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The Role of Biochar Amendments on Soil Properties, Waste Water Treatment and Carbon Sequestration A: Review

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Abstract

Biochar is the by-product of biomass pyrolysis in an oxygen depleted atmosphere. It contains porous carbonaceous structure and an array of functional groups. Biochar's highly porous structure can contain amounts of extractable humic-like and fluvic-like substances. Moreover, its molecular structure shows a high degree of chemical and microbial stability. The physical and chemical properties of biochar are highly dependent on pyrolysis temperature and process parameters, such as residence time and furnace temperature, as well as on the feedstock type. Recent increases in atmospheric greenhouse gas levels require that novel approaches are undertaken to mitigate impacts of climate change, such as management practices conducive to improved soil carbon sequestration. Water usage has been rising immensely with growing population and industrial activities in both developed and developing countries. This resulted in deterioration of water sources as various contaminants such as dyes toxic heavy metals, organic compounds like detergents, phenols, dyes, pesticides in addition to the other persistent organic pollutants are increasingly being dumped into the water bodies. Recently, char derived from biological materials under oxygen free condition, popularly known as "biochar" has been recently been introduced as an effective sorbent for various toxins. Biochar application as a soil amendment is motivated by its capacity to enhance crop yields and alter the soil physical, chemical and biological properties, such as soil water holding capacity, pH, cation exchange capacity, nutrient retention, and organic carbon. Biochar has been recently recognized as multifunctional material related to carbon sequestration, contaminant immobilization, greenhouse gas reduction, soil fertilization, and water filtration. Accordingly, biochar is presented as a promising soil amendment of high economic and environmental value.

Keywords: Amendment, Carbon, Pollutant, Pyrolysis and Surface area
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1. Introduction

Biochar is a carbon rich material obtained from thermochemical conversion (slow, intermediate, and fast pyrolysis or gasification) of biomass in an oxygen-limited environment (Yadav and Jagadevan, 2019). It can be produced from a range of feedstock, including forest and agriculture residues, such as straw, nut shells, rice hulls, wood chips/pellets, tree bark, and switch grass (Abukari, 2014). Biochar has been described as a possible tool for soil fertility improvement, potential toxic element adsorption, and climate change mitigation (Diatta *et al.,* 2020). Biochar, a product of the thermal degradation of organic materials in the absence of air (pyrolysis), is distinguished from charcoal in terms of usage (Rao *et al.,* 2016). An increase in pH provides a wide range of benefits in terms of soil quality, notably by improving the availability of nutrients to plants, and in some cases it reduces the availability of detrimental elements such as Al and Fe and exchangeable acidity (Ippolito *et al.,* 2012). Biochar application as a soil amendment is motivated by its capacity to enhance crop yields and alter the soil physical, chemical and biological properties, such as soil water holding capacity, pH, cation exchange capacity, nutrient retention, and organic carbon (Thies and Rillig, 2012).

In an effort to reduce the concentrations of greenhouse gases in the atmosphere in order to reduce the potential effects, considerable attention has been paid to soil management practices (Mbow *et al.,* 2017). Improving cropland management practices such as reduced tillage and residue retention has the potential to reduce agricultural greenhouse gas emission irrespective of type of cultivation (Bai *et al.,* 2019). Recent increases in atmospheric greenhouse gas levels require that novel approaches are undertaken to mitigate impacts of climate change, such as management practices conducive to improved soil C sequestration. Nitrogen fertilization and crop residue retention play a major role in greenhouse gases emission. Soil carbon sequestration through the application of recalcitrant C-rich biochar is mentioned as a suitable means to mitigate climate change (Howard *et al.,* 2014).

