Review

Biochar Production, Modification, and Its Uses in Soil Remediation: A Review

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Abstract: Soil remediation is the act of removing or reducing the availability of contaminants from soil. In the case of agriculture, soil remediation targets the removal of pollutants, including residual pesticides/herbicides, hydrocarbons, and toxic heavy metals. This is often done by chemical treatments with multiple washes or excavation of soils, which are costly and time-consuming. Therefore, finding cheaper, less time-consuming remediation methods is highly desirable. In this review, we will examine the addition of biochar as an effective method of soil remediation. Biochar is a carbon-rich material derived from burning biomass in an oxygen-limited environment with benefits such as high cation exchange capacity, large surface area, neutral to alkaline pH, and some nutritional content. Biochar can also be a sanctuary for naturally occurring microbes and can be inoculated with specific microbes for contaminant breakdown. The physical and chemical characteristics of biochar combined with biological activity can help bind and promote the degradation process of these contaminants without the need to use hazardous chemicals or remove a large amount of soil. Biochar, and the microbes they house, can bind these contaminants through electrostatic attraction, sorption, precipitation, and bioaccumulation, reducing their availability to the surrounding environment. However, the characteristics of biochar and its biological activity can vary depending on the feedstock, pyrolysis temperature, and time the mass is heated. Therefore, some of these traits can be modified through pre or post-treatments to suit their intended use, allowing for biochar to be made for specific contaminants. This review hopes to increase interest in biochar research to fill in missing gaps of information that could make biochar production cheaper and more consistent, as it offers a greener way to clean up contaminants in soil.

Keywords: biochar; pyrolysis; cation exchange capacity; specific surface area; soil remediation

1. Method of Research

A thorough literature search was performed using keywords such as biochar, engineered biochar, biochar modification, soil contaminants, soil remediation, biochar in soil health improvement, heavy metals in soil, organic pollutants, soil-plant microbe interactions, microbial remediation of soil contaminants, soil restoration, sustainable agriculture. A comprehensive search was done for available electronic information resources in the Agricola, Web of Science, and Science Direct databases, and the most appropriate and up-to-date research and review studies were considered in our review.

2. Introduction

Soil remediation is needed in lands contaminated intentionally or accidentally due to anthropogenic or naturally occurring activities. Examples of human activities that can cause soil contamination include military operations, mining, waste disposal, over-fertilization, and overuse of pesticides or herbicides. Natural disasters such as hurricanes, floods, and earthquakes can lead to soil contamination, releasing naturally occurring or synthetic products [1]. Soil contaminants include organic pollutants (polycyclic aromatic hydrocarbons (PAHs), pesticides, herbicides, and fertilizers) and heavy metal(loid)s (arsenic, cadmium,

chromium, cobalt, copper, lead, mercury, nickel, and zinc) [2]. Remediation is required for these pollutants as they can reduce soil fertility and crop production, thereby reducing the viability of food production. Often these contaminants are carcinogenic, mutagenic, or toxic to the plants and the animals that accumulate them, causing sickness or mutations as they move up the food chain [3]. These contaminants should be of serious concern to the general populace and government organizations interested in public health outcomes.

Many methods of soil remediation presently used include physical, chemical, and biological methods. Physical remediation includes excavation, heating, or leaching but is expensive and can have secondary issues. Chemical treatments use immobilization, modification, reduction, and cleaning/washing, but treatments can become a pollutant to the soil they are applied to. Bioremediation using microbes or plants has the least amount of negative side effects but can be affected by external factors such as weather and have a long repair cycle compared to physical or chemical treatments [4]. Thus, more cost-effective or a combination of remediating actions must be taken to reduce negative side effects, and biochar can play a significant role in these efforts.

Biochar is a carbon-rich material created from heating biomass in an oxygen-deprived environment through pyrolysis. The feedstock can range from woody materials to biosolids and often be broken up into three categories, organic waste (OW), crop residue (CR), and woody biomass (WB) [5]. When these different raw materials are transformed into biochar, they have carbon content ranging from 40–80%, and additional modifications can be performed, changing the CEC and structure of the biochar [6]. While most of the C is in aromatic compounds and unavailable for microbial use, there is a small fraction that is labile and bioavailable (<10%) depending on the conditions of pyrolysis [7]. The C that is not readily available is bound in aromatic compounds, creating large sheets (amorphous forms, turbostratic carbon, and graphene sheets) that form macro and micropores (2 mm–2 μm), providing biochar a large specific surface area (SSA) ranging from 1.5–500 m^2/g [7–9]. This porous structure can store water and improve water retention in course textured soils by reducing pore space, and improving water movement in clay soils by increasing pore size [7,10]. Biochar's bulk density ranges from 0.2–1.0 g/cm^3 with an average bulk density around 0.5 g/cm^3 and reduces the bulk density of the mineral-heavy soil when applied [7,11]. Soils that are fine textured have shown improved aggregate stability with additions of biochar [7].

