



Production, Structural properties Nano biochar and Effects

Nano biochar in soil: A review

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Abstract

Due to greenhouse gas emissions and land-use change, the world climate and its geographical climate are changing. Due to population growth and increasing industrial and agricultural activities, the emission of carbon compounds and gases into the environment is increasing. For this reason, in addition to wasting energy, the environment is also polluted. With proper management and technology, the emission of such gases can be reduced to carbon solids. These carbon solids, called "biochar", have a variety of applications in various industries, including agriculture. Bio char can be transformed into Nano biochar by applying processes. In this case, the physical and chemical properties of this valuable material increase and the reduction of pollutant emissions, soil remediation, energy production and waste control is done in a more favorable way. In the recent past, the area under cultivation increased in order to increase agricultural production. This practice has now changed somewhat, and researchers and farmers are looking for ways to increase production per unit area. However, increasing production per unit area in some cases leads to pressure on the cultivated land. In this case, if not properly managed, over-harvesting of nutrients from the soil will occur and after a certain period of time, the soil will be depleted of such valuable elements. In such cases, one of the most effective ways is to add soil remedies. These modifiers are added to improve the physical, chemical, and biological conditions of the soil. One of these substances, which also increases the efficiency of fertilizer and irrigation water, is biochar. Biochar can also be called Nano biochar due to its structural properties. The addition of Nano biochar improves the plant culture environment and helps in proper soil management.

Keywords: Nano biochar, biological conditions, soil, environment, energy production, soil remediation, pollutant emissions.

1. Introduction

Although the contribution of each of the factors influencing climate change is unclear, greenhouse gas emissions are undoubtedly one of the most important. In recent years, the increase in human activities has led to the production and emission of such gases [1-5]. One way to absorb and separate carbon is to remove greenhouse gases from the output of industrial plants and store them in safe tanks [6-10]. Emissions of carbon dioxide from the soil also have

adverse effects on the global carbon cycle and ecosystem [11-13]. Soil organic carbon (SOC) is the largest carbon reservoir and is twice the amount of carbon in the atmosphere [14-17]. Preservation or emission of soil organic carbon is one of the important factors affecting the concentration of atmospheric carbon dioxide [18-22]. Carbon sequestration in soil is a slow process but is an effective natural strategy to moderate the concentration of carbon dioxide in the atmosphere

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[23-26]. Estimates suggest that small changes in soil organic carbon have significant effects on atmospheric carbon dioxide concentrations; A 5 % change in SOC can change more than 16 % of atmospheric carbon dioxide [27-31]. Agricultural soils usually lose a significant amount of organic carbon due to improper cultivation and plowing [32-36]. For this reason, changes in plowing methods, suitable fallow, the use of deep-rooted plants, and carbon sequestration in the soil can increase soil organic carbon content. In the meantime, carbon sequestration is done in different ways [37-42]. Table 1 lists several of these methods and the advantages and limitations of each. Among the mentioned methods, the method from which the carbon produced has long-term effects and has considerable stability against chemical and biological agents is more appropriate [43-45]. Biochar has these properties and due to its use, in addition to reducing soil organic matter, increasing and reducing carbon dioxide from the soil, by improving the physical and chemical properties of the soil, the growth rate and yield will increase [46-50]. The production of more and more not agricultural products is global demand. Intensification of agricultural activities over time has led to erosion and reduced soil fertility [51-53]. Some traditional agricultural methods also reduce the amount of soil organic matter (SOM), in which case the soil structure is plunged into the abyss of destruction [54-57]. As a result, the retention of nutrients and water in the soil is reduced. Organic farming methods also improve soil fertility indices such as SOM and pH by about 5 to 34% depending on environmental conditions compared to conventional methods. Therefore, it is necessary to prevent excessive degradation and erosion of agricultural soils by adding modifiers to the soil [58-61]. Biochar can be mentioned as a material for improving soil conditions. Biochar, obtained from the pyrolysis of plant materials, has a crystalline structure [62-65]. The biochar compound can be divided into three parts: resistant carbon, sensitive carbon, and ash. This material has many Nanopores and pores and due to the stability of its carbon (having an aromatic structure), it is resistant to biodegradation. As a result, microorganisms cannot use the carbon in it as an energy source [66-70]. The H / C and O / C ratios in biochar are less than 0.6 and 0.4, respectively, and the lower these ratios are, the better the biochar is formed, the better the carbonization of the plant material is done, and the better [71-73]. It is