Water usage has been rising immensely with growing population and industrial activities in both developed and developing countries (Malmqvist and Rundle, 2002). This resulted in deterioration of water sources as various contaminants such as dyes toxic heavy metals, organic compounds like detergents, phenols, dyes, pesticides in addition to the other persistent organic pollutants are increasingly being dumped into the water bodies (Hanafi and Sapawe, 2020). These contaminants reach water bodies through various industrial activities, including mining, electrolysis, metallurgy, battery manufacture, metal finishing, electroplating, electro-osmosis, pigment manufacture and tanneries (Haris *et al.,* 2021). Owing to this, different biological and physico-chemical treatment techniques have been proposed to remediate heavy metal-bearing contaminated waters (Gunatilake, 2015). Recently, char derived from biological materials under oxygen free condition, popularly known as “biochar” has been recently been introduced as an effective sorbent for various toxins (Senthilkumar and Prasad, 2020). Biochar is a stable carbon-rich product synthesized from biological materials through different heating methods above the decomposition temperature (Kambo and Dutta, 2015). Biochar is produced through thermal degradation of organic components in absence of O_2 or under limited oxygen conditions (pyrolysis). In recent years, owing to the inherent biochar properties such as surplus surface binding sites hydroxyl, carboxyl, phenolic hydroxyl and carbony groups, porous surface, high cation exchange capacity and its surface area, this organic amendment be utilized as an efficient and practical sorbent for remediation (Kharel *et al.,* 2019).

Biochar has been recently recognized as multifunctional material related to carbon sequestration, contaminant immobilization, greenhouse gas reduction, soil fertilization, and water filtration. Accordingly, biochar is presented as a promising soil amendment of high economic and environmental value (Racek *et al.,* 2020).

2. The Role of Biochar

2.1. Soil Physical properties

Several soil benefits arise from the physical properties of biochar. The highly porous nature of biochar results from retaining the cell wall structure of the biomass feedstock. A wide range of pore sizes within the biochar results in a large surface area and a low bulk density. Biochar incorporation can alter soil physical properties such as structure, pore size distribution and density, with implications for soil aeration, water holding capacity, plant growth, and soil workability (Downie *et al.,* 2012). Evidence suggests that biochar application into soil may increase the overall net soil surface area and consequently, may improve soil water and nutrient retention and soil aeration, particularly in fine-textured soils. Biochar has a bulk density much lower than that of mineral soils (~0.3 Mg m^{-3} for biochar compared to typical soil bulk density of 1.3 Mg m^{-3}) therefore, application of biochar can reduce the overall total bulk density of the soil which is generally desirable for most plant growth. Increased surface area, porosity, and lower bulk density in mineral soil with biochar can alter water retention, aggregation, and decrease soil erosion (Amer, 2017). Water retention of soil is determined by the distribution and connectivity of pores in the soil matrix, which is largely affected by soil texture, aggregation, and soil organic matter content. Biochar has a higher surface area and greater porosity relative to other types of soil organic matter, and can therefore improve soil texture and aggregation, which improves water retention in soil. These starting physical properties in biochar occur at a range of scales and affect the proportion of water than can be retained (Verheijen, 2010).

2.2. Soil Chemical properties

2.2.1. Soil organic carbon

Soil organic C (SOC) content is one of the key indicators of soil fertility. Increasing SOC content is one of the main means to decrease the carbon dioxide (CO_2) concentration in the atmosphere. Biochar was responsible for the high soil Biochar addition could increase the formation and stabilization of soil micro aggregates that often play a greater role in providing physical protection to SOC than macro aggregates. Adding biochar to the soil may therefore help trap SOC within aggregates and reduce the decomposition of SOC, and C occlusion within aggregates might be one of the main reasons for the stabilization of SOC in biochar-amended soils. Manure-derived biochars, having higher labile C concentrations than those of plant biomass–derived biochars, could be mineralized to a greater extent and show higher positive priming effects on native SOC mineralization (Ouyang *et al.,* 2013), whereas biochars produced from grasses can exert greater effects on native SOC mineralization than those from hardwoods.