Besides being rich in C, biochar contains small amounts of nitrogen (0.5–2%), phosphorus (1–4.5%), potassium (0.5–8%), and calcium (0.1–8.5%) [7]. P and N are not as readily available directly at application as N is often bound in heterocyclic structures, while P is associated with cations depending on their presence in the feedstock and at higher pH levels [7,12]. K and Ca are more available and can help reduce toxic metals by substituting with them on aromatic rings [12,13]. Many functional groups (carboxyl, lactone, lactol, quinine, chromene, anhydride, phenol, ether, pyrone, pyridine, pyridone, and pyrrole) are present on the aromatic rings that can interact with soil contaminants [14,15]. The large quantity of O-containing functional groups creates a cation exchange capacity (CEC) that ranges from 3–200 $cmol_{c+}/kg$, with a median value of 35.4$cmol_{c+}/kg$ and is considered one of the significant factors in heavy metals or cationic organic pollution sorption to biochar [7,9,14]. Biochars added to soils often increase nutrient retention due to the increased CEC [7]. These functional groups and elements' presence in biochar generate alkaline pH levels as high as 10 [5]. This allows biochar to be considered a liming agent with a calcium carbonate equivalence range of 5–30% and is shown to help increase the soil pH, which can reduce the availability of aluminum and manganese [7]. Biochar also enhances nutrient retention and plant uptake, thus increasing the nutrient-use efficiency [16,17].

Additions of biochar are also beneficial to microbial communities due to their numerous and small pores, labile C, and alkaline pH. The pores of biochar act as a safe habitat for fungi and bacteria due to their size and water-holding capacity, providing protection from predators that cannot fit into micropores and desiccation [7] Biochar created from certain feedstocks and at specific temperatures has labile C compounds that can act as a

substrate for microbial growth and a primer for soil organic matter breakdown [7]. The pH changes from biochar application can change the microbial communities in the soils they are applied to, as bacteria generally prefer near neutral pH and fungi generally prefer acidic or alkaline conditions, eventually leading to further changes up the food chain [7]. Biochar has been shown to improve the physical, chemical, and biological properties of many soils, particularly degraded and nutrients poor soils, as illustrated in Figure 1, and these properties are important factors in the remediation of toxins [7].
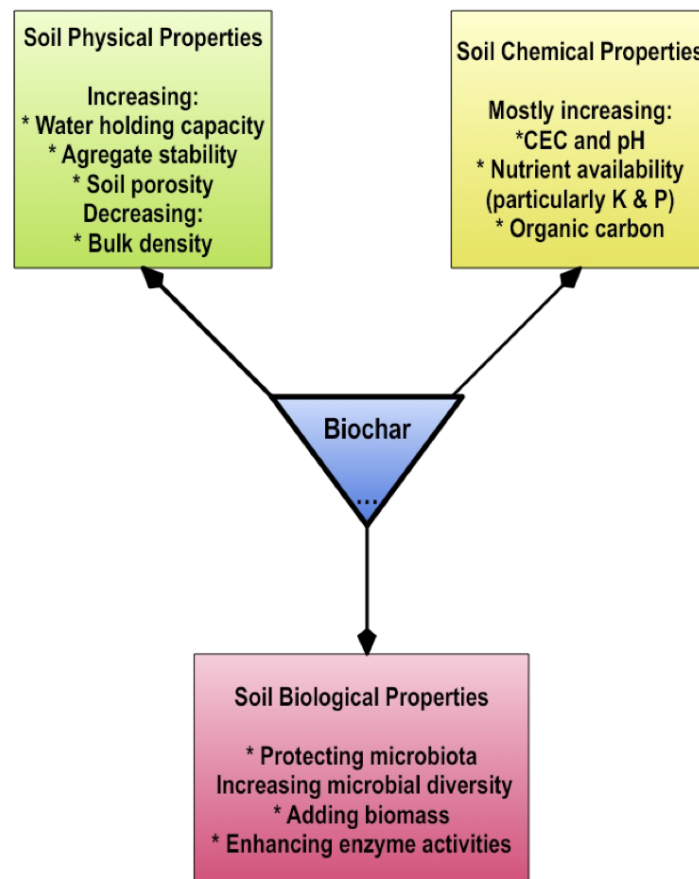

Figure 1. Beneficial effects of biochar on soil physical, chemical, and biological properties.

