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Review

Biochar-Assisted Bioengineered Strategies for Metal Removal: Mechanisms, Key Considerations, and Perspectives for the Treatment of Solid and Liquid Matrixes

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Abstract: Biochar has drawn the scientific community's attention during the last few years due to its low production value and unique physicochemical properties, which are helpful for numerous applications. The development of biotechnological processes for the remediation of heavy metal environmental pollution is one central research avenue in which biochar application has shown promising results, due to its positive effect on the bacteria that catalyze these activities. Biochar stimulates bacterial activity through adsorption, adhesion, electron transport, and ion exchange. However, before biochar implementation, a complete understanding of its potential effects is necessary, considering that those interactions between biochar and bacteria may help improve the performance of biological processes designed for the remediation of environmental pollution by metals, which has been historically characterized by limitations related to the recalcitrance and toxicity of these pollutants. In this review, the key biochar–microorganism interactions and properties of unmodified biochar with the potential to improve metal bioremediation in both solid (mine tailings, polluted soils) and liquid matrixes (metal-laden wastewaters) are summarized. Knowledge gaps regarding the mechanisms involved in remediation strategies, the effect of long-term biochar use and the development of improved biochar technologies and their combination with existent remediation technologies is summarized. Additionally, an up-to-date summary of the development of biochar-assisted bioengineered strategies for metal passivation or removal from solid and liquid matrixes is presented, along with key perspectives for the application of biochar-based biotechnologies at full scale during the treatment of mining effluents in the real scale.

Keywords: biochar; bioremediation; soil; water treatment; metal removal; metal bioremediation

1. Introduction

Environmental problems regarding toxic metal contamination have encouraged the development of reclamation strategies for the mitigation of the related negative effects that these contaminants have on the environment. In recent years, biochar has emerged as a promising material to be implemented in engineered solutions for metal removal. Biochar is defined as a fine-grain product rich in organic carbon, which is obtained from the thermal decomposition of biomass and waste under conditions of limited oxygen (pyrolysis) [1]. The approach of the waste-to-resource process applied to obtain biochar as a by-product can contribute to environmental sustainability and may help to develop a circular economy [2].

Initially, biochar was used for promoting carbon sequestration and agricultural gains; however, the promising results found using this material for pollutant removal as well as the number of publications of indexed articles has seen exponential growth from 2005 and onwards [3,4] (Figure 1).

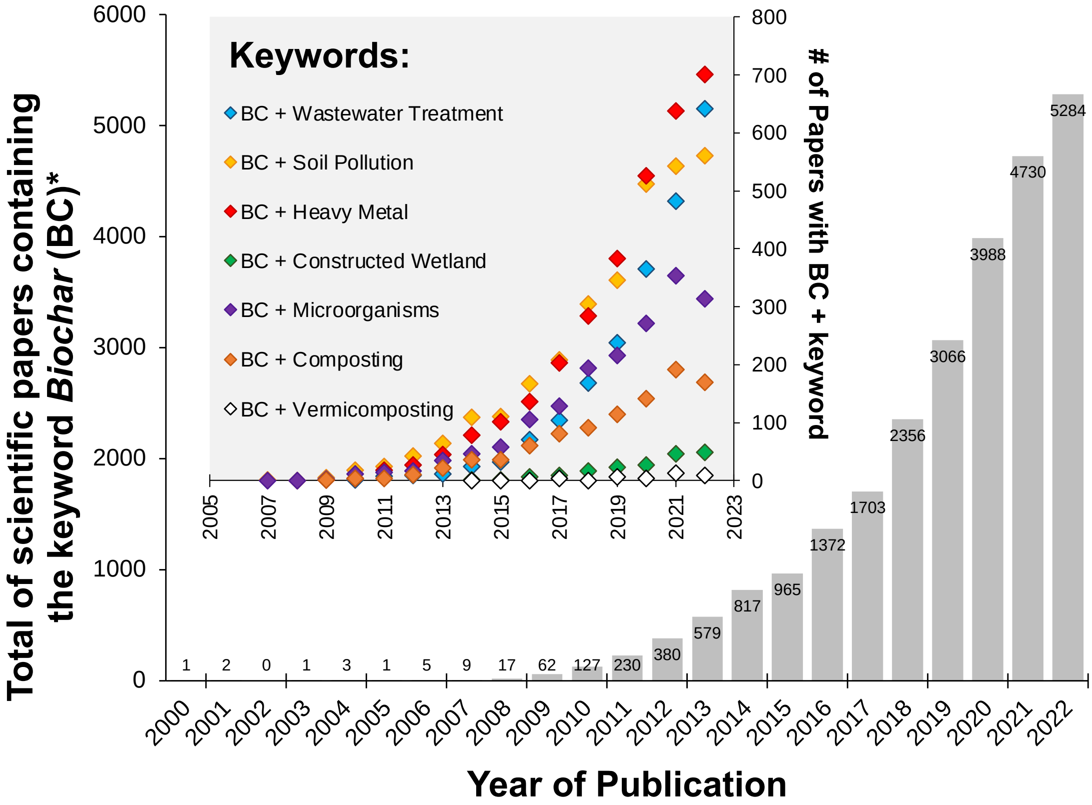

Figure 1. SCOPUS-based bibliographic analysis of the scientific interest in biochar (BC) and its relationship with scientific fields related to heavy metals, pollutant remediation, and microbiology. *The total number of published scientific papers per year was obtained using biochar as the search keyword (bars). * BC stands out for biochar. The insert displays the number of papers in which BC and keywords for the different scientific fields relevant for this review are present in the literature. Search results as of October 2022.

In particular, metal removal by biochar has been successfully demonstrated and it has been associated with its properties, which are influenced by production parameters such as the pyrolysis temperature, residence time, and feedstock type, amongst others [3]. Hence, the physicochemical properties of biochar constitute a central aspect of it, since they are indispensable to promoting specific interactions with microorganisms, which can be exploited for biotechnological applications. Because of this, ongoing research has focused on modifying biochar by different methods to improve these material interactions according to the properties conferred by the production parameters or modifying agents. However, some methods of activation to produce engineered biochar may imply higher preparation costs and a detailed study of biochar–microorganism interactions.

A number of studies have been developed with the aim of contributing to the advance of reclamation strategies in different environmental matrixes affected by metals. However, biochar use has not achieved practical or large-scale applications, which is mainly because there is still a need to understand the mechanisms involved, biochar's long-term role, and to improve the combination of biochar with other technologies [5].

