3 g^{-1}	50 mg kg^{-1}	*Brassica chinensis* L.	0 0.5% 1.0% 2.5% 5.0%	0.83 0.71 0.60 0.54 0.41	[40]
Bamboo residues	400 °C, –	pH EC CEC	9.16 3.24 µS cm^{-1} 56 cmol(+) kg^{-1}	50 mg kg^{-1}	*Brassica rapa* L.	0 0.5% 1.0% 1.5%	1.29 0.99 0.71 0.49	[41]
Bamboo residues	400 °C, –	pH EC CEC	9.16 3.24 µS cm^{-1} 56 cmol(+) kg^{-1}	50 mg kg^{-1}	*Zea mays* L.	0 0.5% 1.0% 1.5%	0.77 0.57 0.48 0.33	[41]

Organic fertilization of the contaminated soil has a very positive effect on its parameters, on micro- and macro-elements content, and on plant growth. Many researchers are considering the possibility of using biochar as an environmentally friendly soil amendment. The addition of biochar resulted in a significant reduction in the concentration of Cd, Cr, and Pb in the maize roots and shoots in proportion to the amount of biochar (1% or 2%) added to the soil, as found by Saleem et al. [33]. Similarly, *B. chinensis* L. grown in the freshly Cd contaminated soil (10 mg kg^{-1}) accumulated proportionally lower amounts of this metal in the leaves and roots with the increasing application of wheat straw biochar. The reduction in Cd uptake between plants growing in untreated and biochar-treated (1%) soils reached 95% and 86% for the roots and shoots, respectively [42].

Radziemska et al. [61] showed that toxic metals were available to *L. perenne* L. despite the soil supplementation with biochar. The application of 3% willow biochar positively affected the growth of this grass, which efficiently took up Cr, Cu, Pb, and Zn from the industrially contaminated soil, significantly increasing their concentration in the roots and decreasing in the soil compared to the treatments without biochar. Interestingly, this supplementation with biochar did not change the concentrations of Hg and As in the soil or in the grass roots and shoots, even in relation to the control plants growing in the unenriched soil. Radziemska et al. [61] explained this through the greater affinity of these elements to the active sites of biochar than to the plant roots. Even small amounts of biochar, such as 100 or 200 mg kg^{-1}, modified the Cd uptake by *Bidens pilosa* L. Manori et al. [11] showed that the Cd bioconcentration factors in the roots and shoots were significantly higher when plants were grown in soil supplemented with biochar than without. However, translocation from the roots to shoots was lower when the biochar dose was increased. The efficiency of metal accumulation depends not only on the amount of biochar added to the soil, but also on the plant species and the type of metal. This was demonstrated by Medyńska-Juraszek et al. [34], who tested the bioaccumulation of Cd, Cr, Cu, Ni, Pb, and Zn by common vegetables (dill, lettuce, parsley, radish, and spinach). In general, wheat straw biochar dose-proportionally reduced the bioaccumulation coefficient values of Cd, Cu, Pb, and Zn in radish leaves, Cd, Pb, and Zn in spinach, Cd, Cr, Cu, Ni, and Pb in parsley, and Cu, Pb, and Zn in lettuce. It improved the effect of bioaccumulation of Ni and Cr in dill, spinach, and radish leaves [34]. Interesting reports by Zhu et al. [72] indicate that biochar (3%) did not significantly affect Cd translocation from the soil to the roots of cotton bushes grown in the soil contaminated with Cd (1, 2, and 4 mg kg^{-1}). However, reduced Cd translocation from the roots to the stems and increased translocation from the stems to the leaves was observed. These changes in Cd translocation correlated strongly and positively with the dominance of bacteria such as Actinobacteria, α-Proteobacteria, γ-Proteobacteria, Bacteroidia, Bacilli, Chloroflexia, and Gemmatimonadetes.

Therefore, in phytoremediation procedures, as well as in analyses of metal toxicity to plants, it is necessary to take into account the plant root exudates, which modulate the physical, chemical, and microbiological properties of the rhizosphere (soil under the direct influence of roots), significantly altering the bioavailability of metals and even their biogeochemical properties. The quality and quantity of the root exudates is related to plant species, growth stage, weather conditions, etc., thus the extent and trend of changes that may occur in the root sphere can be difficult to predict [73]. Depending on the final effect to be achieved (phytostabilization/phytoextraction), consideration should also be given to appropriate support for plant growth in the contaminated soils.

