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Review

Biochar as a Green Sorbent for Remediation of Polluted Soils and Associated Toxicity Risks: A Critical Review

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Abstract: Soil contamination with organic contaminants and various heavy metals has become a global environmental concern. Biochar application for the remediation of polluted soils may render a novel solution to soil contamination issues. However, the complexity of the decontaminating mechanisms and the real environment significantly influences the preparation and large-scale application of biochar for soil ramification. This review paper highlights the utilization of biochar in immobilizing and eliminating the heavy metals and organic pollutants from contaminated soils and factors affecting the remediation efficacy of biochar. Furthermore, the risks related to biochar application in unpolluted agricultural soils are also debated. Biochar production conditions (pyrolysis temperature, feedstock type, and residence time) and the application rate greatly influence the biochar performance in remediating the contaminated soils. Biochars prepared at high temperatures (800 °C) contained more porosity and specific surface area, thus offering more adsorption potential. The redox and electrostatic adsorption contributed more to the adsorption of oxyanions, whereas ion exchange, complexation, and precipitation were mainly involved in the adsorption of cations. Volatile organic compounds (VOCs), dioxins, and polycyclic aromatic hydrocarbons (PAHs) produced during biochar pyrolysis induce negative impacts on soil alga, microbes, and plants. A careful selection of unpolluted feedstock and its compatibility with carbonization technology having suitable operating conditions is essential to avoid these impurities. It would help to prepare a specific biochar with desired features to target a particular pollutant at a specific site. This review provided explicit knowledge for developing a cost-effective, environment-friendly specific biochar, which could be used to decontaminate targeted polluted soils at a large scale. Furthermore, future study directions are also described to ensure a sustainable and safe application of biochar as a soil improver for the reclamation of polluted soils.

Keywords: biochar; bio-availability; heavy metals; pyrolysis; soil contamination; toxicity

1. Introduction

Recently, more soils have been noticed to be polluted with inorganic and organic chemicals globally due to residues discharged from agricultural practices, industrial processing, manures and biosolids application, mining activities, inefficient management of fertilizer and pesticides, and wastewater irrigation (Figure 1) [1,2]. More eco-environmentally suitable substitutes, such as biochar application as waste handling approaches, are required to reduce increasing soil pollution [2]. Contaminants in the soils are dangerous to agricultural production and ecosystems and a severe risk to public health due to their entrance into the ground water and food web [3]. Da Silva et al. reported that approximately 80% of wastewater is released into the environment at a global scale without any treatment [4]. Furthermore, about 9 million premature deaths have been reported due to environmental pollution globally [4]. Approximately four million sites, including mines and industrial sites, energy generation plants, agricultural lands, and landfills, have become potentially polluted in most European countries. Consequently, soil pollution has become a critical issue that needs urgent action to protect the soil [5]. Mitigation of such environmental problems has been prioritized in the European Green Deal (EGD) program, aiming to achieve climate neutrality for Europe by 2050, which is a framework for implementing many climate- and environmental-related targets in major sectors [6,7]. The EGD targets also encompass soil protection aspects which emphasize improving the deteriorating condition of European soils [8]. Furthermore, the new "European Union Soil Strategy for 2030" harvesting benefits of healthy soils for food, people, nature, and climate has provided a roadmap for the future handling of the soil [7]. The EGD also supports the implementation of Sustainable Development Goals (SDGs) defined by the United Nations (UNEP, 2015). The new EU Soil Strategy strengthens the SDG target 15.3, aiming to combat desertification and restore degraded soils and lands [7]. In mainland China, fast economic growth has also caused many environmental problems in recent decades. Around 30 million hectares of fertile land have been exposed to metal pollution, representing about 25% of the total farming land in China. Massive attempts have been made to remediate the contaminated soils, as revealed by increasing research literature on the remediation of soil contamination [8]. Bioremediation, integrated remediation, and chemical and physical remediation approaches have been applied to manage the polluted soils [2]. Moreover, optical composite materials (OCMs) and ligand-based composite hybrid materials (CMHs) are also considered as potential materials for sustainable waste management [9–11]. According to Das et al., biochar is a product produced from pyrolysis of feedstock obtained from forestry and agricultural residues [12]. Biochar addition to the soil is assumed to have a high potential to increase carbon (C) sequestration because C in the biochar has an aromatic structure and is more intractable to the ecosystem [13,14]. Usually, biochar has a high pH and cation exchange capacity (CEC), which can increase soil fertility [15]. Numerous authors have also reported that biochars have great capability to remove the chemicals in soils [2,16].

This review study provided an overview of recent approaches in the reclamation of polluted soils and biochar effects on the bio-availability and mobility of the soil pollutants, along with the removal mechanism of pollutants by biochar from polluted soils. Moreover, the toxicity risks associated with biochar addition to unpolluted agricultural soils and its mitigation methods are also discussed, and future research directions regarding biochar application for the reclamation of polluted soils have also been described.

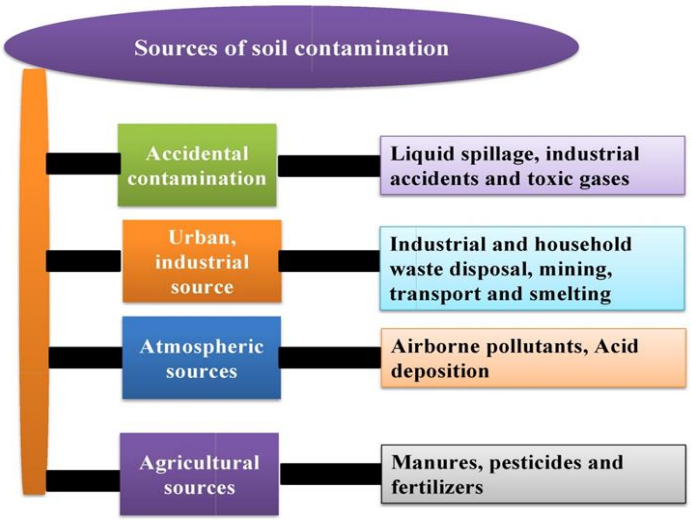

Figure 1. Sources of soil contamination.

2. Materials and Methods

Online search engines including Google Scholar, Web of Science, and Scopus were used to retrieve data on the remediation of polluted soils with biochar. Different keywords were used to collect the literature including "soil pollution, soil remediation, organic and inorganic pollutants, heavy metal pollution, biochar for soil remediation, health risks". The primary source data for this review were published papers, and the criteria for the inclusion of articles were: (i) research/review papers published in English-language journals; (ii) and those which contained information about soil contamination with organic and inorganic pollutants and its ramification with biochar. Articles containing ambiguous information or that were outside the main scope of this review were excluded during the screening process.

3. Biochar Application to Polluted Soils

Biochar has the ability to treat the polluted soil with organic and inorganic elements, decrease the soil nutrient leaching loss, and amend the physiochemical attributes of soil.

Improving the Soil Traits

The soil improvement under biochar application is mostly reflected in the amendment of soil organic matter (SOM), the improvement of nutrient dynamics and utilization rate, and the amendment of acidic soil and soil erosion [14]. Moreover, biochar traits, such as higher surface area and porosity, enhance the water-holding capacity (WHC), the soil porosity and soil capacity, and the porous structure of biochar, which make it a better habitat for the soil microbial population (Figure 2). Biochar application can efficiently improve the structure of soil, decrease the moisture content loss because of structure runoff and filtration, and enhance soil-available water [17]. Montagnoli et al. [18] reported that the biochar's higher porosity has strong water retention ability, and the slow discharge of water contents from biochars can significantly enhance the water conservancy properties of degraded soil. Biochar incorporation into the soil can enhance the pH levels, possibly due to the biochar's higher base cation composition, such as Na^+, K^+, Mg^{2+}, and Ca^{2+}. Biochar ash content is comprised of carbonates and hydroxides, and these substances' dissolution expedites the soil pH increase of enhancement [19]. The negatively charged surface functional groups of biochar can greatly adsorb cations and support an increase in the soil's CEC [20]. Oni et al. reported that the composition of feedstocks determines the biochar CEC during pyrolysis mechanism [21]. Jain et al. [22] reported the immobilization of metal ions in the soil via substituting cations on the biochar, and these cations enter into the soil and enhance the pH. Therefore, the elevation of soil pH and CEC induced through biochar might be due to the decline of metal ions bio-availability. Therefore, biochar is frequently applied for

soil reclamation polluted by cationic-trace components [22]. Biochar contains essential nutrients, such as Ca, Mg, K, P, and N. These elements are necessary for plant growth and development, and the release of these nutrients stimulates or accelerates the growth of plants [23]. Biochars produced from different feedstocks also varied in nutrient substances, for example, biochar derived from grass seed had a higher amount of P, whereas biochars derived from wood contained more Mg and Ca [24]. Moreover, the biochar's strong WHC can decrease nutrient leaching, modify the nutrient dynamics, stimulate the root nodule, and accelerate the plant growth and immobilization of N [25]. Furthermore, the minimum dose of biochar needed to maintain plant growth also varies because of the diversity in the heavy metal and nutrient concentration of polluted soils [26]. The higher amount of organic and inorganic pollutants in soils causes a disturbance in soil enzyme activity or functionalities, and the microbial population may be seriously damaged [27]. Applying biochar can improve the habitats of the microbial community, by influencing the structure, diversity, microorganism's activity, and nutrient availability [28]. Torabian et al. reported that compared to the biochars pyrolyzed at high temperatures, biochars derived at low temperatures were more contributive to soil microorganism's growth because they comprised N and more DOC [29]. Gul et al. described that biochar can indirectly influence the P and N cycling reaction of microbes by altering the soil environment and structure of the microbial community, and can promote the plant rhizobial exchanges [30]. Therefore, adding biochar contributes to soil microbial activity, which may benefit plant growth and development [31]. In general, biochar improves the physicochemical traits of soil and is comprised of nutrients necessary for microbial and plant growth. Hence, biochar application is a potential material for the ecological reclamation of polluted soils with inorganic and organic elements.

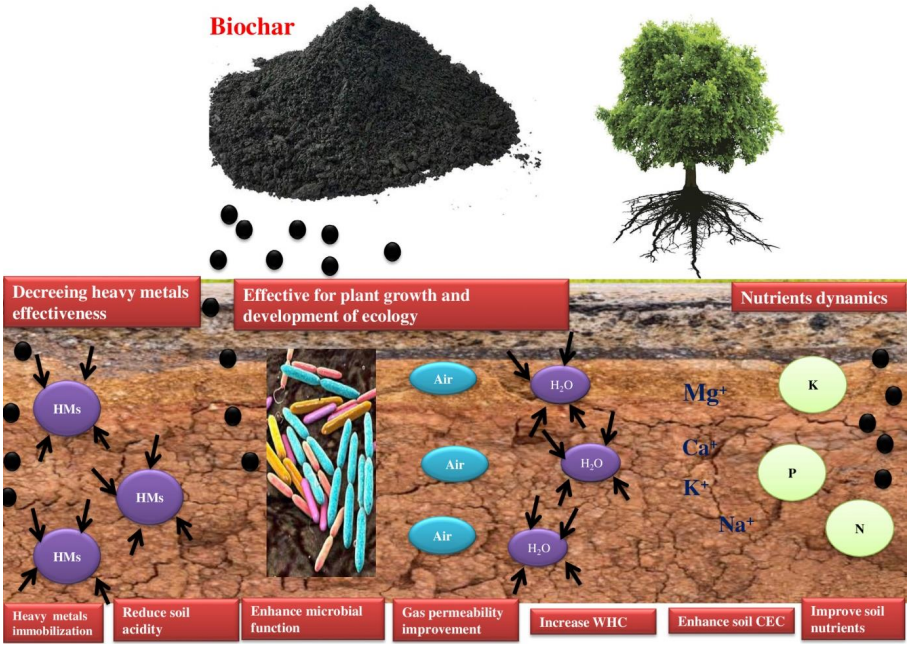

Figure 2. Mechanism of soil amendment by biochar.

4. Biochar Applications for Remediation of Soils Contaminated with Heavy Metals

Heavy metals persist for a long time and are not bio-degradable in polluted soils. The elimination of metals from contaminated soils is time-consuming and expensive. In situ metal stabilization through soil amendments, such as compost and lime, is usually employed to decrease the bio-availability of metals and decrease plant uptake [32]. Biochars can stabilize heavy metals, amend the quality properties of polluted soil, and significantly reduce the uptake of various metals in crops [33]. Thus, biochar application can be a potential solution for the reclamation of soils polluted with heavy metals. Metals stabilization in

soils with biochar addition may involve different mechanisms, as explained in Figure 3. Taking lead ions (Pb^{2+}) as an instance, many researchers proposed different mechanisms for the sorption of lead ions through biochar produced from sludge that may include: (i) the exchange of heavy metal with Mg^{2+}, Ca^{2+}, and other cations present in biochar, representing inner-sphere complexation and co-precipitation complexation with mineral oxide and complexed humic matter of biochar; (ii) surface complexation of heavy metals with various functional groups as well as inner-sphere complexation with free-hydroxyl of mineral oxides and other surface precipitation; and (iii) surface precipitation and van der Waals adsorption ensuring the Pb^{2+} stabilization [34]. In the case of acidic polluted soils, depending on the biochar type and presence of exchangeable cations, such as Ca^{2+}, K^{+}, Mg^{2+}, and Na^{+} in biochar, these could govern the exchange of cations with heavy metals during the sorption process and may enrich the stabilization process [35]. Ennaji et al. [36] also illustrated that the exchange of heavy metal with K^{+}, Na^{+}, Mg^{2+}, and Ca^{2+} from sludge-derived biochar was the main process responsible for this exchange in their work, but the contribution of monovalent cations (K^{+}, Na^{+}) was negligible. Thus, it could be stated that under actual field conditions, the biochar-derived sorption process in metal-polluted soils is mainly dependent on soil type and the cations present in both biochar and soils; consequently, metal remediation in polluted soils may differ. Mahmud et al. [37] demonstrated that the mineral constituents, e.g., phosphates and carbonates in the biochar, play a substantial role in stabilizing the metals in soil because these salts can precipitate with metals and lessen their bio-availability. Chen et al. suggested that the primary mechanism for dairy manure-based biochar to retain lead was the precipitation of insoluble lead phosphates [38]. Usually, during biochar preparation, water-soluble Mg, Ca, and P content increase when heated at 200 °C, but these reduced at high temperatures perhaps because of the higher crystallization of P-Mg-Ca. This was evident during the formation of whitlockite when the production temperature was elevated to 400 °C, thereby ensuring the smooth precipitation of lead. Biochar's alkalinity can also stimulate metal precipitation in the soils [38]. In 2022, Palansooriya investigated the pH variation of the biochar and got a mean value of pH 8.0. With similar biomass materials, the pH value of biochar increases with the preparation temperature due to higher ash contents in the biochar [39]. Thus, many biochars are basic in nature, having a mulching effect that helps decrease the mobility of the heavy metals in polluted soils [40]. Conversely, the removal capacity of the same type of biochar differs with different kinds of heavy metals.

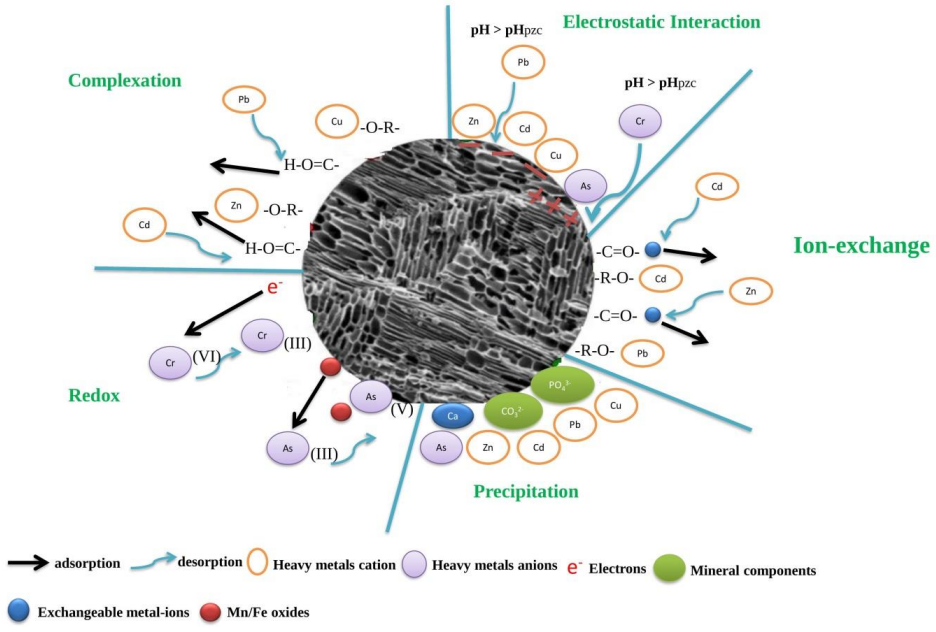

Figure 3. Heavy metals adsorption and immobilization mechanism by biochars in polluted soil.

4.1. Influence of Biochar on the Mobility of Heavy Metals

The application of biochar can decrease the mobility of various heavy metals in polluted soils (Table 1), which minimizes the risk of plant uptake. Various studies have presented that bamboo-derived biochar can remove chromium, nickel, mercury, cadmium, and copper from contaminated soil and water [41]. Biochar obtained from dairy residue prepared at a 300 °C pyrolysis temperature was more effective in sorbing lead than biochar prepared at 400 °C because biochar pyrolyzed at 300 °C had a greater concentration of soluble phosphate [42]. Since biochar properties depend on feedstock type and pyrolysis conditions, a single type of biochar cannot be universally used to reclaim polluted soils containing different heavy metals. Thus, when biochar is to be applied as an amendment for the reclamation of polluted soils, care must be taken about the type of heavy metals, biochar production temperature, residence time, moisture content, and the type of feedstock employed. The influence of biochar on metal bio-availability differs with biochar type and different kinds of heavy metals. Alipour et al. reported that when zinc and cadmium polluted soil was ameliorated by hardwood biochar, the concentration of zinc and cadmium in pore water decreased [8]. Concentrations of extractible zinc and arsenic in soil become higher with the biochar addition rate, whereas the concentration of extractible lead reduced, copper did not modify, and cadmium exhibited an inconsistent trend. They determined that the removal of metals on biochar with primary loadings up to 200 µmol at 7 pH took place in this order: lead > copper > cadmium > zinc > arsenic [43,44]. Singh et al. described that the biochar addition can decrease the discharge of heavy metals due to the redox reaction of heavy metals [44]. For instance, adding chicken manure-derived biochar in chromate-polluted soils increased the decline of mobile chromium hexavalent to less mobile chromium trivalent, thus reducing the leaching of chromium. The reduction in the leaching of chromium trivalent is accredited to adsorption as chromium hydroxide is produced from the release of hydroxide ions (OH^-) during the chromium hexavalent reduction mechanism [44] (Figure 3).

