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Mitigation of Soil Salinity using Biochar Derived from Lignocellulosic Biomass

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Soil salinisation is recognised as a serious form of soil degradation, affecting crop production and compromising food security. It is crucial to remediate the negative impacts of soil salinisation to improve the associated soil functions. Various organic and inorganic amendments are used for saline soil remediation. Biochar, known as the porous solid carbonaceous material produced at elevated temperatures ranging from 300 °C to 1,000 °C under oxygen deficit condition, is gaining considerable attention. Biochar is widely reported to enhance the sorption of nutrients and reduce nutrient leaching from the soil. Biochar application is effective in improving the physical, chemical and biological properties of saline soil. Limited studies were reported on the role of biochar to mitigate soil salinity, especially in terms of their adsorption mechanisms. This paper review the various role of biochar, derived through the pyrolysis of fibrous biomass, to improve the physical properties (soil porosity, soil aggregation, water holding capacity, hydraulic conductivity and organic carbon content) and chemical properties (pH, electrical conductivity, exchangeable sodium percentage and sodium adsorption ratio) of saline soil. Physical adsorption and ion exchange are found to be the most common remediation mechanisms of saline soil by biochar.

1. Introduction

Soil salinisation is a global issue owing to its severe impact on agricultural productivity and sustainability. In arid or semi-arid area, excess ions such as sodium (Na^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), chlorides (Cl^-) and sulfates (SO_4^{2-}) accumulate to form saline soil, causing the impairment of plant growth and development. About 831 Mha arable land is affected by soil salinity, and salinisation is predicted to impact 50 % of the total world land by 2050 (Wang et al., 2003). Various reasons such as low precipitation, weathering of native rocks, irrigation with saline water, low rainfall, high surface evaporation and poor cultural practices have contributed to the expansion of saline soil (Shrivastava and Kumar, 2015).

In the arid or semi-arid area, sodium chloride (NaCl) which is known as common salt, accumulates to form saline soil. Soil salinity that occurs under all climatic conditions, due to natural and human-induced actions, has imposed ion toxicity, osmotic stress, nutrient deficiency and oxidative stress on plants (Shrivastava and Kumar, 2015). These impacts can cause further deterioration of their physical, chemical and biological properties. When the soil water contains too much salt, water may flow from the plant roots back into the soil, leading to dehydration of the plant. This can compromise plant yield or leading to plant death. It is crucial to solve the salinity problem to minimise economic loss and improve food security.

Biochar has attracted considerable attention as a soil amendment. It is identified as a sustainable and low-cost technology that can be used to remediate saline soil. Biochar is a porous solid carbonaceous material produced by thermal decomposition of biomass under oxygen-limited conditions at a temperature ranging from 300 °C to 1,000 °C. It is produced by heating a wide variety of feedstock such as agricultural wastes, grasses, leaves, manure, sludge, and fruit peel. The addition of biochar into saline soil could restore the soil organic

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carbon, which improves soil quality and enhances the growth of plants or microorganisms. Biochar is a stable carbon-rich material. It exhibited promising adsorption potential owing to its large surface area and presence of surface functional groups, which can be used to remediate soil contaminated by hazardous molecules (Meri et al., 2017). Biochar also improves the physicochemical properties of saline soils and enhancing crop production.

Intensive research has been reported on the use of biochar in improving saline soil and plants. There are still gaps in deciphering such remediation mechanisms of the biochar. Physical adsorption and ion exchange on the biochar surfaces are found to be the most common mechanisms reported to remediate saline soil. There is a lack of insights on how the surface functionality of biochar could affect salt removal from saline soils. As the remediation mechanism involves multiple adsorptions mechanisms such as the different functional groups, high degree of porosity and extensive surface area, more detailed mechanisms regarding these physical adsorptions and ion exchanges are needed. This paper reviews on the potential mechanisms of biochar addition to improving the physical properties (soil porosity, soil aggregation, water holding capacity, hydraulic conductivity and organic carbon content) and chemical properties (pH, electrical conductivity, exchangeable sodium percentage and sodium adsorption ratio) of saline soils, which leads to the remediation effect of biochar. Little work has been done to determine the effects of pyrolysis conditions, biomass structure and surface area on surface functionality of biochar for salt removal. This review summarised the effect of different functional groups from biochar produced under different pyrolysis condition that is responsible for salt sorption.