For these reasons, this review is focused on the interactions and potential applications of biochar obtained from wastes without modification. Based on the most relevant information found in the literature, the direct and indirect synergistic biochar–microorganism interactions promoting the development of biotechnologies for heavy metal removal will be summarized and discussed. The importance of biochar's physicochemical properties for its application in bioprocesses, as well as those characterization techniques needed to elucidate such properties and future research requirements, are addressed. The implications and perspectives to innovate in microbial-biochar-based solutions are examined, highlighting the influence of this material in microbial communities. Among the technologies discussed, special attention is given to constructed wetlands as a nature-based solution that can incorporate biochar to deal with metal removal. This review aims to provide crucial aspects of biochar–microorganism utilization for metal remediation strategies in environmental matrices.

2. Critical Properties of Biochar in Its Interaction with Microorganisms

The performance and efficiency of all biochar-microorganism interactions with the potential to be exploited for toxic metal remediation will ultimately rely on the physicochemical characteristics of the biochar employed, which may be highly variable, depending on its source and synthesis process (Table 1). As will be discussed later (Section 3), all biochar–microorganism interactions originate from the capacity of microorganisms (mainly bacteria) to employ the physicochemical and physical assets of biochar, such as its adsorption capacity, porous surface, and/or electroactive functional groups, to guarantee their survival and proliferation by running their metabolism. By doing this, microbial activity reliant on biochar's presence may result in beneficial changes in the surrounding environment in which these phenomena take place with the direct or indirect consequence of affecting the toxic metal speciation and/or redox state, which will result in their passivation. Due to their vital relevance in the selection of biochar for bioengineered options, the main physicochemical characteristics of biochar in its interaction with microorganisms are described (Table 1).

Table 1. Summary of proposed relevant linkages between biochar's physicochemical characteristics and the interaction with microorganisms involved in mechanisms for potentially toxic metal(loid) stabilization/remediation.

Biochar–Microorganism Interaction	Mechanism of Metal (Loid) Stabilization	Key Biochar Properties	Factors Determining Key Biochar Properties
Electron-shuttling-mediated reactions. Biochar-mediated interspecies electron transfer.	▪Change in the redox state of non-toxic metals (i.e., Fe and Mn). ▪Catalyzing the production of minerals with high sorption capacity (i.e., siderite and toxic metal co-precipitation. ▪Change in the redox state of toxic metals (acting as an electron shuttle for microorganisms). ▪Change in soil/tailing mineralogy.	▪Amount and type of redox-active functional groups. ▪Electron-exchange capacity. ▪Redox potential.	▪Feedstock material. ▪Pyrolysis conditions (temperature and atmosphere) ▪Aging process.
Microbial shelter.	Growth stimulation of key microorganisms catalyzing metal transformations.	▪Surface area. ▪Porosity, pore size, and pore distribution. ▪Specific surface area. ▪Labile carbon content. ▪Content of inorganic nutrients (N, P, etc.).	▪Feedstock material. ▪Pyrolysis conditions (temperature and atmosphere). ▪Activation process

Table 1. *Cont.*

Biochar–Microorganism Interaction	Mechanism of Metal (Loid) Stabilization	Key Biochar Properties	Factors Determining Key Biochar Properties
Biofilm development on biochar's surface.	Serving as an attachment surface for the development of biofilms of key microorganisms catalyzing metal transformations.	▪Particle size. ▪Porosity. ▪Absence of toxic organic compounds formed during pyrolysis. ▪Hydrophobic/hydrophilic nature.	▪Feedstock material ▪Pyrolysis temperature
Decrease in heavy metal toxicity towards microorganisms.	Facilitation of microbial growth and metabolic activity by diminishing metal/metalloid toxicity.	▪Adsorption capacity. ▪Cation-exchange capacity. ▪Immobilization/buffer capacity.	▪Feedstock material ▪Pyrolysis temperature ▪Particle size ▪Ash content ▪O-group content
Indirectly improving key microbial activity by improving the soil quality.	Facilitation of microbial growth and metabolic activity by improving soil quality.	▪Adsorption capacity. ▪Cation-exchange capacity. Nutrient content.	▪Feedstock material ▪Ash content

2.1. Adsorption Capacity

Toxic metal adsorption by biochar may alleviate metal toxicity towards microorganisms, allowing microorganism–metal interactions that may improve mechanisms by which metal removal can be achieved. Adsorption mechanisms for the removal of toxic metals by biochar include ion exchange, surface complexation, electrostatic interactions, precipitation, and π-π e- donor/acceptor interactions [6]. Key biochar characteristics promoting metal adsorption are surface area, surface charge, ash content, and oxygen content (O-groups). The main factors promoting the obtention of biochar with high adsorptive capacities are the type of feedstock, pyrolysis conditions, and activation/modification of the material. When used as a feedstock, sewage sludge waste, and manure, the biochar presented a higher surface area, ash content (mainly Ca, Mg, P, Fe), and oxygen content than most wood-chip- or agricultural-waste-derived biochar, thus showing superior adsorption capacity towards heavy metals [7,8]. Due to this, agricultural waste, after an anaerobic digestion process, has proved to be a more suitable feedstock to produce biochar than undigested waste [9]. Biochar produced at elevated pyrolysis temperatures (>600 °C) also tends to have higher ash content and surface areas; therefore, its adsorption capacity towards heavy metals surpasses the capacity of those produced at temperatures <500 °C [10]. The activation of biochar, addressed in the previous section, is a common approach to increase the surface area and oxygen content of the material, both factors having a paramount role in the adsorption of heavy metals; however, ash content has a more important role on the adsorption capacity. Therefore, most of the modifications (commonly carried out after an activation process) are aimed at increasing this value by impregnating biochar with different minerals, such as $CaCO_3$, FexOx, MnOx, and MgO [11–14]. Key analytical tools for verifying the adsorption capacity of biochar for biotechnological applications focused on metal removal are adsorption assays at a controlled temperature/pH, aided by adsorption models, such as the Langmuir, Freundlich Temkin, and Dubinin–Radushkevi models, and sequential extraction assays to determine the extent of the different adsorption mechanism of biochar. Qualitative characterizations such as XRD, EDS, and FTIR are also commonly employed to identify the adsorption of heavy metals onto biochar.