4.4. Effect on the Soil Microbiota

Microorganisms are living elements of the soil solid phase and form specific communities depending on the soil type, climatic zone, vegetation, human influence, and accumulated pollutants. These dynamic communities respond to changes in their habitat and modify it themselves [24]. One of the most powerful factors is the root secretions, which contain mineral and organic compounds that stimulate the growth of microorganisms. These compounds initiate the formation of microcolonies and biofilms. Microorganisms in such structures are much less susceptible to toxins. The chemical composition of these secretions can eliminate certain species and stimulate the growth of others, indirectly affecting the mobility and bioavailability of various elements, including metals [73]. It is not without reason that microorganisms are considered to be the driving force of biogeochemical cycles of essential major elements (C, O, H, N, P, S), minor elements (Ca, Mg, K), and trace elements (e.g., Co, Cu, Fe, Mn), as well as toxic elements (e.g., Cd, Hg, Pb). The balance between the mobilization and stabilization of elements in the soil, or the shift of this balance in one direction or the other, depends on the number, activity, and diversity of soil microorganisms [74]. Soil microbial diversity is characterized using traditional plate methods based on the kinetics of visible colony formation or microplate methods (e.g., Biolog EcoPlate™) based on the metabolic profiles. However, both only allow for the analysis of culturable microorganisms [75,76].

The 16S rRNA gene amplicon sequencing method, on the other hand, is culture independent [77]. It allows us to estimate the richness of the operational taxonomic units (OTUs), the relative abundance of the primary phyla in the microbial community, the microbial community structure at the genus/species level, as well as to predict the functions of microorganisms in the habitat [59,63,70,72]. One of the most popular indices is the Shannon index, which is used to describe biodiversity at the species and metabolic levels, as well as on the basis of the kinetics of formation of visible colonies (Equation (3)).

$$H = -\sum_{i=1} (p_i \cdot \ln p_i) \quad (3)$$

where p_i expresses: (a) the ratio of the a abundance of species i to the total abundance, (b) the ratio of the OD590 substrate i to the sum OD590 of all wells, or (c) the ratio of the number of colonies on day i to the total number of colonies.

Microbial diversity, as described by the Shannon index, increased significantly with the amount of biochar added (from 4.60 to 6.31) to the soil contaminated with 10 mg Cd kg^{-1} [42]. The Shannon index was significantly higher in the soil supplemented with willow biochar (increase of 0.13–0.36 units) than in non-treated soil [61]. An increase in the value of this index was also found by Wang et al. [63] and Zhu et al. [72]. Although the Shannon index gives an indication of the magnitude and the direction of change (decrease/increase) in the diversity of the soil bacterial community, it does not provide too much detail. The effect of biochar on soil microorganisms is diverse. It can stimulate the growth of all microorganisms or only selected groups. For this reason, more attention is being paid to more detailed analyses of OTUs.

The total number of OTUs was not always higher in the biochar-enriched soil than in the control, but changes in diversity were always observed after the addition of biochar [61,63,72]. For example, the addition of jarrah wood biochar had no significant effect on the OTU richness in the rhizosphere of *Atriplex nummularia* L. growing in saline-alkaline soil, but an upward trend was observed, especially at 10% biochar. After the biochar addition (5% or 10%) to the rhizosphere of this plant, the relative abundance of phyla such as Actinobacteria, Firmicutes, and Chloroflexi increased, but Proteobacteria decreased [59]. Proteobacteria, as the dominant phylum in the unamended soil, was also dramatically reduced, but Actinobacteria, Firmicutes, and Bacteroidetes were apparently increased in the biochar-treated soil contaminated with 10 mg Cd kg^{-1} [42]. Genus richness (Table 5) in this soil was significantly higher following wheat straw biochar supplementation compared to the control soil. Their abundance in the soil without biochar was comparably lower. Bacterial abundance was associated with the amount of Cd bioavailability, which also decreased after biochar application [42].

Table 5. Dominated bacteria genus in Cd-contaminated soil supplemented with 1% biochar [42].

