Chapter 23

Biochar-mediated soils for efficient use of agrochemicals

Ahamed Ashiq and Meththika Vithanage
Ecosphere Resilience Research Center, Faculty of Applied Sciences, University of Sri Jayewardenepura, Nugegoda, Sri Lanka

23.1 Introduction

Biochar is of great interest in remediation strategies due to the great environmental and economic benefits it pertains. It is characterized by its large surface area, porous structure, abundant functional groups, and mineral components, which make it promising both in soils and aqueous media (Ahmad et al., 2014b; Lehmann et al., 2009; Rajapaksha et al., 2014; Vithanage et al., 2018). Biochar is a carbonaceous material produced from the pyrolysis of biomass residue under limited oxygen environment. Its water-retention capacity and highly porous structure make it a unique both in terms of a sorbent and as a material for environmental remediation (Atkinson et al., 2010; Orr et al., 2016; Zhu et al., 2017). Usage of biochar as an additive has been studied by many to mitigate anthropogenic climate changes through carbon sequestration while providing soil fertility and enhanced soil production. This old-aged strategy was accompanied by the utilization of char-based materials into the soils whose true potential of agronomic worth and environmental benefits has been identified quite recently (Glaser et al., 2002; Lehmann, 2007). Application of biochar to nutrient-poor soils has been a practice for centuries and has been recognized recently as an attractive option for remediation strategy. Both as sorption of organic or inorganic pollutants and a slow-release material for fertilizer and pesticides are its applicability in soils. Thus the chemical and physical properties of biochar to be utilized for soil and agrochemicals mainly depend on the feedstock used and the pyrolysis conditions such as the heating rate and temperature.

Numerous studies have been focused and highlighted the potential benefits of using biochar as soil amendments (Fig. 23.1). However, most of them include using biochar as a mitigation strategy for global warming through

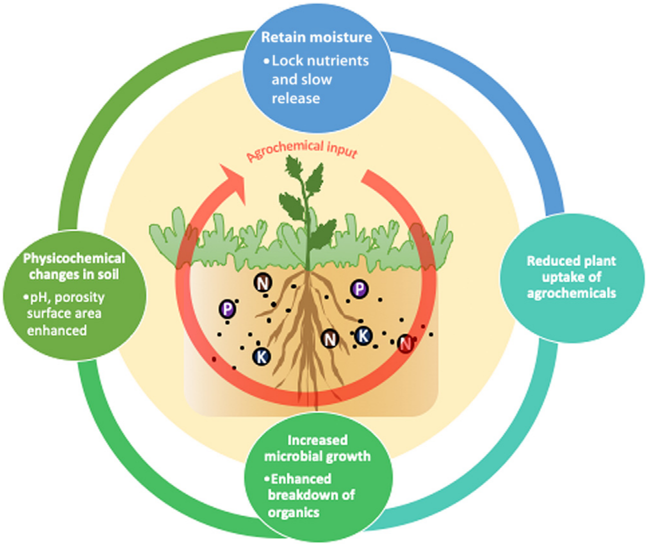

FIGURE 23.1 Overview of the major advantages in biochar-amended soils.

the application in soil and the stability of it in the soil matrices and aqueous media (Kookana, 2010; Kookana et al., 2011; Varjani et al., 2019). The utilization of biochar in all other aspects of agrochemical remediations as in fertilizers and pesticides has been studied to the minimum. Thus the main motivation of this chapter is to give a different perspective of biochar applicability in terms of pesticides remediation and a comprehensive understanding about the agricultural implications concerning the remediation of excess fertilizers and pesticides by biochar. Besides giving a brief review on the biochar properties, types and modes of production, this chapter focused on the limitation of using biochar for soil amendments and as agrochemical remediation and narrowed to provide the future research directions in the field.

23.1.1 Influence from sources, properties, and production technologies

Thermochemically converting available biomass to produce an extensive carbonaceous product have been captivating attention for reducing greenhouse emissions and in increasing soil fertility in a remarkably environmental friendly way. Biochar-production processes have tremendous effects on the physicochemical characteristics of the char. In general, biochar produced at high temperatures (600°C–700°C) demonstrates high aromaticity and organized carbon layers with few hydrogen and oxygen-based functional groups (Novak et al., 2009; Uchimiya et al., 2011), whereas biochar produced at lower temperatures (300°C–400°C) have numerous organic content along with functional groups (Glaser et al., 2000; Novak et al., 2009; Rajapaksha et al., 2016).

Biochar sourced from biomasses can be characterized from purpose-grown, that is, food crops, sludge and then from waste biomasses. Utilizing the wastes directly links with the environmental sustainability of resources. Common wastes mainly include agricultural residues, food crops, manures, and sludge wastes that can be reutilized for synthesizing biochar (Lee et al., 2018; Wang and Wang, 2019). Employing these biomasses for biochar production could not only be an ecofriendly strategy but also reutilizing the waste resources (Ashiq et al., 2019; Sohi et al., 2010).

In agricultural areas the decline in soil quality is observed with extensive application of agrochemicals, which may lead to a loss of organic content in soils (Varjani et al., 2019). Microbes and other enzymes in soils provide sources to improve soil quality, and application of biochar can have detrimental effects, as explained earlier. Sewage sludge–derived biochar, in a study, have shown an increase in biochemical properties, that is, dehydrogenase activity through a decrease in the beta-glucosidase activity (Paz-Ferreiro et al., 2012). The amendments made in the soil are easily accessed through the soil biochemical properties as they are too sensitive with the little changes in the organic contents. They measure the key microbial reactions and thereby understanding the biogeochemical effects of biochar addition it possessed on the plant growth (Bandara et al., 2017; Paz-Ferreiro et al., 2012).