2.2. Surface Area and Porosity

Biochar's higher surface areas are associated with high porosity. In combination with a high concentration of redox functional groups, the catalytic effect that such biochar may have in microbially mediated reactions might be significantly boosted. Metal adsorption capacities are also positively affected by high surface areas and high porosity. Multiple studies have shown that these characteristics are derived from the type of feedstock [15–17] and the pyrolysis conditions used for biochar production [2,18,19]. The parameters associated with the pyrolysis process, such as temperature, heating rate, and atmospheric conditions, have been deemed factors contributing to high surface areas. For instance, temperatures of up to 500 to 600 °C have resulted in biochar with surface areas of up to ~100 m^2/g biochar [15,18,20]. In addition, high heating rates (400 °C/min) have been associated with 10 to 15% increases in the microporous characteristic of biochar, which is indispensable for increased surface areas [16]. Concerning atmospheric conditions during biochar pyrolysis, using an inert atmosphere, e.g., N_2, Ar, or He, results in a material with a lower surface area compared to the material obtained in an air-limited atmosphere at the same temperature. In the contrary case, using an air-limited atmosphere leads to a material with a higher surface area, which is desirable for several aspects in the context of biotechnological applications [19]. Characterizing the porosity and surface characteristics of biochar by N_2 adsorption isotherms at 77 K and the use of the Brunauer-Emmett-Teller method (BET) for the estimation of the specific surface area is indispensable to developing sustainable biotechnological processes for metal removal.

2.3. Electron-Exchange Capacity

Oxygenated functional groups (O-groups), for instance, quinone moieties (C=O), have been shown to correlate with the electron-exchange capacity (EEC) of biochar in biotechnological applications [21]. Thus, biochar with a high content of O-groups is desirable for biochar–microorganism applications relying on the catalytic effect of biochar as an electron acceptor, donor, or shuttle. Pyrolysis temperatures of up to 300 °C, rapid heating rates, and air-limited atmospheres (instead of an inert atmosphere) have been shown to importantly increase the number of O-groups in biochar [15,22]. A common practice to increase the content of O-groups in biochar is to submit it to an activation process that could be either chemical or physical [23–25]. Physical activation consists in using high temperatures and an oxidizing atmosphere, such as water vapor, O_2, or CO_2 [23,26]. Meanwhile, chemical activation involves using oxidizing agents such as HNO_3, H_2SO_4, KOH, NaOH, H_3PO_4, K_2CO_3, and H_2O_2 at low temperatures (50–80 °C) [23]. Another essential factor that determines the O-group content and speciation is the aging of the biochar, which is a process that can occur naturally in time under different conditions, such as high temperatures, an oxidizing environment, or the presence of microorganisms. Generally, more aged biochar shows a higher concentration of O-groups [27,28] due to the oxidation/degradation of labile or poorly fixed C; because of this, biochar produced using a higher pyrolysis temperature, shows a higher degree of aromaticity and presents an increased resistance towards aging [28]. Common techniques to validate the EEC of carbonaceous materials, to verify their suitability for mediating microbial reactions, are mediated electrochemical analysis using a three-electrode system and redox mediators for the direct determination of the EEC, or Boehm titrations for the indirect determination of the EEC by quinone/hydroquinone quantification. Verifying this redox activity is an essential part of developing biotechnological approaches for the removal of concerning metals.

3. Biochar-Microorganism Interactions Promoting Heavy Metal Removal

3.1. Biochar-Mediated Microbial Redox Reactions

Analogously to that documented for natural and engineered carbonaceous materials such as redox-active natural organic matter (a.k.a., humic substances) and activated carbon [29,30], biochar possesses important redox activity due to its richness in electron transfer moieties. Such moieties may include phenolic species, quinone functional groups, and polycondensed aromatic structures, amongst others [21,31]. Chemical moieties in biochar are generated during its production through the pyrolysis of lignin and cellulose. Depending on its nature, amount, and distribution, these moieties can result in biochar with variable electrochemical properties, namely cation- and electron-exchange capacities

(CEC and EEC, respectively) as well as different redox potential values [32,33]. The redox activity of biochar can be described as the capability of this material to (i) donate electrons for reduction in more oxidized compounds, (ii) accept electrons from the oxidation of more reduced compounds, or (iii) act as an electron shuttle by transporting electrons during redox reactions occurring in the surrounding environment [34–36]. The reactions in which biochar can intervene, due to its redox activity, can be biological (microbial) or chemical in nature. Hence, many mechanisms by which biochar could promote the passivation of potentially toxic metals are possible and will be discussed below (Figure 2).

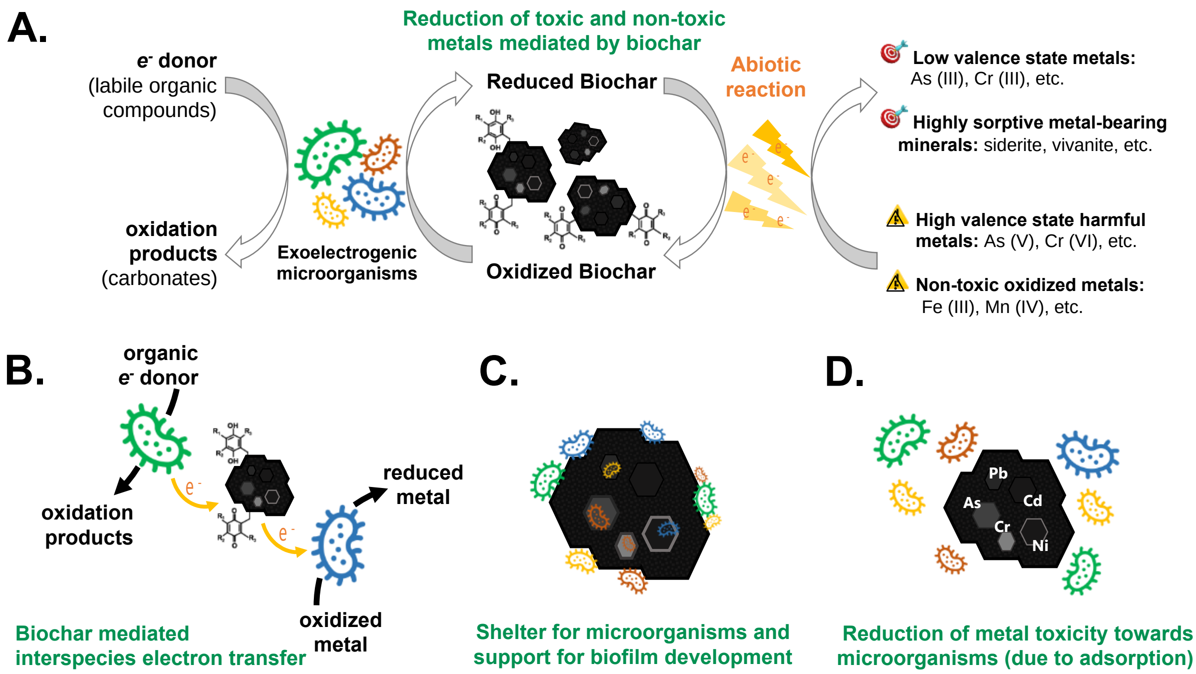

Figure 2. Mechanisms of biochar–microorganism interactions with a positive impact on the passivation or immobilization of potentially toxic metals/metalloids. (**A**) displays the mechanism of electron shuttling mediated by biochar resulting in the chemical reduction of toxic and non-toxic metals and metalloids, (**B**) displays the mechanism of biochar mediated interspecies electron transfer for the reduction of metals and metalloids, (**C**) depicts biochar serving as the shelter for microorganisms growth and biofilm formation, and (**D**) depicts a reduction in the toxicity of metals towards microorganisms due to adsorption of metals onto the biochar's surface.