Table 1. Effect of different biochars on the mobility of various heavy metals in soil.

Biochar Type	Application Rate	CEC (cmol/kg)	pH	Pollutant	Effect	Reference
Sugarcane	1–10%	69.6	9	Arsenic	Application of sugarcane can decrease concentration of arsenic with the enhance in pH	[30]
Beet	—	—	9.5	Lead, nickel, and cadmium	Beet biochar can efficiently decrease the concentration of various metals in soil, decreasing the amounts of lead, nickel, and cadmium by 87, 26, and 57%, respectively	[33]
Hardwood	—	—	9.9	Zinc and cadmium	Harwood biochar causes enhancement in a soil's pH, also concentrations of zinc and cadmium in the leachate are decreased by 45 and 300 times	[8]
Orange peel	10%	29.47	10.24	Cadmium	The 10% application rate of orange peel biochar reduced the concentration of cadmium by 71%	[39]
Sludge	4%	2.36	9.5	Lead	A 4% biochar addition can reduce lead migration significantly	[16]
Lantana and Parthenium	3%	–	8.7	Chromium, lead, copper, nickel, zinc, iron, and cadmium	Heavy metals' (Cr, Cd, Cu, Pb, Ni, Zn, Mg, and Fe) bio-accumulation rate and mobility exhibited a significant reduction after biochar application relative to the control	[35]
Rice straw	5%	–	9.5	Zinc, lead, copper, and cadmium	Heavy metals concentrations were significantly lower in rice straw biochar treated soils, 5% rice straw biochar treatment reduced the concentration of zinc, lead, copper, and cadmium by 6, 34, 17, and 11%	[38]

Table 1. *Cont.*

Biochar Type	Application Rate	CEC (cmol/kg)	pH	Pollutant	Effect	Reference
Rice straw	1%	–	8.7	Lead	After biochar addition the concentration of available lead was decreased by 23.6% compared to control	[39]
Wheat straw	5%	10.4	10.6	Cadmium and lead	The biochar reduced filtrate heavy metals level by 89% to 95% (cadmium) and 93% to 99% (lead) compared with the control	[40]
Orchard prunings	2%	27.5	9.2	Arsenic, cadmium, copper, lead, and zinc	Biochar increased soil arsenic and metal mobility via changing the soil pH, dissolved organic carbon, and phosphorus	[41]
Oak wood	5%	24.2	10.2	Lead	Significantly decreased water-soluble, exchangeable, and PBET-extractable lead in soil	[29]
Rice husk	1%	–	9.4	Cadmium, copper, nickel, and zinc	Metal mobility was increased via biochar-introduced dissolved organic carbon	[22]
Wood	1, 2, and 5%	–	10.2	Cadmium	Decrease in cadmium leaching damage by more than 90%	[21]
Hardwood	3%	–	8.7	Zinc and cadmium	Zinc concentration decreased 45- and 300-fold; decrease in cadmium in soil pore water by 10-fold in column leaching tests	[17]
Bamboo	1%	–	9.1	Cadmium	Mutual influence of electro-kinetic, elimination of extractable cadmium by 80% with 2 weeks	[8]
Hardwood	5%	7.43	8.7	Arsenic, cadmium, copper, lead, and zinc	Biochar surface insulation increased arsenic and copper mobility in soil, little effect on lead and cadmium	[27]
Wheat straw	0.5, 1, and 5%	–	10.5	Cadmium and lead	The biochar addition changed 2.3% to 9.84% of the exchangeable cadmium fraction lead to residual fractions	[13]
Stinging nettle	1–10%	–	9.87	Copper and arsenic	Reduced copper leaching, but affected little on arsenic mobility	[23]
Hardwood	1%	24.8	9.17	Cadmium, arsenic, copper, and zinc	Decreased cadmium and zinc while increased arsenic and copper in soil pore water	[4]
Eucalyptus wood	3%	–	8.71	Cadmium	Biochar decreased 0.01 M $CaCl_2$-extractable soil cadmium	[33]
Poultry manure	0.5 and 1%	–	10.47	Cadmium, copper, and lead	NH_4NO_3-extractable and pore water cadmium and lead reduced in spiked soil; copper, lead, and zinc in plant roots and shoots reduced	[23]
Cottonseed hull	1–10%	–	9.67	Cadmium, copper, nickel, and lead	Greatly reduced the concentrations of all the metals in solution relative to un-amended soil	[20]
Poultry litter	1, 2, and 5%	11.84	8.47	Copper, cadmium and nickel	Biochar increased Cd and Ni, but reduced Cu sorption by soil. DOM-removed biochar further enhanced all metal sorption	[3]
Hardwood	1–5%	–	9.87	Copper and lead	Significantly decreased soil pore water concentrations of copper and lead	[20]
Hardwood	1%	17.48	10.01	Nickel and zinc	Biochar decreased metal leaching by 80% and enhanced the residual portion in soil	[14]

4.2. Influence of Biochar on Heavy Metals Bio-Availability

The bio-availability of various metals indicates the toxicity in soils and the potential hazard of contaminating the human food-web. The bio-availability of contaminants regulates their degradation and eco-toxicology in polluted soils. Bio-availability is defined as a pollutant fraction representing the availability of a chemical agent to a living organism for eco-toxicology, assimilation, and degradation expression [33]. Many studies showed that applying biochar is more efficient in immobilizing heavy metals, thereby decreasing their phytotoxicity and bio-availability (Table 2). Liu et al. assessed the ability of biochar addition to amend the heavy metals toxicity in pit-tailings [45]. They used biochar prepared from orchard prune residues at 0%, 1%, 5%, and 10% rates. WHC, CEC, and pH level were increased with increasing biochar application rates, and the bio-availability of zinc, lead, and cadmium of mine-tailings was reduced, while cadmium showed the maximum

reduction. According to Montagnoli et al. [18], applied biochar produced from cotton stalks improved the cadmium-polluted soil. The findings suggested that biochar obtained from cotton stalks can decrease the bio-availability of soil cadmium by co-precipitation or an adsorption mechanism. According to another study, the effects of sewage sludge-derived biochar on metals bio-availability and solubility in Mediterranean farming soil were compared with untreated sewage sludge (not charred). The biochar applications decreased the plant accessibility of lead, cadmium, zinc, and nickel when equated to sewage application [46]. Table 2 summarizes the outcome of various biochars on the uptake volume of pollutants and the bio-availability of contaminants. Biochar produced from green waste and chicken manure significantly reduced lead, copper, and cadmium uptake by Brassica juncea. It was also found that the decline in plant metal concentration was increased with increasing biochar rates, except for copper concentration. Biochar produced from rice proved more effective to immobilize lead and copper than cadmium [47]. Hence, when the sole objective of biochar addition is to immobilize various metals, special attention should be paid to selecting suitable feedstock and the production temperature of biochar. Gamboa et al. conducted a pot experiment and used activated biochar of wood in the soil spiked with metals to examine the biochar's effect on the accessibility of zinc, lead, copper, and cadmium to corn [48]. Biochar addition reduced the concentration of copper, cadmium, and arsenic in corn shoots, but the effect of biochar addition was inconsistent on zinc and lead concentrations in corn shoots. Soil pH is closely associated with the bio-availability of metals in the soil. The addition of biochar can improve the CEC and pH of soil, and consequently increase the immobilization of various metals in the soil [49]. Siles et al. [50] conducted a study using biochar obtained from cow manure and mussel shell to decrease the lead toxicity in prominently lead-polluted soil in South Korea. Lead bio-availability in soil was reduced by 76% with biochar application. An increase in adsorption capacity and a rise in soil pH were considered the result of the reclamation effect of biochar. For instance, lead bio-availability in soil was reduced up to 93% with shell biochar, a mulching material. At present, many studies revealed that various kinds of biochars can decrease heavy metals' bio-availability and their mobility. However, most of this research is carried out under controlled environments (under greenhouse and laboratory experiments). Therefore, to fully utilize the biochar potential as a reclamation agent, large-scale field studies should be conducted.

Table 2. Effect of biochar addition on bio-availability of heavy metals in soils.

Biochar	Preparation Temperature (°C)	Heavy Metals	Outcome	Reference
Chicken waste	550	Chromium	Increased soil Cr(IV) reduction to Cr(III)	[18]
Eucalyptus	500	Zinc, cadmium, copper, and arsenic	Reduction in zinc, cadmium, copper, and arsenic in corn shoots	[20]
Sewage sludge	550	Zinc, lead, nickel, copper, and cadmium	Substantial decrease in plant availability of these metals	[38]
Hardwood	400	Arsenic	Noteworthy reduction of arsenic in foliage of the Silver-grass	[29]
Chicken waste	500	Lead, copper, and cadmium	Notable decrease of lead, copper, and cadmium accumulation by *Brassica juncea*	[14]
Rice straw	450	Lead, copper, and cadmium	Substantial decrease in concentration of lead, copper, and cadmium in polluted soil	[3]
Orchard residue	600	Lead, copper, cadmium, and zinc	Notable decrease of bio-available lead, copper, cadmium, and zinc, with cadmium showing utmost reduction	[35]
Maize straw	550	Cadmium	Decrease of bio-availability of cadmium in soil through co-precipitation or adsorption process	[18]

Table 2. *Cont.*

Biochar	Preparation Temperature (°C)	Heavy Metals	Outcome	Reference
Wheat straw	450	Cadmium and lead	Bio-available cadmium and lead were reduced by 4.48% to 10.69% (Cd) and 11.74% to 16.42% (Pb) in surface soil (0 to 4 cm)	[34]
Hardwood	400	Cadmium, lead, and arsenic	Reduced cadmium and zinc concentrations, but not arsenic in soil leachate	[48]
Poultry litter	350	Copper, cadmium, and nickel	Biochar enhanced cadmium and nickel, but decreased copper sorption via soil. Dissolved organic matter-removed biochar further increased all metal sorption	[19]
Rice straw	500	Cadmium, lead, and zinc	Biochar decreased soil bio-available and vegetable metals and enhanced plant biomass yield	[36]
Oak wood charcoal	450	Cadmium and copper	Charcoal reduced soil-available, leachable, and bio-accessible cadmium and copper	[39]
Rice straw	350	Cadmium	Soil pH increased, exchangeable cadmium reduced, but Fe-oxide and OM-bound cadmium enhanced	[17]
Rice husk	500	Mercury	Rice husk feedstock can expressively decrease the transport of mercury in soil	[50]
Poultry manure	400	Copper	Decrease the concentration of Cu in soil pore water and soil, diminish the transferable contents of Cu in the plants, and enhances the residual state in plants contents as well as organic substance binding	[26]
Fruit bunches	550	Lead, copper, and cadmium	When the application rate was 20%, the content of Cd in brassica aerial parts reduced by around 90% and Pb content reduced by 95% as well as copper content reduced by 63%	[18]
Oak branches	500	Lead	Pb bio-availability in soil reduced by 15 and 76%	[50]
Orchard residue	500	Arsenic	Arsenic components in roots of tomato reduced by around 70%	[14]
Wheat straw	450	Cadmium and lead	Concentration of bio-availability of cadmium and lead was decreased 13.84% to 16.15% and 4.02% to 13.40% in 4 to 8 cm soil	[32]
Miscanthus	700	Copper, lead, zinc, and cadmium	pH changes upon biochar amendment, the results exhibited that biochar decreased extractability of copper, lead, and zinc, but not of Cd	[50]
Rice straw	500	Cadmium, zinc, lead, and arsenic	Biochar reduced cadmium, zinc, and lead, but increased arsenic in soil pore water and rice	[41]
Orchard prunings	350	Arsenic, cadmium, copper, lead, and zinc	Reduced free metals yet elevated arsenic and dissolved organic carbon-associated metals in soil pore water	[22]
Sewage sludge	450	Arsenic, cadmium, cobalt, chromium, copper, nickel, lead, and zinc	Decreased soil EDTA-extractable and bio-accumulated arsenic, chromium, cobalt, nickel, and lead, but increased the portions of others	[39]
Soybean straw	300	Copper, lead, and antimony	Biochar immobilized lead and copper, but mobilized antimony	[25]
Rice straw	350	Cadmium	Lettuce cadmium content decreased in lightly contaminated but not in heavily contaminated soil	[42]

5. Immobilization and Adsorption Mechanisms

Biochar contains a porous structure, active surface functional groups, high pH, and aromatic components. These characteristics play a significant role in the reclamation

process of metals in the soil, such as precipitation, complexation, electrostatic interaction, ion exchange, redox, and physical adsorption (Figure 3).

5.1. Physical Adsorption (Van der Waals Adsorption)

The physical adsorption mechanism is also called van der Waals adsorption due to the interaction among adsorbent and adsorbate molecules. This adsorption is primarily induced by intermolecular forces and is usually reversible. Van der Waals adsorption of the heavy metals on biochar is generally influenced by pore volume, surface energy, and specific surface area of the biochar (adsorbent) [51]. Biochars produced at higher temperatures contain greater pore volume and specific surface area, offering a significantly large contact area to the heavy metal ions, thus improving the van der Waals adsorption of biochar. For instance, switchgrass- and pine wood-derived biochar at 300 °C and 700 °C can efficiently immobilize uranium and copper with van der Waals adsorption [52]. Heavy metal ions, including zinc, cadmium, and arsenic, are immobilized on the biochar surface by van der Waals adsorption [53].

5.2. Ion Exchange

Ion exchange represents the selective exchange of transferable metal ions, such as K^+, Mg^{2+}, Na^+, and Ca^{2+}, on the surface of biochar through metal ions. The ion exchange efficiency primarily depends on the chemical properties of biochar surface. The ion exchange capacity between metal cations and biochar particles can be improved via higher cation exchange capacity (CEC). The higher cation exchange capacity of biochar is observed at 200–350 °C pyrolysis temperatures, because higher temperatures reduce the acidic carbon/oxygen and oxygen-comprising functional groups, which decreases the CEC of biochar [54]. Zaman et al. studied the reclamation procedures of mercury and zinc through shell-derived biochar at 170–185 °C [55]. They found that the acidic oxygen-comprising functional groups on the surface of biochar, including -OH and -COOH, can exchange with Hg^+ and Zn^{2+} ions to discharge ionizable protons, as shown in the complying equations:

i. $2\text{-COOH} + ZN^{2+} = \text{-(COO)}_2\ Zn + H^+$
ii. $2\text{-COH} + ZN^{2+} = \text{-(CO)}_2\ Zn + 2H^+$

Biochar's ion exchange capacity is closely associated with soil pH. When the soil solution pH is lower than the biochar's pH at PZC (point of zero charge), more metal ions are attracted to the biochar surface by the ion exchange method [56]. According to the Tomczyk et al. [57] investigation, the biochar derived by the hydrothermal process has plenty of oxygen-containing functional groups, which helps in the adsorption of copper (Cu^{2+}) ions through physical adsorption and ion exchange. Oxygen-containing functional groups can enhance the adsorption and enrichment of the pollutants near the cathode, thereby improving the degradation efficiency

5.3. Electrostatic Interactions

A highly negatively charged biochar surface can increase electrostatic interaction among metal cations and soil particles to immobilize heavy metals with electrostatic attraction. This electrostatic interaction of biochar and metals mainly depends upon the point of zero charge (PZC) of biochar, the pH of the soil solution, and the ionic and valence radii of the heavy metal [58]. Applying biochar to soils increases the soil pH and CEC, which also increases the electrostatic attraction between soil particles and metal ions [59]. Qiu et al. reported that the reclamation effect of rice- and wheat stalk-derived biochars is more pronounced compared to activate C because the incorporation of biochar induced a remarkable increase in the soil cation exchange capacity and shifted the zeta potential–pH curves in a negative direction that caused an increase in electrostatic attractions between negatively charged biochar and Pb (II) ions (Pb^{2+}). Hence, electrostatic attraction is a well-known process for biochar to immobilize the heavy metals in the soil [60].

5.4. Complexation

The biochar surface is enriched with oxygen-comprising functional groups, including -OH, -COH, and -COOH, which make a complex with metal ions to generate stable complexes. Biochar prepared at a low pyrolysis temperature contains ample oxygen-comprising functional groups, immobilizing the heavy metals more efficiently via metal complexation. The amount of oxygen-containing functional groups in biochar augments with time, which is caused by the carboxyl formation and oxidation of the biochar surface [59]. Complexation can be formed between the C=O ligand of oxygen-comprising functional groups and positively charged metal cations. For example, Pb (II) ions surface complexation with free hydroxyl and carboxyl functional groups and inner-sphere complexation of Pb (II) ions with hydroxyl functional groups of mineral oxides, as given in the below equations (iii to v) [60]:

iii. $\text{-COOH} + Pb^{2+} + H_2O \rightarrow \text{-COOPb}^{+} + H_3O^{+}$

iv. $\text{-OH} + Pb^{2+} + H_2O \rightarrow \text{-OPb}^{+} + H_3O^{+}$

v. $> \text{C-COOH} + M^{n} \rightarrow > \text{C-COOM}^{+} + H_3O$

The oxygen-comprising functional groups in biochar significantly enhance the ligands on the soil surface to immobilize various metals by establishing heavy metal–ligand complexes [61]. In another experiment, Bandara et al. examined the reclamation processes of Cr through biochar derived from sugar beet tailing. They found that complexation is the primary process responsible for Cr reclamation [17].