2.2.2. Soil reaction (pH)

The addition of biochar to soils generally increases soil pH. Biochars with the highest proportions of ash, produced at the highest temperatures, from mineral rich source materials, result in the greatest increases in soil pH. This is unsurprising since the addition of minerals (e.g., lime) to soils is routinely carried out to raise soil pH and increase the availability of plant nutrients such as P, Ca and Mg (although lime can reduce the availability of some micronutrients such as Fe and Zn) (Ippolito *et al.,* 2012). By raising the pH of a soil, the mobility and availability of metals decrease due to less competition between H^+ and Mn^+ for sorption sites. In biochar amended soils, the decrease in metal mobility at a higher pH cannot be explained by the sorption of metals on the surface of biochar alone, there is also an increase in sorption to other soil surfaces. This is because an increase in soil pH also leads to an increase in the pH-dependent CEC of organic matter, clay minerals and oxyhydroxides present in soils. A decrease in metal mobility after raising the pH is also due to the precipitation of metals as insoluble mineral species (hydroxides, phosphates, carbonates, etc.). Metal immobilization due to increases in pH can only be considered temporary as it is not known how long the elevation of soil pH persists in soils after biochar application (Hanafi and Sapawe, 2020).

2.2.3. CEC (Cation Exchange Capacity)

The pyrolysis of organic matter and subsequent exposure to the atmosphere leads to the oxygenation of biochar surfaces. This oxygenation results in the formation of oxygen containing functional groups carboxyl, hydroxyl, phenol and carbonyl over the vast internal surface area of the biochar. These functional groups give rise to a considerable negative charge and a high CEC (Cation Exchange Capacity). The CEC of biochars first increases and then decreases with increasing pyrolysis temperatures with a peak CEC of up to 45 $cmol_ckg^{-1}$ generally occurring between 250 and 350°C, depending on the source material (Yadav and Jagadevan, 2019). The lower CEC observed after higher temperature pyrolysis is concurrent with a lower oxygen: carbon ratio and a decrease in the abundance of oxygenated (acid) functional groups which are likely to be responsible for the high CEC and metal retention in <500ºC pyrolysis temperature biochar. The considerable capacity for metal immobilization demonstrated by low temperature (<500ºC), faster. There is evidence to suggest that much of the CEC of biochars pyrolyzed at low temperatures may arise due to the presence of non-carbonized organic matter. This non-carbonized fraction may be a particulate constituent of the biochar or be sorbed to the surface of biochar, thereby increasing the surface charge density (Tomczyk *et al.,* 2020).

2.2.4. Nitrogen

Nitrogen loss to the environment from intensively managed agricultural production systems cause negative feedbacks to environmental and human health, such as water eutrophication, ozone depletion, and contamination of drinking water. Biochar addition to the soil can be beneficial both to the environment and to the crop productivity. Some studies showed that biochar application markedly increased soil N retention, which was due to decreased leaching and increased recovery of applied fertilizer Nitrogen. Moreover, the growth of soil microorganisms that promote the complete denitrifcation or dissimilatory reduction of nitrate to ammonium may potentially be enhanced by the addition of biochar, thereby reducing N losses to leaching or gaseous fluxes. The effect of biochar on soil N cycling may also be related to biochar application rate or the particle size of biochar as well as field management. Soil mineral N concentrations as well as N concentrations in leachates decrease after biochar application, probably due to increased microbial immobilization and reduced nitrifcation activity. Biochars produced at high temperatures (≥500°C) induced greater net N mineralization and lower N immobilization than those produced at low temperatures (≤400°C); as a result, biochars produced at low temperatures may induce less mineral N leaching loss and greater soil N retention. In addition, application of fresh biochar produced from wheat straw by slow pyrolysis increased net N mineralization, whereas application of biochar produced through fast pyrolysis led to N immobilization but until recently, few studies have examined the effect of rate of biochar pyrolysis (slow versus fast) on soil N dynamics (Xiao and Meng, 2020).