3. Biochar Generation and Characterization

During the pyrolysis process, factors such as the highest treated temperature (HTT), heating duration, and speed to reach the HTT affect biochar's chemical and physical properties [9]. Pyrolysis occurs in an oxygen-limited or N_2 rich environment and can occur in pit kilns and homemade kilns designed for slow pyrolysis or mechanical reactors such as fluidized beds, stirred or moving beds, and vacuum pyrolysis systems designed for fast pyrolysis [7,18].

Pyrolysis temperature ranges from 300–1100 °C during the process, and the HTT can be reached quickly (fast pyrolysis) at $\geq$100 °C/s or slowly (slow pyrolysis) at 10 °C/min. The residence time spent to burn the feedstock changes based on the desired HTT. Once HTT is reached residence time using fast pyrolysis can take as quickly as 1–5 s, while slow pyrolysis can take days to get a finished product [7,9,19]. Fast pyrolysis is mainly used for bio-oil production, yielding less biochar, as the main focus is creating energy or gasification [18]. Slow pyrolysis is used for biochar production as the residence time is longer and heating is slower, leaving more biochar at the end of the process [9]. The pyrolysis temperature will change the biochar structure, CEC, pH, and the presence of bio-oils left on the final product [20,21]. The CEC of biochar is larger at lower temperatures

(300–500 °C) due to increased functional groups, alkaline elements, and volatile matter on the biochar surfaces, though bio-oils presence reduces the surface area, as they block or fill micropores [3,5,7]. At the higher temperature range (500–1100 °C), biochar CEC is reduced as functional groups on the aromatic structure degrade, and the volatile matter is burned off through the heating process [3,5]. Higher temperatures, up to 750 °C, increase the biochar's specific surface area (SSA) as more volatiles are burned away, leaving behind a more hydrophobic aromatic structure [5]. The pH of biochar is also higher when treated at this temperature range and can reach up to 10 depending on the feedstock [5]. This increase in pH is a result of increased carbonization, and different carbonate compounds with elements present in the feedstock [9].

At lower temperatures, the C forms amorphous carbon sheets, and as the temperature increases, the carbon begins to become organized into turbostratic crystallites and graphene sheets, accounting for the increase in SSA and hydrophobic nature [9,22]. These structures are all composed of aromatic C rings that become more organized as temperature increases. When pyrolysis temperatures reach or pass 700–750 °C, the biochar pore structure begins to crumble, reducing biochar surface area as more C begins to burn off [7,23].

The feedstock type affects the biochar properties. As mentioned, the materials used to create biochar are broken into three main categories. Organic waste (OW) biochar is derived from compost, manure, and biosolids, often higher in volatile matter and ash content than WB or CR [24]. OW biochar often has high CEC levels, large amounts of surface functional groups, neutral to high pH, and negative zeta potential, especially at low HTT temperatures (300–500 °C), as zeta potential increases (smaller negative or even positive) with higher temperatures [25–27]. Zeta potential is the measurement of charge across the surface of a particle (it is negative if the particle carries negative charge), and the higher the charge, the more interaction between the surrounding solution and the material [26]. WB is often created from sawdust or other woody materials and has higher amounts of cellulose and lignin (reducing degradation from microbial activity), with the final product usually low in volatile matter and ash content, rich in micropores (high SSA) and high pH at HTT < 550 °C [28]. CR biochar is created from spoiled fruits and vegetables, seeds, and any remains or unusable part of a crop after harvest. Biochars derived from these products are similar to WB biochar but are not as rich in lignin and cellulose, resulting in a reduced aromatic ring structure. These biochars are between the WB and OW, having similar volatile matter and ash content to OW biochar at a lower HTT but high SSA and pH at a high HTT [5].

Feedstock particle size can also affect the biochar's chemical and physical properties at lower temperature pyrolysis (300 °C). The larger the feedstocks particle size (5–10 mm), the more dissolved organic content is left in the biochar, while the smaller (0.5–2 mm) particle sizes have higher pHs [29]. These feedstock size dependant variables change though as temperatures pass 600 °C, leading to all sizes having similar pH and dissolved organic content [29]. Feedstock moisture content can reduce the heating speed, requiring more energy to complete the process, and 15–20% moisture content is recommended for wood kilns. In sealed/pressurized kilns, water can increase yields when added to the feedstock before and during pyrolysis, especially under pressurized conditions [30].