5.5. Precipitation

Biochars can co-precipitate with heavy metal cations to produce insoluble carbonates and phosphates to immobilize heavy metals in soils [62]. A higher pyrolysis temperature (more than 400 °C) of hemicellulose and cellulose in plant feedstock generally produces alkaline biochar to facilitate metal precipitation in soil [63]. On the other hand, biochar produced from animal manure contains higher ash contents, namely sulfur, silicon, phosphorus, potassium, sodium, magnesium, and calcium, which can react with heavy metals and form insoluble minerals [64]. For instance, cow manure-derived biochar possesses an ample number of phosphates that can immobilize lead in the soil due to pyromorphite formation. Another study presented that biochar derived from dairy manure adsorbs Pb from an aqueous medium via surface sorption (13 to 16%) and precipitation (84 to 87%) [65]. Lopez et al. compared the mechanisms and effects of cadmium, zinc, copper, and lead adsorption through rice- and cow-bone-derived biochar. They found that the leading adsorption process is precipitation among metal cations and carbonate or phosphate. These findings propose that precipitation can efficiently immobilize metals [66].

5.6. Redox

The redox reaction is an important mechanism through which biochar immobilizes heavy metals. Functional groups on biochar surfaces can undergo redox reactions with metal ions, which, in turn, change their toxicity. For instance, biochar can decrease the more toxic Cr (VI) to comparatively less toxic Cr (III) and then immobilize Cr (III) on the surface via a complexation process [20]. In this process, biochar performs as an electron donor to provide electrons from surface functional groups and graphitic structure to Cr (VI) [8]. Thus, during polluted soils' remediation, the biochar electron-giving ability can decrease metals, including TI, Sb, and As, which can increase their bio-availability [32]. Many researchers have obtained a better performance for the adsorption of arsenic on biochars modified with Mn and Fe oxides [64]. The process is that manganese oxide on the biochar oxidizes As (II) to form As (V), and then manganese arsenate precipitates and causes them to be adsorbed onto the surface of biochar [65]. In the study by Lin et al. [67], As (III) was adsorbed with a composite of BC-Mn-Fe, and its adsorption capacity was four times better than the pristine biochar, but the adsorption mechanism was significantly affected by pH because the sorption impact of the composite for arsenic was weakened by an electrostatic repulsion under alkaline environments. In brief, the heavy metal immobilization through biochar is

mainly due to the chemical reaction of heavy metals with surface functional groups. Heavy metal adsorption through biochar may have multiple processes working simultaneously. Though researchers have investigated the heavy metal adsorption mechanism on biochar via various techniques, it is still presently challenging to expose the adsorption mechanism precisely at a molecular level.

6. Remediation of Soils Contaminated with Organic Pollutants through Biochar Application

Soils become contaminated with organic pollutants due to farming practices, mismanagement of wastes, and industrial and anthropogenic activities. Many organic contaminants are mutagenic or carcinogenic, and some are recalcitrant to degradation [66]. Organic pollutants can be either emerging organic contaminants or persistent organic pollutants (POPs). Organic pollutants have wide applications as they are used in pesticides, industrial processes, and in the manufacturing a wide range of commodities (pharmaceuticals, additives, and solvents). According to the World Health Organization (WHO), well-known persistent organic contaminants include polychlorinated biphenyls, polychlorinated dibenzo-p-dioxin, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated dibenzofurans [67,68]. Usually, POPs accumulate in the soil horizons enriched with organic matter and retain themselves for several years. Emerging pollutants are thought to have harmful impacts on wildlife and humans. For instance, personal care products (triclosan and trimethoprim), naturally occurring estrogenic steroid hormones and phthalate acid esters, and pharmaceutical products are regarded as emerging organic contaminants [69]. Biochars have been observed to be very efficient in the removal of various anthropogenic and natural organic pollutants. Previous studies have reported that having a high SSA, an aromatic nature, a micropore volume, and an ample number of polar functional groups in the biochar substance has been observed to be effectual in the uptake of different organic compounds, such as, PAHs, emerging pollutants (steroid hormones), and pesticides [32]. However, biochar having a large SSA, being highly porous and having an aromatic nature, a micropore volume, and sufficient polar functional groups proved effective for the adsorption of contaminants [70]. Biochar can decrease the organic compound bio-availability by the sorption process and minimize the hazard of the contaminants polluting the human food chain and ground water. However, the fate of these sequestered pollutants in the environment is still unclear. Future studies should fill this gap by conducting biochar-based soil reclamation trials under field conditions.

6.1. Influence of Biochar on the Adsorption of Organic Contaminants

The sorption behavior of contaminants to biochar depends on the process controlling the concentration of organic contaminants in polluted soils. Consequently, other mechanisms, including leaching, degradation, volatilization, and bio-availability of the pollutants, are also affected (Table 3). Most of the biochar–soil interactions are regulated by the high SSA of biochar. This characteristic of biochar is influenced mainly by the type of feedstock biomass and pyrolysis conditions used for biochar preparation [71]. The pyrolysis temperature greatly influences the biochar desorption and adsorption of organic contaminants in the soil. Nkoh et al. [72] investigated the phenanthrene ($C_{14}H_{10}$) uptake isotherms with wood-derived biochars from the species Betula pendula and Pinus sylvestris. The isotherm data revealed higher phenanthrene sorption for materials that experienced high pyrolysis temperatures. Such an increase in sorption also occurs with the increased SA of biochar prepared at elevated temperatures. Duan et al. stated that eucalyptus wood-based biochar prepared at 800 °C has more micropores than biochar produced at 400 °C, lacking a microporous structure [73]. They concluded that biochar pyrolyzed at 800 °C showed a greater tendency to adsorb diuron ($C_9H_{10}C_{l2}N_2O$) in the soil as compared to biochar produced at 400 °C. A higher pyrolysis temperature causes an increase in micropore volume and SSA through a progressive degradation of the organic materials (cellulose, lignin) and the formation of vascular bundles or a channel structure.

Some amorphous carbon structures also form during pyrolysis due to the degradation of cellulose. It has been reported that micropores may be formed by amorphous carbon structures. A higher pyrolysis temperature causes the release of volatile matter and creates more pores [74]. Woody biochars contain higher porosity (due to higher lignin and cellulose content) compared to the biochars prepared from crop residues, which causes a difference in the biomass cell structure, composition, size, and shape [11]. The biochar produced at 650 °C had a much greater adsorption potential, but a lower desorption capability of terbuthylazine in the soils as compared to biochar prepared at 400 °C. As explained above, micro-porosity and high SSA make biochar an effective sorbent for various organic pollutants. These properties of biochar may alter with time after their application to the soils, and this phenomenon is known as the aging of biochar [72]. The association between biochar and soil constituents (clay minerals and natural organic compounds) facilitates the biochar aging process. It has been found that organic matter (OM) is responsible for blocking the biochar micropores, thereby inhibiting the sorption of organic pollutants [73]. Fedeli et al. investigated the effect of soil contamination by using different concentrations of gasoline on oat (*Avena sativa* L.) and tested the effect of biochar supply to the polluted soils on the performance of oat plants [9]. The results showed that adding 5% (*w*/*w*) biochar (a carbon-rich byproduct of wood biomass pyrolysis) to the 6% and 10% polluted soils to test whether adding biochar had a beneficial effect on oat performance greatly reduced the negative effects caused by gasoline on all the investigated parameters [9]. Wang et al. [75] noticed that biochar-increased soil adsorption of terbuthylazine (herbicide) is higher in a soil with low OM content than soil with high OM content. It is inferred that the higher amount of dissolved organic compounds in OM-enriched soil may compete for biochar sorption sites with terbuthylazine. The adsorption capacity of biochar produced from pine-wood was continuously decreased after biochars were inoculated with soil for one month [74]. In another study [76], desorption-sorption behavior of weed killers was observed in soil either amended with aged biochars or pristine biochars under field conditions for 3 years. Aged biochar's sorption capacity was decreased up to 46% for the diuron herbicide. All these investigations revealed that biochar aging affects its characteristics, which lowers its capacity to absorb pollutants of interest. Hence, a better understanding of the biochar aging mechanism is important to determine an optimum biochar application rate and frequency for an effective remediation plan.

Table 3. Influence of biochar's addition on the sorption of organic contaminants in soils.

Biochar	Preparation Temperature (°C)	Organic Pollutant	Influence	Reference
Poultry waste	300	Herbicides	Poultry biochar showed great sorption capacity for norflurazon and fluridone	[76]
Eucalyptus	800	Diuron	Increases the adsorption of pesticides with biochar reaction time with soil and addition rate	[77]
Pinewood	600	Phenanthrene, PAHs	Sorption ability enhanced with preparation temperature	[78]
Woodchip	450	Acetochlor and Atrazine	Adsorption of Acetochlor and Atrazine enhanced 1.5 times	[79]
Green waste	450	Atrazine	Biochar increased pesticide adsorption	[80]
Eucalyptus	400	Carbofuran and chlorpyrifos	Higher pyrolyzed and higher rates of addition to soils led to tougher adsorption of pesticide	[76]
Wheat straw	250	Norflurazon and fluridone	Wheat straw biochar showed great sorption capacity for norflurazon and fluridone	[75]

Table 3. *Cont.*

Biochar	Preparation Temperature (°C)	Organic Pollutant	Influence	Reference
Swine manure	250	Norflurazon and fluridone	Swine manure biochar showed great sorption capacity for norflurazon and fluridone	[78]
Pine needles	700	PAHs	Capacity of sorption enhanced with production temperature	[75]
Sugarcane residue	500	Ethinylestradiol	Increased steroid sorption and desorption retardation in both soils; reduced steroid microbial mineralization	[81]
Hardwood	400	PAHs	Decreased both total and bio-available PAHs in soil; likely resilient PAHs sorption via biochar and increased PAHs microbial degradation	[82]
Willow	600	PAHs	Biochar decrease bio-accessible PAHs in the soil; biochar decreased soil toxicity to springtail and bacteria, but not phytotoxicity	[83]
Sewage sludge	350	PAHs	Decreased the bio-accumulation of PAHs; likely resilient PAHs sorption via biochar by partition	[84]
Soft wood	450	Polychlorinated Biphenyls	Biochar decreases Polychlorinated Biphenyls bio-availability by resilient sorption	[18]
Maize stover	300	Polychlorinated dibenzo-p-dioxins	Biochar significantly decreased soil particulate organic matter-extractable and bio-available polychlorinated dibenzo-p-dioxins; biochar immobilizes soil polychlorinated dibenzo-p-dioxins through sorption	[85]
Bamboo	700	Pentachlorophenol	Residual Pentachlorophenol in and Pentachlorophenol leaching losses from soil columns were reduced; sorption of Pentachlorophenol through biochar mainly by partition	[86]
Rice straw	500	Petroleum	Soil microbial degradation of petro-hydrocarbon enhanced by 20%	[87]
Hardwood	800	Tylosin	Enhanced tylosin adsorption at greater biochar rate; more tylosin was non-desorbable in greater pH soil	[88]
Olive residues	400	Metalaxyl and Tebuconazole	Biochar decreased degradation and leaching of fungicides in soil	[89]
Hardwood	600	Simazine	Simazine biodegradation inhibited and leaching decreased	[90]
Pinewood	350	Phenanthrene	Sorption of phenanthrene on wood biochar was less evident; sorption on biochar was more evident in low-organic carbon soils	[91]
Stinging nettle	300	Phenanthrene	Biochar enhanced phenanthrene degradation by up to 44%	[92]
Pinewood	350	Phenanthrene	The biochar application enhancing phenanthrene sorption to soil depended on biochar and soil organic carbon	[33]
Bamboo	500	Diethyl phthalate	90% sorption of diethyl phthalate was noticed	[93]

Figure 4 illustrates the biochar interaction mechanisms proposed for organic contaminants.

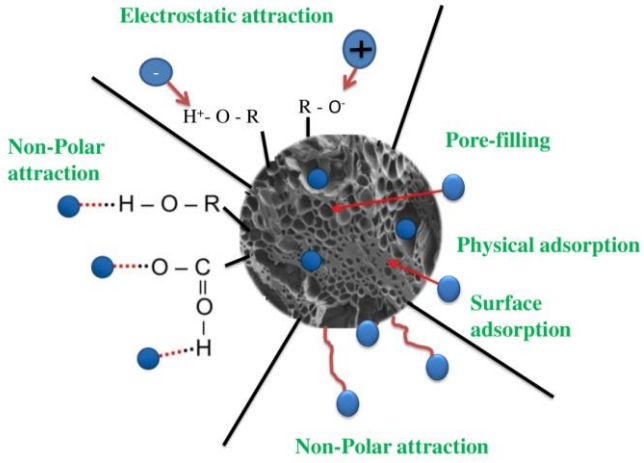

Figure 4. Biochar interaction mechanisms proposed for organic contaminant removal.

6.2. Biochar Effect on Bio-Availability of Organic Contaminants

Many studies revealed that biochar-amended soil can facilitate the absorption of various organic pollutants, decreasing their uptake through the plants. The addition of biochar in lesser amounts to soil can markedly decrease the accumulation of organic contaminants and other pesticides in plants (Table 3) [77]. Rana et al. [78] demonstrated that enhancing the biochar quantity in the soil can decrease the bio-availability of weed killers. They noticed that a minimum application rate (0.1%) of biochar in soil could significantly decrease the diuron bio-availability. Ref. [37] observed the effect of two different biochars on the bio-availability of sulfentrazone and S-metolachlor herbicides. They noticed that biochar with high SSA can significantly decrease the bio-availability and efficiency of weed killers for weed control. According to another study, biochar derived from rice straw added to phenanthrene-polluted soil substantially decreased the phenanthrene uptake through corn seedlings [79]. Ref. [80] reported a 50% decrease in soil pore water concentration of polycyclic aromatic hydrocarbons in biochar-amended soil. The sorption, bio-availability, and dissipation of hexachlorobenzene via wheat stalk biochar were investigated by [66]. They reported that the sorption of hexachlorobenzene through biochar was 42-fold higher than in control soil, thereby decreasing the volatilization and Eisenia foetida (earthworm) uptake of hexachlorobenzene from soil.

7. Biochar Attributes Affecting the Remediation of Polluted Soils

Biochar impact on various pollutants, such as heavy metals and organic contaminants in soils, depends on soil attributes, biochar characteristics, particle size, and the addition amount of biochar as well as biochar pyrolysis condition from different types of biomasses.

7.1. Physiochemical Attributes of Polluted Soils

The pH of the soil is the most significant parameter in the pollutant's stabilization process. Under a lower pH environment, a large concentration of hydrogen ions exist in the soil contributing to its electrostatic repulsion with positively charged metal cations, and hydrogen ions compete with these cations for sorption sites. Thus, the mobility of metals in contaminated soils with lower pH is typically stronger [81]. The alkaline carbonates and hydroxide groups released via biochar in contact with water in soils elevate the soil pH [39]. Under alkaline conditions, heavy metals are liable to undergo sorption reactions with O-comprising functional groups in biochar and generate precipitates with phosphate and carbonate [31]. An increase in soil pH can increase the biochar stabilization capacity for heavy metals. Nonetheless, not all detrimental compounds can be immobilized in a higher

soil pH condition [36]. For instance, high concentrations of OH- in alkaline nature soils would undergo competitive sorption with the negatively charged oxyanion. As creatine is easily desorbed from the soil particle surface under a higher pH environment [20], this shows that soil pH is a critical parameter affecting the impacts of biochar.

Various redox conditions can control heavy metal's adsorption via biochar addition [82]. Several studies on alterations in redox potential were conducted in flooded conditions. Many researchers observed significant alterations in pH after the addition of biochar to upper mining-contaminated soil, but no effect when biochar was applied to lower mining-polluted soils, and hypothesized that the hydric regime hydration process might change the biochar impacts on the pH of the soil [83]. Lian et al. reported that biochar derived from sewage sludge created an apparent rise in residual constituents of cadmium under flooding environments, and thus, they concluded that hydrophobic environments were the main factor influencing the effective metals immobilization via biochar application [84]. Additionally, continuous drying–wetting cycles of soil can accelerate the biochar aging mechanism, which may enhance the surface O-enriched functional groups, therefore maintaining the metals' immobilization efficiency of biochar [20]. Other parameters in the soil also have impacts on the metal immobilization efficiency of biochar [84]. For instance, biochar addition sometimes raises copper migration in mining-polluted soils with higher zinc contents [78]. Additionally, some metals, such as copper, can bind organic matter to create stable complexes, and the mobility of these metals is restricted in the soils [85].

7.2. Physicochemical Characteristics of Biochars

Various factors may affect the chemical attributes of biochars, such as feedstock types, pyrolysis conditions, dissolved organic carbon content, and the SSA of biochar. These aspects can influence the biochar performance for polluted soils. The feedstock can influence the biochar attributes and affect its removal process and outcome on various metals (Table 4). Different feedstocks lead to changes in biochar ash content, which, in turn, impacts its pH and remediation ability [86]. The efficacy of adsorption and the immobilization of mercury are also correlated to applied biochar type [87]. The pyrolysis temperature strongly influenced biochar's physicochemical properties (e.g., surface area, pH, and functional groups) and affected biochar's performance as a soil amendment [88]. The pyrolysis temperature is strongly correlated with changes in the structure and physicochemical properties of biochar. A higher pyrolysis temperature resulted in an increase of surface area, carbonized fractions, pH, and volatile matter, and a decrease of CEC and the content of surface functional groups [89]. It has been found that increasing the pyrolysis temperature causes changes in the biochar surface area and porosity. This is most likely due to the decomposition of organic matter and the formation of micropores. Moreover, the destruction of aliphatic alkyl and ester groups and the exposure of the aromatic lignin core under higher pyrolysis temperatures may result in increased surface area [90]. The heating to temperatures of 350–650 °C breaks and rearranges the chemical bonds in the biomass, forming new functional groups, including carboxyl, lactone, lactol, quinine, chromene, anhydride, phenol, ether, pyrone, pyridine, pyridine, and pyrrole [91]. On the other hand, biochar produced at lower temperatures (300–400 °C) displays a more diversified organic character due to the occurrence of aliphatic and cellulose type structures. As a result, the structure of biochar appears to have more organized C layers (such as graphene structure) and less content of surface functional groups when pyrolysis temperature increases [92]. Zeghioud et al. observed a decreased organic mercury content (43–78%) after three months of cultivation with biochar from various feedstocks. They showed that the removal performance of organic mercury through biochar with a higher N content was greatly effective [94].