2.2.5. Phosphorus and potassium

The concentration of available P in the soil is lower than that of N and K, and sorption of P by soil constituents is a dominant mechanism for P retention in the soil. The application of biochar has been found to increase the retention of P and the availability of P and K in soils the increase is positively related to the biochar application rate. There are two possible explanations for the increase of soil available P content after biochar application: (1) the high P content in the biochar applied and (2) the increased CEC and decreased soluble Al in acidic soils as a result of biochar application would increase P availability in the soil In addition, the incorporation of biochar into agricultural soils can increase the leaching of P and K, at least in the short term. The impact of biochar application on soil dissolved P varies with biochar feedstock type and soil property. For example, the incorporation of poultry litter–derived biochar generally increased $PO4_3^-$-P, whereas pine chip–derived biochar had a minimal or no effect on $PO4_3^-$-P in soil solution (Hossain *et al.,* 2020).

2.3. Soil Biological properties

Biochar stimulates the activity of a variety of agriculturally important soil microorganisms and can greatly affect the microbiological properties of soils (Thies and Rillig, 2012). Soil biological communities are complex assemblages of bacteria, archaea, fungi, algae, protozoa, nematodes, arthropods and a diversity of invertebrates. The presence and size distribution of pores in biochar provides a suitable habitat for many microorganisms by protecting them from predation and desiccation and by providing many of their diverse carbon (C), energy and mineral nutrient needs (Haris *et al.,* 2021). Interactions among the members of these populations and soil chemical and physical properties will determine overall ecosystem function and productivity. With the interest in using biochar for promoting soil fertility, many scientific studies are being conducted to better understand how this affects the physical and chemical properties of soils and its suitability as a microbial habitat. Since soil organisms provide a myriad of ecosystem services, understanding how adding biochar to soil may affect soil ecology is critical for ensuring that soil quality and the integrity of the soil subsystem are maintained. The chemical and physical characteristics of different biochars will add another layer of complexity to soil food web interactions by altering the availability of soluble and particulate organic matter (substrates), mineral nutrients, pH, soil aggregation and the activity of extracellular enzymes and, thus, will affect diversity, abundance and distribution of associated microbial communities. The nature and function of soil microbial communities change in response to many edaphic, climatic and management factors, especially additions of organic matter (Downie *et al.,* 2012). Amending soils with biochar is no exception however, the way in which biochar affects soil biota may be distinct from other types of added organic matter because the stability of biochar makes it unlikely to be a source of either energy or cell C after any initial bio-oils or condensates have been decomposed. Instead, biochar changes the physical and chemical environment of the soil, which will, in turn, affect the characteristics and behaviour of the soil biota. The biochar pores may act as a refuge site or microhabitat for colonizing microbes, where they are protected from being grazed upon by their natural predators or where microbes that are less competitive in the soil environment can become established. The pore size variation observed across biochar particles from different feedstocks and pyrolysis conditions is such that the microflora could, indeed, colonize and be protected from grazing, especially in the smaller pores (Abukari, 2014).

3. Biochar Remediation Inorganic and Organic Pollutant

3.1. Nitrogen leaching

Biochar application to soil has been shown to decrease the loss of N through leaching and gaseous emissions, thereby increasing the N use efficiency by plants ammonia volatilization. The physical surface area and chemical cation exchange capacity characteristics of biochars influence the effectiveness of controlling NH_3 volatilization. biochar can act as soil amendment through capturing NH_3 from the soil. Biochar addition to soil can decrease soil pH, thereby reducing NH_3 volatilization. Biochars with high SA that contains several surface functional groups can capture NH_3. Whereas with NH_3 being an alkaline gas, the acidic surface groups on biochar with their low pH can protonate the NH_3 to form $NH4^+$, thereby promoting their adsorption on to cation exchange sites. The NH_3 sorbed by biochar can subsequently become available for plants (Widowati *et al.,* 2011)