Biochar derived from oakwood and bamboo showed capability in reducing the beta-glucosidase activity with increased biochar application, but in another study, the food crops yield deteriorated when biochar derived from wheat straw biomass is added to the soil. This indicates the source of biochar matters in the crop yield (Demisie et al., 2014; Wu et al., 2013).

The most crucial factors influencing the physical and the chemical properties of the resulting biochar are the feedstock and the pyrolysis conditions (Downie et al., 2009). Wood-based biochar has high lignin content, which makes it have high carbon content, and there is a resistance in the surface of the biochar so formed. This is crucial for soil-based applications, a coarser particle. The temperature and the residence exposure time of the biochar during heating also define the chemical alterations of the final product and also the microstructural arrangements of the layers of carbon (Kookana et al., 2011; Williams et al., 2015; Winsley, 2007). Numerous studies have shown that biochar is highly effective in increasing soil fertility and immobilizing certain contaminant because of its microstructure, charged functional groups, cation-exchange capacity, which is briefly explained below. For the sake of understanding how the amendments of biochar made with soil will influence the soil chemistry, understanding each of these parameters is crucial.

23.1.2 Biochar characteristics: surface area, surface functional groups

The adsorption of organic contaminants as in pesticides solely depends on this very crucial property: the specific surface area. This increases as the pyrolysis temperature increases due to the formation of more micropores. The microporous structure is mostly inherited from the source used, and this is important for the water-retention capacity of the sorbent and the adsorption capacity of the soil (Sohi et al., 2010; Yang et al., 2017; Yu et al., 2006). The temperature of the reactor is the key factor for the surface area, for instance, at 400°C the surface area measured by gas adsorption was found to be 120 m^2/g, whereas at 900°C, the surface area was found to be 460 m^2/g from woody biochar (Sohi et al., 2010). Similarly, from 250°C to 600°C of pyrolytic temperature, the surface area has proven to drastically increase from 0.56 to 14.1 m^2/g (Ding et al., 2014) for sugarcane bagasse-based biochar. This is again quite noticeable for Soybean Stover–based biochar where the surface area increased from 6 to 420 m^2/g at a temperature change from 300°C to 700°C (Ahmad et al., 2012; Vithanage et al., 2015).

For the most part, biochar synthesized at a lower temperature is suggested to have promising results for the controlled release of fertilizers in the soil. The high temperature–derived biochar can be employed as a sorbent for organic contaminant mitigation. These differences make it viable to decide on the right pyrolysis temperature depending on the application to be used. The high surface area at a lower temperature accounts due to a hydrophobic characteristic that may limit the water retention in soils. The celluloses and hemicelluloses during pyrolysis release the volatile matter and increase the formation of the vascular bundle structure in the biochar. This improves the specific surface area and the pore structure of the biochar (Vithanage et al., 2012; Yang et al., 2017). As an instance, corncob biochar showed a variation in the surface area at changes in the pyrolysis temperature from 61.8 to 193 m^2/g due to the decrease in the volatile matter content within the corncob (Liu et al., 2014).

Adsorption properties are directly affected by the surface chemical properties as well, such as oxygen-containing functional groups and thereby are highly sensible to the changes in pyrolytic temperature. With the increase in the pyrolytic temperature the hydrogen and oxygen-containing functional groups are reduce, and further increase in pyrolytic temperature can further reduce the polar functional groups (Pintor et al., 2012). These differences in the chemical properties define the abundance or deficiency of aromaticity or aromatic moieties on the biochar surface, and thus increase hydrophobicity (Ahmad et al., 2012; Chen and Zhou, 2008; Yang et al., 2017). The clear evidence of these functional groups is normally deduced from methods, including Fourier transform-infrared spectroscopy, Raman, X-ray absorption, and X-ray photoelectron (Alam and Alessi, 2018).

Surface functional groups of biochar play a significant role in governing the pH environments, volatile matter, and organic contents and their ability to retain a diversified contaminant (Tang et al., 2013; Uchimiya et al., 2012; Vithanage et al., 2015). For instance, biochar with a high pH is associated to sorb or take up cationic species contaminant, whereas, at a lower pH, a more predominant anionic species is preferred. When it comes to soil amendments, biochar binds with the various cationic nutrients in the soil due to the phenolic and carboxylic functional groups present in the biochar, which further exemplified the cation-exchange capacity of the biochar with the soil (Ahmad et al., 2014b).

23.1.3 Cation-exchange capacity and charge characteristics

Improvement in the cation-exchange capacity in soils after amendments made with biochar has been a general trend. However, depending on the soil types, the availability of cationic nutrients in the soil to bind with the varied functions of the biochar changes with varying organic content in the soils (Chathurika et al., 2016; Tian et al., 2018).

Biochar with a high cation-exchange capacity has a lower tendency to leach out the crucial plant nutrients from soils. The pyrolysis temperature has an inverse effect on the cation-exchange capacity. Cordgrass biochar produced at 200°C has a cation-exchange capacity of 44.5 cmolc/kg and then further reduced to 32.4 cmolc/kg at 550°C pyrolysis temperature (Harvey et al., 2011; Yang et al., 2017). The decreased cation-exchange capacity with increased pyrolysis temperature is attributed to the disappearance of functional groups and, thereby, aromaticity (Li et al., 2017a,b).