In another study, Abdin et al. compared the removal efficiency of biochar derived from mesquite and fishbone for various metals, including Cd, Cu, Zn, and Pb, and they concluded that biochar derived from fishbone has more stabilization ability because it contained ample phosphate [60]. Animal waste-derived biochar showed a higher removal ability than biochar derived from plant residue [76]. For instance, cattle manure-derived

biochar's effect on zinc stabilization was more remarkable than that of biochar derived from rice husk. This may be due to the complex manure composition, as manure-derived biochar has additional surface functional groups [93]. The pyrolysis temperature and conditions have a significant impact on biochar attributes. With the increase in production temperature, ash content, pH value, SSA, and carbon stability are enhanced, while the yield of biochar, functional groups, volatile matter, and O/C and H/C ratio are reduced [95]. Sarfraz et al. [96] reported that high pyrolysis can convert more feedstock into ash content and discharge alkali metal salts. Thus, biochar is often applied to reduce or neutralize the tailing's acidity, stimulating metal's cation adsorption [57]. Biochar pyrolyzed at a high temperature has high porosity and surface area, and polar functional groups, which can remove the mercury more effectively [97]. Various heavy metal cations are easy to combine with phosphate to generate precipitation and develop more stability. It has been found that biochar with more phosphate content has more lead stabilization ability in treating the polluted soils; mostly, lead is immobilized in biochars through creating complexes with phosphate. Moreover, biochar can donate phosphate and enhance the phosphate bio-availability in soil [98], but the chemical traits of P resemble As (V), and thus, increasing the availability of P can contribute more to the discharge of arsenic from soil solid-phase to liquid-phase and enhance the arsenic migration [99].

Smebye et al. reported that the biochar-dissolved organic carbon can influence the interaction between soil and dissolved metals, and also the adsorption and desorption equilibrium [100]. The biochar addition increases the dissolved organic carbon content in polluted soil, while dissolved organic carbon reacts with Sb, As, and ferric oxides, and may create ternary complexes to enhance the toxic metalloid's mobility [96]. Nonetheless, since dissolved organic carbon can accelerate the ion exchange and complexation reaction, biochar with dissolved organic carbon can reduce the diethylenetriaminepentaacetic acid-extractable cadmium content to a greater extent, thus increasing the cadmium immobilization [101]. Biochar surface area has a positive impact on the remediation of polluted soil. Biochar with a larger surface area has a greater contact surface with the soil solution, leading to more reactions with pollutants [77]. Palansooriya et al. noticed that the surface area of biochar derived from lightwood (265.3 m^2/g^{-1}) was greater than biochar derived from pinewood (234.8 m^2/g^{-1}) and it had a significant effect on EC, pH, and the lead amount of soil pore water [60].

7.3. Application Methods/Operating Modes

Biochar addition rates can alter the speciation of heavy metals in polluted soils to various degrees, which can decrease the heavy metal concentration in plant tissues [102]. The addition rate of biochar is negatively interrelated with the amount of contaminating pollutants of Zn, Pb, Cd, and Al in mine-polluted soils [78]. Pandey et al. observed that with enhancing biochar application rates of 1–4% w/w, the Pb and Cd amount of plant shoots reduced from 2.81 mg kg^{-1} and 22.6 mg kg^{-1} to 2.37 mg kg^{-1} and 15.5 mg kg^{-1}, while those of the roots reduced from 15.7 mg kg^{-1} and 16.1 mg kg^{-1} to 8.42 mg kg^{-1} and 11.5 mg kg^{-1} in that order [103]. A 5% biochar application rate could enhance the plant shoot biomass by 29.3%, which might be due to the heavy metal's reduction and the improvement of nutrients and organic matter [104]. However, the plant shoot's biomass reduced by 2.8% when the application rate of biochar reached 10%. It is hypothesized that benzoic acid and ethylene in biochar could accelerate plant growth and seedling development as well as reduce the toxicity [105–128]. Therefore, it is essential to find an appropriate biochar addition rate for phyto-ecology promotion in a cost-effective way in polluted soils.

Biochar with different particle sizes can also affect the soil remediation efficiency, and mostly, small particle sizes have excellent effects on remediation [129]. Medynska-Juraszek observed biochar derived from pinewood with particle size of 0.1–0.4 mm can decrease soil pore water lead amount by 86 and 69%, respectively, in contaminated soil [130]. This is attributed to the finer size biochar having a higher surface area, which also showed

that biochar particle size was more efficient in decreasing the organic-bound metals, but did not influence metal species residual [131]. Moreover, combining the biochar with other treatment measures could play an effective role in contaminated soil. The mixing of lime with 5% biochar caused a significant enhancement of microbial activity in soil and decreased the extractable Zn, Cu, and Al amount compared with biochar application alone [87]. The mixing of technosol and biochar significantly reduced the mobility of Pb from 17 to 2.1, Ni from 47 to 2.3, and Cu from 18 to 1.6 [132]. Siles et al. reported that a combination of iron sulfate and biochar added to soil, accelerated the arsenic release, and immobilized the arsenic effectively [50]. In general, the interaction between heavy metals and biochar depends not only on biomass type and pyrolysis temperature, but also on physiochemical attributes and the soil pollution intensity. Different application methods also play a significant role in a pollutant's mobilization and soil system improvement.

Table 4. The impact of biochar produced from various feedstocks in treating the polluted soils.

Feedstock Type	Pyrolysis Temperature °C	pH	Biochar Addition Dose %	Pollutant Form	Adsorption Rate	Reference
Wheat straw	500	10.6	5	Soil pore water Sb amount	Reduced 44%	[95]
Rabbit manure	450	10.5	10	Cr mobility	Decreased 58%	[107]
Oak wood	400	9.9	5	Ni concentration	Reduced 73%	[108]
Poultry manure	450	10	10	Cr mobility	Decreased 54%	[109]
Wheat straw	550	10	5%	Soil pore water Al mount	Reduced 10%	[106]
Wheat straw	550	10	5	Soil pore water Ni mount	Reduced 49%	[106]
Cocoa husk	600	9.9	5	Mercury fraction	Reduced 79%	[110]
Wheat straw	550	10	10	Pore water As amount	Reduced 83%	[106]
Rabbit manure	600	10.8	10	As amount in soil	Reduced 23%	[110]
Sugarcane bagasse	60	6.1	5	Bio-available mercury extracted	Decreased 31%	[111]
Banana peel	600	9.9	5	Bio-available mercury	Reduced 75%	[113]
Fishbone	600	-	3	Cu concentration	Decreased 66%	[114]
Mesquite-wood	300	-	3	Cu concentration	Decreased 53%	[114]
Wheat straw	550	10	5	Pore water Cu amount	Reduced 46%	[106]
Rice straw	500	10	5	Pore water Cu amount	Eliminated 95%	[115]
Oak-wood	400	9.9	5	Cu concentration	Reduced 98%	[108]
Rabbit manure	450	10.5	10	Cu mobility	Decreased 58%	[94]
Poultry manure	600	10.7	10	Cu mobility	Decreased 25%	[94]
Rabbit manure	600	10.8	10	Total copper content of soil	Reduced 26%	[109]
Wheat straw	550	10	10	Pore water zinc amount	Removed 97%	[106]
Fishbone	600	-	3	Zn concentration	Decreased 55%	[114]
Kiwi pruning	550	11.3	4	Fraction of zinc	Reduced 13.3	[115]
Rice straw	500	10	5	Pore water zinc amount	Eliminated 66%	[118]
Apple tree	500	10.7	-	Zinc availability	Reduced 11%	[38]
Apricot-shell	500	9.2	-	Acid-soluble zinc	Decreased 21%	[38]
Pomelo peel	450	10.2	5	Water-leachable zinc	Reduced 74%	[119]
Pine-wood	500	8.2	5	Labile zinc amount in soil	Decreased 63%	[120]
Rabbit manure	600	10.8	10	Zinc mobility	Decreased 72%	[121]
Poultry manure	450	10	10	Zinc mobility	Decreased 86%	[122]
Mesquite-wood	400	-	3	Pb concentration	Decreased 39%	[114]
Fishbone	600	-	3	Pb concentration	Decreased 43%	[114]
Kiwi pruning	550	11.3	4	Fraction of lead	Reduced 24%	[118]
Wheat straw	550	10	10	Pore water lead amount	Removed 97%	[106]
Rice straw	500	10	5	Pore water lead amount	Eliminated 93%	[123]
Pine-wood	500	9.6	5	Pore water lead amount	Decreased 86%	[124]
Light-wood	500	8.2	5	Pore water lead amount	Decreased 98%	[124]
Rice husk	450	10	5	Water-leachable lead	Reduced 90%	[118]
Pine-wood	500	8.2	5	Labile lead amount in soil	Reduced 45%	[115]
Poultry manure	600	10.7	10	Pb mobility	Decreased 38%	[108]
Rabbit manure	450	10.5	10	Pb mobility	Decreased 32%	[116]
Fishbone	600	-	-	Cadmium amount	Reduced 34%	[116]
Kiwi pruning	550	11.3	4	Fractions of cadmium	Reduced 7.6%	[109]
Bamboo	750	9.5	5	Pore water cadmium amount	Eliminated 43%	[106]
Apple tree	50	10.7	10	Available amount of cadmium	Reduced 19%	[115]
Apricot-shell	500	9.2	10	Available amount of cadmium	Reduced 11%	[117]
Poultry manure	600	10.7	10	Cadmium mobility	Deceased 78%	[126]
Rabbit manure	600	10.8	10	Cadmium mobility	Decreased 29%	[127]
Pinewood	500	8.2	5	Labile cadmium amount in soil	Reduced 62%	[109]

8. Biochar Toxicity and Its Mitigation Methods

8.1. Organic Contaminants in Biochar

Pyrolysis of feedstocks may form a wide range of organic substances, including dioxins, PAHs, and volatile organic compounds (VOCs) [133]. These chemicals in biochar might be a potential drawback because of their toxicity to plants and soil microorganisms [134]. The negative impacts of biochar addition on agriculture or eco-toxicity risk resulting from biochar's inherent impurities [135] necessitate a complete understanding of the formation, bio-availability, and total content of organic contaminants within biochar, including dioxins, PAHs, and VOCs, which would be very significant from an environmental safety point of view.

8.2. Volatile Organic Compounds (VOCs) Formation in Biochar

Volatile organic compounds in biochars are usually obtained from the re-condensation of pyrolysis liquids and vapors, such as the pyrolytic products named bio-oil and syngas (also called pyroligneous acid or wood vinegar, respectively) [125,129]. The feedstocks are mainly composed of inorganic minerals, lignin, cellulose, and hemicelluloses, which vary in different feedstocks. These chemical constituents largely affect yields and characteristics of the decomposition products, such as bio-oil and biochar [130]. Rana et al. comprehensively described the release, distribution, and transformation of the main chemical components, such as S, Cl, P, N, O, H, C, and other metals, during pyrolysis/carbonization procedures as well as biochar evolution, tar, bio-oil, and gas [78]. First, the breaking down of hemicelluloses at temperatures of 200 °C–260 °C generates more volatiles, and less chars and tars than cellulose, and cellulose follows at temperatures of 240 °C–350 °C to create levoglucosan and anhydrocellulose, whereas lignin is the last element to decompose at temperatures of 280 °C–500 °C and with a maximum rate being noticed at 350 °C–450 °C, which yields phenols with the cleavage of carbon and ether linkages [117,118]. Biomass pyrolysis is considered to be a two-stage reaction, in which the products of the first stage break-up reactions (1) and (2) further in the existence of each other to create reactions for secondary pyrolysis yield.

Parallel reactions:

$$\text{Pure biomass} \rightarrow (\text{Volatiles} + \text{gases})_1 \quad (1)$$

$$\text{Pure biomass} \rightarrow (\text{char})_1 \quad (2)$$

$$(\text{Volatiles} + \text{gases})_1 + (\text{char})_1 \rightarrow (\text{Volatiles} + \text{gases})_2 + (\text{chars})_2 \quad (3)$$

Volatile organic compounds release and react with liquids, gases, and char fractions during the pyrolysis process. Thus, a huge range of volatile organic compounds, including low molecular weight organic acids, phenols, alcohols, ethane, and ketones, are re-condensed and trapped in the pores of biochar [96]. These volatile organic compounds in biochar generally are linked with the pyrolysis liquid fraction [46]. For instance, Sarfraz et al. extracted water-soluble organic elements from maize stalk-derived biochar manufactured at 350 °C and 650 °C and characterized them with mass spectrometry, and chromatographic and spectroscopic techniques, in order to establish the linkage between water-soluble organic elements patterns and biochar bulk characteristics in relation to the bio-oil composition [96]. Their findings confirmed that even at the pilot plant scale these aromatic units are created through the interaction between the biochars and pyrolysis vapors and survived into biochar pores, therefore determining the suitability of biochar for environmental applications [96].

8.3. Volatile Organic Compounds (VOCs) Contents in Biochars

Very limited studies have quantitatively or qualitatively studied volatile organic compounds in biochar [136]. We searched for the literature that described the volatile organic compounds profiles and concentrations in biochar, regardless of what kind of

pyrolysis methods were applied, and identified roughly 11 articles listed in Table 5. The pyrolysis parameters (heating temperatures and pyrolysis technology) and feedstock type are also contained in Table 5, as are the techniques used for the detection and extraction of volatile organic compounds in biochars. Additionally, it should be noted that among these studies, most of them were carried out under laboratory conditions to qualitatively determine the influence of several factors on volatile organic compounds formation, and less attention has been paid to quantitative analysis. The total content of volatile organic compounds in biochar was reported by El-Shafey et al. who compared the relative content and VOCs composition in hydrochars produced from woody material, digestate, and wheat straw by hydrothermal carbonization at 190 °C–270 °C [137]. They described that the total amount of volatile organic compounds in the biochar derived at 270 °C ranged between 2000 and 16,000 μg g^{-1} (0.2–1.6 wt%), 300 and 1800 μg g^{-1} of phenols, and 50 and 9000 μg g^{-1} of benzenes. Based on this quantitative examination of volatile organic compounds, the authors recommended that the fresh hydrochar should be optimized for the addition as a soil amendment [138]. Shi et al. studied the formation of VOCs in biochars, the total VOCs content in 152 biochars varied widely, ranging between 0.34 and 16,000 μg g^{-1} [139]. The total content of VOCs also changed with feedstock type and pyrolysis parameters. Moreover, VOCs types detected in biochar largely vary with the pyrolysis parameters and feedstock. For instance, biochar created from the hydrothermal method at a higher temperature usually contained more kinds of volatile organic compounds than those from a lower temperature [140].

Table 5. Reported total and available concentrations of VOCs in biochar.

Biochar Type	Preparation Method	Pyrolysis Temperature °C	VOC Extraction and Detect Method	Total Concentration (μg g^{-1})	Available Concentration (μg g^{-1})	Reference
Corn stalk	Slow pyrolysis	350–650	Aqueous extraction and chromatographic mass spectrometry	88	35–3000	[129]
Pine, lignin, and cellulose	Slow pyrolysis	600–500	Mass spectrometry and electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry	51	28.58–1251	[130]
Softwood pellets	Slow pyrolysis	550	Water extraction, MiniRAE lite VOC analyzer	8	0.9–13.7	[131]
Rice straw, corn stalk, and mushroom	Slow pyrolysis	450	Aqueous extraction gas and chromatographic massspectrometry	Not detected	5200, 7700, and 2100	[132]
Softwood pellets	Slow pyrolysis	550	Carbon disulphide extraction and semi-quantitative analysis	Below detection limit (20 μg g^{-1})-1166	-	[133]
Softwood pellets	Slow pyrolysis	550	Water extraction, MettleToledo thermogravimetric \analysis	Not detected	-	[134]
Garapa wood	Hydrothermal carbonization	150–270	Water extraction	8–71	-	[135]
Masanduba wood	Hydrothermal carbonization	150–270	Toledo thermogravimetric analysis	8–79	-	[87]
Digestate	Hydrothermal carbonization	190–270	Headspace gas chromatography	25–78	2000–16,000	[57]
Switch grass biochar	Fast pyrolysis	450	Toluene extraction	Not detected	-	[137]
Shells, oak, hardwood, sawdust, and corn stover	Fast pyrolysis; slow pyrolysis Gasification, hydrothermal, carbonization, and microwave-assisted pyrolysis	250–800	Headspace thermal desorption and gas chromatographic mass spectrometry	>140	-	[139]

Negative Effect and Standard of Biochar Associated with VOCs

The VOCs amount in biochar is very low (Table 5), but its potential negative impacts on alga, soil microbe, and plants are significant [140]. For instance, the germination of seeds is significantly reduced after exposure to poultry manure-derived biochars, tentatively attributed to the water-soluble organic compounds in biochar [141]. VOCs in biochar also influence soil nutrient cycling, such as P and N, because of their participation in biotic and abiotic reactions known to impact soil quality [142]. Ghidoti et al. reported that phenols contained a fraction of the VOCs in biochar that potentially could be toxic to some microorganisms and constrain their growth in a short time, and hence the VOCs shaped the structure of soil microbial populations [142]. It has been extensively accepted that VOCs are very significant for the evaluation of biochar quality. Nonetheless, although various biochar quality guidelines have been suggested through the European Biochar Certificate [35] and International Biochar Initiative [74], no quantitative data or threshold of volatile organic compounds was comprised. For the sustainable and safe application of biochar, we sturdily suggest that volatile organic compounds should be incorporated among the criteria for the valuation of biochar quality, which needs more attention in this area.