4. Pre and Post-Treatment Methods of Biochar

Biochar for specific soil contaminants can be created with prior knowledge of the contaminant's chemical properties. Pre- and post-treatment of biochar can also be performed through chemical or physical treatments to add or change functional groups, element abundance, and micropore size of the final product [20]. Pre-treatments include loading different metal compounds via impregnation of varying metal salts or oxides ($AlCl_3$, $CaCl_2$, $MgCl_2$, $KMnO_4$, KOH, $ZnCl_2$, $FeCl_3$) so that subsequent pyrolysis generates different nano molecules on the biochar surface changing adsorption capacity by modifying pore volume, polarity and functional groups [31]. Similarly, the impregnation of non-metallic elements (N, S, B, and P) before pyrolysis is shown to improve the adsorption capacity of biochar [32].

Modification is dependent on the toxin in question as metals such as Fe and Mn could be used to help biochar bind anions, something biochar's negatively charged surface area would usually not be efficient at [31]. Another loading method includes growing seeds or cuttings with solutions containing the desired element so the crop can be terminated and turned into biochar containing the selected element creating engineered carbon [33]. One primary concern of these methods is that as the biochar degrades, metal compounds could be released into the system. Co-doping of different elements in metal/metal and non-metal/metal combinations has been of interest recently. Metal/non-metal compounds have been of more interest as they have been shown to reduce the leaching potential of metal ions from biochar [20].

Post-treatment methods include impregnation, precipitation, and heating. Post-treatment coating of biochar involves treating the biochar after pyrolysis with a solution rich in the desired element, followed by evaporation or further pyrolization to bind the product to the surface of the biochar [34,35]. Other post-treatment methods include acid or alkaline washing of the biochar [36]. Acid washing utilizes weak or strong acids (hydrochloric, sulfuric, nitric, phosphoric, oxalic, and citric acid) to increase the amount of acidic functional groups (carboxylic, lactonic, phenolic) and remove impurities from the biochar structure [37]. This treatment can also change the SSA and adsorption capacity of biochar depending on the concentration and acid used [38]. Alkaline washing of biochar utilizes solutions like potassium hydroxide or sodium hydroxide to increase the SSA and oxygen-containing functional groups on the biochar surface [36]. It is crucial to notice that feedstock seems to be an essential factor to consider with alkaline washes. For instance washing with potassium hydroxide reduced bicohar surface area based on the feedstock used to create it [39]. Steam modification occurs after the pyrolysis process and utilizes gaseous water to exchange free active sites forming surface hydrogen complexes (2CH) and oxide sites (CO) [40]. Gas purging utilizes CO_2 to increase the SSA and micropore structure while ammonia gas can be used to add nitrogen-containing groups to the biochar [41]. A combination of the two has also been shown to have increased SSA better than single treatments of either gas alone [42]. This creation process can be mapped out, so choosing what feedstock, and temperature range should be used to create biochar for a particular issue (Figure 2). The modification choice can be made based on the contaminant of concern and what physical or chemical traits are desired (Table 1).

Table 1. Modification of biochar.

| Treatment Type	Pre- or Post-Treatment	Chemical or Physical Modification
Impregnation/Coating	Pre or Post	Increases adsorption capacity (Co-doping reducing leaching potential)
Engineered carbon	Pre	Increases adsorption capacity (without impregnation before pyrolysis)
Acid washing	Post	Removes impurities Introduces acidic functional groups
Alkaline washing	Post	Increases SSA Introduces O-containing functional groups
Steam modification	Post	Increases SSA Pore structure refinement
Gas purging	Post	Increase SSA
Ammination	Post	Increase SSA Introduces N-containing functional groups
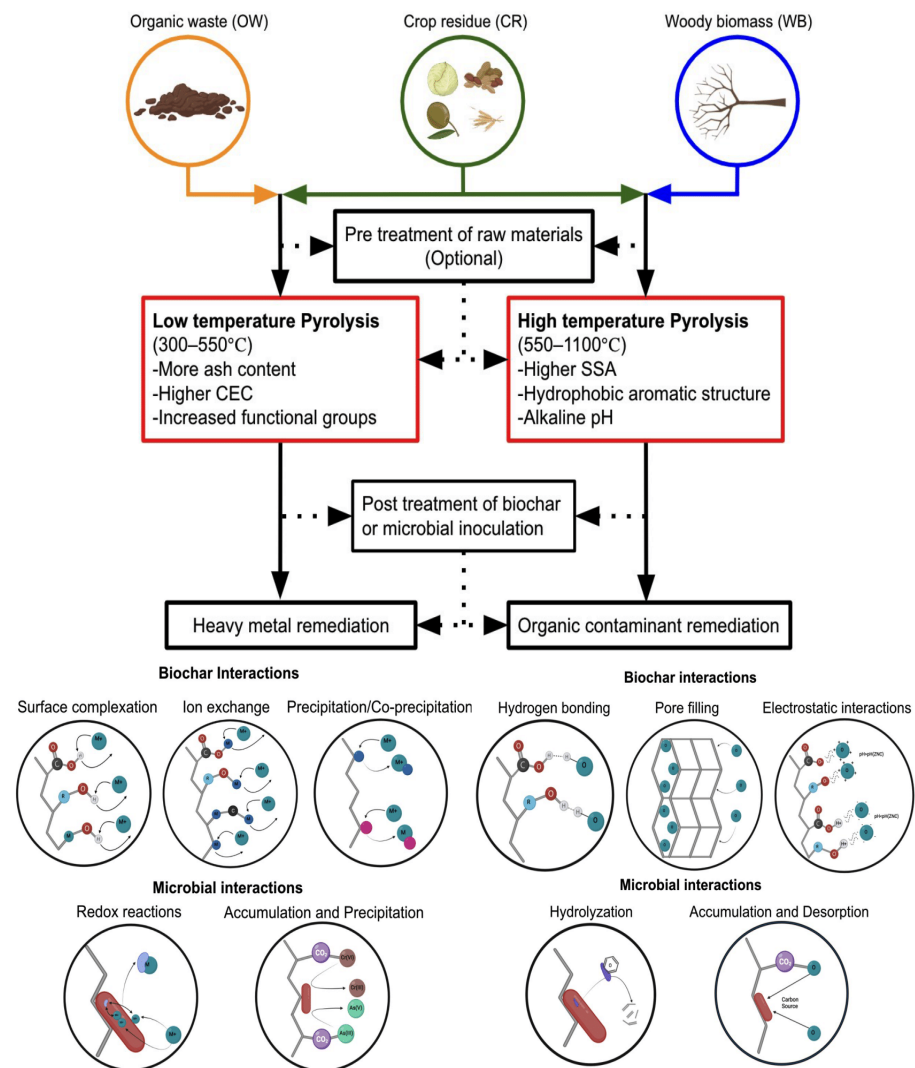
Figure 2. Biochar pipeline, mapping the production process, to choose feedstock, pyrolysis method, and modifications depending on the contaminant type. Figure created with Biorender.com.