Gram Staining	Phylum	Genus
Gram-positive	Actinobacteria	*Actinopolymorpha*
		Mycobacterium
		Promicromonospora
		Rhodococcus
		Streptomyces
		Thermobispora
	Firmicutes	*Lactococcus*
		Thermobacillus
Gram-negative	Proteobacteria	*Hyphomicrobium*
		Inquilinus
		Ochrobactrum
		Thermovum
	Bacteroides	*Prevotella*

Radziemska et al. [61] found that the application of willow biochar mitigated the stresses caused by heavy metal contamination and the freeze–thaw effect in the post-industrial urban soils. Biochar had a protective effect on *Nitrosomonadales*, *Nitrospirales*, or *Verrucomicrobia* bacteria, which are important for efficient nutrient transformations in soils. In addition, *Rhodococcus* sp., *Williamsia* sp., and *Alkalindiges* sp. were the most abundant in the biochar-treated soil. Another example shows that the intensity of changes in microbial diversity and the dominance of specific bacterial groups were not only a result of the addition of biochar, but also evolved over time. Zhu et al. [72] found that in the biochar-treated soil planted with cotton, the abundance of bacteria from the group Gemmatimonadetes was significantly increased in 2019, while α-Proteobacteria and γ-Proteobacteria decreased compared to the soil without biochar. One year later, in 2020, an increase in α-Proteobacteria was observed in the biochar-treated soil, along with an increase in the relative abundance of Bacilli and Actinobacteria. Meta-analyses conducted by Xu et al. [78] showed a positive correlation between the soil amendment of biochar and the abundance of Actinocateria and Proteobacteria, but a negative correlation between the soil amendment with biochar and the abundance of Gemmatimonadetes, Verrcomicrobia, and Acidobacteria.

Increasing the number of saprotrophic bacteria [59,61] and saprotrophic fungi [79] in the soil has a positive effect on the formation and protection of the soil humus, which is extremely important for soil fertility. The abundance of saprotrophs is also very important for plant health as they compete with phytopathogens. Idbella et al. [79] revealed that biochar application significantly altered the structure of the fungal community inhabiting the rhizosphere of the grapevine. An increase in the abundance of saprotrophic and symbiotrophic fungi and a decrease in pathotrophic fungi were observed. In particular, the double application of biochar increased the species richness of *Basidiomycota* yeasts compared to the control soil, while the abundance of putative plant pathogens such as *Phaeoacremonium* sp. and *Aspergillus* sp. was significantly reduced. Nirukshan et al. [80] found significantly higher abundances of saprotrophic and arbuscular mycorrhizal fungi in the biochar-treated soil than in the untreated soil. They also observed an increase in coconut root mycorrhization and P accumulation following biochar application during drought stress. Various microbial metabolites, i.e., siderophores, plant hormone analogues, antioxidants, enzymes, etc., secreted into the soil also stimulate plant growth [57]. On the other hand, the plant root deposits are rich in various organic and inorganic compounds that stimulate the growth, development, and activity of microorganisms in the soil around the roots (rhizosphere) and modify soil parameters within this zone. In this way, the cycle of fundamental interactions that can be observed in the soil-microbe-plant system has been completed (Figure 2).