2. Biochar as an organic soil amendment in saline soil

The possible mechanisms for biochar to amend saline soil are mostly reported as physical adsorption and ionic exchange. This is owing to the unique characteristics of biochar, including high porosity, high surface area, abundant functional groups, high carbon content (Dai et al., 2019). Through these mechanisms, the biochar amendment could hasten salt leaching and decrease the time required to lower the salt concentration to a proper for plant growth. These two mechanisms are reviewed in details as follow.

2.1 Effect of biochar on physiochemical properties of saline soil

In the arid or semi-arid area, sodium chloride (NaCl) which is known as common salt, accumulates to form saline soil. Saline soil exhibits poor physical conditions in which it has poor drainage and low fertility, causing them unfit for agriculture. The Na^+ in the soil promotes slaking, swelling and dispersion of clay, causing the soil aggregates to break down (Dahlawi et al., 2018). Swelling and dispersion cause surface crusting and hard setting of soil, affecting the infiltration and hydraulic conductivity (Dahlawi et al., 2018). Diffuse double layer (DDL) theory can be used to explain the swelling and dispersion behaviour of saline soil. In this theory, the van der Waals forces and electrostatic interaction lead to the attraction and repulsion between ions in soil particles, and soil solution and these forces could affect the pore system and structural stability of soil (Amini et al., 2016). When the exchange sites of the soil particles are saturated with Na^+, the repulsive force increases, and the inter-particulate distance in the DDL becomes greater, causing the dispersion and breakdown of soil aggregates and negatively affects the structure of soil (Amini et al., 2016).

Table 1 shows the effects or mechanisms of biochar amendment into saline soil. Biochar could alleviate salt stress due to its ability to adsorb sodium ions through physical adsorption and ion exchange mechanisms. It adsorbs sodium ions and reduces its hazards, at the same time, releasing mineral nutrients such as Ca^{2+} and Mg^{2+} into the soil. The release of these ions could help to improve the soil quality and crop yield. This review presents the capacity of biochar in enhancing the physiochemical properties of saline soil. It shows more details of biochar adsorption mechanisms that are predominantly responsible for binding salt ions in the soil. The potential of biochar as a feasible adsorbent offers an efficient management approach in agricultural systems, and it could be applied to saline soil elsewhere in the world.

The feedstock presented in Table 1 is categorised into woody biomass and cellulosic biomass-based on their lignocellulosic content. Cellulosic biomass contains approximately 40-50 % of cellulose, 20-30 % of hemicellulose and 10-25 % of lignin (Anwar et al., 2014). Woody biomass contains a higher lignin content (>25%) than cellulosic biomass. Biochar may improve the soil bulk density, porosity, water holding capacity and penetration resistance. The effects of biochar amendment are dependent on the nature of feedstock, pyrolysis conditions and the amount of biochar added to the soil. Biochar derived from cellulosic biomass has a high amount of residual pores and a large exposed surface area (Batista et al., 2018) than other woody biomass. The porous structure of the biochar can decrease the soil bulk density and enhance the aeration of the soil, which produces a rapid turnover of the microorganisms, improving the biodegradation process in soil. Biochar derived from cellulosic biomass could also improve the structure of saline soil through the formation of soil aggregates due to interactions with soil organic matter, minerals and microorganism. Soil aggregation is important to maintain good root growth, movement of soil water and gases to enhance agricultural productivity. The Ca-containing biochar improves soil aggregation and facilitates salt leaching to reduce the Na^+ in soil. The release of Ca^{2+} from biochar displaces the Na^+ from exchangeable sites of saline soil colloids, promoting the leaching of Na^+ out of soil profile (Gunarathne et al., 2020). Since the Na^+ content in soil is lowered, sodium-induced dispersion that could harden soil and block water infiltration is prevented. Biochar improves the total porosity of saline soil being a porous material, which could lead to much faster salt leaching (Yue et al., 2016). A shorter time is required to reduce the salt concentration to a level suitable for crop cultivation. Biochar application also reduces sodium uptake by plants through transient Na^+ binding due to its high adsorption capacity and by releasing nutrients (K^+, Ca^{2+} and Mg^{2+}) into the soil solution (Feng et al., 2018). They further concluded that biochar could effectively reduce the Na^+ accumulation, osmotic stress and ion toxicity in the plant, enhancing the plant growth in saline soil. Biochar treatment could increase the organic carbon content in saline soil. Biochar with high carbon content will increase soil organic matter bonding, enhancing the resistance of soil aggregates to water and physical disturbances (e.g., wet-dry cycles), improving the aggregation of degraded saline soil (Juriga and Šimanský, 2018). The high concentration of soil organic carbon through biochar incorporation has led to more water-stable aggregates.