considered suitable for soil. Biochar ash also contains minerals and macro and microelements [74-77]. The presence of these elements plays a key role in the chemical and aromatic structure of biochar [78-80]. For example, the element nitrogen can be attached to one or two carbon atoms, but the effect of this bond on the behavior of biochar in the soil is unknown [81-83]. Iron-rich biochar formed from plant fertilizers at temperatures above 600 ° C has Fe₃C bonds and ferromagnetic iron clusters [84-86]. Compared to the raw material, biochar is formed at different temperatures, and as this temperature increases, more stable carbon compounds are formed. Increasing the temperature by removing excess material in the raw material leads to an increase in the specific surface area of the biochar [87-90]. The specific surface area of this material is more than 500 m²/gm, which can be increased not by applying a series of physical and chemical processes [10-12]. The addition of such a high specific surface material and resistance to biodegradation affects the physical condition of the soil. It can also affect soil water dynamics and nutrient cycles [91-92]. Figure 1 shows the general effects of biochar in the soil. This article tries to investigate the effect of biochar on the physical and chemical properties of soil [1- 2]

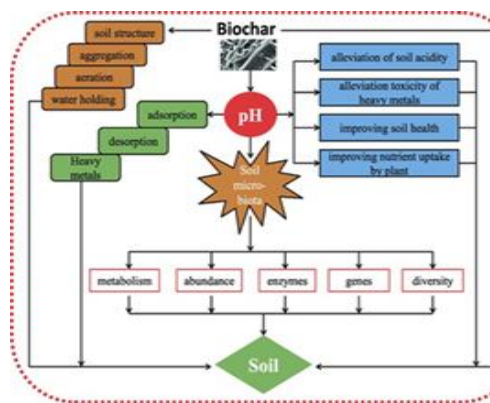


Figure1. Biochar effects in soil [13].

2. Production of Nano biochar

Nano biochar is a carbon-rich material that is formed during the process of pyrolysis and by the carbonization of biomass. The difference between thermal decomposition and combustion is the presence or absence of oxygen (see Figure 2). In the combustion process, biomass can be converted to gases and carbon dioxide, ash mixed with metal oxides, silica, and other volatile inorganic elements by the application of temperature and oxygen [93-94]. If oxygen is removed from the reaction, thermochemical conversion of the biomass takes

place and no carbon dioxide gas is produced. In this case, carbon appears as a solid called biochar. Other products produced in the thermal decomposition process include Liquid bio-oil and Syngas such as hydrogen, methane, and other hydrocarbon gases. In general, thermal decomposition takes place in two modes, fast and slow, and depends on the amount of heat applied to the biomass [95-96]. If the applied temperature is less than $100\text{ }^{\circ}\text{C} / \text{min}$, the thermal decomposition will be slow and the Biochar and Syngas will be the final products of the reaction. Rapid thermal decomposition usually occurs in the presence of temperatures above $1000\text{ }^{\circ}\text{C} / \text{min}$, in which case biofuels are also produced [2].