23.1.4 Biochar stability

Degradation of biochar at a lower pyrolysis temperature is prominent with certain soil types and based on the recalcitrant carbon substrates that are not fully bound at the lower temperatures. The application frequency the soil requires also dictates the stability toward which longevity of biochar still depends on (Sohi et al., 2010; Taherymoosavi et al., 2017). Biochar applicability in soils are normally dictated to be stable at higher temperatures mainly due to the disappearance of the volatile matter from the biomass when pyrolyzed at such high temperatures as discussed previously (Randolph et al., 2017).

Biochar derived from food waste showed less thermal stability at 500°C pyrolytic temperature as they show a small change in the masses when mixed with sandy soils and resulted in a slight increase in the pH and a decrease in the available plant water. As compared to food waste biochar generated at 700°C, the agronomic applications in soils were evaluated and proved no losses with time (Ahmad et al., 2014a,b). However, the biochar at

500°C is mostly used as a liming agent in soils, and further investigations are underway to know its stability in various other soil matrices. The reactions of biochar with soil is a complex and tedious process that varies both physical and chemical properties of the soil matrices along with the biochar (Elkhalifa et al., 2019; Inyang et al., 2016).

23.2 Biochar benefits: abiotic soil components

The environmental fate and the toxicological impacts of the agrochemicals utilized in food crops need to be accessed thoroughly; therefore the ability of biochar to sorb these agrochemicals and contaminants is a vital route to bear on the fate and toxicology in the environment (Williams et al., 2015). The chemical release, uptake, and bioavailability are affected tremendously by the sorption process and hence needs to be further detailed with specific emphasis on the agrochemicals used in the field.

23.2.1 Influence of biochar on soil physical properties

Physical properties of soil such as permeability, porosity, soil compaction, bulk, and soil density improve drastically with biochar applications. When biochar is applied to the soil, the porosity increased. A study by Oguntunde et al. (2008) found that the porosity increased to 50.6% from 47.5% after the biochar have been amended to the soil. This showed improved plant growth and a decrease in the compaction of soil, which enables the roots to go deeper for nutrients (Agegnehu et al., 2017; Tan et al., 2017). Soil density declines with an increase in the ratio of biochar into the soil; as studied in Major et al. (2010) the density decreased to 2.55 g/cm^3. Soil bulk density plays a major role in soil fertility and hardness. High bulk density decreases with increasing the biochar amendments ratios, which results in a higher ventilatory capacity that can enhance the growth of roots, nutrients uptake, and water adsorption. This applies the same for effect on soil density as a whole. Overall, improved air permeability, optimized soil structure, and crop growth are noticed when biochar is applied to the soils (Jien, 2018; Rehrah et al., 2016). Adsorption capabilities of plants for soil nutrients improve with the application of biochar and thus reduce the leaching effect of important nutrients into the deep surface.

The factors, such as feedstock types used, pyrolysis conditions of biochar produced and its applications, that is, application frequency and the particle size of biochar, affect the mentioned benefits of soil amendments with biochar (Alburquerque et al., 2013; Herath et al., 2017; Song et al., 2019). Biochar is also known for its hydrophobic character when the surface is oxidized, so either the water absorbance or water-holding capacity increases in the soil. The soil structure, texture, and the availability of organic matter get influenced by the water retention in the soil amendments with biochar.

Water-retention capacity of soil, aeration, bulk density, and the microbial effects in the soil are all interrelated property to soil amendments with biochar although they are quite dependent on the feedstock of biomass used for biochar preparation and pyrolysis conditions (Tan et al., 2017; Tripathi et al., 2016; Varjani et al., 2019).

23.2.2 Influence of biochar on soil's chemical properties

Biochar addition to enhancing soil fertility is due to the combined beneficial effects biochar has on chemical and biological properties through alteration in the pH, cation-exchange capacity, and the speciation involved in each pesticides molecules. Understanding of the effect of biochar application to soil on nutrient cycling as in carbon, nitrogen, available phosphorous is crucial to improve soil fertility (Atkinson et al., 2010; Lehmann, 2007; Vithanage et al., 2017).

Soil organic matter is the key indicator of soil fertility. The decrease in the carbon dioxide concentration from the atmosphere is due to the increase in the soil organic matter. The organic content is responsible for simulating the microaggregates that are responsible for the stability of the char in soils. The decomposition of the organic matter in the soil is diminished with the application of biochar in soils and thereby accumulating carbon within the aggregates that are responsible for the stabilization of the soil-biochar system (Tan et al., 2017; Yang et al., 2017). The stabilization occurs through storing the organic content within these aggregates formed from the addition of biochar to soils.

The priming effects in soils can be affected negatively or positively through soil amendments made with biochar. The priming effect is caused through microbial community changes that are inculcated when biochar is introduced in the soil, thereby affecting the degradation rates of the native organic content in the soil (Zhu et al., 2017). Upon application of biochar in soils, a negative priming effect mostly occurs due to an alteration in the fungi-to-bacteria ratio as studied in Bamminger et al. (2014), suppressing significantly the degradation of an organic contaminant in soils. This is dependent on the nature of the biochar as well as feedstocks used and pyrolysis conditions on. Carbon content, aromaticity, volatile organic matter, and the active surface availability in the sorbents influence the negative priming, thereby securing the carbon content in the soils through these reserves that develops from amending biochar into the soils (Bamminger et al., 2014; Zheng et al., 2016). Table 23.1 shows the available nutrients for crop plant intake after biochar amendments at different pyrolysis conditions and their cation-exchange capacity.