Table 1: The remediation mechanisms of biochar in saline soil

Feedstocks	Biochar Addition rate	Salinity treatment	Effects/ Mechanisms of biochar addition	References
Hardwood, softwood	0, 5 wt%	0, 25, 50 mM	1)Transient Na+ binding 2) Increase soil water availability 3) Release mineral nutrients	(Akhtar et al., 2015)
Conocarpus wood waste	0, 4, 8 % w/w	7, 18.96 mM	1) Increase soil water availability 2) Release mineral nutrients	(Usman et al., 2016)
Woodchip	75 t/ha	56.03 mM	1) Salt leaching 2) Lower soil EC, ESP and SAR	(Chaganti et al., 2015)
Sawdust	0, 5, 50 t/ha,	30 gm^{-2}	1)Transient Na+ binding 2) Increase soil water availability	(Thomas et al., 2013)
Wheat Straw	0, 2, 4, 8 %	0.7, 1, 3 dSm^{-1}	1) Transient Na+ binding 2) Increase soil water availability 3) Release mineral nutrients	(She et al., 2018)
Rice husk	0, 50 gkg^{-1}	140.6 $meqL^{-1}$	1) Salt leaching 2) Lower soil EC, ESP and SAR 3) Enhance Ca^{2+} and Mg^{2+} in soil solution	(Sadegh-Zadeh et al., 2018)

2.1.1 Impact of biochar on soil electrical conductivity

Other soil physicochemical properties amended by biochar include pH, electrical conductivity (EC), exchangeable sodium percentage (ESP) and sodium adsorption ratio (SAR). The extend of improvement could be affected by the type and concentration of salt (Dahlawi et al., 2018). The excess soluble salt could be reduced through appropriate leaching strategy. Biochar can mitigate high ESP or SAR by amending the organic and inorganic contents in the saline soil (Dahlawi et al., 2018).

EC is a measure of the amount of salt in soil solution and its ability to conduct electricity. As pure water is a poor conductor of electricity, the increase in soluble salts leads to a proportional increase in the EC of the solution. High EC could indicate soil salinisation. Leaching is one of the alternatives to lower excess soluble salt in saline soil, and it should preferably be done when the groundwater table is deep and or drainage is sufficiently rapid. Many studies have reported that biochar permits soluble salt leaching to reduce the EC and salinity of the soil profile. It improves the soil porosity and hydraulic conductivity that accelerated the leaching of salt. Yue et al. (2016) have conducted an experiment to investigate the effects of biochar in salt leaching and its potential as a soil conditioner. They have concluded that the biochar-amended columns discharged efflux 24 d to 40 d earlier than unamended soil. Biochar addition accelerated salt leaching and cut down 56 d to 62 d to wash most salts out of the soil column, which means that a shorter time is required for the EC values of the efflux to be reduced to 5 dSm^{-1} (Yue et al., 2016). The treatment with biochar could improve soil porosity and hydraulic conductivity, which led to the reduction of saline soil EC. Gunarathne et al. (2020) have concluded that the wood chip biochar produced at 500 °C is the most effective in mitigating soil salinity through leaching under excessive irrigation conditions. Huang et al. (2019) reported a significant decrease in soil EC by 9.8 - 36.5 % at incorporation zone and 0.4 - 13.8 % at below incorporation zone of soil under the amendment of woodchip biochar, as compared to the non-treated soil.