5. Remediation Mechanism of Biochar

Biochar's remediation of contaminants is possible because of the chemical and physical characteristics, which can be chosen based on what contaminant needs to be remediated. This information is crucial and will dictate the pyrolysis method used, the feedstock, and if a pre- or post-treatment is needed.

5.1. Remediation of Heavy Metals

Biochar stabilizes heavy metals resulting in reduced solubility and bioavailability of metals, which differs from remediation methods like soil washing, leaching, or excavation of heavy metals [43]. The primary stabilization mechanisms biochar implements are precipitation and the sorption of heavy metals. Such metal stabilization is possible due to biochar's structure, functional groups, and soluble metal salts [5]. Depending on the pH, functional groups are protonated or deprotonated, providing biochar with an electrical charge. Biochar submerged in a solution had an increase of negative charges on the surface of biochar as solution pH was increased from 3 to 8 [44,45]. These negatively charged functional groups adsorb heavy metal cations through electrostatic interactions. It is important to note that biochar produced at a higher temperature has a higher pH zero net charge (ZNC) (pH at which the biochar has zero net charge), explaining why higher

temperature biochar has a lower CEC [25]. This also means that the pH of a biochar-amended soil $<$ pH$_{ZNC}$, there could be positive charge sites on the biochar, allowing for anionic toxic metals to bind to the biochar surface [46]. The aromatic structure of biochar is rich in π electrons allowing for electrostatic attraction on electron-deficient metal cations through π-π interactions [47]. Electrostatic attractions are likely to break over time as they are outer sphere interactions, and the cations remain in the diffusion layer of the biochar [44]. Cations attached to functional groups on the biochar surface can exchange with metals in soil solution through ion exchange or inner sphere interactions. pH and ionic strength of the soil solution dictate whether ion exchange occurs. At low pH, ion exchange reduces, and high ionic strength solutions have reduced exchange as competition in solution increases [46]. Functional groups (carboxyl, carbonyl, and hydroxyl) on the biochar surface increase the CEC of the biochar, and as this increases, so does the ability of the biochar to adsorb metal cations through the exchange of Ca, Mg, K, and Na [48]. Biochar produced at low temperatures has increased functional groups compared to biochar produced at higher temperatures [49]. Anionic toxic metals such as Cr (chromate) and As (arsenate) become more available with additions of biochar, indicating that some combination of phytoremediation with biochar addition could be a useful combination of remediation techniques to appropriately reduce their presence in soils [25,50].