3.2. Reduction in Non-Toxic Metals Mediated by Biochar

One plausible mechanism by which biochar can facilitate the passivation of toxic metals is by catalyzing the reduction in non-toxic metals in solid and liquid wastes, such as mine tailings and polluted waters (Figure 2A). Studies have shown that biochar facilitates and accelerates the microbial reduction in oxidized metals such as ferric iron oxyhydroxides, producing, e.g., ferrihydrite and hematite [37–39]. Such biochar-catalyzed processes have been shown to affect the fate of the ferrous iron produced, forming minerals such as magnetite ($Fe^{II}{}_2Fe^{III}O_4$), vivianite, ($Fe^{II}{}_3(PO_4)_2{\cdot}8H_2O$), and siderite ($Fe^{II}CO_3$), thereby changing the geochemical and mineralogic characteristics of the surrounding environment [40]. These findings highlight the potential that biochar-mediated electron shuttling has in influencing Fe-related biological processes with the potential of changing soil and tailings mineralogy and therefore affect the fate and mobility of nearby heavy metals [41,42]. For instance, it has been widely reported that some toxic metals can co-precipitate with carbonates [43]; a clear example is that siderite has been proven to function as an adsorbent for harmful metals such as (III and V), Pb (II), and Cr (VI) [44–46]. Similarly, phosphates can adsorb and co-precipitate with toxic metals, i.e., vivianite has been reported to incorporate As (III and V) during the microbial reduction in As-bearing Fe(III)-(oxyhydr)oxides [47,48].

Cr(VI) has also been reported to bind into vivianite's surface allowing its removal from aqueous media [49]. Considering this body of evidence, biochar-facilitated reactions that provoke the precipitation of inert minerals and could potentially diminish the impact of toxic metals by transferring them into more stable Fe-bearing mineral phases (e.g., by sorption) not only in polluted soils and mine tailings but also in metal-laden waters [50,51]. It is important to stress that the previously described mechanisms of biochar-mediated metal reduction (Figure 2A) are also likely to occur with other metals, such as Mn(IV) oxides [52]. Therefore, further research must be performed to describe the potential application of biochar with high EEC to remove or passivate potentially toxic metals by exploiting the capability of biochar to promote biological reduction in non-toxic metals widely available in nature (Table 1).

3.3. Reduction in Toxic Metals Mediated by Biochar

Accumulating evidence shows that reduced biochar can effectively catalyze the reduction in potentially toxic metals by acting as an abiotic electron donor [53,54]. For instance, a reduction in Cr(VI) and As(V) by biochar has been recently reported and low-temperature biochar overperformed high-temperature biochar to function as a reductant for metalloids [55]. Considering that many of these metal(oid)s are less mobile and toxic in their lower valence state (e.g., Cr (III)) [56,57], the biochar-driven reduction in toxic metals and metalloids constitutes a highly feasible strategy to eliminate the toxic effects of such contaminants. Interestingly, this remediation strategy could be potentialized if exoelectrogenic microorganisms (with the capacity to employ extracellular electron acceptors, i.e., solid-electron accepting materials), such as biochar-respiring bacteria, reduce the redox-active moieties in biochar over subsequent cycles [58]. This can be possible if suitable organic substrates are available to function as electron donors, which is the case for agricultural soils and certain wastewaters [59,60]. However, in the case of heavy metal and metalloid-polluted matrices, such as mine tailings or mining-derived waters, which are organic-poor, strategies such as amendment with biochar rich in labile organic carbonaceous compounds or the addition of extrinsic organic matter can be employed as an option to promote biological redox reactions mediated by biochar, which can result in the passivation of certain metallic pollutants [61,62]. It is worth mentioning that metalloids such as and Sb have shown to be released after the application of biochar under reducing conditions, which increases their mobility and toxicity; thus, special considerations must be made before implementing strategies exploiting the synergies between microorganisms and biochar if they are to be applied in multi-metal contaminated systems including As and Sb [63].

3.4. Biochar-Mediated Interspecies Electron Transfer

Recent research has unveiled a novel role for biochar, which takes advantage of its electron-exchange capacity to make possible syntrophy between different microbial taxa, which otherwise could not interact due to physiological and metabolic limitations (Chen et al., 2014a). Such a phenomenon, called biochar-mediated interspecies electron transfer (B-IET), has been shown to link microorganisms' metabolisms to accomplish oxidation and reduction in compounds that are impossible to degrade for each of the microorganisms alone [29,64]. Although the development of B-IET-based processes has gained attention to improve processes only involving organic substrates [65,66], to the best of our knowledge, the implementation of this mechanism in metal-remediation strategies has not been evaluated. Despite this, the B-IET mechanism has the potential to allow or improve the electron flow between microorganisms, for instance, by forming bacteria–biochar–bacteria conductive networks, with the ultimate consequence of changing the oxidation state of metallic pollutants, which can result in their detoxification or passivation (Figure 2B). As well as for the two previously described mechanisms (reduction in non-toxic and toxic metals), the application of bioremediation strategies based on B-IET mechanisms would be benefitted by using biochar with high electron-exchange capacities, and suitable redox potentials would ensure rapid microbial kinetics and metal-reduction rates (Table 1).

3.5. Biochar as a Microbial Shelter and Biofilm Carrier

One crucial function of biochar with excellent potential for improving microbial heavy metal remediation is its capacity to serve as shelter for microbial growth (Figure 2C) and its suitability for nourishing biofilm development [67,68]. Such ability partially originates from some physical characteristics of biochar, such as its high porosity and large specific surface area, which provides microorganisms with plenty of multi-size pores to attach, colonize, and obtain protection from external stressors such as toxic compounds [42,69]. Additional characteristics of biochar, such as its sorption and cation-exchange capacities, help boost microbial growth due to pH buffering and the sorption of inhibiting organic and inorganic compounds, thus promoting microbial growth [70,71] (Figure 2D). Further studies have shown that biochar can provide microorganisms with several nutrients, such as N, P, K, and Mg, but also with organic C, which not only improves the growth of microorganisms on its surface but also in the surrounding location (the so-called "charosphere") [71,72]. Examples of the successful application of biochar for the development of biofilms in metal-removal systems include the successful elimination of Cd and Pb from wastewater employing food-waste-based biochar [73] and the simultaneous immobilization of Fe, Al, and As and the removal of organic contaminants from water originating from mining processes [74]. Several parameters during pyrolysis (i.e., the pyrolysis atmosphere, heating rates, and use of oxidizing agents), as well as distinct stock sources for biochar production, have been identified as creating biochar with high surface areas and porosities (Table 1).