In contrast, some researchers demonstrated that the EC reduction is due to 1) the adsorption or retention of Na on the surfaces of biochar or the physical entrapment of salts in its fine pores, and 2) biochar-induced reduction in upwards movement of saline water (biochar cover reduced evaporation) resulting in decreased accumulation of salt on the soil surface (Dahlawi et al., 2018). Läuchli and Grattan (2007) reported that these studies were conducted in pots filled with soil salinised with NaCl as the only salt, which could not represent most of the saline soil. Although pot experiments enable more precise control of the environmental variables, the results are not always reproducible in the field, causing difficulty in interpreting the results to the actual field situation. Akhtar et al. (2015) found that biochar has excellent capability to adsorb salt ions; its adsorption capacity over time is limited. The salt ions adsorbed by biochar or entrapped in its fine pores could be released back into the soil after some times, depending on the biochar type, aging time and strength of adsorption (Dahlawi et al., 2018). The results of pots experiment may not be applied to the field trial. Since the soil is artificially salinised by using NaCl as the only salt, the extrapolation is afflicted with uncertainty. Different biochar has different EC values, and the soil EC could vary significantly with the biochar added. Further research and large-scale testing under field conditions using natural saline soil with different textures and salinities are required to confirm the validity of these studies.

2.1.2 Impact of biochar on pH, exchangeable sodium percentage and sodium adsorption ratio

Biochar amendment has been reported to improve soil quality by increasing the soil pH. This situation can be demonstrated when the pH of added biochar (pH >7.0) is higher than the pH of the soil pH <5.5 (Dai et al., 2017). There may be different pictures on alkaline soils. The pH of soil could decrease when low-pH biochar is added. The initial pH of biochar may be an important determinant of the changes in pH of saline soil. The final pH of biochar-soil mixture could also be affected by the pH of the soil itself. Another explanation for the pH reduction in saline soil was due to the high CEC of biochar added. The high CEC of biochar promoted the adsorption of cations such as K^+, Ca^{2+} and Mg^{2+} by the plants, resulting in hydrogen ions (H+) release from the root zone to compensate charge balance. Lin et al. (2015) discovered that pH value did not differ significantly between control and biochar-treated saline soil. The exact implications of biochar on the pH of saline soil are not well understood. Since the biochar could retain in the soil for an extended period of time, long term studies are required to investigate the mechanisms responsible for pH changes using the soil of different texture, different types of biochar, the extent and type of salinity, different plant species and various ways of farm management and cultural practices (Dahlawi et al., 2018).

ESP is the percentage of exchangeable sodium concerning cation exchange capacity (CEC), and it is used to indicate the relative amount of Na^+ present on the soil surface. SAR is an indicator to identify the salinity of the soil. Na^+ is likely to be adsorbed at cation exchange site in the soil at the expense of other cations such as Ca^{2+} and Mg^{2+}. Both Ca^{2+} and Mg^{2+} are predominant cations at the soil exchange site that could improve soil flocculation, leading to better permeability and aeration in the soil. When Na^+ is present in the soil, it replaces Ca^{2+} and Mg^{2+}, causing soil dispersion and infiltration problems. SAR is calculated as the ratio of Na^+ to Ca^{2+} and Mg^{2+} while a low sodium content in the soil gives a low SAR value. High SAR can bring about soil deterioration and infiltration problems.