8.4. Formation of Polycyclic Aromatic Hydrocarbons (PAHs) in Biochars

Several studies described the formation of polycyclic aromatic hydrocarbon in biomass pyrolysis; the depiction of polycyclic aromatic hydrocarbon in biochar is very complex. Several reaction mechanisms have been suggested and the production process of polycyclic aromatic hydrocarbons during pyrolysis has been well-reviewed [143]. As stated via them, the broadly accepted process is a H^- abstraction acetylene addition, in which gaseous C_2H_x radicals or intermediates including ethene and ethyne that are produced from the cracking of biomass lignin, hemicelluloses, and cellulose undergo a chain of bi-molecular reactions to form greater poly-aromatic ring structures. That is why the polycyclic aromatic hydrocarbon content is sorbed on raw biochar surge when enhancing the residence time and heating temperature. Moreover, Zhang et al. reported that polycyclic aromatic hydrocarbon is generated via two main ways based on heating temperature [144]. At more than 500 °C, polycyclic aromatic hydrocarbons are produced from uni-molecular cyclization, dealkylation, dehydrogenation, and aromatization of cellulosic and ligneous components in biomass. The native compounds, including H_2S, CH_4, CO_2, and H_2O, are removed and aromatized structures are retained, which then face a direct nuclear condensation with further cyclization. At less than 500 °C, a free radical way followed through pyrosynthesis into bigger aromatic structures produces polycyclic aromatic hydrocarbon.

8.4.1. Total and Available Amounts of Polycyclic Aromatic Hydrocarbon in Biochar

Some recent studies have analyzed the content of polycyclic aromatic hydrocarbon in a huge number of biochars obtained from several feedstocks and pyrolytic conditions at an industry and laboratory scale (Table 6). Odinga et al. measured the total polycyclic aromatic hydrocarbon of 11 biochars produced from various feedstocks, such as cow manure, poultry litter, paper sludge, leaves, and wood, but the amounts were below the limit of detection [93]. Zhang et al. stated that the total content of polycyclic aromatic hydrocarbon dominated with methylnaphthalenes and naphthalene in a birch biochar was 10 $\mu g\ g^{-1}$, but benzo[a]anthracene and benzo[a]pyrene were not noticed or their concentrations were below the detection limit (<0.1 $\mu g\ g^{-1}$) [144]. Lopez et al. reported that the total polycyclic aromatic hydrocarbon content of nine pulp sludge biochars varied from 0.4 to 236 $\mu g\ g^{-1}$ [66]. The biochar sample produced at 450 °C for 60 min was noticed to comprise the maximum concentration of polycyclic aromatic hydrocarbon (236 $\mu g\ g^{-1}$). Duan et al. assessed the influence of heating temperature on freely dissolved polycyclic aromatic hydrocarbon contents in sludge biochars and observed that their amount is very low, with a range of 81–126 ng L^{-1} [73].

Table 6. Reported total and available concentrations of PAHs in biochars.

Feedstock	Fabrication Method	Pyrolysis Temperature °C	PAH Extraction Method	Total PAHs Concentration (μg g^{-1})	Reference
Sludge	Microwave heating pyrolysis	400–800	Acetone and dichloromethane extraction	23–65	[141]
Rice husk Spruce wood Beech wood Sugar beet Elephant grass Wheat husks Paper sludge Sewage sludge Pine wood	Slow pyrolysis	400–800	Acetone extraction	1.0–11.3	[78]
	Slow pyrolysis	400–750	Toluene extraction	0.4–1987	[145]
Sewage sludge	Slow pyrolysis	500–700	Heptane and acetone extraction	0.6–1.1	[57]
Pine wood	Slow pyrolysis	250–700	Dichloromethane extraction	0.19–0.86	[87]
Miscanthus Wheat straw Sida hermaphrodita Willow Softwood pellets Willow chips Miscanthus chips Demolition wood *Arundo donax* Straw pellets Willow	Slow pyrolysis	500–700	Toluene extraction	0.6–1.5	[66]
	Slow pyrolysis	350–750	Toluene extraction	1.2–100	[140]
Wheat straw Elephant grass	Slow pyrolysis	350–650	Accelerated solvent extractor	3.5–39.9	[133]
Pulp sludge	Slow pyrolysis	450–550	Hexane extraction and Sodium sulfate	0.4–236	[90]
Rice husk Fraxinus excelsior	Slow pyrolysis	300–600	Triethylamine, acetone, and hexane	9.56–64.65	[131]
Coconut shell Elephant grass	Slow pyrolysis	350–650	Accelerated solvent extractor	1.124–28.339	[47]
Distiller grains	Slow pyrolysis	350–400	Cyclohexane extraction	1.2–19	[9]
Ponderosa pine wood Tall fescue straw	Slow pyrolysis	100–700	Toluene-methanol extraction	0.05–30.2	[87]
Digested dairy manure Elephant grass	Slow pyrolysis	250–900	Toluene extraction	0.07–45	[97]
Coniferous wood Coniferous Vine wood	Slow pyrolysis	350–750	Toluene, methanol, dichloromethane, acetone, ethanol, propanol, hexane, and heptane extraction	9.1–355	[73]
Hardwood Rice straw	Slow pyrolysis	300–450	Dimethylsulfoxide extraction	10	[66]
Maize Bamboo Redwood Poplar wood	Slow pyrolysis	300–600	Pressurized liquid extraction	0.08–8.7	[11]
Spruce wood Wheat straw	Slow pyrolysis	400–525	Dichloromethane extraction	33.7	[146]
Varnish wastes Olive oil Solid waste Waste lube oils Paper waste Sewage sludges Polyethylene	Gasification	400–1050	Dichloromethane extraction	0.598–16.33	[11]

8.4.2. Negative Effect of Biochar Associated with Polycyclic Aromatic Hydrocarbons

Though low total concentrations and much lower concentrations of bio-available polycyclic aromatic hydrocarbon have usually been detected in biochar (Table 6), some studies paid special attention to the negative influence of polycyclic aromatic hydrocarbon released from biochar because of their mutagenic, teratogenic, and carcinogenic traits. A few organisms, including earthworms, protozoa, alga, and plants, were used to assess the toxicological impacts of biochar associated with polycyclic aromatic hydrocarbon [145]. For instance, ref. [140] observed that polycyclic aromatic hydrocarbon in aqueous extracts of biochar produced through higher-temperature gasification is at least partly accountable for the decrease in seedling growth. Stefaniuk et al. examined biotoxicity tests of three higher pyrolytic-derived biochars extract solutions (Acorus calamus, saw dust, and rice husk) on an animal (Caenorhabditis elegans), a plant (Triticum), and a microbe (Pseudomonas

aeruginosa) [11]. Little toxic impact on all the examined organisms was noticed for the biochars produced from sawdust and rice husk, whereas biochar produced from Acorus calamus shows substantial toxicity on all the examined organisms, probably because of those certain small aromatic molecules. [78] reported that the polycyclic aromatic hydrocarbon can have bactericidal characteristics that would disastrously affect the function and structure of the soil microbial community [78]. For example, ref. [146] revealed that the remaining polycyclic aromatic hydrocarbon in low temperature-prepared biochars played a key role in decreasing the emission of N_2O through inhibiting denitrification. Patel et al. reported that the biochars had a toxic property toward tested organisms, owing to the relatively great amount of polycyclic aromatic hydrocarbon (1.124–28.339 $\mu g\ g^{-1}$) retained in the biochars [144]. Nonetheless, although various studies attributed the negative effects of biochar on soil microbes to the sorbed pollutants, such as VOCs and PAHs [147], limited data are available in this area. More research is needed to thoroughly understand the adverse impacts of biochar-sorbed VOCs and PAHs on the function and structure of the soil microbes, and the underlying mechanisms. These efforts will prominently help create better quality biochar.

8.5. Presence of Dioxins in Biochar

Dioxins belong to the family of chlorinated composites, such as polychlorinated dibenzo furans, and polychlorinated dibenzo dioxins that share characteristics and chemical structures that are mostly created on solid surfaces during carbonization when the temperature is between 200 and 400 °C, and the pyrolysis time in seconds [148]. Dioxins are ubiquitous and extremely toxic compounds; originally, they were supposed to be completely of anthropogenic origin [78]. Until now, very little information has been revealed on concentrations of dioxin in biochar. Aside from determining the concentration of PAHs, ref. [140] detected dioxins retained in various biochars and noticed that concentrations of total dioxin were extremely low (92 pgg^{-1}) and the concentrations of bio-available dioxins were below the detection limit. Furthermore, the biochars derived from food waste contained a higher concentration of dioxins as compared to other biochars, possibly owing to the higher chlorine content in food wastes. ref [78] stated that polychlorinated dibenzo furans concentration varied among biochars manufactured at different pyrolysis temperatures, and the maximum concentrations of polychlorinated dibenzo furans (612 pgg^{-1}) were found in a biochar created at 300 °C [78]. Nonetheless, Diao et al. conceived that dioxins should be examined in their biochars that contain the highest amount of PAHs (236 μgg^{-1}), but no compounds were detected within the lowest detection limit (0.1 pgg^{-1}), which might be accredited to the clean feedstock without heavy metals and chlorine [97]. Moreover, the maximum permissible thresholds for dioxins within biochars have been developed by UBC (20 $ngkg^{-1}$), EBC (20 $ngkg^{-1}$), and IBI (17 $ngkg^{-1}$). Still, the information about the presence of dioxins in biochar is inadequate to develop any general assumptions, and more studies are required in the future.

8.6. Presence of Heavy Metals in Biochar

8.6.1. Presence of Heavy Metal Total Contents in Biochar

Generally, biochar products consist of mineral and carbon elements, and minerals include various types of heavy metals, such as As, Cu, Cd, and Pb, which generally result from the feedstock [88]. Heavy metals in the feedstock are mostly concentrated and accumulated in biochar during carbonizing [149]. Alipour et al. stated that the levels of toxic metals, such as Se, As, Cr, Ni, Cd, and Pb, in the different biochars varied with the carbonization parameters, and these metals were observed to be enriched in biochars [8]. The major concerns of these metals in biochar mainly involve As, Cr, Ni, Zn, Mn, Cu, Cd, and Pb. Zheng et al. found big differences in heavy metals' total contents among the biochars, which are closely associated with the inherent minerals in green waste, production waste, animal manure, and sewage sludge [149]. Green waste-derived biochars, such as grass, wood dust, and crop straw comprise rather lower contents of the As, Cr, Ni, Zn, Mn,

Cu, Cd, and Pb relative to the biochars derived from production waste, animal manure, and sewage sludge, indicating their lesser potential risk as soil remediation/treatments. Zaman et al. reported that the total contents of As, Cr, Ni, Zn, Mn, Cu, Cd, and Pb in biochar derived from sewage sludge were in the range of 3–51 $mgkg^{-1}$, 54–1378 $mgkg^{-1}$, 47–924 $mgkg^{-1}$, 540–3360 $mgkg^{-1}$, 400–1540 $mgkg^{-1}$, 145–2360 $mgkg^{-1}$, 2.5–10 $mgkg^{-1}$, and 40–500 $mgkg^{-1}$, respectively [55]. Zheng et al. found that the Zn, Cd, Cr, Ni, and Cu concentrations in biochars produced from animal manure and sewage sludge are extremely higher [150]. Particularly, arsenic is present in a huge portion of manure and sewage sludge biochars and exceed its safe level (300 $mgkg^{-1}$) for agricultural usage. Thus, an exhaustive risk study of heavy metal contents in the biochar is pivotal before their addition as soil remediation.

8.6.2. Presence of Heavy Metal Speciation in Biochar

The heavy metals' eco-toxicity/bio-availability in the environment are well-known to mainly depend on the chemical speciation of metals. The Bureau of Reference (BCR) and Tessier sequential extraction are extensively employed to determine the chemical speciation of the metals in the sediments and soils [151]. The comparable chemical speciation of the heavy metals is detailed in Table 7. Recently, these two techniques (BCR and Tessier) were also used for analyzing the potential and direct influence of fractions of heavy metals in the biochars [140]. Several studies confirmed that the biochars showed lower contents of the direct influence fractions in the heavy metals (F1 + F2 fractions in the Bureau of Reference extraction, and F1 + F2 + F3 fractions in the Tessier extraction) related with the feedstock/biomass, and the direct influence fraction was converted into comparatively stable fractions [9]. Gasco et al. observed that the direct influence fraction in biochar produced by low temperatures gradually reduced with the rising temperature [152]. Contrary to this, liquefaction biochar manufactured at comparatively slow pyrolysis did not comply with this temperature-reliant tendency. Oni et al. reported that the heavy metals' chemical speciation in biochar may be regulated via molecular speciation of intrinsic heavy metals in the biomass and the species conversion during biomass carbonizing [21]. Nonetheless, recently, the studies regarding the heavy metals' molecular species in biochars are comparatively limited. Copper-glutathione and copper-citrate were leading species in manure-derived biochar, and for pyrolyzed products, the content of these two species of copper was decreased, while Cu2S, CuS, and CuO could be observed using micro-SXRF. Fedeli et al. also reported the fraction of zinc bound to an organic substance, such as zinc-acetate and zinc-citrate, in the carbonous materials reduced corresponding to feedstock (40–76% vs. 26–69%), and zinc sulphide enhanced by 6.6–25% [10]. The conversion of zinc and copper organic substance fractions into their mineral fractions is primarily owing to the creation of aromatic and crystalline C phase from carbonizing the amorphous organic C. Moreover, [140] stated that the presence of several heavy minerals species in biochars derived from manure, such as $C_{10}H_{12}Cr_2N_2O_7Cr_2O_3$, $Ca_{7.29}Pb_{2.21}(PO_4)_3(OH)$, $Cu_3(PO_4)(OH)_3$, and $ZnMn_2O_4$. Furthermore, a portion of mineral fractions may be capsulized in porous structures and C matrices of the biochars and the minerals react with feedstock C to create organic and inorganic composites. These heavy metal fractions in biochar can be conceived to be comparatively resilient to bio-utilization and solubilization. Generally, the transformation of heavy metals' molecular speciation during the varied carbonization conditions and processes of biomass conversion into biochar and the related mechanisms require to be further studied. These are useful and critical for predicting and understanding the potential fate and the heavy metals' bio-availability in the biochar in environment.

Table 7. Relationships among chemical speciation (BCR and Tessier Extraction) and eco-toxicity/bio-availability of heavy metals [11].

BCR Extraction	Tessier Extraction	Eco-Toxicity/Bio-availability
Acid soluble and exchangeable fraction F1	Exchangeable fraction F1 Carbonate fraction F2	Direct influence/effect
Reducible fraction F2	Mn/Fe oxide fraction F3	
Oxidizable fraction F3	Organic substance-bound fraction F4	Potential influence/effect
Residue fraction F4	Residue fraction F5	No impact

8.6.3. Multiple Environmental Risks of Biochar Correlated with Various Heavy Metals

Assessing the impurity degree and measuring the environmental risk of heavy metals present in biochar is critical before their addition as soil amendment. Very limited research has paid attention to the environmental risk of heavy metals present in biochars derived from grass residues, wood, and crops, mainly owing to low heavy metal content in these biochars [106]. The heavy metals' potential risk was evaluated in previous studies. The risk assessment code [87] is a speciation index that measures the environmental risk of single-metal basing on Tessier and BCR extractions (Table 8). Penido et al. reported that the biochars derived from sewage sludge had varied risk assessment code values, indicating diverse risks in the environment [147]. Most of the collected data indicated that the sewage sludge-derived biochars have the risk range from low to extreme high. However, there were numerous studies that stated no risk of Cr, Cu, Cd, and Pb in biochars. Likewise, the sewage sludge-derived biochars and the liquefaction biochars had comparatively lower risk assessment code values of the heavy metals [147]. The geo-accumulation index, risk index, and potential ecological/environmental risk factors are often used to show the potential risk of heavy metal contents (Table 8). Nie et al. demonstrated the different geo-accumulation index values of more than 0 for zinc, copper, and cadmium (un-polluted), and 4.3 to 4.5 for lead (heavily to very polluted). The diverse ecological risk values were 0 to 4.8 (low risk) for cadmium, copper, and zinc, and 150 to 176 for lead (considerable to higher risk). The varied ecological risk values were 155 to 180 for all of the examined heavy metals (moderate risk) in biochars derived from sewage sludge at low temperatures [127]. Divergently, cadmium was at a greatly polluted and very high risk level with an ecological risk and geo-accumulation index of 630 to 735 and 3.8 to 4, while lead was at un-polluted and lower risk level with ecological risk and geo-accumulation index of less than 0 in biochars derived from sewage sludge through liquefaction at low temperatures [21]. For the pyrolyzed biochars, it is usually considered that the degree of contamination and potential risk of various heavy metals can be reduced by increasing the pyrolytic temperature, as shown with lower risk indices, the ecological risk, and the geo-accumulation index for low temperature-derived biochar The sewage sludge-derived biochars showed different potential ecological/environmental risks. Low potential ecological/environmental risk (ecological risk of 1.9 to 17) of Cr, Ni, Zn, Cu, and Pb in the biochars derived from sewage sludge was demonstrated by Zheng et al.while cadmium exhibited higher risk (ecological risk of 370 to 460) in biochars prepared at low temperatures, and moderate or low risk (ecological risk of 48 to 107) in biochars produced at high temperatures [149]. El-Naggar et al. reported that the Cr, Ni, and Pb in biochars produced at 400–600 °C from sewage sludge possessed lower potential ecological/environmental risk (ecological risk of 0.81 to 40). The potential ecological/environmental risk of copper was high for low temperature-prepared biochars (ecological risk of 276), considerable for biochars prepared at 450 and 500 °C (ecological risk of 130 to 150), and low for biochars derived at 550 and 600 °C (ecological risk of 60 to 75), and zinc was at the lower risk level with the ecological risk range of 50 to 60 [46]. These differences in the potential risks and impurity degrees of various heavy metals in sewage sludge biochars may be closely related with the heavy metals' original species in the biomass and the conversion of heavy metals' species during the carbonization process.