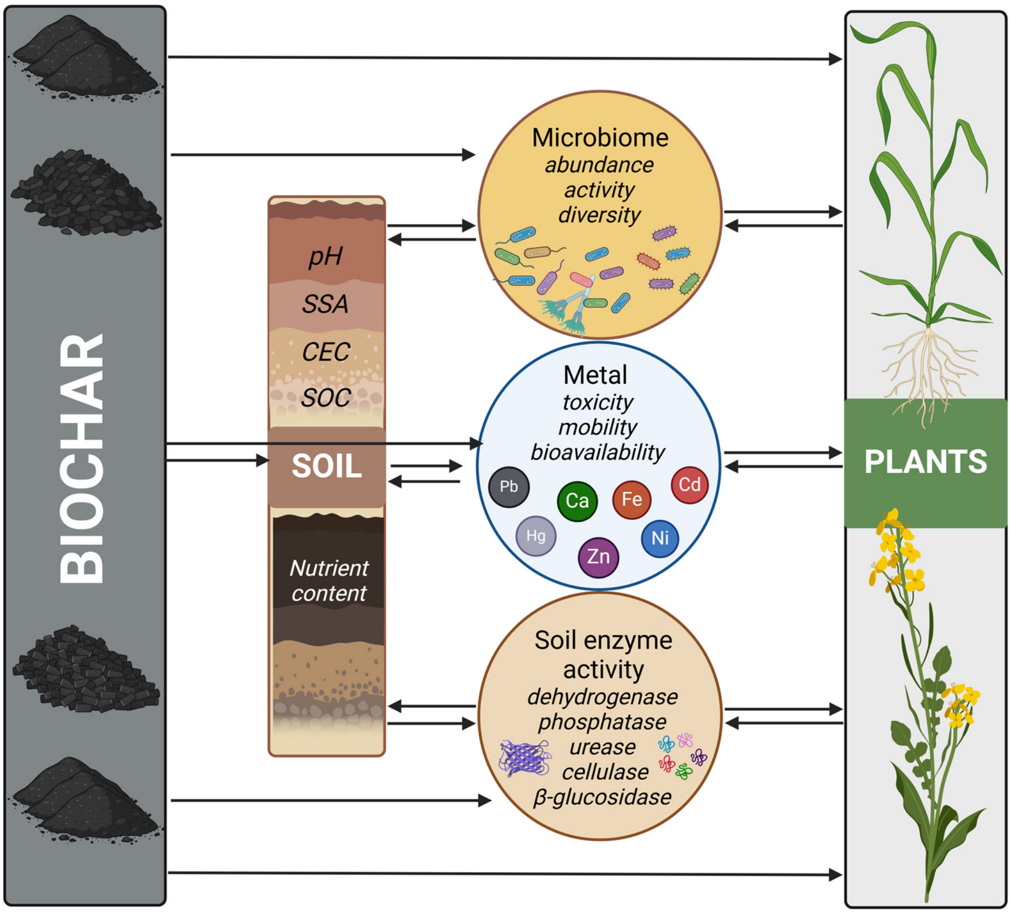

Figure 2. Scheme showing the potential effect of biochar on the interactions that exist in the soil-microbe-plant system. SSA—specific surface area, CEC—cation exchange capacity, SOC—soil organic carbon based on [24,25,29,53–68,71–82]. Created in https://BioRender.com (accessed on 15 January 2025).

4.5. Activity of Enzymes in Biochar-Treaded Soils

Soil enzymatic activity is used as an indicator of microbial activities [81], as it is very sensitive to metal stress and significantly decreases with increasing heavy metal content in the soils [53]. For example, dehydrogenases are the enzymes of the respiratory chain and are considered a reliable indicator of the oxidative activities of soil microorganisms [81]. They are positively correlated with the total soil microbial activity but negatively correlated with the degree of soil pollution, and are therefore used to determine the total soil microbial activity [53,81]. They are a good indicator of the changes caused by the addition of biochar to the soil. It was observed that the activity of soil dehydrogenases increased significantly in proportion to the dose of biochar added to the Cd-contaminated soil (20, 40, and 80 mg Cd kg^{-1}) [82]. This suggests that biochar, by stabilizing heavy metals and reducing stress, may have a positive effect on the soil enzyme activity and consequently on the nutrient cycling.

Soil enzymes are the biomolecules associated with proliferating cells of microorganisms (such as dehydrogenases) or as an extracellular molecule adsorbed to clay minerals or complexed with humic colloids [81]. First, as an efficient adsorbent, biochar, like clay minerals and humic substances, can adsorb enzymes, significantly reducing their activity but increasing their resistance to proteolysis and denaturation. Second, it can bind the substrates for enzymes, preventing their association with the active site of the enzyme. Thus, the effect of biochar on soil enzymes can be diversified. Therefore, the enzyme immobilization by biochar added to the Cd-contaminated soil (20 mg kg^{-1}) could be the reason for the decrease in urease activity. An experiment conducted by Manori et al. [11] showed that urease activity decreased proportionally to the dose of biochar used (100 or 200 mg kg^{-1}). Other reports show an opposite trend. Urease activity in the unpolluted soil with much higher doses of peanut shell biochar (from 1% to 5%) and with mineral fertilization (K, Ca, and N in a 2:1:1 ratio) was significantly higher (about 18%) than in the control soil without biochar [63]. Urease activity was also higher after application of 2% switchgrass biochar than in the control soil [60].