A large number of studies reported that biochar is effective in reducing the ESP or SAR of saline soil through various mechanisms. The mechanisms are depending on the soil-plant-biochar properties. According to Chaganti et al. (2015), biochar could reduce the ESP by providing Ca^{2+} ions to replace Na^+ in saline soil. The amendment of soil with biochar could improve soil structure and porosity, which promoting the leaching of Na^+ and leading to lower ESP or SAR of saline soil (Yue et al., 2016). Kim et al. (2016) also concluded that the application of biochar might increase the soil CEC, favouring the adsorption Na^+ and lowering the ESP of saline soil. Biochar has a high concentration of organic carbon; the biochar incorporation would increase the soil surface charge density, causing more Ca^{2+} than Na^+ being adsorbed on the soil and a decline in ESP of soil (Kim et al., 2016). They further stated that the changes of SAR values are based on the proportion of Na^+ and Ca^{2+}, while the content of both cations may vary depending on the biochar types. The rate of biochar application will also affect the SAR values of saline soil. Fernandes et al. (2019) have discovered the increase in the SAR value, which is 0.27 $mmol_cL^{-1}$in soil treated with 30 t/ha of biochar. Caution is needed when selecting the type of feedstock and pre-testing is required to analyse the Na^+ content of biochar before its application into the saline soil. The biochar with high Na^+ content should be avoided in the reclamation of saline soil.

2.2 Possible mechanisms for Na^+ adsorption on biochar

Physical adsorption is a process in which biochar utilises its surface characteristics such as surface area and porosity so that the salt ion could be adsorbed onto the surface of biochar or diffused into its micropores. Fathy et al. (2017) concluded that the intensity of the physical adsorption is related to three factors: 1) the nature and properties of the adsorbent, such as pore structure, and the presence of functional groups; 2) the nature of the adsorbate, such as its polarity, pKa, size, molecular weight, functional groups present; and 3) the condition of the soil solution, such as pH and ionic strength. The concentration of salt ions and the temperature during the adsorption process will affect the adsorption capacity as well. High pyrolysis temperature could enlarge its pores volume and expand its surface area, and providing higher binding sites for salt ions. Rostamian et al. (2018) reported the network of pores is classified into macropores (diameter >50nm), mesopores (diameter 2-50 nm) and micropores (<2 nm). The adsorbate that is smaller than the pore diameter of the adsorbent could assess to the internal surface of the adsorbent, increasing the adsorption capacity. Rostamian et al. (2018) have reported that the rice husk biochar with a mean pore size of 2.2 nm is effective in removing the Na^+ with a radius of about 0.178 nm.

Another potential mechanism of salt removal is ion exchange. Previous studies have shown that the adsorption of salt ion is related to CEC of biochar. The CEC value is closely related to the concentration of oxygenated functional groups on the surface of biochar but varies with feedstocks and combustion conditions. Yavari et al. (2019) reported that palm oil empty fruit bunch (EFB) biochar has high CEC value of 83.90 cmol/kg due to the presence of oxygenated and polar functional groups such as hydroxyl, carboxyl and carbonyl groups on the external surface of biochar. It was assumed that these functional groups participated in salt adsorption. The surface hydrophilicity of biochar can be related to the O/C ratio. The higher the O/C ratio, the more polar the surface functional groups, the higher the adsorption capacity of the biochar. Chan et al. (2008) found that the increase in CEC in soil with the addition of biochar has occurred through two mechanisms: 1) high surface area of the biochar to cation adsorption; 2) the presence of high charge density on biochar surface to retain positive ions like Na^+.

3. Conclusions

Biochar amendment could improve soil porosity, soil aggregation, water holding capacity, hydraulic conductivity and its organic carbon content. It also reduces the soil's EC, SAR and ESP by Na adsorption, showing a positive effect on the physicochemical properties of saline soils. It shows more details of biochar adsorption mechanisms that are predominantly responsible for binding salt ions in the soil. Such positive effects are contributed by the physical adsorption and ion exchange of biochar owing to its large surface area and oxygenated functional groups. In terms of the soil pH, there is still some confusion regarding the exact implications of biochar. These discrepancies could be due to different soil texture, different types of biochar, the extent and type of salinity, different plant species and various ways of farm management and cultural practices. The mechanisms responsible for pH changes should be further investigated. Extensive research is required to classify the detailed mechanisms such as the functional groups to affect the salt removal rate from the soil and the possible saturation effect. Such understanding is essential to design the application rate of biochar to achieve further the desired level of salt removal in the saline soil. Long term data collection is essential to fully understand the mechanism, by different functional groups, for salt removal in soil by biochar as derived from other biomass and under different pyrolysis conditions.

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