4. Applications for Solid Matrixes Treatment

4.1. Mine Tailing Bioremediation/Metal-Containing Solid Waste

Metal-containing solid waste originates as a by-product of industrial activities as the result of metal utilization in processes, such as tailings, slags, and sludges [75]. However, there are also other wastes that can be contaminated with metals, for example, municipal solid waste, electronic waste, and used batteries [76,77]. Because of the presence of toxic metals, these wastes are hazardous and represent environmental problems [75]. Moreover, there is a large amount of them; as an example, global estimates of tailings production by 2000 were hundreds of thousands per tonnes per day [77], while the total worldwide amount of e-waste reached 41.8 million tons in 2015, and it was projected to increase by 21% to 50 million tons by 2018 [78].

Some solid wastes need to be managed by stabilization, which refers to the immobilization of the hazardous materials or reductions in their solubility through appropriate reactions [79]. Other metal-containing solid wastes can be considered as a source of valuable metals for recovery [80] and leaching is the method required. Hence, it is crucial to understand biochar's properties and interactions as well as its interactions with microorganisms to obtain the desired results and to avoid undesirable effects.

4.2. Tailing Stabilization

Regarding remediation, the use of biochar as a carrier for functional microorganisms promotes physicochemical and microbial reactions, and this can be an integral approach and serve as a bio-augmentation method [81] which can be useful for mine-tailing remediation. Even more detailed studies are needed to understand the response of microorganisms; some studies have confirmed that biochar application and the coexistence of indigenous microorganisms can effectively reduce the bioavailability of heavy metals [82]. Another study observed that inoculated seedlings of native plant species and biochar synergistically improve the establishment of mycorrhizal fungi in mine tailings [83]. Moreover, the combined use of organic amendments and biochar is suggested because of their complementarity; results showed that the mix better supports a more diverse microbial population, which may favor the resilience of the system against environmental stressors [84]. In addition, the protection of bacteria from metals by biochar has also been confirmed; for instance, P-abundant biochar provided a P source (the most common limiting nutrient) to support microbial growth while bacteria (*Enterobacter* sp.) secrete more organic acids to drive P release [85]. Studies have also reported beneficial changes driven by biochar such as pH, nutrient retention, and water-holding capacity, which would favor its use on mine wastes to help the establishment of a green cover [86].

Nevertheless, particular attention to oxyanionic metalloids has to be paid since some results have suggested biochar's inability to immobilize As and Sb [87]. This issue could be addressed by immobilizing resistant bacteria onto biochar in a similar way as has been undertaken with activated carbon [88]. However, further studies need to be developed to find the adequate conditions to achieve immobilization and better understand the long-term effect of biochar on the microbial community. Other strategies such as sulfate-reduction combined with long-term submergence for the disposal of mine tailings could be enhanced [89] by the addition of biochar and this requires further studies.

4.3. Leaching from Metal-Containing Solid Waste

Biochar's use as an exogenous mediator to regulate the redox reactions of bioleaching has been found to enhance efficiency. For instance, Fe-mediated bioleaching was significantly promoted by biochar, facilitating redox action between Fe(II) and Fe(III), which resulted in effective leaching of Cu from printed circuit boards using aerobic activated sludge as an inoculum. Two dominant functional species, identified as *Alicyclobacillus* spp. and *Sulfobacillus* spp., were suggested to cooperate in the Fe-mediated bioleaching system [90]. Besides this, copper and nickel bioleaching from spent mobile-phone printed circuit boards by *A. thiooxidans* was improved by adding biochar as a catalyst, obtaining 98% of copper and 82% of nickel by indirect bioleaching. The better performance in the presence of biochar was explained as due to both galvanic interactions between biochar and solid waste [91].

Additionally, an enhanced effect of biochar on the bioleaching of stone-coal tailings by *Thiobacillus ferrooxidans* has been studied and the authors refer to two main aspects: (i) The store of nutrients and microenvironment for inhabitation by free microorganisms due to the porous structure of biochar; and (ii) The promotion of electron transfer by biochar, improving the oxidation ability of *T. ferrooxidans* on Fe^{2+} [92].

For practical application, the study of the operating conditions is necessary to assess the appropriate dosage and ratios as well as understanding and promoting the role of biochar as a mediator, facilitating the electron transfer in solution and to bacteria that may lead to bacterial growth and process enhancement.

4.4. Polluted Soil Bioremediation

Regarding soil treatment, phytoremediation is an approach in which biochar–microorganism interactions can be exploited to achieve improved remediation efficiencies. For instance, during the 2010s, numerous investigations demonstrated the potential of plant-growth-promoting bacteria (PGPB) to enhance the effectiveness of phytoremediation. In the late 2010s, research was specific to heavy-metal-resistant plant-growth-promoting bacteria (HMRPGPB), which had statistically superior heavy-metal-removal efficiencies than non-metal tolerant PGPB [93]. However, medium-term and large-scale experiments showed a nutrient deficit due to the rapid assimilation of nutrients by HMRPGPB, coupled with adverse habitat conditions. Eventually, both bacteria and plants were damaged and thus unable to continue removing metals, and these metals could be released back into the soil [94]. In these cases, the combination of biochar with HMRPGPB becomes relevant. As mentioned before, biochar improves the retention of organic matter and nutrients such as nitrogen and phosphorus. Additionally, biochar amendment improves the phytoremediation of heavy metals by reducing bioavailability and phytotoxicity, increasing phytostabilization.

The use of biochar as a carrier or shelter of microbial strains has gained attention in the last years. The capability of biochar to retain nutrients and provide an enhanced habitat for microorganisms and biofilm development is crucial for improving phytoremediation strategies.

Although HMRPGPB are usually isolated from contaminated sites, either directly from soils or from the rhizosphere of metal-accumulating plants, taxonomic studies have revealed that the most abundant genera are *Pseudomonas*, *Bacillus*, *Rhizobium*, and *Klebsiella*, which are widely available for biotechnological purposes. These bacterial genera are nitrogen fixers and thus provide nitrogen to the rhizosphere so plants can use it for its cellular structures, alleviating nitrogen depletion in sites with the presence of heavy metals. In addition, when HMRPGPB are combined with biochar, they can reduce soil N_2O emission, which also increases nitrogen retention in the soil [95].