These reasons are principal for the utilization of pesticides in the growth of food crops, and its reduction or remediation are the primary goals in agroeconomics. Biochar amendments to soil influences pesticides

TABLE 23.1 Available nutrients of biochar for crop plant uptake produced with different feedstocks.

Feedstocks	Pyrolysis conditions (°C)	pH	Phosphorous (mg/kg)	Potassium (mg/kg)	Calcium (mg/kg)	Magnesium (mg/kg)	CEC (cmol/kg)	References
Pine	500	7.8	18.0	4931.3	1352.9	280.7	NA	Majeed et al. (2018)
Bamboo	600	9.8	77.6	2614.2	128.9	194.8	15.3	Siddiqui et al. (2016)
Poplar	400	7.8	145.78	7739.06	1237.60	613.5	NA	Majeed et al. (2018)
Rice husk	350	6.6	24.7	1.1	–	–	1.7	Oladele et al. (2019)
Corn straw	500	7.3	851.1	4954.8	–	–	36.8	Li et al. (2019)

CEC, Cation Exchange Capacity

transformation in many pathways, which will be detailed in the later sections. To summarize further the benefits (Joseph and Taylor, 2014; Zhu et al., 2017) are as follows:

- Biochar is utilized as an ingredient in an organic or mineral fertilizer.
- Biochar utilized as an ingredient in chemical fertilizer to persist the nutrients further in soil and stop the leaching of the nutrients.
- Improve the uptake of plant roots for these nutrients though the microaggregates obtained from the soil amendments made with biochar.

23.2.3 Sorption−desorption of pesticides

The surface of the biochar has charges that occur through the varied functional groups present in them; they get adsorbed mostly through electrostatic adsorption with the immediate pollutants or other organic and inorganic matter in contact with them (Gan et al., 2012). The oxygen-containing functional groups such as carboxylic groups, hydroxyl groups, or ketonic groups develop on the surface of the biochars at different production technologies and thus desorbs/adsorbs when bounded with soil. These active functional groups on the active sites get negatively charged to the most extent and thus are known to have a high cation-exchange capacity than the soils. Cation-exchange capacity is an important indicator for soil quality, and higher the cation exchange capacity (CEC) higher is the improved nutrient uptake in soil by the plants (Agegnehu et al., 2017; Tan et al., 2017).

As mentioned about the physicochemical properties of biochar, its strong sorption capabilities for pesticides in the soil environment has been known to proven promising in many studies. The most prominent properties for the sorption−desorption property includes porosity, surface area, surface charge, pH, surface functional groups, carbon content, and the aromaticity present on the biochar (Pignatello et al., 2017). The mineralogical aspects and the priming effect of biochar applicability on soil also play a great role in the sorption−desorption mechanisms for pesticides' sorption on biochar. Two main sorption processes occurs for biochar with soil: surface adsorption and partitioning. Surface adsorption is through stable chemical bonds formed with the ions or organic compounds with the functional groups formed at the surface of the biochar and thus adsorbed at the surface. Ideally, as the biochar prepared has a higher pyrolysis temperature, the adsorption capacity is higher for varied pesticides. However, the major factors for pesticides sorption are biochar properties (surface area, porosity, and aromaticity), pesticides molecular dimensions, hydrophobicity, soil properties, and the environmental factors (Khorram et al., 2016a,b; Pignatello et al., 2017).

For macromolecular pesticides the probability for biochar to adsorb them is lower due to the accessibility of the pores in the biochar used, while electron donor and acceptor interactions can play a major mechanism for polar compounds (Ali et al., 2018). Hydrophobic pesticides increase their adsorption on biochar due to the aliphatic bonds present in the biochar and aromatic structures that bind well with the pesticides. However, clay such as bentonite structures that are present in the influences of the soil in the sorption−desorption of pesticides and drastically interact with the biochar being amended with the soil (Ali et al., 2019; Liu et al., 2018).

Depending on the bioavailability of pesticides by the plants, desorption of pesticides can take place and gets leached into the surface groundwater. The sorption process is ideally a reversible process, and the desorption process is much difficult, a phenomenon known as hysteresis (Khorram et al., 2016b). It is a widespread phenomenon known for pesticides interactions. Swelling of a sorbent during the sorption process is a common route where there is a micro- or macropore deformation for the pesticides to adsorbs, and the other interaction is the functional groups present on the biochar surface bind with the pesticides (Khorram et al., 2015; Sopeña et al., 2012).