Biochar addition has often been shown to decrease total N_2O emission from soils treated with N sources such as manures, urea, and composts. Denitrifcation is the biological process leading to increased N_2O emission from soil. Elevated mineral N in soils, the substrate for N_2O production, is generally associated with higher N2O emissions. Research suggests that possible explanations for reduced N_2O loss from biochar-treated soils include reduced denitrifcation, complete denitrifcation, or a combination. A decrease in denitrifcation is likely to occur due to sorption of mineral N compounds (NH^+_4, $NO3^-$) to biochar surface and lattice, thus reducing the substrate for denitrifcation. Complete denitrifcation, leading to N_2 emission due to biochar addition, was explained by enhanced aeration, the presence of labile C in biochar, and elevated soil pH and enhanced microbial activities (Obia *et al.,* 2015)

3.2. Phosphorus leaching

Excessive application of P fertilizers has caused leaching of P from agricultural felds to aquatic systems. Nutrient leaching not only poses a threat to environmental health but also may deplete soil fertility, accelerate soil acidification, increase fertilizer costs, and reduce cropyield. Biochar has proven to alter P availability in soils by reducing P leaching through sorption and adsorption characteristics. The addition of hardwood biochar produced using slow pyrolysis to typical mid-western agricultural soils significantly reduced total P leaching by 69%. Similarly, in a column study, biochar produced from Brazilian pepperwood at 600°C reduced the total amount of phosphate in the leachates by ~20.6% (Lyu *et al.,* 2016). Application of peanut hull biochar increased the amount of phosphate in the soil solution by 39%. The possible mechanisms suggested for the influence of biochar on P availability are a change in soil pH and the subsequent influence on the interaction of P with other cations, or enhanced retention through anion exchange. In the natural environment, P is strongly adsorbed onto the surface of Fe(III) (hydr)oxides in soils. Addition of biochars reduced the amount and rate of P sorbed onto ferrihydrite (the most effective Fe oxide for P). Chen et al. (2011) demonstrated that biochars with magnetized Fe^{3+}/Fe^{2+} had enhanced phosphate sorption compared to nonmagnetic biochars.

4. Organic Pollutant

In recent years, the incidence of soil contamination is increasing globally Approximately 3.5 million sites in industrial and mine areas, landfills, energy production plants, and agricultural land are potentially contaminated. Soil contamination with organic pollutants is usually caused by industrial activities or inadequate management of pesticides and chemicals in agricultural production and from household waste. Many organic pollutants are recalcitrant and may accumulate in soils where they can enter the human food chain or harm ecosystems. Organic pollutants released from industrial and agricultural processes or household products include persistent organic pollutants (POPs), emerging organic pollutants, and some pesticides Biochar has been used as an amendment to absorb and retain organic contaminants in soils. High porosity and large surface area enable biochars to adsorb organic pollutants, and adsorption onto biochars can reduce the bioavailability of organic pollutants and reduce the risk of these pollutants entering the human food chain or leaching into ground water (Hanafi and Sapawe, 2020). Soils with high organic carbon have higher adsorption and weaker desorption capacity than the low organic carbon soils. However, soil organic matter can easily release most of the pollutants to the environment again. Addition of a soil amendment, such as biochar, may enhance the adsorption capacity of soil. The ability of biochar to adsorb organic pollutants is related to the feedstock biomass, the conditions under which the biochar is produced, and the types of organic pollutants present in the contaminated soils (Hanafi and Sapawe, 2020).