Depending on the soil conditions and enzyme type, biochar may have a different effect on the soil enzyme activity. The protective effect of biochar, by neutralizing toxic metals, can increase enzyme activity. For example, alkaline phosphatase activity was significantly higher after biochar treatment than in the untreated Cd-contaminated soils [11], as was β-glucosidases activity [82]. The activity of invertase, polyphenol oxidase, and catalase also increased with increasing biochar content in the uncontaminated soil [63]. Comparison by Zaid et al. [60] of the activity of key enzymes in the carbon (β-glucosidase, cellulose, dehydrogenase), phosphorus (acid and alkaline phosphatase), sulfur (arylsulfatase), and nitrogen (arylamidase, urease) cycles showed that they were more affected by season than by biochar fertilization. Significant differences were observed between the activity of these enzymes in spring (April) and summer (August). Analyzing the putative C, N, and P cycle in the rhizosphere of *A. nummularia* L. (saline-alkaline soil), Howell et al. [59] found that jarrah wood biochar (5% or 10%) did not significantly affect the relative abundance of genes involved in the transformation of P and N compounds, while controlling those important for the carbon cycle. In particular, the relative abundance of α-amylase genes decreased, but β-galactosidase, endoglucanase, and β-glucosidase genes increased. In the N cycle, the ammonification potential decreased, but the potential of denitrification increased [59].

4.6. Plant Growth Promotion and Stress Mitigation

Biochar added to the soil cannot eliminate heavy metals, but it can reduce their toxic effect in a habitat. Thus, metals are still there, but in a different, less harmful form, and this can make it easier for plants to grow and develop in a contaminated area. In vitro tests showed that wheat straw biochar significantly stimulated the germination of cucumber, carrot, lettuce, and tomato seeds in a dose-dependent manner. This biochar was also shown to ameliorate the stress caused by the addition of $Cd(NO_3)_2$ solution and to significantly increase seed germination [42]. Plants grown in the contaminated soil also respond well to biochar amendment. The fresh and dry mass, as well as the height, of *Brassica chinensis* L. were significantly increased when the dose of wheat straw biochar added to the soil contaminated with 10 mg Cd kg^{-1} was increased from 0.2% to 1% [42]. Similarly, the biomass of perennial ryegrass [61] and maize [33] used for biochar-assisted phytoremediation of metal-contaminated soils was significantly higher than that of plants grown in the soil without biochar. The use of 2% rice husk biochar also increased the length of root and shoot (by 22% and 23%, respectively) and the fresh biomass (by 22% and 15%, respectively) of rice growing in Cd-contaminated soil compared to the control without biochar [83]. However, biochar does not always improve plant growth under stressful conditions. For example, saltbush (*A. nummularia* L.) growing in jarrah wood biochar-treated saline-alkaline soil did not significantly change the shoot and root biomass compared to the control plants [59], nor did *B. pilosa* L. growing in Cd-contaminated soil with biochar supplementation [11]. Most importantly, in these cases, biochar did not inhibit plant growth. It is also worth noting that there are examples of the use of biochar having an inhibitory effect on plant growth. Such observations were made by Simiele et al. [12]. *Populus euramericana* L. clone I45/51 and *Salix purpurea* L. achieved significantly lower root and shoot mass after the application of 3% biochar than those growing in soil not remediated with this material [12].

During phytoremediation of the metal-contaminated soils, plants are exposed to abiotic stress, the effects of which can be detected at the biochemical level. These changes in the plant tissues clearly correlate with the level of metal toxicity. Plants under stress synthesize significantly less chlorophyll than plants not exposed to such influences. A decrease in chlorophyll content leads to disturbances in the photosynthetic system, and therefore chlorophyll is a suitable indicator of declining plant health [84–86]. However, contrary pigment data have also been reported. For example, under Cu excess, the chlorophyll content in *Phaseolus coccineus* L. increased [87,88]. Kara et al. [82] found a significant increase in chlorophyll a and b concentrations in *Triticum aestivum* L. grown in soil contaminated with 80 mg Cd kg^{-1}, proportional to the sludge biochar dose. Similarly, rice grown in Cd-contaminated soil (15 or 20 mg Cd kg^{-1}) supplemented with 2% rice husk biochar contained more chlorophyll *a* and *b* as well as carotenoids (17%, 25%, and 26%, respectively) than plants grown in untreated soil [83]. The relative water content, as a parameter reflecting the state of the plant water management under stress conditions, in wheat leaves also increased significantly with the increasing level of the sludge biochar content in the soil [82]. The results of da Cruz Ferreira et al.'s [89] study showed that the application of biochar from açaí seeds (5 and 10%) was efficient in remediation and improvement of the growth of Brazilian mahogany plants grown in Cu-contaminated soils (200, 400, and 600 mg Cu kg^{-1}), but the final effects strongly depended on the proportions between biochar and Cu doses. For example, the height was independent from biochar level and Cu concentration, whereas photosynthesis was positively stimulated only at the lowest levels of biochar and Cu, but a number of leaves were elevated at 5% biochar supplementation and up to 400 mg Cu kg^{-1}.