Table 8. Indices for the ecological risk assessment [9].

Geo-Accumulation Index	Degree of Contamination	Ecological Risk	Risk Degree	Risk Index	Risk Degree	Risk Assessment Code	Risk Degree
Less than 0	Unpolluted	Less than 40	Low risk	Less than 150	Low risk	Less than 1	No risk
0 to 1	Unpolluted to moderately unpolluted	40 to 80	Moderate risk	150 to 300	Moderate risk	1 to 10	Low risk
1 to 2	Moderately polluted	80 to 160	Considerable risk	300 to 600	Considerable risk	10 to 30	Middle risk
2 to 3	Moderately to greatly polluted	160 to 320	High risk	More than 600	High risk	30 to 50	High risk
3 to 4	Heavily polluted	More than 320	Very high risk			More than 50	Very high risk
4 to 5	Heavily to extremely polluted						
More than 5	Extremely polluted						

8.7. Possible Methods to Mitigate or Avoid the Biochar Contamination

In order to mitigate the negative impacts on the soil system, it is important to produce biochar with low levels of pollutants, such as heavy metals, VOCs, and PAHs. Nonetheless, most of the published literature has focused on the creation, transformation, and amount of these pollutants [146], but few of them cared about how to avoid their creation. Thus, the careful selection of unpolluted feedstock is very essential to avoid these impurities. Furthermore, pyrolytic conditions such as residence time and heating temperature mainly affect the creation and amount of pollutants in biochar; therefore, the good feedstock should prudently match with carbonization technology that has suitable operating conditions, i.e., specifically residence time and temperature range. For instance, based on the data collected on 46 biochars comprised of polycyclic aromatic hydrocarbon, the study in [140] proposed that the biomass selection and appropriate matching with the carbonization technology is important to ensure the fabrication of uncontaminated biochar. Similarly, ref. [73] advocated that biochar created with unpolluted feedstock at high pyrolysis (500 °C–550 °C) for 30 or 120 min meet the IBI guidelines of polycyclic aromatic hydrocarbon. In this regard, controlled equipment or an industrial reactor is highly suggested for this purpose, instead of a traditional kiln [97]. Generally, organic contaminants are retained on biochar during its fabrication from the re-condensation of pyrolysis liquids and vapors [57]. Therefore, one possible approach to decrease VOCs and PAHs in biochar is to pivot and collect liquids and gases separately, as suggested by [9], which is a huge challenge for developing the scaled and modern reactors for biochar fabrication. Haider et al. verified that the complete elimination of gas-phase pyro-synthesized polycyclic aromatic hydrocarbon resulted in biochars with low polycyclic aromatic hydrocarbon levels [78]. As well as the reactor, inert gases (CO_2 and N_2) are employed to cleanse gases from the pyrolytic system, which is also a better technique to reduce VOCs or PAHs in biochar [153]. After biochar creation, post-treatment approaches, such as composting and drying, are employed to decrease the impurities in biochar. Abate et al. dried the biochar samples and observed that the upsurge of drying temperature from 100 to 300 °C induced the total diminution of all polycyclic aromatic hydrocarbon content in biochars [151]. Biochar composting with organic materials, including biogas residue, agricultural straw, and dairy manure, is suggested as a practicable technique for generating biochar-based amendments to control these inherent insufficiencies associated with pollutants [147]. Nonetheless, available data about VOCs or PAHs contents in the composted biochar is scanty. Furthermore, the post-treatment approach will enhance the biochar production cost, which is not beneficial for the application of biochar. Thus, apart from selecting an unpolluted biomass, it is essential to reduce the pollutants during biochar fabrication.

9. Future Research Perspectives

Biochar application as a promising strategy for reclaiming polluted farming soils requires various aspects to be clarified and well-established. Various gaps in the literature have been identified and further studies to fill these knowledge gaps include:

1. To date, most of the studies regarding biochar application for the reclamation of polluted soils primarily focus on a small plot, greenhouse, and laboratory experiments. Large-scale experiments are needed before commercial-scale reclamation projects are employed.
2. Since biochar properties differ with different pyrolysis temperatures and feedstock materials, the optimization of biochar production systems is crucial to prepare designer biochar products to be applied efficiently for a particular remediation project.
3. The weak desorption and strong sorption of contaminants in biochar shows that biochar causes the self-sequestration of contaminants. The addition of biochar may contribute to pollutant accumulation in ameliorated soils, but, the long-term environmental fate of the sequestered pollutants is still unclear.
4. Biochar's capacity to sequester or adsorb contaminants declines with time due to the aging mechanism. A better understanding of the biochar aging mechanism is necessary for future research. This could help advocate appropriate application rates and frequency for improved reclamation programs.
5. At present, limited information is available regarding the role of biochar in decreasing the leachability and bio-availability of contaminants via sorption and speeding-up the dissipation of various organic pollutants in soil. Future studies are needed to investigate the feasibility of biochar-based dissipation of organic contaminants.
6. IMT combined with biochar showed promising potential in cleaning the soils polluted with organic contaminants. Therefore, biochar preparation to facilitate the optimum production of a microbial carrier should be emphasized.

10. Conclusions

This paper provided an in-depth analysis of the immobilization and adsorption mechanisms of heavy metals and organic pollutants through biochar application across diverse environmental conditions. Biochar can plausibly reduce the bio-availability and efficiency of organic contaminants and heavy metals in contaminated soils by changing the soil conditions. Biochar production conditions (pyrolysis temperature, feedstock type, and residence time) and the application rate greatly influence the biochar performance in remediating the contaminated soils. Biochar's efficacy for soil pollutants relies on the surface groups, pore size distribution, and ion-exchange capacity. Biochars prepared at high temperatures (800 °C) contained more porosity and specific surface area, thus offering more adsorption potential. The redox and electrostatic adsorption contributed more to the adsorption of oxyanions, whereas ion exchange, complexation, and precipitation were mainly involved in the adsorption of cations. Soil pH was the dominant factor influencing the remediation efficacy of biochar. On the other hand, impurities (VOCs, dioxins, PAHs, and heavy metals) produced during pyrolysis may induce toxicity in biochar and negatively affect the soil alga, microbes, and plants. Residence time and heating temperature mainly affect the creation and amount of pollutants in biochar; therefore, a careful selection of good feedstock matching with the carbonization technology is necessary to mitigate biochar toxicity. This review presented a comprehensive understanding of biochar-based mechanisms involved in the remediation of polluted soils and mitigation methods to reduce biochar toxicity. It would help to prepare a specific biochar with the desired features to target a particular pollutant at a specific site. This review provided explicit knowledge for developing a cost-effective, environment-friendly specific biochar, which could be used to decontaminate targeted polluted soils at a large scale.

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References

1. Yahaya, S.M.; Abubakar, F.; Abdu, N. Ecological risk assessment of heavy metal-contaminated soils of selected villages in Zamfara State, Nigeria. *SN Appl. Sci.* **2021**, *3*, 168. [CrossRef]
2. Cara, I.G.; Țopa, D.; Puiu, I.; Jitareanu, G. Biochar a promising strategy for pesticide-contaminated soils. *Agriculture* **2022**, *12*, 1579. [CrossRef]
3. Ahn, Y.; Yun, H.S.; Pandi, K.; Park, S.; Ji, M.; Choi, J. Heavy metal speciation with prediction model for heavy metal mobility and risk assessment in mine-affected soils. *Environ. Sci. Pollut. Res.* **2020**, *27*, 3213–3223. [CrossRef]
4. Da Silva, E.; Gao, P.; Xu, G.M.D.; Tang, X.; Ma, L.Q. Background concentrations of trace metals As, Ba, Cd, Co, Cu, Ni, Pb, Se, and Zn in 214 Florida urban soils: Different cities and land uses. *Environ. Pollut.* **2020**, *264*, 114737. [CrossRef] [PubMed]
5. Ai, S.; Yang, Y.; Ding, J.W.; Bai, X.; Bao, J.X.W.; Zhang, Y. Metal exposure risk assessment for tree sparrows at different life stages via diet from a polluted area in north western China. *Environ. Toxicol. Chem.* **2019**, *38*, 2785–2796. [CrossRef]
6. Bashir, S.; Ali, U.; Shaaban, M.; Gulshan, A.B.; Iqbal, J.; Khan, S.; Husain, A.; Ahmed, N.; Mehmood, S.; Kamran, M.; et al. Role of sepiolite for cadmium (Cd) polluted soil restoration and spinach growth in wastewater irrigated agricultural soil. *J. Environ. Manag.* **2020**, *258*, 110020. [CrossRef]
7. Gelardi, D.L.; Li, C.; Parikh, S.J. An emerging environmental concern: Biochar-induced dust emissions and their potentially toxic properties. *Sci. Total Environ.* **2019**, *678*, 813–820. [CrossRef] [PubMed]
8. Alipour, M.; Asadi, H.; Chen, C.; Besalatpour, A.A. Fate of organic pollutants in sewage sludge during thermal treatments: Elimination of PCBs, PAHs, and PPCPs. *Fuel* **2022**, *319*, 123864. [CrossRef]
9. Fedeli, R.; Alexandrov, D.; Celletti, S.; Nafikova, E.; Loppi, S. Biochar improves the performance of Avena sativa L. grown in gasoline-polluted soils. *Environ. Sci. Pollut. Res.* **2022**, *2*, 1. [CrossRef]
10. Kumar, R.; Verma, A.; Shome, A.; Sinha, R.; Sinha, S.; Jha, P.K.; Vara Prasad, P.V. Impacts of plastic pollution on ecosystem services, sustainable development goals, and need to focus on circular economy and policy interventions. *Sustainability* **2021**, *13*, 9963. [CrossRef]
11. Hasan, M.M.; Kubra, K.T.; Hasan, M.N.; Awual, M.E.; Salman, M.S.; Sheikh, M.C.; Awual, M.R. Sustainable ligand-modified based composite material for the selective and effective cadmium (II) capturing from wastewater. *J. Mol. Liq.* **2023**, *371*, 121125. [CrossRef]
12. Das, S.K.; Ghosh, G.K.; Avasthe, R. Application of biochar in agriculture and environment, and its safety issues. *Biomass Convers. Biorefinery* **2020**, *13*, 1359–1369. [CrossRef]
13. Allohverdi, T.; Mohanty, A.K.; Roy, P.; Misra, M. A Review on Current Status of Biochar Uses in Agriculture. *Molecules* **2021**, *26*, 5584. [CrossRef]
14. Stefaniuk, M.; Tsang, D.C.; Ok, Y.S.; Oleszczuk, P. A field study of bioavailable polycyclic aromatic hydrocarbons (PAHs) in sewage sludge and biochar amended soils. *J. Hazard. Mater.* **2018**, *349*, 27–34. [CrossRef]
15. Sun, J.; Cui, L.; Quan, G.; Yan, J.; Wang, H.; Wu, L. Effects of biochar on heavy metals migration and fractions changes with different soil types in column experiments. *BioResources* **2020**, *15*, 4388–4406. [CrossRef]
16. Taraqqi-A-Kamal, A.; Atkinson, C.J.; Khan, A.; Zhang, K.K.; Sun, P.; Akther, S.; Zhang, Y.R. Biochar remediation of soil: Linking biochar production with function in heavy metal contaminated soils. *Plant Soil Environ.* **2021**, *67*, 183–201. [CrossRef]
17. Ambaye, T.G.; Vaccari, M.; van Hullebusch, E.D.; Amrane, A.; Rtimi, S. Mechanisms and adsorption capacities of biochar for the removal of organic and inorganic pollutants from industrial wastewater. *Int. J. Environ. Sci. Technol.* **2021**, *18*, 3273–3294. [CrossRef]
18. Montagnoli, A.; Baronti, S.; Alberto, D.; Chiatante, D.; Scippa, G.S.; Terzaghi, M. Pioneer and fibrous root seasonal dynamics of Vitis vinifera L. are affected by biochar application to a low fertility soil: A rhizobox approach. *Sci. Total Environ.* **2021**, *751*, 141455. [CrossRef]
19. Amin, M.A.; Haider, G.; Rizwan, M.; Schofield, H.K.; Qayyum, M.F.; Zia-ur-Rehman, M.; Ali, S. Different feedstocks of biochar affected the bioavailability and uptake of heavy metals by wheat (*Triticum aestivum* L.) plants grown in metal contaminated soil. *Environ. Res.* **2023**, *217*, 114845. [CrossRef]
20. Chen, C.K.; Chen, J.J.; Nguyen, N.T.; Le, T.-T.; Nguyen, N.-C.; Chang, C.-T. Specifically designed magnetic biochar from waste wood for arsenic removal. *Sustain. Environ. Res.* **2021**, *31*, 29. [CrossRef]

21. Oni, B.A.; Oziegbe, O.; Olawole, O.O. Significance of biochar application to the environment and economy. *Ann. Agric. Sci.* **2019**, *64*, 222–236. [CrossRef]
22. Jain, S.; Mishra, D.; Khare, P.; Yadav, V.; Deshmukh, Y.; Meena, A. Impact of biochar amendment on enzymatic resilience properties of mine spoils. *Sci. Total Environ.* **2016**, *544*, 410–421. [CrossRef] [PubMed]
23. Brtnicky, M.; Datta, R.; Holatko, J.; Bielska, L.; Gusiatin, Z.M.; Kucerik, J.; Hammerschmiedt, T.; Danish, S.; Radziemska, M.; Mravcova, L.; et al. A critical review of the possible adverse effects of biochar in the soil environment. *Sci. Total Environ.* **2021**, *796*, 148756. [CrossRef] [PubMed]
24. Cameselle, C.; Gouveia, S.; Cabo, A. Enhanced Electro kinetic Remediation for the Removal of Heavy Metals from Contaminated Soils. *Appl. Sci.* **2021**, *11*, 1799. [CrossRef]
25. Azeem, M.; Ali, A.; Jeyasundar, P.; Li, Y.M.; Abdelrahman, H.; Latif, A.; Li, R.H.; Basta, N.; Li, G.; Shaheen, S.M.; et al. Bone-derived biochar improved soil quality and reduced Cd and Zn phytoavailability in a multimetal contaminated mining soil. *Environ. Pollut.* **2021**, *277*, 116800. [CrossRef]
26. Carvalho, J.; Nascimento, L.; Soares, M.; Valerio, N.; Ribeiro, A.; Faria, L.; Silva, A.; Pacheco, N.; Araújo, J.; Vilarinho, C. Life Cycle Assessment (LCA) of Biochar Production from a Circular Economy Perspective. *Processes* **2022**, *10*, 2684. [CrossRef]
27. Chandola, D.; Rana, S. *Biochar for Environmental Remediation*; Biochar—Productive Technologies, Properties and Applications; Elsevier: Amsterdam, The Netherlands, 2023. [CrossRef]
28. Hamid, Y.; Tang, L.; Hussain, B.; Usman, M.; Gurajala, H.K.; Rashid, M.S.; He, Z.; Yang, X. Efficiency of lime, biochar, Fe containing biochar and composite amendments for Cd and Pb immobilization in a co-contaminated alluvial soil. *Environ. Pollut.* **2020**, *257*, 113609. [CrossRef]
29. Torabian, S.; Qin, R.; Noulas, C.; Lu, Y.; Wang, G. Biochar: An organic amendment to crops and an environmental solution. *AIMS Agric. Food* **2021**, *6*, 401–415. [CrossRef]
30. He, E.; Yang, Y.; Xu, Z.; Qiu, H.; Yang, F.; Peijnenburg, W.J.; Wang, S. Two years of aging influences the distribution and lability of metal (loid) s in a contaminated soil amended with different biochars. *Sci. Total Environ.* **2019**, *673*, 245–253. [CrossRef]
31. Altaf, R.; Altaf, S.; Hussain, M.; Shah, R.U.; Ullah, R.; Ullah, M.I. Heavy metal accumulation by roadside vegetation and implications for pollution control. *PLoS ONE* **2021**, *16*, e0249147. [CrossRef]
32. Treto-Suarez, M.A.; Prieto-Garcia, J.O.; Mollineda-Trujillo, A.; Lamazares, E.; Hidalgo-Rosa, Y.; Mena-Ulecia, K. Kinetic study of removal heavy metal from aqueous solution using the synthetic aluminum silicate. *Sci. Rep.* **2020**, *10*, 10836. [CrossRef]
33. Krzyszczak, A.; Dybowski, M.P.; Czech, B. Formation of polycyclic aromatic hydrocarbons and their derivatives in biochars: The effect of feedstock and pyrolysis conditions. *J. Anal. Appl. Pyrol.* **2021**, *160*, 105339. [CrossRef]
34. Ullah, A.; Tahir, A.; Rashid, H.U.; Ur Rehman, T.; Danish, S.; Hussain, B.; Akca, H. Strategies for reducing Cd concentration in paddy soil for rice safety. *J. Clean. Prod.* **2021**, *316*, 128116.
35. Chang, Y.C.; Xiao, X.F.; Huang, H.J.; Xiao, Y.D.; Fang, H.S.; He, J.B.; Zhou, C.H. Transformation characteristics of polycyclic aromatic hydrocarbons during hydrothermal liquefaction of sewage sludge. *J. Supercrit. Fluids* **2021**, *170*, 105158. [CrossRef]
36. Ennaji, W.; Barakat, A.; El Baghdadi, M.; Rais, J. Heavy metal contamination in agricultural soil and ecological risk assessment in the northeast area of Tadla plain, Morocco. *J. Sed. Environ.* **2020**, *5*, 307–320. [CrossRef]
37. Mahmud, U.; Salam, M.B.; Khan, A.S. Ecological risk of heavy metal in agricultural soil and transfer to rice grains. *Discov. Mater.* **2021**, *1*, 10. [CrossRef]
38. Chen, X.; He, H.Z.; Chen, G.K.; Li, H.S. Effects of biochar and crop straws on the bioavailability of cadmium in contaminated soil. *Sci. Rep.* **2020**, *10*, 9528. [CrossRef]
39. Pande, V.; Pandey, S.C.; Sati, D.; Bhatt, P.; Samant, M. Microbial Interventions in Bioremediation of Heavy Metal Contaminants in Agroecosystem. *Front. Microbiol.* **2022**, *13*, 824084. [CrossRef]
40. Eckert, E.; Kovalevska, O. Sustainability in the European Union: Analyzing the Discourse of the European Green Deal. *J. Risk Financ. Manag.* **2021**, *14*, 80. [CrossRef]
41. EBC. *European Biochar Certificate Guidelines for a Sustainable Production of Biochar*; European Biochar Foundation (EBC): Arbaz, Switzerland, 2012.
42. Egamberdieva, D.; Jabbarov, Z.; Arora, N.K.; Wirth, S.; Bellingrath-Kimura, S.D. Biochar mitigates effects of pesticides on soil biological activities. *Environ. Sustain.* **2021**, *4*, 335–342. [CrossRef]
43. Sinduja, M.; Sathya, V.; Maheswari, M.; Dhevagi, P.; Kalpana, P.; Dinesh, G.K.; Prasad, S. Evaluation and speciation of heavy metals in the soil of the Sub Urban Region of Southern India. *Soil Sediment Contam. Int. J.* **2022**, *31*, 974–993. [CrossRef]
44. Singh, C.; Tiwari, S.; Singh, J.S. Biochar: A Sustainable Tool in Soil Pollutant Bioremediation. Bioremediation of Industrial Waste for Environmental Safety; In *Biological Agents and Methods for Industrial Waste Management*; Springer: Berlin, Germany, 2020; Volume II, pp. 475–494.
45. Liu, M.; Almatrafi, E.; Zhang, Y.; Xu, P.; Song, B.; Zhou, C.; Zeng, G.; Zhu, Y. A critical review of biochar-based materials for the remediation of heavy metal contaminated environment: Applications and practical evaluations. *Sci. Total Environ.* **2022**, *806*, 150531. [CrossRef] [PubMed]
46. El-Naggar, A.; Chen, Z.; Jiang, W.; Cai, Y.; Chang, S.X. Biochar effectively remediates Cd contamination in acidic or coarse-and medium-textured soils: A global meta-analysis. *Chem. Eng. J.* **2022**, *442*, 136225. [CrossRef]
47. Esfahani, A.R.; Zhang, Z.; Sip, Y.Y.L.; Zhai, L.; Sadmani, A.H.M.A. Removal of heavy metals from water using electrospun polyelectrolyte complex fiber mats. *J. Water Process Eng.* **2020**, *37*, 101438. [CrossRef]