The presence of heavy metals generates changes in pH and oxidation-reduction potentials in soils, which raises the content of insoluble phosphate species unavailable to plants. Some HMRPGPB species solubilize phosphates through phosphatase enzymes to monobasic and dibasic phosphates (HPO_4^{2-} and $H_2PO_4^{-}$), which are the most accessible forms for plants [96,97]. More precisely, the bacteria involved in such solubilization are metal tolerant, and the degree of phosphate solubilization is correlated with bacterial abundance. The use of biochar increases the surface area for a greater establishment of bacterial colonies, in this case, HMRPGPBs. Thus, biochar can promote greater assimilation of phosphorus by plants.

The presence of heavy metals also has adverse effects on potassium availability. For instance, pH and redox conditions may lead to a non-exchangeable forms of phosphorus [98]. Acidic soils (pH < 5.0) with oxidizing conditions (>250 mV) favor the solubilization of heavy metals and make nutrients non-exchangeable [99]. In addition, heavy metals substitute potassium from the stomata in dissolved phases, which is an initial mechanism during metal poisoning, mainly occurring with lead and cadmium [100]. The addition of biochar makes the potassium contained in the substrate more exchangeable [101]. In addition, heavy metals competing with potassium for the stomata in plants can be adsorbed onto biochar. Coupling these effects of biochar with the presence of HMRPGPB, potassium solubility could be enhanced.

In a previous paper by [102], strain SNB6 was isolated from a highly cadmium-contaminated soil and immobilized on biochar, and added to *Chrysopogon zizanioides* L. Results revealed that a micro-ecology system was formed. The findings were very encouraging, as the consortium resulted in a higher bacterial cell count and higher enzyme activity near the rhizosphere was responsible for stabilizing heavy metals [102]. The trends indicate that the synergism between biochar and HMRPGPB should be studied in detail, as it is a promising green approach to remediate and recover heavy metals from contaminated soils.

Aspects such as the type of raw material, temperature and pyrolysis time, and proportions added to soils are crucial. Zhou et al., (2021) investigated the community succession of heavy-metal-resistant bacteria and bacterial activity in composting poultry manure. The results indicated that adding 5–7% biochar increases the abundance of bacterial communities; the immobilization of heavy metals was higher and even the composting efficiency was improved [103].

Once the benefits of combining biochar with heavy-metal-tolerant bacteria have been identified, further studies will be required to optimize results and understand limitations or effects in the long term.

4.5. Biochar Application in Composting/Vermicomposting Processes

During the last years, the application of biochar during the stabilization of the composting of biological wastes has drawn considerable attention from the scientific community [104] (Figure 1). To take advantage of the physicochemical properties of biochar, which confer a high affinity for metals [82], this material has been added to the processes of composting and vermicomposting, in which it reduces the mobility of metals, such as Ni, Pb, Zn, and Cu [105]. It has been proposed that via mechanisms involving precipitation,

ion exchange, increase in pH, and electrostatic interactions, biochar possess the capability to reduce the bioavailability of toxic metals during the composting/vermicomposting process [106]. In this way, biochar reduces the toxicity of these metals to the microorganisms and to the worms involved in the vermicomposting process [107]. Therefore, the application of biochar results in beneficial effects to the vermicomposting process such as a higher degradation of organic matter and a reduced concentration of heavy metals in the resulting compost [108].

5. Applications for Liquid Matrixes Treatment

5.1. Bioreactors

The implementation of technologies that combine biochar and microorganisms in synergy for metal removal in water is still to be exploited. For instance, water can be treated by biochar–microorganism interactions in different configurations of bioreactors, constructed wetlands, hybrid processes, and permeable reactive barriers (Figure 3).