Precipitation reactions are also an essential part of heavy metal detoxification by biochar. Most biochar is alkaline and increases the soil solution pH, thus increasing the hydroxyl density on the biochar surface adsorbing Al or Mn [10]. This allows for more hydroxyl-metal precipitates, thereby reducing the availability of the heavy metals in soil solution. Precipitates can also form from the mineral or ash content of biochar such as CO_3^{2-}, PO_4^{3-}, SO_4^{2-} and SO_3^{2-}. Phosphate and sulfate can be bound through ligand exhchange or precipitation on the biochar surface through feedstock choice, modification (impregnation or co-doping), and pyrolization temperature [47,51,52]. P sorption increases with higher temperature produced biochar, due to an increase in aromatic C and loss of O-containing functional groups, replaced with P and S. Precipitation can occur with these anions and carbonates with metals such as Hg (S specific), Zn, Pb, Cu, or Cd, forming more stable bonds than surface complexation or π-π bonds [51–53].

Biochars' structure and functional groups all play a role in the electron transfer capacity. Phenols are the functional groups important to biochar's reduction/oxidation (redox) potential [54]. Phenolic bonds donate electrons to reduce species such as Cr^{6+}, as biochar phenolic bonds peak FTIR spectra measurements disappear after being used for treating toxic Cr^{6+} to non-toxic Cr^{3+} [55]. As mentioned before, as pyrolysis temperature increases, the structure of biochar becomes more aromatic, resulting in increased π electron availability. These allow quick electron transfers between the surrounding metals and biochar structure [55]. This reducing potential can also be an issue, as Hg can become methylated if redox potential increases [56]. This is related to Fe reduction as Fe hydroxides are created under redox conditions [57]. This showed some potential relationship between Fe and Hg under redox conditions that have been theorized for some time [58]. When biochar was added to a rice paddy with fluctuating water levels, Methylated Hg increased, which is toxic to humans showing that there are instances when biochar should not be implemented based on environmental factors [55].

Biochar usage in long-term experiments has been shown to be successful in reducing heavy metal availability. In rice paddies, Cd accumulation in rice was reduced after one season with applications of biochar, with the best results at an application rate of 40 tons/ha that lasted for three growing seasons or two years [59]. As biochar was only applied once, there was an upward trend in accumulation as growing seasons continued, showing that multiple applications are probably necessary to maintain healthy levels in crops [59]. Similar findings were found when biochar was applied to fields growing pak choi (Chinese cabbage), reducing Cd and Pb concentrations below limits for consumption in their edible parts when applied at 3 tons/ha [60].

5.2. Remediation of Organic Pollutants

To treat organic pollutants (antibiotics, fuels, oils, pesticides, and persistent organics) with biochar, it is essential to know if the contaminant in question is hydrophobic, polar, or cationic, as this can be a factor in what type of biochar is needed for treatment. Once the biochar is incorporated into the soil, these pollutants will bind to the surface or inside the pores and degrade over time or through microbial stimulation due to labile carbon addition from biochar [7,61].

Organic pollutants can react with the aromatic structure of biochar through the electrostatic attraction of nonpolar (London dispersion forces) or polar (dipole-dipole) forces, increasing potential with more surface area. Hydrogen bonding is possible through the biochar structure's C, N, H, and O-containing functional groups [44]. pH_{ZNC} can be changed to more neutral, negative, or positive through post-biochar treatments if the pollutant in question is polar, or ionized [46]. If the biochar material chosen was high in metal compounds or was pre- or post-treated, then the presence of metal compounds on the biochar surface can also play a role in polar or ionized pollutant complexation in biochar surface or precipitate in soil solution [62]. In the case of ionized impurities, some inner sphere adsorption can occur, reacting with functional groups and reducing their availability in solution [53]. Finally, π electrons on the aromatic structure of biochar can create π-π electron donor interactions, the stronger bonds occurring between oppositely polarized molecules [47].

Physical adsorption plays a vital role in nonionic pollutant cleanup, and SSA and micropore size play a huge role in the capacity of biochar to adsorb contaminants with this method [63]. As biochar SSA increases, the porosity, aromaticity, and hydrophobicity increase [44]. This means that higher-temperature treated biochar is favored for pollutant clean-up [64]. This was shown as biochar derived from the same feedstock but at different temperatures had different sorption capacities of Deisopropylatrazine, as the higher temperature (700 °C) biochar had more adsorption capacity than low temperature (300 °C) produced biochar [65]. This experiment also showed that steam modification had a more drastic effect on adsorption than temperature alone, as the greater surface area of the steamed biochar allowed for more storage of volatile compounds [65].

6. Microbial Interactions with Biochar

Microbes are also crucial to soil contamination remediation as biochar acts as a sanctuary for bacteria and fungi due to its porous nature [66]. Biochar additions have been shown to increase specific bacterial communities native to the soils they are amended [12,67]. Biochar can also be loaded with specific microorganisms for a contaminant and is considered one of the more promising methods of remediation as this combines bioremediation with biochar applications to increase effectiveness [50].