23.2.4 Retention and release of nutrients in biochar

The growing need of curbing the hunger of the increased world population while protecting the environment has posed challenges to develop sustainable products. This caused an increase in the usage of inorganic chemical fertilizers that are not only used for improving the soil fertility but also for maintaining the yield increases (Foley et al., 2005; Liu et al., 2010). Thus the application can lead to overexploitation of the soil nutrients through excess nitrogen-containing compounds present in the soil, which further leads to organic matter mineralization and decrease in the available carbon content in the soil, which is crucial for plant growth (Agegnehu et al., 2017). Appropriate levels of soil organic matter and ensuring the right biological and agricultural requires to grow crops are crucial for productivity strategies. This includes the inclusive of both fertilizers, organic and inorganic, with keeping the productivity and efficiency of crops in order for different soil types. Such demands led to realizing the exploitability of biochar in several studies for agronomic benefits, soil-degradation problems, soil acidity, carbon sequestration, soil quality and acidity, etc., along with the usage of composite amendments with different soil types (Chathurika et al., 2016; Foley et al., 2005; Liu et al., 2010).

Traditionally, agrochemicals, when used in soils in huge quantities, have negative repercussions to both the soil fertility and the environment (Bajpai and Giri, 2002; Saruchi et al., 2019). Slow and restricted release of these agrochemicals is vital and one of the most studied among researchers. Reduction of indiscriminate usage of pesticides is necessary due to its failure to reach the target food crops due to leaching, evaporation of the active ingredient, hydrolysis, deposition, and degradation. Controlled release formulations of agrochemicals for releasing the active ingredient at a delayed rate thereby increase the crop growth without jeopardizing the soil ecosystems (Mattos et al., 2017; Wani et al., 2019).

Biochar, due to its high soil organic content and its ability to sequester carbon as previously discussed, is utilized as a slow release of the active ingredient in the fertilizer via encapsulating the nitrogen. Sequestering pesticides in soils using biochar have drawn substantial attention in recent years. Apart from the temperature and the biomass sources used to produce biochar to adsorb pesticides from soils, organic matter, pH, clay content in soils, and cation-exchange capacity of soils closely correlate with the sorption capacity. It is due to these factors that pesticide degradation in soils reduces to a significant extent after the soils have been amended with the biochar. Diuron, a urea-based compound primarily used as an herbicide to control the germinating grasses and broad-level weeds, showed a reduction in inhibition rates after soils were made to amended with biochar (Yang et al., 2006; Yu et al., 2006). Biochar reduces the freely dissolved pesticides in the soils, thus controlling the bioavailability of pesticides residue for the other organisms in soils. The accumulation of pesticides can be reduced to a great extent and thereby reduce the ecotoxicological impact of pesticides and other organics present in the soil ecosystems. These effects of biochar on the release of fertilizers in soils could change the course of fertilizer applications to soil and its frequencies. However, the sorption capacity of biochar decreases over time as it ages over time, depending on the source of feedstocks and the nature of the nutrient utilized in the soils. This could lead to the increased desorption rates, leaching of the active ingredients, and the bioavailability for plant uptake (Khorram et al., 2016a,b). Fig. 23.2 shows a scheme of

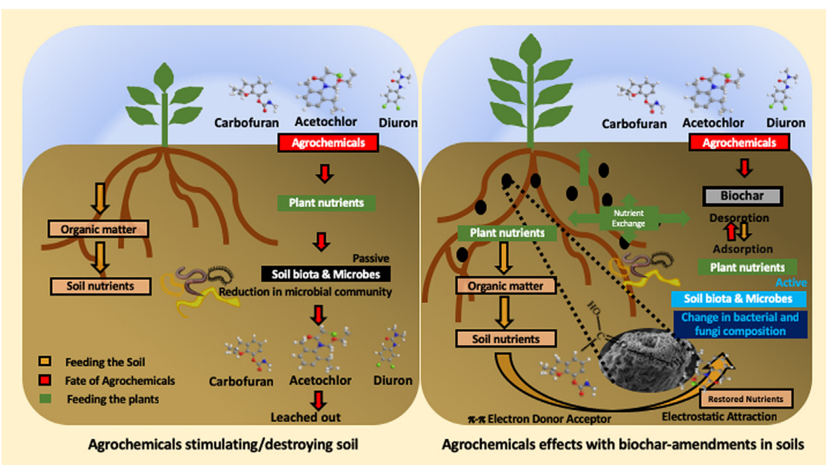

FIGURE 23.2 A schematic diagram showing biochar amendments effects with soil on the environmental repercussions of using agrochemicals.

utilizing biochar amendments in soils and its effects on several nutrients and soil biotas. Wood chips biochar and rice hull biochar have been used in Li et al. (2018a,b), to study the fate of acetochlor in soil, used as herbicides for a variety of crops as in corn, peanuts, soybean, and cotton. Its bioaccumulation in plants without amendments can have drastic risks in the food chain as it is highly disruptive to the reproductive and nervous system. However, when biochar is amended in soils, it has shown increased sequestration of acetochlor, which resulted in the bioavailable fractions of the organic pollutants and the pesticides. The same study showed the increased bioaccumulation of acetochlor in plants when biochar is kept for more than 20 days, which is the shortcoming of using biochar as a soil amendment (Khorram et al., 2017; Li et al., 2018a,b).

A variety of other gases including carbon dioxide, oxygen, and nitrogen gets dissolved with water within those pores. Aerobic or anaerobic conditions occur on these pores depending on the diffusion rates of these gases and the extent of surface sorption of the other nutrients. Where oxygen is sufficiently available, energy generation is through aerobic reactions where the metabolic breakdown takes place within the pores of the biochar (Quilliam et al., 2012; Zhu et al., 2017). Carbon dioxide concentration elevates when insufficient oxygen is present and then facultative aerobes develop to use anaerobic pathways to give nitric oxide, nitrous oxide and nitrogen (denitrification process) (Bamminger et al., 2014; Randolph et al., 2017). Thus the presence of available oxygen for diffusion decides as to which mode of pathways for the microbes to develop or in large part, microbes make their hospitable environments where the pore is free of other occupants or other aerobic/anaerobic conditions (Cederlund et al., 2017; Lehmann et al., 2011). These effects in the microbial activity upon biochar amendments in soils are further discussed in the later part of the chapter.