5. Waste water treatment

Wastewaters originate from several sources, including domestic sewage (municipal wastewater) agricultural, urban, and industrial effluents; and storm water. Wastewater irrigation has many beneficial effects, such as groundwater recharging and nutrient supply to plants disposal of industrial and domestic waste materials, including wastewaters and biosolids, are the major sources of metal(loid) enrichment in soils and have potential to leach into groundwater (Malmqvist and Rundle, 2002). Wastewater treatment requires vast quantities of activated carbon. Improved, inexpensive, tailor made, and readily regenerated adsorbents are required. This requirement has led to extensive research concerning the identification of suitable and relatively cheap materials for the production of low-cost adsorbents that are capable of removing significant quantities of metal(loid) ions from aqueous solutions (Hanafi and Sapawe, 2020). Biochar is a pyrogenic C-rich material, derived from thermal decomposition of biomass in a closed system with little or no Oxygen supply. Biochar has been extensively studied in the past few years for its potential for C sequestration and for its ability to enhance the nutrient level of soils as well as for its positive effect on plant growth (Diatta *et al.,* 2020). Biochar is now widely studied for its metal(loid) sorption efficiency in soils and water. Biochar is negatively charged, and there is thus considerable exchange of cationic ions, such as K^+, Na^+, and $Ca^{2+,}$ in the biochar matrix. This property facilitates the sorption of cationic organic contaminants by ion exchange and subsequently electrostatic attraction (Ippolito *et al.,* 2012). Cationic dyes are a group of typical organic contaminants that can be sorbed by biochar through ionic electrostatic attraction. For example, Rhodamine B, a popular cationic dye, in water was effectively removed by both biochar and activated carbon. However, biochar was slightly more effective due to the Rhodamine B-biochar electrostatic attraction. In contrast, biochar is not as effective at sorption of anionic organic contaminants because of electrostatic repulsion. The use of biochar as a low cost sorbent to remove organic and inorganic contaminants from aqueous solutions is an emerging and promising wastewater treatment technology (Haris *et al.,* 2021).

6. Carbon sequestration

The increasing atmospheric concentrations of carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) are of major concern when considering future climates. For all three, cycling, production, consumption, or storage is linked substantially with soils. Anthropogenic activities (eg, fossil fuel emission, industry) and natural phenomena (such as carbon cycle, organic matter mineralization) are the major contributors of these biogenic greenhouse gases and are considered to be the main influence of global climate (Wuebbles, 2009). In view of the growing evidence on global climate change and an urgent need to reduce atmospheric CO_2 emissions or to remove carbon from the atmosphere. Biochar, a carbon-rich material obtained by pyrolysis of organic matter, has been a focus of wide attention due to its potential to mitigate climate change via carbon (C) sequestration and reduction of greenhouse gas emissions (Bai *et al.,* 2019). The potential of biochar as a viable tool to carbon sequestration has recently been centered on the common discourse of climate change. Biochar has been pointed out to enhance carbon sinks, especially in dry regions. However, the degree with which biochar achieves carbon sequestration depends on various factors. Most importantly, it depends on the desired soil carbon content and the rate of carbon dioxide removal from the atmosphere. There are considerable large sizes of arable lands (estimated at 6% of the earth's surface); thus, they require relatively high amounts of biochar to be incorporated therein. Since it takes long to sequester carbon dioxide from the atmosphere, the predisposition asserted by industrial activities makes the process even longer. To rehabilitate the environmental greenhouse gas emission biochar has the potential to sequester carbon, sustainable land use change and pollution controls are indispensable (Howard *et al.,* 2014).

7. Conclusion

Biochar is a carbon rich material obtained from thermochemical conversion (slow, intermediate, and fast pyrolysis or gasification) of biomass in an oxygen-limited environment. It can be produced from a range of feedstock, including forest and agriculture residues, such as straw, nut shells, rice hulls, wood chips/pellets, tree bark, and switch grass. Biochar application as a soil amendment is motivated by its capacity to enhance crop yields and alter the soil physical, chemical and biological properties, such as soil water holding capacity, pH, cation exchange capacity, nutrient retention, and organic carbon. Biochar has been recently recognized as multifunctional material related to carbon sequestration, contaminant immobilization, greenhouse gas reduction, soil fertilization, and water filtration. Accordingly, biochar is presented as a promising soil amendment of high economic and environmental value.

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