48. European Commission. Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of Regions. In *New EU Forest Strategy for 2030*; European Commission: Brussels, Belgium, 2021.
49. Zhang, X.; Wells, M.; Niazi, N.; Bolan, N.; Shaheeng, S.; Hou, D.; Wang, Z. Nanobiochar-rhizosphere interactions: Implications for the remediation of heavy-metal contaminated soils. *Environ. Pollut.* **2022**, *299*, 118810. [CrossRef]
50. Siles, J.A.; Garcia-Romera, I.; Cajthaml, T.; Belloc, J.; Silva-Castro, G.; Szakova, J.; Tlustos, P.; Garcia-Sanchez, M. Application of dry olive residue-based biochar in combination with arbuscular mycorrhizal fungi enhances the microbial status of metal contaminated soils. *Sci. Rep.* **2022**, *12*, 12690. [CrossRef]
51. Ghosh, D.; Maiti, S.K. Biochar-assisted eco-restoration of coal mine degraded land to meet United Nation Sustainable Development Goals. *Land Degrad.* **2021**, *32*, 4494–4508. [CrossRef]
52. Yang, X.; Liu, L.; Tan, W.; Liu, C.; Dang, Z.; Qiu, G. Remediation of heavy metal contaminated soils by organic acid extraction and electrochemical adsorption. *Environ. Pollut.* **2020**, *1264*, 114745. [CrossRef]
53. Zahed, A.M.; Salehi, S.; Madadi, R.; Hejabi, F. Biochar as a sustainable product for remediation of petroleum contaminated soil. *Curr. Res. Green Sustain. Chem.* **2021**, *4*, 100055. [CrossRef]
54. Ghosh, D.; Maiti, S.K. Invasive weed-based biochar facilitated the restoration of coal mine degraded land by modulating the enzyme activity and carbon sequestration. *Restor. Ecol.* **2022**, e13744. [CrossRef]
55. Zaman, A.; Irfan, M.; Khan, A.M.; Ali, H.; Iqbal, N.; Ahmad, I.; Fawad, M.; Muhammad, F. Toxicity assessment and phytostabilization of contaminated soil by using wheat straw-derived biochar in tomato plants. *Gesunde Pflanz.* **2022**, *74*, 705–713. [CrossRef]
56. Hu, Y.; Yu, W.; Wibowo, H.; Xia, Y.; Lu, Y.; Yan, M. Effect of catalysts on distribution of polycyclic-aromatic hydrocarbon (PAHs) in bio-oils from the pyrolysis of dewatered sewage sludge at high and low temperatures. *Sci. Total Environ.* **2019**, *667*, 263–270. [CrossRef]
57. Tomczyk, A.; Sokołowska, Z.; Boguta, P. Biochar physicochemical properties: Pyrolysis temperature and feedstock kind effects. *Rev. Environ. Sci. Biotechnol.* **2020**, *19*, 191–215. [CrossRef]
58. Giarikos, D.G.; Brown, J.; Razeghifard, R.; Vo, D.; Castillo, A.; Nagabandi, N.; Gaffney, J.; Zelden, M.; Antakshinova, A.; Rodriguez, S.; et al. Effects of nitrogen depletion on the biosorption capacities of Neochloris minuta and Neochloris alveolaris for five heavy metals. *Appl. Water Sci.* **2021**, *11*, 39. [CrossRef]
59. Glab, T.; Gondek, K.; Mierzwa, H.M. Biological effects of biochar and zeolite used for remediation of soil contaminated with toxic heavy metals. *Sci. Rep.* **2021**, *11*, 6998. [CrossRef]
60. Palansooriya, K.N.; Sang, M.K.; Igalavithana, A.D.; Zhang, M.; Hou, D.; Oleszczuk, P.; Sung, J.; Ok, Y.S. Biochar alters chemical and microbial properties of microplastic-contaminated soil. *Enviro. Res.* **2022**, *209*, 112807. [CrossRef] [PubMed]
61. Ji, X.; Wan, J.; Wang, X.; Peng, C.; Wang, G.; Liang, W.; Zhang, W. Mixed bacteria-loaded biochar for the immobilization of arsenic, lead, and cadmium in a polluted soil system: Effects and mechanisms. *Sci. Total Environ.* **2022**, *811*, 152112. [CrossRef]
62. Gong, X.; Huang, D.; Liu, Y.; Zeng, G.; Chen, S.; Wang, R.; Xu, P.; Cheng, M.; Zhang, C.; Xue, W. Biochar facilitated the phytoremediation of cadmium contaminated sediments: Metal behavior, plant toxicity, and microbial activity. *Sci. Total Environ.* **2019**, *666*, 1126–1133. [CrossRef]
63. Gouma, V.; Tziasiou, C.; Pournara, A.D.; Giokas, D.L. A novel approach to sorbent-based remediation of soil impacted by organic micropollutants and heavy metals using granular biochar amendment and magnetic separation. *J. Environ. Chem. Eng.* **2022**, *10*, 107316. [CrossRef]
64. Blenis, N.; Hue, N.; Maaz, T.M.; Kantar, M. Biochar Production, Modification, and Its Uses in Soil Remediation: A Review. *Sustainability* **2023**, *15*, 3442. [CrossRef]
65. Heuser, I. Soil Governance in current European Union Law and in the European Green Deal. *Soil Sec.* **2022**, *6*, 100053. [CrossRef]
66. Lopez, J.E.; Arroyave, C.; Aristizabal, A.; Almeida, B.; Builes, S.; Chavez, E. Reducing cadmium bioaccumulation in Theobroma cacao using biochar: Basis for scaling-up to field. *Heliyon* **2022**, *23*, e09790. [CrossRef] [PubMed]
67. Lin, L.N.; Song, Z.G.; Khan, Z.H.; Liu, X.W.; Qiu, W.W. Enhanced As(III) removal from aqueous solution by Fe-Mn-La-impregnated biochar composites. *Sci. Total Environ.* **2019**, *686*, 1185–1193. [CrossRef]
68. Hamid, Y.; Tang, L.; Sohail, C.M.I.X.; Hussain, B.; Aziz, M.Z.M.; Usman, M.; He, Z.L.; Yang, X. An explanation of soil amendments to reduce cadmium phyto-availability and transfer to food chain. *Sci. Total Environ.* **2019**, *660*, 80–96. [CrossRef]
69. Gul, S.; Whalen, J.K. Biochemical cycling of nitrogen and phosphorus in biochar amended soils. *Soil Biol. Biochem.* **2016**, *103*, 1–15. [CrossRef]
70. Kumar, A.; Joseph, S.; Tsechansky, L.; Privat, K.; Schreiter, I.J.; Schueth, C.; Graber, E.R. Biochar aging in contaminated soil promotes Zn immobilization due to changes in biochar surface structural and chemical properties. *Sci. Total Environ.* **2018**, *626*, 953–961. [CrossRef] [PubMed]
71. Guo, M.; Song, W.; Tian, J. Biochar-facilitated soil remediation: Mechanisms and efficacy variations. *Front. Environ. Sci.* **2020**, *8*, 183. [CrossRef]
72. Nkoh, J.N.; Fidelis, O.A.; Edidiong, O.A.; Abdulaha-AlBaquy, M.; Shamim, M.; Elijah, C.O.; Renkou, X. Reduction of heavy metal uptake from polluted soils and associated health risks through biochar amendment: A critical synthesis. *J. Hazard. Mater. Adv.* **2022**, *6*, 100086. [CrossRef]
73. Duan, C.; Ma, T.; Wang, J.; Zhou, Y. Removal of heavy metals from aqueous solution using carbon-based adsorbents: A review. *J. Water Process Eng.* **2020**, *37*, 101339. [CrossRef]

74. Dihan, M.R.; Nayeem, S.A.; Roy, H.; Islam, M.S.; Islam, A.; Alsukaibi, A.K.; Awual, M.R. Healthcare waste in Bangladesh: Current status, the impact of Covid-19 and sustainable management with life cycle and circular economy framework. *Sci. Total Environ.* **2023**, *871*, 162083. [CrossRef]
75. Wang, L.; Ok, Y.S.; Tsang, D.C.; Alessi, D.S.; Rinklebe, J.; Wang, H.; Mašek, O.; Hou, R.; O'Connor, D.; Hou, D. New trends in biochar pyrolysis and modification strategies: Feedstock, pyrolysis conditions, sustainability concerns and implications for soil amendment. *Soil Use Manag.* **2020**, *36*, 358–396. [CrossRef]
76. Gwenzi, W.; Chaukura, N.; Noubactep, C.; Mukome, F.N. Biochar-based water treatment systems as a potential low-cost and sustainable technology for clean water provision. *J. Environ. Manag.* **2017**, *197*, 732–749. [CrossRef] [PubMed]
77. Joseph, S.; Cowie, A.L.; Van Zwieten, L.; Bolan, N.; Budai, A.; Buss, W.; Lehmann, J. How biochar works, and when it doesn't: A review of mechanisms controlling soil and plant responses to biochar. *GCB Bioenergy* **2021**, *13*, 1731–1764. [CrossRef]
78. Rana, A.; Sindhu, M.; Kumar, A.; Dhaka, R.K.; Chahar, M.; Singh, S.; Nain, L. Restoration of heavy metal-contaminated soil and water through biosorbents: A review of current understanding and future challenges. *Physiol. Plant* **2021**, *16*, 33724481. [CrossRef] [PubMed]
79. Gujre, N.; Mitra, S.; Soni, A.; Agnihotri, R.; Rangan, L.; Rene, E.R.; Sharma, M.P. Speciation, contamination, ecological and human health risks assessment of heavy metals in soils dumped with municipal solid wastes. *Chemosphere* **2021**, *262*, 128013. [CrossRef]
80. Lebrun, M.; Miard, F.; Nandillon, R.; Leger, J.C.; Hattab Hambli, N.; Scippa, G.S.; Bourgerie, S.; Morabito, D. Assisted phytostabilization of a multicontaminated mine technosol using biochar amendment: Early stage evaluation of biochar feedstock and particle size effects on as and Pb accumulation of two Salicaceae species (Salix viminalis and Populus euramericana). *Chemosphere* **2018**, *194*, 316–326. [CrossRef]
81. Lian, J.; Zhao, L.; Wu, J.; Xiong, H.; Bao, Y.; Zeb, A.; Tang, J.; Liu, W. Foliar spray of TiO_2 nanoparticles prevails over root application in reducing Cd accumulation and mitigating Cd-induced phytotoxicity in maize (*Zea mays* L.). *Chemosphere* **2020**, *239*, 124794. [CrossRef]
82. Kharel, G.; Sacko, O.; Feng, X.; Morris, J.R.; Phillips, C.; Trippe, K.; Kumar, S.; Lee, J.W. Biochar Surface Oxygenation by Ozonization for Super High Cation Exchange Capacity. *ACS Sustain. Chem. Eng.* **2019**, *19*, 16410–16418. [CrossRef]
83. Ghodszad, L.; Reyhanitabar, A.; Maghsoodi, M.R.; Lajayer, B.A.; Chang, S.X. Biochar affects the fate of phosphorus in soil and water: A critical review. *Chemosphere* **2021**, *283*, 131176. [CrossRef]
84. Tedoldi, D.; Charafeddine, R.; Branchu, P.; Thomas, E.; Gromaire, M.C. Intra- and inter-site variability of soil contamination in road shoulders-Implications for maintenance operations. *Sci. Total Environ.* **2021**, *769*, 144862. [CrossRef]
85. Lomaglio, T.; Hattab Hambli, N.; Miard, F.; Lebrun, M.; Nandillon, R.; Trupiano, D.; Scippa, G.S.; Gauthier, A.; Motelica Heino, M.; Bourgerie, S.; et al. Cd, Pb, and Zn mobility and (bio)availability in contaminated soils from a former smelting site amended with biochar. *Environ. Sci. Pollut. Control Ser.* **2018**, *25*, 25744–25756. [CrossRef] [PubMed]
86. Simiele, M.; Lebrun, M.; Miard, F.; Trupiano, D.; Poupart, P.; Forestier, O.; Scippa, G.S.; Bourgerie, S.; Morabito, D. Assisted phytoremediation of a former mine soil using biochar and iron sulphate: Effects on as soil immobilization and accumulation in three Salicaceae species. *Sci. Total Environ.* **2020**, *710*, 136203. [CrossRef] [PubMed]
87. Nedjimi, B. Phytoremediation: A sustainable environmental technology for heavy metals decontamination. *SN Appl. Sci.* **2021**, *3*, 286. [CrossRef]
88. Katiyar, R.; Chen, C.W.; Singhania, R.R.; Tsai, M.L.; Saratale, G.D.; Pandey, A.; Patel, A.K. Efficient remediation of antibiotic pollutants from the environment by innovative biochar: Current updates and prospects. *Bioengineered* **2022**, *13*, 14730–14748. [CrossRef]
89. Liang, J.; Ye, J.; Shi, C.; Zhang, P.; Guo, J.; Zubair, M.; Chang, J.; Zhang, L. Pyrolysis temperature regulates sludge-derived biochar production, phosphate adsorption and phosphate retention in soil. *J. Environ. Chem. Eng.* **2022**, *10*, 107744. [CrossRef]
90. Lahori, A.H.; Guo, Z.Y.; Zhang, Z.Q.; Li, R.H.; Mahar, A.; Awasthi, M.K.; Shen, F.; Sial, T.A.; Kumbhar, F.; Wang, P.; et al. Use of biochar as an amendment for remediation of heavy metal-contaminated soils: Prospects and challenges. *Pedosphere* **2017**, *27*, 991–1014. [CrossRef]
91. Gu, S.; Zhang, W.; Wang, F.; Meng, Z.; Cheng, Y.; Geng, Z.; Lian, F. Particle size of biochar significantly regulates the chemical speciation, transformation, and ecotoxicity of cadmium in biochar. *Environ. Pollut.* **2023**, *320*, 121100. [CrossRef]
92. Hasan, M.N.; Salman, M.S.; Hasan, M.M.; Kubra, K.T.; Sheikh, M.C.; Rehan, A.I.; Awual, M.R. Assessing sustainable Lutetium (III) ions adsorption and recovery using novel composite hybrid nanomaterials. *J. Mol. Struct.* **2023**, *1276*, 134795. [CrossRef]
93. Odinga, E.S.; Gudda, F.O.; Waigi, M.G.; Wang, J.; Gao, Y. Occurrence, formation and environmental fate of polycyclic aromatic hydrocarbons in biochars. *Fund Res.* **2021**, *1*, 296–305. [CrossRef]
94. Zhang, F.; Zhang, G.; Liao, X. Negative role of biochars in the dissipation and vegetable uptake of polycyclic aromatic hydrocarbons (PAHs) in an agricultural soil: Cautions for application of biochars to remediate PAHs-contaminated soil. *Ecotoxicol. Environ. Saf.* **2021**, *213*, 112075. [CrossRef]
95. Haider, F.U.; Wang, X.; Zulfiqar, U.; Farooq, M.; Hussain, S.; Mehmood, T.; Mustafa, A.; Naveed, M.; Li, Y.; Liqun, C.; et al. Biochar application for remediation of organic toxic pollutants in contaminated soils; An update. *Ecotoxicol. Environ. Saf.* **2022**, *248*, 114322. [CrossRef] [PubMed]
96. Sarfraz, R.; Li, S.W.; Yang, W.H.; Zhou, B.Q.; Xing, S.H. Assessment of physicochemical and nutritional characteristics of waste mushroom substrate biochar under various pyrolysis temperatures and times. *Sustainability* **2019**, *11*, 277. [CrossRef]