In addition, toxic metals induce oxidative stress, which also weakens the plant and slows down the mechanisms directly aimed at neutralizing metal toxicity. Oxidative stress induces the formation of reactive oxygen species, e.g., H_2O_2, $O_2^{\bullet -}$ (Figure 3), which damage the cell membrane as a result of lipid peroxidation, and the malondialdehyde (MDA) formed in this reaction is an indicator of the level of stress [84,85]. Studies by Kara et al. [82] showed that with the increasing Cd-contamination in the soil without application of sludge biochar, the concentration of MDA in *T. aestivum* L. also increased, but in plants grown in soil with application of biochar, this type of response to stress was significantly attenuated. For example, when there was no biochar in the soil, the amount of MDA in wheat was 14.1 mg kg^{-1}, but in plants grown in the soil with biochar, it was 11.3 mg kg^{-1}. A reduction in lipid peroxidation was observed in plants growing in soils with different levels of Cd contamination and in linear proportion to the biochar dose, both in the sandy loam and clay loam soils. The decrease in MDA content was also observed by Ali et al. [83] in shoots of rice grown in the Cd-contaminated soil (15 or 20 mg Cd kg^{-1}) supplemented with 2% rice husk biochar compared to the treatments without biochar.

Proline is another indicator of oxidative stress. The presence of proline increases stress tolerance, e.g., by neutralizing reactive oxygen species [84,85]. The accumulation of proline in the leaves of *B. pilosa* L. growing on the Cd-contaminated soil was indicative of Cd-induced stress, irrespective of the dose of pine needle biochar (an average 13.8 µmoles g^{-1}). In contrast, only 8.2 µmoles g^{-1} of proline was found in the leaves of the plant growing on the Cd-contaminated soil without biochar. Manori et al. [11] explained this by the stimulation of the biochemical defense mechanisms that reduce oxidative stress in the presence of biochar in the soil. Plants also neutralize reactive oxygen species using an enzymatic antioxidant system that includes superoxide dismutase (SOD), catalase (CAT), guaiacol peroxidase (GPX), ascorbate peroxidase (APX), peroxidase (POD), and other enzymes [30,87,88,90–93]. Ali et al. [83] found that Cd added to the soil at concentrations of 15 and 20 mg kg^{-1} significantly reduced the activity of POD (20% and 55%, respectively), SOD (25% and 49%, respectively), APX (14% and 38%, respectively), and CAT (21% and 47%, respectively) in the rice roots compared to the uncontaminated soil. A similar reduction in the activity of these enzymes was observed in rice shoots. However, 2% rice husk biochar added to the Cd-contaminated soil increased the POD, SOD, APX, and CAT activity in both the roots and shoots of rice [83]. Thus, biochar enhanced the activity of enzymatic antioxidants and reduced oxidative stress in plants induced by Cd contamination.