23.3 Influence of microorganisms and fertility on biochar application

Soil microorganisms get benefited through the application of biochar in soils as it provides nutrients that are adsorbed on the surface and gets its habitats from the porous structure of the biochar. The nutrient cycle, catabolism, and soil organisms get affected by the changes in the growth rate of these microorganisms as in bacteria and fungi. Bacterial species such as *Pseudomonas* and *Bacillus* spp. have been reported to have stimulated growth with the application of biochar in soils (Li et al., 2017a,b; Ralebitso-Senior and Orr, 2016). The physicochemical properties changes in soil upon addition of biochar, for instance, the soil pH, organic carbon content, and the cation-exchange capacity (Lehmann et al., 2011). The mechanisms driving the change of microbial process in the soils amended with biochar are intensely studied. It has proven to have increased bacterial diversity and a decrease in the fungal diversity in the soils, thereby increasing the phylogenetic diversity in bulk soils (Song et al., 2013). Implementation of biochar in soils is also said to enhance the growth of arbuscular mycorrhizal fungi, which enhances the soil fertility in abundance (Zheng et al., 2016). Improving the free available N2 in the agroecosystem is the key improving he fertility of the soil, and increased biochar application has led to the increased nodulation that provides areas for free-bacterial growth catalyzed by nitrogenase, which thereby captures the nitrogen from the air to give NH_3. This increased N_2 fixation is done through rhizobia in legumes and thus produced diverse colonization of mycorrhizal fungi and other organisms that promotes the plant's growth in soil (Kolton et al., 2011; Quilliam et al., 2013a). Consequently, the intrinsic properties as in the soil pH, sequestration of available carbon, and the availability of micronutrients can be altered through the changes in the microbial activity; all of which gets influenced through the application of biochar in soils.

23.3.1 Habitat for soil organisms

Soil bacterial community and the nutrient transformation have a significant influence when biochar is added to the soil. Rich pores and high specific areas not only favor the soil microbes to diversify, colonialize, and refuge but also upgrade their habitats by improving their aerobic conditions and water and nutrient-retention conditions (Masiello et al., 2015; Ralebitso-Senior and Orr, 2016; Tian et al., 2018). Depending on the feedstock used, pyrolysis conditions and posttreatment is done, biochar is not a uniform substance, especially when it comes to amending with soils. It behaves differently on the soil biota. Biochar influence on the microbial communities is strongly influenced by the residence time in which the biochar was added to the soils and the characteristics of the receiving soil. The application of fresh biochar or the biochar that have been preeffected by biotic and abiotic conditions of the soil affect the soil biota (Ahmad et al., 2014b; Lehmann et al., 2011).

Organic matter, nutrient availability, soil mineralogy and texture, pH/electrochemical conditions, presence of toxins, variations in the soil moisture are all the influential factors that trigger the abundance and diversity of microbial communities in biochar-amended soils. Since water is said to be a universal biological solvent, its availability in pores increases the habitability of microbes (Zheng et al., 2016; Zhou et al., 2019). High amounts of volatile matters in biochars gets mineralized over time, and the water-holding capacity in those pores increases, thus retaining more moisture. This provides surfaces for microbes to colonize, and the different minerals get adsorbed over time. Thus, as biochar ages, surface charge increases, clays from the parent soil find their domain within the pores along with other minerals, microbes form their metabolites, and other organic substances begin to cote onto the pore structures, ultimately leading to blocking over time. These processes reciprocate over a cycle and create their biomes in the biochar-amended soils (Li et al., 2019; Quilliam et al., 2013a; Wang and Wang, 2019).

23.3.2 Microorganism community and activity

Soil microbial activity, soil bacteria-to-fungi ratio, and soil enzymatic activities change to a significant extent in biochar-amended soils, and this shapes the whole microbial community entities of soil. With several techniques utilized to test the microbial activity and its communities, there have been changes in the presence of *Acidobacteria*, *Actinobacteria*, and *Verrucomicrobia*, all of which are produced in abundance with the application of biochar. As the aging periods advance for biochar-amended soil, colonization of fungal hyphae and bacterial cells on the surfaces and in the pores improved as studied in Quilliam et al. (2013b). Cocultures of *Geobacter metallireducens* and *Methanosarcina barkeri* bacterial cells were found attached by themselves on the biochar surface for 20 days of application (Quilliam et al., 2013a; Zhu et al., 2017). Rhizobacteria in soils transform the organic S and P into its bioavailable forms, thereby producing *Lolium perenne* that promotes the growth of other microbes and facilitates more of this kind of inorganic conversions. This becomes possible only if biochar is capable of providing the available nutrients to soils for such mechanisms of soil fertility and microbial growth (Mukherjee and Zimmerman, 2013; Zhu et al., 2017).