6.1. Microbial Loading

After choosing a specific microbe, loading them onto biochar is the next step before application to soil. This can occur through adsorption, entrapment, or covalence to the biochar. Adsorption occurs between surface functional groups of the microbes and biochar and can be improved further by modification of the biochar [68,69]. The entrapment of microbes relies on using natural or synthetic polymers to create housing around biochar that has been inoculated. Sodium alginate is often used for this purpose and is effective, but it reduces the size of particles able to enter the structure of biochar [70]. Covalence is considered the most complicated of these loading methods as it chemically bonds microbes to the surface of the biochar, leading to strong microbe-biochar binding and stability [71].

6.2. Heavy Metal Microbial Remediation

Microbes interact with heavy metals through intercellular adsorption, precipitation of heavy metals, and increasing redox potential of valence elements. Strain Bacillus cereus WHX-1 has been found to reduce Cr^{6+} to the nontoxic form Cr^{3+}. When biochar is

inoculated with this strain, there is an increased reduction of Cr^{6+} to Cr^{3+} when added to soil, more than biochar alone [72]. As^{3+} is another toxic element that can be oxidized to its less toxic form As^{5+} through microbial interaction [73]. When biochar inoculated with phosphorus solubilizing Bacillus sp. is added to soils rich in As^{3+}, plant health outcomes are increased due to the reduced amount of As accumulation in the plant biomass [74]. Heavy metal-resistant strains of microbes have been inoculated onto biochar that performs biosorption of heavy metal elements such as Cd, reducing them or binding them under anaerobic and aerobic conditions [75,76]. This occurs through metabolic action and through mechanisms such as ion exchange, complexation, and chelation [77]. Finally, bacterial strains have been identified that create different secretions that can precipitate metal ions in soil solution, making them nontoxic to the plants growing in the soils where these precipitates reside [78,79].

6.3. Organic Pollutant Microbial Remediation

The contaminants that microbial-inoculated biochar has been used to remediate include benzenes, hydrocarbons, pesticides/herbicides, and antibiotics. Microbes can break down these products through desorption, dehalogenation, and hydrolysis [70]. Microbes create enzymes to break down the organic contaminants connected to the biochar surface resulting in the bioaccumulation or breakdown of the contaminant. When *Alcaligenes faecalis* WZ-2, a microbial strain isolated from a tebuconazole (a fungicide) contaminated soil, was immobilized on biochar; it reduced the half-life of tebuconazole in the soil in half, resulting in a restoration of the enzymatic activity in these soils [80]. Experiments in soil and in water have shown multiple strains of microbes attached to biochar reduce benzene compound's availability and half-life [81,82]. Antibiotics are slow to degrade in sterile soils, and the degradation increases with the addition of microbes and a carbon source showing that microbes are essential to speed up antibiotic breakdown [83]. Degrading hydrocarbons with microbes inoculated on biochar is essential as the biochar draws in hydrocarbons into its pores, increasing the degradation process due to the microbial presence [84]. In combination with biochar, microbes are essential for removing organic contaminants due to their enzyme activity, breaking down carbon structures in the soil.

7. Biochar Efficacy

Biochar remediation in long-term field trials has had overall success, but there are instances where there are negative side effects or a completely negative outcome, likely related to abiotic and biotic factors. Abiotic factors such as soil type, weather, and redox potential can begin to reduce the effectiveness of biochar over long periods of time [85]. After applying biochar at 15 tons/ha, soil pH changed back to its original levels after two years showing that the liming effects slowly reduced over time [86]. In lands spoiled by Pb, Cd, and Zn, applications of wood-based biochar at 5% (*v/v*) did not increase plant health or reduce plant uptake of these heavy metals [87]. This could be due to the use of wood-based biochars, as their CEC levels are generally lower, and when remediation is needed for heavy metal toxins, biochar with a high CEC is more likely to reduce metal availability. Under anaerobic conditions, soils with biochar additions have higher levels of soluble heavy metals than soils without, meaning areas with long periods of rain or flooded soils should not have biochar added [88]. Biotic factors such as plants, microbiota, and earthworms can also have negative effects on biochar's immobilization of heavy metals. Plants can release their own exudates that increase the availability of heavy metals; some theorize cationic metals attached to biochar could be freed by these exudates back into the soil but increase the immobilization of anionic toxins [89]. Earthworms can eat biochar, breaking it down and releasing any heavy metals attached to it back into the soil [90]. Microbial metabolism can increase heavy metal availability through exudates, similar to plant roots, and can release heavy metals attached to the biochar surface back into soil solution [85]. Biochar, as discussed before, can increase and change microbial communities. In rice paddies, Cr release was increased while Fe reduction occurred when