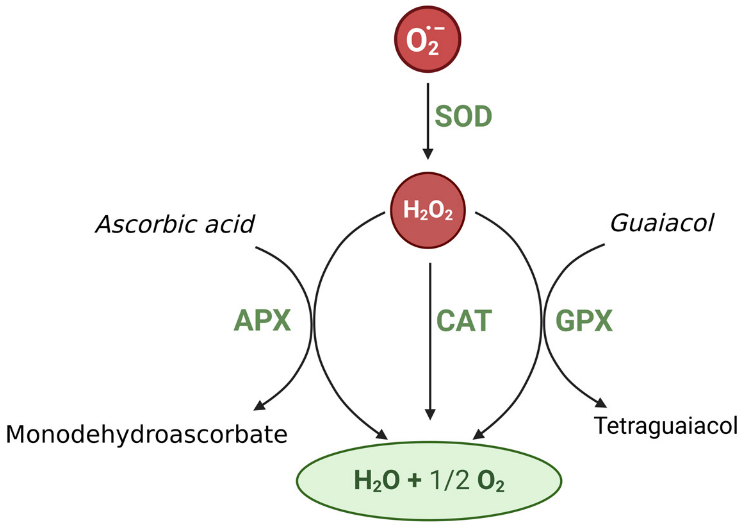

Figure 3. Simplified scheme of reactive oxygen species neutralization in plant cells by superoxide dismutase (SOD), catalase (CAT), ascorbate peroxidase (APX), and guaiacol peroxidase (GPX) based on [90–92]. Created in https://BioRender.com (accessed on 15 January 2025).

5. Risks of Biochar Use

Despite the many benefits of using biochar as a soil amendment, as discussed above, many scientists have questions about whether the long-term use of biochar will have a negative impact on the environment, particularly on the quality and quantity of agricultural products. Meta-analyses of scientific sources conducted by Ndirangu et al. [94], Brtnicky et al. [95], Gelardi [96], and Xiang et al. [97] report that there is a risk of the formation and release of toxic compounds during the production, transport, storage, and application of biochar.

One of the problems is the presence of contaminants in the organic feedstocks (e.g., sewage sludge and municipal solid waste) used in biochar production. Concentrations of heavy metals and metalloids in sewage sludge vary between regions or countries and are significantly higher in industrial areas. In general, sewage sludge contains Zn, Cu, Ni, Cr, As, Pb, Cd, and others [98–100], which are concentrated during pyrolysis, and their concentration in the biochar is increased by 20–100% compared to those in the sludge [98]. Moreover, biochar produced from municipal solid waste may contain also glass, textiles, and hard and film plastic contaminants in addition to metals [101,102]. The pyrolysis process also leads to the accumulation of harmful compounds such as polycyclic aromatic hydrocarbons (mutagenic and carcinogenic compounds) and persistent free radicals (induce the formation of toxic reactive oxygen species), dioxins and furans (carcinogenic compounds), and other potentially toxic elements [95–97,99]. Unfortunately, all harmful compounds can be leached out of biochar over time and can be toxic to microbiota, plants, soil fauna, and humans. However, it is worth noting that the pollutants immobilized in biochar are more stable than those found in sewage sludge or municipal waste. For example, the leaching of heavy metals from biochar was significantly decreased compared to raw sludge because they move from the bioavailable fraction to the residual fraction during thermal transformation [98].

Changes in the soil microbial community caused by the release of toxic compounds from biochar can have direct or indirect negative effects on the biocenotic balance as well as the course of biogeochemical cycles of C and N [95,97]. The fact that microbial activity is stimulated by biochar can also have a negative effect. Microorganisms can accelerate the mineralization of soil organic matter, thereby reducing the humus content in the soil and increasing the emission of CO_2 or CH_4 (greenhouse gases) during the aerobic or anaerobic transformation of carbon compounds, respectively. The intensification of nitrification and denitrification processes in the soil can also lead to the emission of other greenhouse gases such as nitrous oxides [97,102]. Radziemska et al. [61] found the positive effect of biochar on *Nitrosomonadales* and *Nitrospirales* (nitrifying bacteria), which could also potentially increase nitrous oxides emissions.

Biochar is not a homogeneous material. It contains particles of different sizes, from 5 μm to 5 mm [103]. Attention is drawn to the possibility of emission and air pollution by microbiochar (about 1 μm) and nanobiochar (up to 100 nm) dust particles during biochar crushing, transport, and application [97] or from biochar amended soils [96]. The size of the particles makes them dangerous to humans, as they can penetrate the respiratory system and be a source of toxic substances. Brtnicky et al. [95] concluded that the high porosity and large specific surface area of biochar can cause strong immobilization of nutrients, reducing their availability to plants. The result may be a reduction in yield. The high sorption capacity of biochar can also reduce the effectiveness of agrochemicals (e.g., herbicides applied to the soil) by reducing their bioavailability and requiring greater amounts of them [95,102].