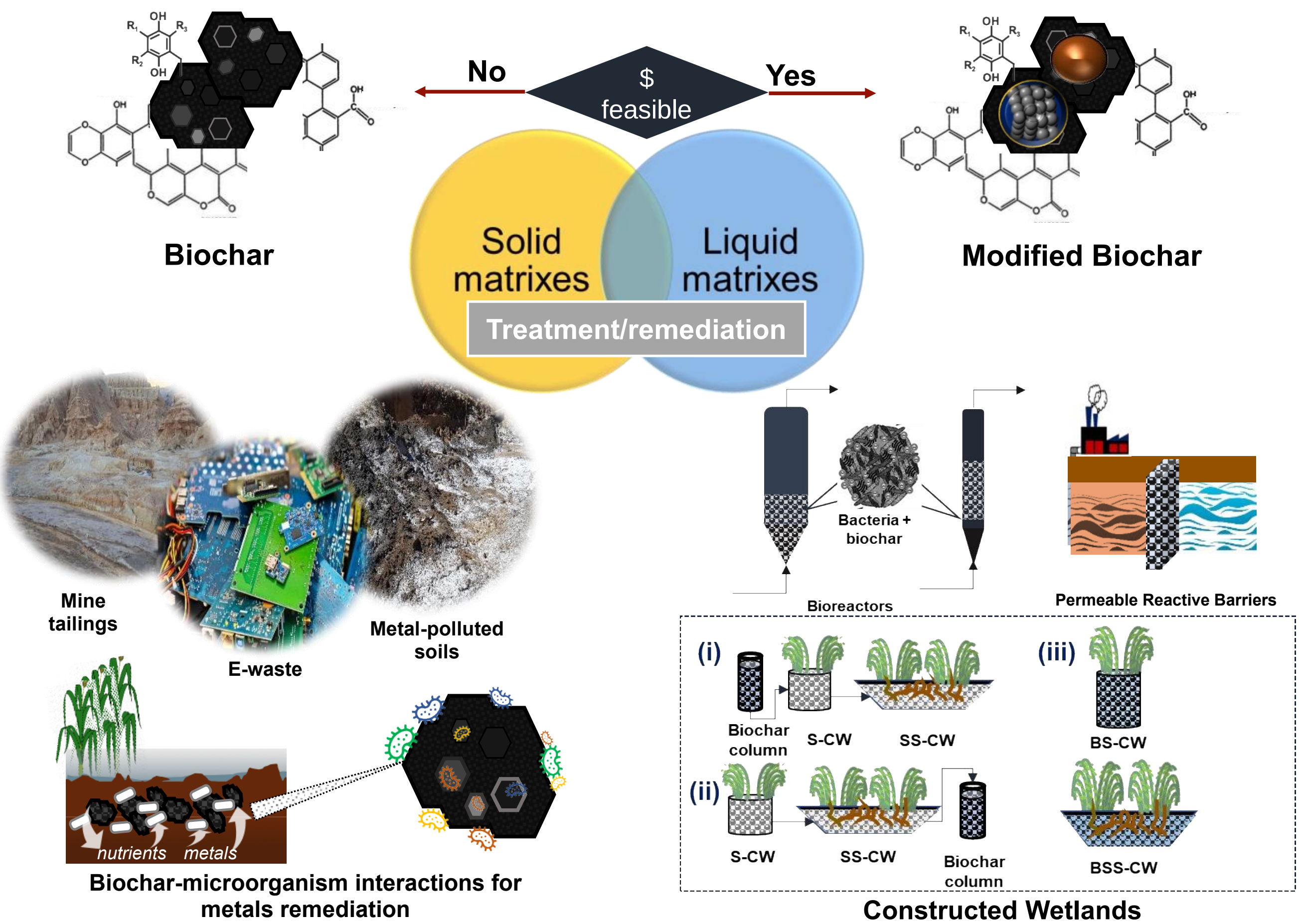

Figure 3. Metal removal by microbial-biochar/modified biochar-based solutions for solid and liquid matrixes. S-CW (surface-flow constructed wetland), SS-CW (subsurface-flow constructed wetland), BSS-CW (biochar-filled subsurface-flow constructed wetland), BS-CW (biochar-filled surface-flow constructed wetland).

The use of biochar and microorganisms in bioreactors can include two approaches: (i) Using biochar as support for microorganisms, involving the prior growing of bacterial consortium onto biochar, which would increase density of bacteria and accelerating removal; or (ii) Adding biochar to interact with bacteria over time. So far, all research has been carried out at laboratory scale and mostly in batch systems.

For instance, in [103], batch reactors of bacterial cells immobilized on biochar were implemented. This treatment showed higher cell density and significantly higher cadmium removal compared to reactors without biochar. On the other hand, a plug flow reactor inoculated with *Stenotrophomonas maltophilia*, and immobilized on corn-stalk biochar, for the removal of Cu(II), demonstrated that the number of microorganisms loaded on biochar decreases as the pyrolysis temperature increases, while the removal of metal increased with the reduction in biochar particle size [104].

A beneficial aspect in reactors where the organic load is a key design parameter is the effect of bacterial protection from metal stress by biochar. The results obtained by [105] using biochar with a P content of 1.32% (obtained from rice-husk and pig-manure mixture 70–30%) and added to *Enterobacter* sp. for the removal of Cd2+ revealed positive feedback between P-enriched biochar, which provides a P source to support microbial growth, and *Enterobacter* sp., which secretes more organic acids to drive P release. Finally, this allowed the organic load to remain constant. Similarly, a batch reactor with composites of *Bacillus subtilis* and biochar was tested for the removal of Cd(II) in water and demonstrated that corn-stalk-, peanut-shell-, and pine-wood-derived biochar pyrolyzed at 500 °C alleviated Cd toxicity for *B. subtilis* to a certain extent, with constant organic and hydraulic loads [106].

Different reactor configurations, such as up-flow anaerobic blanket (UASB) or column batch, may be used, although the increase in bacterial density would modify some design and operating parameters. For example, in up-flow systems, it is necessary to consider the increase in the weight of the fluidized biomass. However, this can be overcome by applying the established design equations for these types of reactors. In addition, variables such as organic load could have more desirable values; therefore, lower hydraulic residence times could be required.

In situ remediation of surface and groundwater can be accomplished by innovating in permeable reactive barriers filled with biochar (B-PRB) or immobilized bacteria-biochar [109,110]. In this application the biochar can be mixed with slow-release nutrient particles to facilitate microbial activity [109]. Biochar as a filling material can remove metals by adsorption, and biomass can be supported on biochar to accelerate remediation.

5.2. Constructed Wetlands

An additional technology for metal removal from waters that takes advantage of the interaction between biochar and microorganisms are constructed wetlands (CWs). In CWs, biochar is used as packing material or as support media. Different configurations have been explored for the implementation of CWs for metal removal. For instance, CWs can be used as a first stage or pre-treatment unit or as a final stage or post-treatment unit. As a first stage unit, biochar would help to increase the pH and diminish certain metal concentrations. This design would avoid microbial inhibition, plant damage, or clogging of the CW. The advantages provided by biochar can result in improving the water treatment of acid mine drainage or heavily polluted industrial waters. As a final stage unit, the use of biochar in CWs allows one to achieve high-quality treated waters. Furthermore, the use of biochar as substrate/supporting media in CWs promotes biochar–microorganism interactions, as explained in the following sub-sections.

5.2.1. Use of Biochar in Constructed Wetlands for Metal Removal

Biochar implementation as part of treatment systems for metal removal in rural areas and/or with minimum energetical and operational costs are promising. Constructed wetlands (CWs) are nature-based solutions that can be used for the treatment of different wastewaters. This technology is accepted as a secondary treatment alternative to activated sludge, anaerobic reactors, trickling filters, and stirred reactors, among others. CWs are characterized by biotic (i.e., microbial consortium and macrophyte plants) and abiotic (i.e., packing media) components but mainly by their interactions. For instance, the packing media are responsible for contaminant adsorption and the presence of bacteria promotes biosorption, which increases the removal of contaminants. Vegetation also interacts with microorganisms in the rhizosphere through oxygen, carbon dioxide, nutrients, enzymes and organic-exudate exchange [111].

Metal removal in CWs involves mechanisms depending on packing-material–microorganism–vegetation interactions. The main processes are cationic exchange, adsorption to particulate matter, carbonate precipitation, direct plant assimilation, metal complexation, biosorption, reduction, and precipitation [112]. Additionally, biofilm development on packing media and the rhizosphere enhance the tolerance mechanisms of microorganisms towards metals through vacuolar transport, sulfur gene regulation (metabolism-detoxification) [89,113], etc. Hence, the implementation of biochar as packing media in CW systems offers advantages for metal removal.

Moreover, some authors have reported a beneficial effect on vegetation promoted by biochar. The authors of [114] reported a twofold increase in biomass vegetation by biochar addition, as compared to a control without biochar: 0.6 kg/m^2 and 0.3 kg/m^2, respectively. Thus, phytoremediation (a mechanism occurring in CWs) for metal removal can be stimulated by biochar and applied in scenarios as an acid mine drainage treatment. Nevertheless, few studies on the use of biochar in CWs for the treatment of metal-containing wastewaters are available. In this context, [115] studied the removal routes of heavy metals from mining-impacted water by biochar-filled CWs. Their results indicated that the biochar system exhibited higher levels of metal retention as compared to the control system (without biochar), 280 mg/L Cu-400 mg/L Cr and 160 mg/L Cu-75 mg/L Cr, respectively. Although the study demonstrated that the role of macrophytes was insignificant, an increase in the plant biomass growth was observed, which also suggests that under specific operational conditions, the phytoextraction of metals could be favored.