97. Lu, K.; Yang, X.; Gielen, G.; Bolan, N.; Ok, Y.S.; Niazi, N.K.; Xu, S.; Yuan, G.; Chen, X.; Zhang, X.; et al. Effect of bamboo and rice straw biochars on the mobility and redistribution of heavy metals (Cd, Cu, Pb and Zn) in contaminated soil. *J. Environ. Manag.* **2017**, *186*, 285–292. [CrossRef] [PubMed]
98. Mak-Mensah, E.; Sam, F.E.; Safnat Kaito, I.O.I.; Zhao, W.; Zhang, D.; Zhou, X.; Wang, X.; Zhao, X.; Wang, Q. Influence of tied-ridge with biochar amendment on runoff, sediment losses, and alfalfa yield in northwestern China. *Peer J.* **2019**, *9*, e11889. [CrossRef]
99. Manikandan, S.K.; Pallavi, P.; Shetty, K.; Bhattacharjee, D.; Giannakoudakis, D.A.; Katsoyiannis, I.A.; Nair, V. Effective Usage of Biochar and Microorganisms for the Removal of Heavy Metal Ions and Pesticides. *Molecules* **2023**, *28*, 719. [CrossRef]
100. Smebye, A.; Ailing, V.; Vogt, R.D.; Gadmar, T.C.; Mulder, J.; Cornelissen, G.; Hale, S.E. Biochar amendment to soil changes dissolved organic matter content and composition. *Chemosphere* **2016**, *142*, 100–105. [CrossRef]
101. Pandey, B.; Suthar, S.; Chand, N. Effect of biochar amendment on metal mobility, phytotoxicity, soil enzymes, and metal-uptakes by wheat (*Triticum aestivum*) in contaminated soils. *Chemosphere* **2022**, *307*, 135889. [CrossRef]
102. Medynska-Juraszek, A.; Rivier, P.A.; Rasse, D.; Joner, E.J. Biochar affects heavy metal uptake in plants through interactions in the rhizosphere. *Appl. Sci.* **2020**, *10*, 5105. [CrossRef]
103. Mihai, F.C.; Gundogdu, S.; Markley, L.A.; Olivelli, A.; Khan, F.R.; Gwinnett, C.; Gutberlet, J.; Reyna-Bensusan, N.; Llanquileo-Melgarejo, P.; Meidiana, C. Plastic Pollution, Waste Management Issues, and Circular Economy Opportunities in Rural Communities. *Sustainability* **2022**, *14*, 20. [CrossRef]
104. Shaheen, S.M.; El-Naggar, A.; Wang, J.; Hassan, N.E.; Niazi, N.K.; Wang, H.; Tsang, D.C.; Ok, Y.S.; Bolan, N.; Rinklebe, J. Biochar as an (Im) mobilizing agent for the potentially toxic elements in contaminated soils. In *Biochar from Biomass and Waste*; Elsevier: Amsterdam, The Netherlands, 2019; pp. 255–274.
105. Konczak, M.; Gao, Y.; Oleszczuk, P. Carbon dioxide as a carrier gas and biomass addition decrease the total and bioavailable polycyclic aromatic hydrocarbons in biochar produced from sewage sludge. *Chemosphere* **2019**, *228*, 26–34. [CrossRef]
106. Osadebe, A.U.; Uzoma, G.C.; Ogugbue, C.J.; Okpokwasili, G.C. Effect of Feedstock Type on Biostimulation Efficiency and Microbial Community Structure during Biochar-Facilitated Remediation of Petroleum Contaminated Soil. *Bioremediat. Sci. Technol. Res.* **2022**, *10*, 1. [CrossRef]
107. Ippolito, J.A.; Cui, L.; Kammann, C.; Wrage-Monnig, N.; Estavillo, J.M.; Jain, S.; Khare, P.; Mishra, D.; Shanker, K.; Singh, P.; et al. Biochar aided aromatic grass Cymbopogon martini (Roxb.) Wats. vegetation: A sustainable method for stabilization of highly acidic mine waste. *J. Hazard. Mater.* **2020**, *390*, 121799.
108. Luisa Alvarez, M.; Mendez, A.; Paz Ferreiro, J.; Gasco, G. Effects of manure waste biochars in mining soils. *Appl. Sci.* **2020**, *10*, 3393. [CrossRef]
109. Murtaza, G.; Ahmed, Z.; Dai, D.Q.; Iqbal, R.; Bawazeer, S.; Usman, M.; Rizwan, M.; Iqbal, J.; Akram, M.I.; Althubiani, A.S.; et al. A review of mechanism and adsorption capacities of biochar-based engineered composites for removing aquatic pollutants from contaminated water. *Front. Environ. Sci.* **2022**, *10*, 2155. [CrossRef]
110. Ma, J.W.; Wang, H.; Luo, Q.S. Movement-adsorption and its mechanism of Cd in soil under combining effect of electrokinetics and a new type of bamboo charcoal. *Environ. Sci.* **2007**, *28*, 1829–1834.
111. Wijitkosum, S.; Jiwnok, P. Elemental composition of biochar obtained from agricultural waste for soil amendment and carbon sequestration. *Appl. Sci.* **2019**, *9*, 3980. [CrossRef]
112. Zeghioud, H.; Fryda, L.; Djelal, H.; Assadi, A.; Kane, A. A comprehensive review of biochar in removal of organic pollutants from wastewater: Characterization, toxicity, activation/functionalization and influencing treatment factors. *J. Water Process Eng.* **2022**, *47*, 102801. [CrossRef]
113. Mosko, J.; Pohorely, M.; Cajthaml, T.; Jeremias, M.; Robles-Aguilar, A.A.; Skoblia, S.; Beňo, Z.; Innemanová, P.; Linhartová, L.; Michalíková, K.; et al. Effect of pyrolysis temperature on removal of organic pollutants present in anaerobically stabilized sewage sludge. *Chemosphere* **2021**, *265*, 129082. [CrossRef]
114. Mumivand, H.; Izadi, Z.; Amirizadeh, F.; Maggi, F.; Morshedloo, M.R. Biochar Amendment Improves Growth and the Essential Oil Quality and Quantity of Peppermint (*Mentha* × *piperita* L.) Grown Under Waste Water and Reduce Environmental Contamination of Waste Water Disposal. *J. Hazard. Mater.* **2022**, *446*, 130674. [CrossRef]
115. Murtaza, G.; Ditta, A.; Ullah, N.; Usman, M.; Ahmed, Z. Biochar for the Management of Nutrient Impoverished and Metal Contaminated Soils: Preparation, Applications, and Prospects. *J. Soil Sci. Plant Nutr.* **2021**, *21*, 2191–2213. [CrossRef]
116. Li, Y.; Shao, M.; Huang, M.; Sang, W.; Zheng, S.; Jiang, N.; Gao, Y. Enhanced remediation of heavy metals contaminated soils with EK-PRB using β-CD/ hydrothermal biochar by waste cotton as reactive barrier. *Chemosphere* **2022**, *286*, 131470. [CrossRef]
117. Zhang, G.; Guo, X.; Zhu, Y.; Liu, X.; Han, Z.; Sun, K.; Ji, L.; He, Q.; Han, L. The effects of different biochars on microbial quantity, microbial community shift, enzyme activity, and biodegradation of polycyclic aromatic hydrocarbons in soil. *Geoderma* **2018**, *328*, 100–108. [CrossRef]
118. Narayanan, M.; Ma, Y. Influences of Biochar on Bioremediation/Phytoremediation Potential of Metal-Contaminated Soils. *Front. Microbiol.* **2022**, *9*, 929730. [CrossRef] [PubMed]
119. Zhao, M.; Ma, D.; Ye, Y. Adsorption, separation and recovery properties of blocky zeolite-biochar composites for remediation of cadmium contaminated soil. *Chin. J. Chem. Eng.* **2021**, *54*, 272–279. [CrossRef]
120. Kong, L.; Liu, J.; Han, Q.; Zhou, Q.; He, J. Integrating metabolomics and physiological analysis to investigate the toxicological mechanisms of sewage sludge-derived biochars to wheat. *Ecotoxicol. Environ. Saf.* **2019**, *185*, 109664. [CrossRef]

121. Zhen, M.; Tang, J.; Li, C.; Sun, H. Rhamnolipid-modified biochar-enhanced bioremediation of crude oil-contaminated soil and mediated regulation of greenhouse gas emission in soil. *J. Soils Sediments* **2021**, *21*, 123–133. [CrossRef]
122. Zheng, H.; Liu, B.; Liu, G.; Cai, Z.; Zhang, C. Potential toxic compounds in biochar: Knowledge gaps between biochar research and safety. In *Biochar from Biomass and Waste*; Elsevier: Amsterdam, The Netherlands, 2019; pp. 349–384.
123. Novak, J.M.; Ippolito, J.A.; Ducey, T.F.; Watts, D.W.; Spokas, K.A.; Trippe, K.M.; Sigua, G.C.; Johnson, M.G. Remediation of an acidic mine spoil: Miscanthus biochar and lime amendment affects metal availability, plant growth, and soil enzyme activity. *Chemosphere* **2018**, *205*, 709–718. [CrossRef]
124. Plaimart, J.; Acharya, K.; Mrozik, W.; Davenport, R.J.; Vinitnantharat, S.; Werner, D. Coconut husk biochar amendment enhances nutrient retention by suppressing nitrification in agricultural soil following anaerobic digestate application. *Environ. Pollut.* **2021**, *268*, 115684. [CrossRef]
125. Prodana, M.; Silva, C.; Gravato, C.; Verheijen, F.G.A.; Keizer, J.J.; Soares, A.M.V.M.; Loureiro, S.; Bastos, A.C. Influence of biochar particle size on biota responses. *Ecotoxicol. Environ. Saf.* **2019**, *174*, 120–128. [CrossRef]
126. Qin, J.; Wang, X.; Ying, J.; Lin, C. Biochar Is Not Durable for Remediation of Heavy Metal-Contaminated Soils Affected by Acid-Mine Drainage. *Toxics* **2022**, *10*, 462. [CrossRef]
127. Nie, C.; Yang, X.; Niazi, N.K.; Xu, X.; Wen, Y.; Rinklebe, J.; Ok, Y.S.; Xu, S.; Wang, H. Impact of sugarcane bagasse-derived biochar on heavy metal availability and microbial activity: A field study. *Chemosphere* **2018**, *200*, 274–282. [CrossRef] [PubMed]
128. Nissen, R.; Khanal, G.; Elsgaard, L. Microbial Ecotoxicity of Biochars in Agricultural Soil and Interactions with Linear Alkylbenzene Sulfonates. *Agronomy* **2021**, *11*, 828. [CrossRef]
129. Rahim, H.U.; Akbar, W.A.; Alatalo, J.M. A comprehensive literature review on cadmium (Cd) status in the soil environment and its immobilization by biochar-based materials. *Agronomy* **2022**, *12*, 877. [CrossRef]
130. Rinklebe, J.; Shaheen, S.M.; El-Naggar, A.; Wang, H.; Du Laing, G.; Alessi, D.S.; Sik Ok, Y. Redox-induced mobilization of Ag, Sb, Sn, and Tl in the dissolved, colloidal and solid phase of a biochar-treated and un-treated mining soil. *Environ. Int.* **2020**, *140*, 105754. [CrossRef] [PubMed]
131. El-Shafey, E.I. Removal of Zn (II) and Hg (II) from aqueous solution on a carbonaceous sorbent chemically prepared from rice husk. *J. Hazard. Mater.* **2010**, *175*, 319–327. [CrossRef]
132. Shen, X.; Meng, H.; Shen, Y.; Ding, J.; Zhou, H.; Cong, H.; Li, L. A comprehensive assessment on bioavailability, leaching characteristics and potential risk of polycyclic aromatic hydrocarbons in biochars produced by a continuous pyrolysis system. *Chemosphere* **2022**, *287*, 132116. [CrossRef]
133. Rauret, G.; Lopez-Sanchez, J.F.; Sahuquillo, A.; Rubio, R.; Davidson, C.; Ure, A.; Quevauviller, P. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *J. Environ. Monit.* **1999**, *1*, 57–61. [CrossRef]
134. Rawa, B.B.R.T.; dan Efektivitasnya, M. Biochar-Materials for Remediation on Swamplands: Mechanisms and Effectiveness. *J. Sumberd. Lahan* **2021**, *15*, 13–22.
135. Alhar, M.A.M.; Thompson, D.F.; Oliver, I.W. Mine spoil remediation via biochar addition to immobilise potentially toxic elements and promote plant growth for phytostabilisation. *J. Environ. Manag.* **2020**, *277*, 111500. [CrossRef]
136. Ganie, Z.A.; Khandelwal, N.; Tiwari, E.; Singh, N.; Darbha, G.K. Biochar-facilitated remediation of nanoplastic contaminated water: Effect of pyrolysis temperature induced surface modifications. *J. Hazard. Mater.* **2021**, *417*, 126096. [CrossRef]
137. Huccet, V.; Alperen, M.; Sulem, S.D. Changes in the Heavy Metal Levels in Highway Landscaping and Protective Effect of Vegetative Materials. *Appl. Environ. Soil Sci.* **2021**, *9*, 8884718.
138. Yang, F.; Wang, B.; Shi, Z.M.; Li, L.; Li, Y.; Mao, Z.Q.; Liao, L.Y.; Zhang, H.; Wu, Y. Immobilization of heavy metals (Cd, Zn, and Pb) in different contaminated soils with swine manure biochar. *Environ. Pollut. Bioavailab.* **2021**, *33*, 55–65. [CrossRef]
139. Ren, X.; Tang, J.; Wang, L.; Sun, H. Combined effects of micro plastics and biochar on the removal of polycyclic aromatic hydrocarbons and phthalate esters and its potential microbial ecological mechanism. *Front. Microbiol.* **2021**, *12*, 647766. [CrossRef]
140. Tomczyk, B.; Siatecka, A.; Jędruchniewicz, K.; Sochacka, A.; Bogusz, A.; Oleszczuk, P. Polycyclic aromatic hydrocarbons (PAHs) persistence, bioavailability and toxicity in sewage sludge-or sewage sludge-derived biochar-amended soil. *Sci. Total Environ.* **2020**, *747*, 141123. [CrossRef] [PubMed]
141. UNEP GOAL 15: Life on Land. 2015. Available online: https://www.unep.org/explore-topics/sustainable-development-goals/why-do-sustainable-development-goals-matter/goal-15. (accessed on 25 February 2023).
142. Ghidotti, M.; Fabbri, D.; Hornung, A. Profiles of volatile organic compounds in biochar: Insights into process conditions and quality assessment. *ACS Sustain. Chem. Eng.* **2017**, *5*, 510–517. [CrossRef]
143. United Nations Environment Programme. UNEP Tackling Global Water Pollution. 2020. Available online: https://www.unenvironment.org/explore-topics/water/what-we-do/tackling-global-water-pollution (accessed on 25 February 2023).
144. Patel, A.K.; Singhania, R.R.; Pal, A.; Chen, C.W.; Pandey, A.; Dong, C.D. Advances on tailored biochar for bioremediation of antibiotics, pesticides and polycyclic aromatic hydrocarbon pollutants from aqueous and solid phases. *Sci. Total Environ.* **2022**, *817*, 153054. [CrossRef] [PubMed]
145. Varjani, S.; Kumar, G.; Rene, E.R. Developments in biochar application for pesticide remediation: Current knowledge and future research directions. *J. Environ. Manag.* **2019**, *232*, 505–513. [CrossRef]
146. Zhang, M.; Liu, Y.; Wei, Q.; Gu, X.; Liu, L.; Gou, J. Biochar application ameliorated the nutrient content and fungal community structure in different yellow soil depths in the karst area of Southwest China. *Front. Plant Sci.* **2022**, *13*, 1020832. [CrossRef]

147. Penido, E.S.; Martins, G.C.; Mendes, T.B.M.; Melo, L.C.A.; do Rosario Guimaraes, I.; Guilherme, L.R.G. Combining biochar and sewage sludge for immobilization of heavy metals in mining soils. *Ecotoxicol. Environ. Saf.* **2019**, *172*, 326–333. [CrossRef]
148. Zhang, W.; An, Y.; Li, S.; Liu, Z.; Chen, Z.; Ren, Y.; Wang, S.; Zhang, X.; Wang, X. Enhanced heavy metal removal from an aqueous environment using an eco-friendly and sustainable adsorbent. *Sci. Rep.* **2020**, *10*, 16453. [CrossRef]
149. Zheng, X.; Xu, W.; Dong, J.; Yang, T.; Shangguan, Z.; Qu, J.; Li, X.; Tan, X. The effects of biochar and its applications in the microbial remediation of contaminated soil: A review. *J. Hazard. Mater.* **2022**, *438*, 129557. [CrossRef]
150. Abate, A.; Setegn, H.; Digafe, A.; Kamaraj, M. Comparative Utilization of Dead and Live Fungal Biomass for the Removal of Heavy Metal: A Concise Review. *Sci. World. J.* **2021**, *2020*, 5588111.
151. Ahmad, M.; Ok, Y.S.; Rajapaksha, A.U.; Lim, J.E.; Kim, B.Y.; Ahn, J.H.; Lee, S.S. Lead and copper immobilization in a shooting range soil using soybean stover-and pine needle derived biochars: Chemical, microbial and spectroscopic assessments. *J. Hazard. Mater.* **2016**, *301*, 179–186. [CrossRef] [PubMed]
152. Gasco, G.; Alvarez, M.L.; Paz Ferreiro, J.; Mendez, A. Combining phytoextraction by Brassica napus and biochar amendment for the remediation of a mining soil in Riotinto (Spain). *Chemosphere* **2019**, *231*, 562–570. [CrossRef] [PubMed]
153. Lima, J.Z.; Ogura, A.P.; da Silva, L.C.M.; Nauerth, I.M.R.; Rodrigues, V.G.S.; Espindola, E.L.G.; Marques, J.P. Biochar-pesticides interactions: An overview and applications of wood feedstock for atrazine contamination. *J. Environ. Chem. Eng.* **2022**, *10*, 108192. [CrossRef]