biochar was added, and the abundance of a species of Geobacter, an iron-reducing bacteria, was also increased with the addition of pig manure biochar [91]. The metabolites from these bacteria are known to release Cr and As into soil solution, producing an instance of biochar increasing a native species of bacteria that negatively affected the plant's outcome [91]. In a seven-year field trial in a vineyard, biochar additions at 22 tons/ha did not reduce the availability of naphthalene but increased it, showing that the biochar pyrolysis method could have been related to this impact, as the pyrolysis temperature was at 500 °C, and higher temperature biochar can bind organic contaminants efficiently compared to lower temperature pyrolysis [92,93]. When used as an additive with phytoremediation of land contaminated with organochlorine pesticide, reduced the availability in the soil, in turn reducing the amount of uptake by the plant, showing that biochar is not always synergistic with other remediation techniques [94]. These instances point out why more research is needed to find out how different biochars and modifications can be used to reduce these problems.

8. Cost of Biochar

Biochar production is not cheap or considered financially viable at this moment [95]. It has many benefits outside of soil remediation, such as carbon sequestration and nutrient retention, and could become more affordable as the technology surrounding its creation becomes cheaper or is subsidized by governments [96]. The overall goal for biochar production is to become a loop, utilizing the waste from agriculture or waste facilities to be turned into more biochar, as has occurred in European countries [97]. A cost-benefit analysis using an orchard system's waste and a mobile pyrolysis unit was created, finding that biochar cost was around 450–1850$ per ton created [98]. This could change over time, as carbon credits could offset these costs to 193–234$ per ton. This price cut would be great for farmers as the cost is around 600–1300$ per ton on average in the US, which is too expensive for most farmers to utilize [99]. These costs do not account for modification or microbial inoculation either, and this could easily push the price past a point where farmers would consider using this as a product. Luckily some modification can be cheaper like industrial grade acid and alkaline washes but cost for other modifications are not as clear [100]. Reducing the cost of the production of biochar itself should be a priority by investing in the technologies involved. Investigations into microbial species that naturally occur or are genetically modified organisms for specific needs should be further researched.

9. Conclusions

When a contaminant is found, it is essential to identify which material would be best to use, what temperature range and residence time are needed for making biochar, and if a pre- or post-treatment is needed. THis is especially important, as pointed out in the biochar efficacy section, as choosing the wrong place, or biochar type could have no effect or lead to issues after application. When concerned about heavy metal contamination or cationic pollutants, biochar created from OW or CR at low-temperature pyrolysis is recommended. These biochars have higher CEC due to the functional group's presence, high pH from mineral content, and higher volatile matter. These properties help adsorb and precipitate metals, reducing their availability in soils. When concerned about polar, ionized, or hydrophobic organic pollutants, CR or WB biochar at high-temperature pyrolysis is recommended. These biochars have increased porosity, and large SSA is necessary to bind hydrophobic molecules to their aromatic surfaces. Post- and pre-treatments allow the biochar to become even more specific for particular issues. Post- and pre-treatments can take a feedstock that may not be preferential for treatment and make it more feasible, making more waste streams available for use.

Further, if a microbe species is known to reduce the availability of the contaminant, it could be inoculated on biochar to increase remediation speed and quantity. More research should also be prioritized in finding bacteria or fungi that release heavy metals from biochar stabilization, as these species will need to be identified before applying biochar

to soil as they will mitigate it's effectiveness. Biochar has the potential as an efficient material for heavy metal and organic pollutant remediation and could also be combined with bioremediation techniques to remove heavy metals through heavy metal accumulating plants possibly. Biochar degradation is one of the major concerns with its use, and with bioremediation, there could be a combination that makes up for the other's shortcomings.

Biochar's malleable nature and physical and chemical properties make it a great additional remediation tool. In the right situation, it can reduce the availability of a toxin while providing nutrient retention and water retention. If its stability issues could be better understood, then it could provide these benefits to the soils it has been added to for years. Long-term field trials using modified biochar would be extremely useful to grasp what is actually occurring in soils rather than in a lab. Getting more consistent data showing how often biochar should be applied would be useful as most long term trials apply once and look at effects over multiple years.

The cost of biochar production and modification still needs to be improved before it can become affordable for farmers worldwide. This is especially important as modification can have drastic effects on the capacity of biochar to stabilize or bind contaminants. Biochar production can turn waste streams into a usable resource and is a product that many farmers should be considering for a remediation method. The fact that cost is the main concern for most farmers means that biochar producers should be researching ways to reduce costs if they want their products to be widely sold and distributed.

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