Plants become resistant to certain selected pathogenic bacteria, fungi, viruses, insects, and nematodes for which it develops a self-attributed phenomena in its roots system known as the induced systemic resistances (ISR) (Elad et al., 2010). *Bacillus*, *Pseudomonas*, and *Trichoderma* are all well-known species of soil microorganisms that mediate the ISR process for many food crops as in tomatoes, pepper, and bean plants. Significant growth of members of *Actinobacteria* and *Bacteroidetes* phyla were found in the biochar-amended soils through characterization techniques on rRNA gene analysis utilized to understand the difference with nonamended soils. Applied biochar in soils ISR to fungal pathogens *Botrytis cinereal* (gray mold) and *Leveillula Taurica* (powdery mildew) on pepper and tomatoes (Dieter and Geneviève, 2005; Vallad and Goodman, 2004). This indicates the resistance involved against fungal species through biochar-amended soils (Kolton et al., 2011; Mukherjee and Zimmerman, 2013; Vallad and Goodman, 2004).

Biochar behaves differently across diverse phylotypes. The changes in the microbial community structure, composition, and diversity are profusely different for different soil biota. Soils having varying carbon content, pH levels in soils or a diverse range of habitats through the pores have a competitive edge with the other microbial groups within the same soil and thus lead to overall microbial community structural and composition changes.

23.4 Biochar on the accessibility of agrochemicals in soils

The fate of organic contaminants or pesticides per se is strongly dependent on the dissolved organic matter content present in the biochar as discussed in the previous sections and eventually leads to the alterations in the activity of the microbial communities. Recent studies on biochar have been more focused on the accessibility of the pesticides by pant and soil biota with biochar-amendments and the limits and frequency of biochar applicability without risking the environmental implication of having the excessive pesticides leaching out of the system (Ali et al., 2018; Mattos et al., 2017).

23.4.1 Bioavailability of agrochemical for plant uptake

Surface runoff and leaching of pesticides from agricultural fields are one of the major objectives of biochar-amendments in soils. However, their reduction should effectively be available for plants nutrients. Biochar has proven its effectiveness because of its large surface area, nano-porosity, and the affinity to take up large organic contaminants. Widely used pesticides such as carbofuran and chlorpyrifos to control soil insects and pests have been studied in Yu et al. (2009) for bioavailability of plant uptake in biochar-amended soils. Decreased bioavailability for plant uptake was observed through the lesser residue of these pesticides present in spring onions planted in amended soils as compared with the unamended soil that may be due to the degradation using the organic content in the biochar that sequesters the free available pesticides present in the system. Norflurazon, nonionizable herbicides, applied to cotton shows a strong affinity to soils but when applied in biochar amended soils shows lesser affinity due to the cumulative effects it has on the pH of the soil and other physicochemical alterations in soils. Biochar derived from wood at a wide range of temperatures were investigated in Sun et al. (2011), to see the effect of the uptake of Norflurazon by plants along with the effect in pH. Adsorption of the herbicide increases at neutral pH due to $\pi-\pi$ electron donor interactions between biochar and the herbicide sorbate. Biochar contains aromatic rings, which are the source of $\pi-\pi$ electron rich that provides for the electronegativity to bind with the electron-deficient Norflurazon (Ahmed et al., 2017). This increases the adsorption affinity of the herbicides without further leaching into the groundwater system (Sun et al., 2011; Tareq et al., 2019).

Plant growth has been shown to stimulate at a remarkable rate after soil amendments are made with biochar. This increasing rate is attributed to the higher nutrient release rate, as explained in the previous section and the extended water-holding capacity. Biochar releases the required nutrient to the soil at a rate that is required for the plant growth and provide both macros—as in potassium and phosphorous and micronutrients as in copper and further enhance the other physicochemical properties as in pH of the soil, water retention capacity and the aeration of the soil particles. Carboxy group formation and other oxygen-containing functional groups on the biochar surface after oxidation result in an increased affinity to adsorb cationic nutrients (Ca^{2+}, Mg^{2+}, and K^{+}). Increase in the weight and height of the corn grown on amended soil with hull biochar studied in Rogovska et al. (2014) in comparison with unamended soils indicates that the added fomesafen has not been leached into the corn food crops and thus shown lesser residue of the same. Fewer studies on plant uptake of pesticides have been briefed in Table 23.2.

23.4.2 Pesticides uptake by other soil fauna

Earthworms alter the physicochemical and biological aspects of the soil. Microbial communities get triggered when earthworms continue to burrow and feed in soils for organic matters and nutrients. Bioavailability of pesticides in earthworms decreased through biochar amendments by adsorbing, most of the pesticides, and declined food consumption by earthworms (Khorram et al., 2017). Dermis contact of earthworms with the pesticides or through food intake are the pathways through which pesticides gets ingested in earthworms. Biochar amendments make the pesticides less bioavailable to soils and thus make the decomposition at a faster rate for the earthworms (Hickman and Reid, 2008).

Chlorantraniliprole studied in Wang et al. (2012) are an insecticide belonging to the anthranilic and phthalic diamide group. Biochar produced from red gum chips was amended with soil to see the bioavailability of the insecticides in the soils and further uptake behavior in earthworms. The study revealed that the biochar dominated the sorption of the insecticides, and remarkedly reduced the uptake of chlorantraniliprole by the earthworms (Sanchez-Hernandez et al., 2019; Wang et al., 2012).