These are just a few examples of the negative environmental impacts of biochar (Figure 4), which show that the positive effects are not always achievable. For this reason, it seems important to introduce appropriate standards for the quality of organic feedstocks and production conditions for biochar to ensure the high quality of this product, as well as appropriate certificates confirming that it is free from harmful compounds and is safe for use in agriculture and environmental protection. It is also important to introduce appropriate legislation specifying the permissible levels of metals, metalloids, PAHs, dioxins, and others in both the raw material and the biochar [104]. It is important to estimate the amount of biochar that can be applied per hectare per year, depending on its potential risk index (low < 150, moderate 151–300, considerate 300–600, high > 600 [98]), the granulometric type of soil (sand clay, silt [105]), and its use for agricultural or non-agricultural purposes, as is in the case with the sewage sludge application [106].

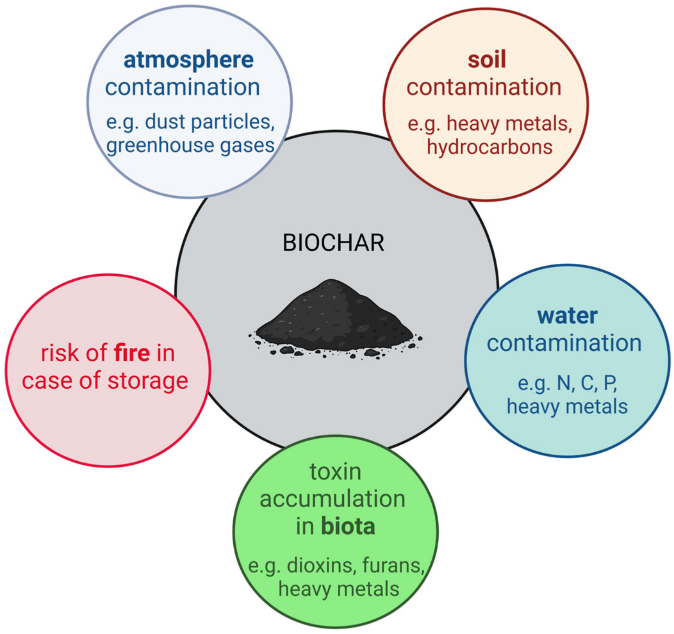

Figure 4. Potential risks associated with the production, transportation, storage, and use of biochar based on [95–97,107]. Created in https://BioRender.com (accessed on 15 January 2025).

The biochar market is so important to global industry that detailed reports are prepared on current analyses and forecasts [108,109]. The biochar market grew by more than 16% in just one year, from USD 2.51 billion in 2023 to USD 2.93 billion in 2024. It is expected to grow steadily to reach USD 7.42 billion by 2030, which is 2.5 times the growth compared to 2024 [109]. European and American authorities such as the European Commission [110] and the United States Department of Agriculture [111] work on the regulatory aspects of the safe production and application of biochar to implement quality standards for industrial practices. Their work is widely promoted on the Internet [112].

6. Conclusions

In general, the use of biochar can be expected to improve soil parameters. Biochar increases soil pH, surface area, and adsorption capacity, all of which determine the increased immobilization of metals by the solid phase of the soil and the reduction of bioavailability and toxicity of metals contaminating the soil. The same factors that reduce the bioavailability and toxicity of metals also increase the activity, number, and diversity of microorganisms. Microorganisms are an important element in the bioremediation of the metal-contaminated soils, and their stimulation by the addition of various materials to the soil, such as biochar, activated carbon, liming, clay minerals, and organic and mineral fertilization (e.g., NPK), can stimulate mechanisms that modify the toxicity, mobility, and bioavailability of metals and metalloids. In addition, the biomass of microorganisms forms an important surface area with a significant sorption capacity for metals. Metals are immobilized on the surface of living or dead microbial cells by ion exchange adsorption, complexation, and precipitation. Living and metabolically active microbes can accumulate metals intracellularly. Therefore, by stimulating the growth and activity of soil microorganisms, biochar added to soil increases its bioremediation potential. Both alone and in interaction with microorganisms, biochar also has a positive effect on plant growth, so it can support phytoremediation and restoration of plant cover in degraded areas. However, anyone who uses biochar must be very careful and be aware of the dangers that can result from improper application.

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