The design parameters for CWs filled with biochar for metal removal are not standardized, but there is literature with the fundamentals for this purpose (Pat-Espadas et al., 2018; Yu et al., 2021) and different practical applications at laboratory and field level are reported [116]. All this available information can be incorporated into the CW design parameters that are mainly based on flow concepts in porous media.

Thus, based on the information available, data from different studies were analyzed to obtain the range values for different parameters for selected metals shown in Table 2. Criteria for packing material and vegetation selection were ascertained according to the recommendations by [117,118]. Hence, information analysis was limited to CWs applied for metal removal filled with gravel, volcanic rock, or river stone and the vegetation considered was *Typha latifolia*, *Phragmites australis*, or *Juncus effusus*. For biochar parameters presented in the data analysis, different feedstock and pyrolysis temperatures for biochar production were included but modified biochar were not considered.

Table 2. Theoretical comparison of heavy metal removal in CWs filled with biochar and traditional packing media based on hydraulic calculations and adsorption capacity.

Parameter	Biochar	Constructed Wetland		Constructed Wetland Filled with Biochar (10% *v*/*v*)	Observations and References
		Whole System	Package Media		
Porosity	0.8–0.11	0.3–0.55		0.27–0.39	n = 10 [52,61,75,85,89,91,110,111,119,120]
Hydraulic conductivity, $mm^3/(mm^2\ d)$	0.9–5.7	38–87		2.6–43	n = 10 [52,61,75,85,89,91,110,111,119,120]
Pb removal	2.4–12.5 mg/g	44.2–68%	47–52% 1.2–5.4 mg/g	67–76%	n = 6 Biochar < 500 °C [10,11,21,29,52,61]
Pb removal	6.1–42.5 mg/g	26–52%	12–21% 1.2–5.4 mg/g	56–71%	n = 6 Biochar > 500 °C [10,11,21,29,52,75]

Table 2. *Cont.*

Parameter	Biochar	Constructed Wetland		Constructed Wetland Filled with Biochar (10% *v*/*v*)	Observations and References
		Whole System	Package Media		
Cr removal	3–27 mg/g	35–55.8%	14–19% 1.9–6 mg/g	41–65%	n = 8 [46,55–59,61,107]
Cu removal	0.5–14 mg/g	8–36%	5–28% 0.7–10.3 mg/g	22–45%	n = 7 [27,61,75,85,91,104,110]
Hg removal	0.5–2.3 mg/g	5–75%	0.5–53% 0.2–1.3 mg/g	12–83%	n = 3 [110,111,120]
Cd removal	0.6–40 mg/g	35–67%	18.6–57.6% 0.5–11.5 mg/g	45–76%	n = 9 [14,20,72,101,105,106,119,120]
Zn removal	4.5–38 mg/g	57–100%	1.2–63% 4.2–13 mg/g	67–100%	n = 4 [52,75,110,119]
As removal	1.8–3.2 mg/g	75–99%	1.4–43% 0.2–1.7 mg/g	79–99%	n = 4 [55,57,110,119]

The calculations for biochar-filled CW efficiency were performed considering metal removal by the material (g metal/g material), by mass balance, and considering the volume and the phytoextraction reported for the vegetation. Additionally, the following considerations were applied: (i) The biochar is 10% *v*/*v* of the total packing media; (ii) Porosity-value criteria to be considered for practical implementation are 0.35, since system clogging is not recommendable; (iii) Pre-treatment of the influent was not considered; (iv) Data for the wastewater from mining tailings and synthetic water (pH below 6.0 and sulfate concentration of at least 200 mg/L) were considered.

According to the calculations as shown in Table 2, heavy metal removal in CW systems can be improved by the addition of biochar as packing media. However, it is important to consider the synergistic effect of microorganisms, vegetation, and packing media, as explained in the following section.

5.2.2. Scenario of Beneficial Microorganism—Biochar Interactions in Constructed Wetlands

Microorganisms' capacity for metal removal includes biosorption, bio-accumulation, and metal reduction. Moreover, some genera such as *Klebsiella*, *Actinoplanes*, *Agrobacterium*, *Pseudomonas*, or *Rhizobium* are plant-growth-promoting rhizobacteria, providing molecules of interest to the roots, and generating hormones for plants that reduce the toxicity of pollutants such as heavy metals [121].

Furthermore, the use of biochar and bacteria has been proved to increase metal removal. For instance, [122] reported that cadmium removal by composites of *Bacillus subtilis* and biochar was higher than only biochar: 62% and 33%, respectively. Moreover, bacteria accounted for only 25% removal in control experiments without the addition of biochar. Another study demonstrated that viable *Bacillus cereus* RC-1 immobilized on biochar derived from rice straw, chicken manure, and sewage sludge for Cd^{2+} removal was improved by bacteria contribution, while different removal mechanisms were obtained depending on the biochar feedstock—mainly ion-exchange and complexation [123].

More studies on the interactions of CW components and the effect of using metal-tolerant microorganisms are needed for biochar-filled CWs, with appropriate experimental designs to document the synergic effect. For instance, [124,125] demonstrated that the presence of metal-resistant bacteria in CW systems enhanced the removal and decreased the metal toxicity (by changing metal speciation).

Another interesting phenomenon to study is the biofilm formation on biochar (influenced by the porosity and pore size) and the role of extracellular polymeric substances.

For example, exopolysaccharides from cyanobacteria have been added to wastewater-treatment systems to efficiently remove Cd, Pb, and Cu [126]. Hence, areas of opportunity are available to upgrade CW systems using biochar.

6. Perspectives and Conclusions

The studies regarding biochar applications involving microorganisms are in development, and it is crucial to document biochar properties that stimulate microbial processes. This understanding is necessary for the future development of large-scale applications. Some of the challenging aspects for which to generalize results are, for example, the variety of biochar feedstocks and the temperature of pyrolysis. As the use of biochar is increasing, modified or engineered materials are being explored; however, some of the methods are still too expensive to be considered for practical applications. Hence, it is promising to explore methods and options, such as the biological and green synthesis of nanoparticles, which could facilitate the implementation or use of modified biochar at lower costs, especially for target and concerning metals.

In the literature review of the mechanisms of biochar during the removal of heavy metals, chemical reactions and the sorption of heavy metals were identified and suggest that biochar can function as a pretreatment or post-treatment of constructed wetlands to maximize removal efficiencies.

Further studies focused on long-term applications are necessary, as the potential applications of these technologies are promising, but an integral approach is needed. Moreover, studies including the complex but real environmental conditions and factors (such as greenhouse gas emissions, microbial activity, biochar, and nutrients' fate) are necessary to evaluate the effects, either positive or negative, of the addition of biochar.

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