23.5 Drawbacks and implication of biochar-amended soils

Beneficial aspects of utilizing biochar as an amendment to soil have been well studied in the literature. However, its drawback it has on soils is sparsely revived. Although it has proven to utilize as a tool to combat excessive nutrients leaching to the surface ground waters or giving the right habitat for the microbes, it also has an inhibitory effect on soil aging and causes a declining effect on the soil−water systems that required a reduced nutrient cycling (Anderson et al., 2011). This has been proven in Anyanwu et al. (2018), where the nutrient availability has changed the biota−biochar

TABLE 23.2 Growth rate variables and bioavailability of agrochemicals in biochar-amended soils.

Biochar types	Biochar-production conditions	Soil type for biochar amendment	Agrochemical used	Plant growth variables improvements	References
Wood pellets	Pyrolysis temperature at 500°C slow rate	Silt loam	Aminocyclopyrachlor	Plant residue upon digestion proved no pesticides residue in plants, thereby all adsorbed by the biochar in soil	Cabrera et al. (2014)
Biochar derived from forest logging residue	Pyrolysis temperature at 500°C for 40 min	Karst soil	NPK fertilizer (N: 46.7%; P: 12.2–61.7; K: 63.2%)	Soil microbial growth enhanced. Growth of Firmicutes pertained in soil amended with biochar	Zhou et al. (2019)
Biochar derived from rice hull	Pyrolyzed at 500°C with 15°C/min heating rate and held for 4 h	Loamy clay	Oxyfluorfen	Decreased oxyfluorfen uptake by soybean plants by 18%–63% after addition of rice hull biochar. Aging of biochar for 6 months further decreased the uptake by 2.3 fold compared with fresh biochar amended soils	Wu et al. (2019)
Corn straw biochar	450°C slow heating rate for 4 h		Atrazine	Enhanced adsorption capacity of biochar and 28% residual pollutant reduction. This due to the electron donor acceptor interactions with biochar and the atrazine sorbate	Zhao et al. (2013)
Cassava waste biochar	200°C slow rate for 2 h and then 750°C for 3 h	Latosol	Atrazine	Adsorption improved by 36 fold and the release of atrazine from the biochar amended soil is due to the pH alterations and thus greater affinity for adsorption at increasing pH	Li et al. (2018a,b)
Soybean straw biochar	500°C for 6 h	Loamy sand	Organochlorine	Alteration in the soil microbial properties and strong adsorption of pesticides that reduced the accessibility of the pesticide and thus enhanced microbial masses	Ali et al. (2018)
Red gum wood–derived biochar	850°C slow rate pyrolysis	Sandy loam	Carbofuran and chlorpyrifos	Improved growth in the spring onion food crop with soil amendments and lesser residue of pesticides of up to 25% reduction in the onions due to sequester of pesticides by the biochar	Yu et al. (2009)

interactions at different environmental conditions and an alteration in the mechanisms involved in the nutrient binding with biochar.

Rice husk biochar used in the study caused the phytochemical properties of soils to change that resulted in a decreased earthworms' survival in soils over time. Another soil fauna has shown a declining growth when biochar is amended in soils where they have toxic effects on the growth of *Enchytraeidae* and *Collembola* due to the decline in soil pH. This has been further justified to not only change in the physicochemical property of the soil but also to decline survival rates of these species due to climatic factors, bioavailability, and the soil types to which the amendments have been made (Domene, 2016; Feigl et al., 2010). Aged biochar implemented in soils has also shown negative effects in the growth of earthworms and fungi. The root biomass of *Oryza sativa* and *Solanum lycopersicum* showed lesser growth upon biochar amendments in soils due to the reduced thermal diffusivity instilled in biochar. This is also dependent on the soil types, which can differ from regions having different temperate soils. Furthermore, soil nutrients can act as a competitor for nutrients that could further facilitate precipitation with phosphate, thereby competing with the availability of phosphorous in soils (Xu et al., 2016). This is highly dependent on the production of biochar that can alter the stability of biochar and the phosphorous contents in soils (Kavitha et al., 2018; Xu et al., 2016). Adsorption of Fe is another drawback of biochar amendments with soil that has proven counterproductive in the plant growth and soil fertility (Joseph et al., 2018). Detrimental effects of biochar applications in agricultural soils become significant to figure out in terms of biomass sources used for biochar production, pyrolysis temperatures, application rate in soils, and the economic feasibility of utilizing the biochar and agrochemical at hand all of which are crucial to consider when making modification to soils (Kavitha et al., 2018; Khorram et al., 2015).

23.6 Future research needs

Agrochemicals are no doubt classified as hazardous compounds that are priority pollutants as well. Their usage is time and again proven to be effective and further consolidated when amendments are made with soil in the study and the biochar. However, the scope of biochar applications for remediation of pesticides needs to be further studied, and the gaps concerning the biochar-production conditions with the application in soil amendments need carefully addressing. Unintended consequences specifically due to the deterioration of soil fertility and growth of microbes that promotes the fertility and plant growth upon biochar amendments need to be tackled. Aging effects of biochar as the amendments are prolonged in the soils needs to be further studied concerning the nutrient release mechanisms and its uptake by plants. The enzymatic activity in different soil condition and biochar-types and pyrolysis conditions needs further exploration.

Overall, agrochemicals in the environments can be remediated using biochar and have potentially positive effects in soils concerning enriched soil fertility, waste managements, habitats for the microbial organisms that facilitate the food crops growth and carbon sequestration. Negative implications and unintended consequences of long-term agronomic effects are essential to fully elucidate its potential in soil and plant growth.

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