1.1. Structural properties of Nano biochar

Biochar is formed from polycyclic aromatic hydrocarbons in which 6 carbon atoms are bonded together in a ring. The presence of such an aromatic structure makes Biochar stable against biological and chemical changes [97]. In addition to carbon, biochar is composed of other elements such as hydrogen and oxygen. Depending on the raw material used to produce the biochar, different minerals such as nitrogen, phosphorus, and sulfur can also be present. This carbon substance has many functional groups such as hydroxyl, ketone, ester, aldehyde, amino, nitro, and carboxyl. Bio chars, on the other hand, contain significant amounts of Humic Acids and fulvic organic acids. Depending on the composition and heterogeneous level of the biochar, these materials may exhibit hydrophilic or hydrophobic properties and have alkaline or acidic properties. For this reason, bio chares have the ability to combine with organic and inorganic materials [98-99]. In the conversion of plant biomass to Nano biochar, the intrinsic and internal structure (Phototaxy) of the plant is preserved and this is very important because the vascular system of plants has a special order and is composed of strong cell walls that the final biochar inherits (See Figure 3). In Nano biochar, the size of the pores is divided into three categories: (1) macropores with a diameter of more than 50 nm, (2) mesoporous with a diameter between 2 and 50 nm, and (3) micropores (Microspores) With a diameter of less than 2 nm.

Table1. Different methods of carbon sequestration increase soil organic carbon [2].

Carbon sequestration method's	properties
Absorption and storage by plants	A simple method but the return of carbon to the atmosphere by plant decomposition
Cultivation without plowing and crop rotation	It takes a long time.
Crop cover with deep roots	A simple method but with short-term effects
Use of biochar	Stable and long-lasting, need further research
Geologic sequestration	Very high cost and sophisticated technology

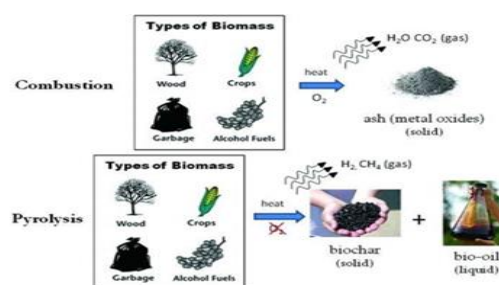


Figure 2. Difference between combustion process and thermal decomposition [2].

In general, micrometer porosity plays the role of transmitting air into the biochar and can act as a place where microorganisms can perform their activities well and protect themselves against adverse conditions. In micrometric and micrometer porosities, adsorption/desorption of organic and inorganic ions and molecules takes place. This increases the biochar capacity to store nutrients in the soil [22-25]. The specific surface area of Nano biochar is much higher than that of clay particles (more than $1500\text{ m}^2/\text{gm}$). Nano biochar properties such as elemental composition, porosity percentage, particle or pore size, and the presence of degradable hydrocarbons are a direct function of the parameters of the thermal decomposition process and the type of biomass. The structure of Nano biochar porosity strongly depends on the applied temperature [26-27]. High temperatures and how long the biomass is affected are very important. These factors determine the amount of Nano biochar produced from the biomass. Basically, at a certain temperature, volatile compounds and components are released from the biomass, which leads to the formation of not micrometer pores[100-101]. In general, the sum of the total specific surface area and not micrometer pores increases with increasing temperature. The maximum specific surface area occurs in the temperature range of $650\text{ to }850\text{ }^{\circ}\text{C}$.

There are several reasons for this, but the most important is the presence of a liquid consisting of hydrocarbons, resins, alcohols, and other compounds (Tars) that during the production process of Nano biochar, prevents the formation of not micrometer pores and with the disappearance of this material at an average temperature of 750 ° C, more not micrometer pores are created and the specific surface area increases more effectively. In lignin-based Nano biochar, the amount of ash in the raw material affects carbonization. By reducing this amount of ash, the produced Nano biochar shows better properties and characteristics. The presence of lipid compounds, Humic Acid, and folic acid reduces the porosity of biochar [28]. Depending on the type of primary biomass in some samples, the cellular structure melts under heat and becomes plastic. This phenomenon can prevent the formation of not micrometer pores in biochar. Of course, the rate of increase in temperature also affects the melting of the cell structure. Studies on pinewood show that if the rate of increase is 20 ° C / s, Nano biochar is formed with the appropriate structure, but if this increase in temperature is done rapidly at a heating rate of 500 ° C / s, the cellular structure of the melt is formed and not micrometer pores will not be able to form. A series of physical and chemical processes also increase the specific surface area of the Nano biochar, which is called "biochar activation". Physical activation methods include the use of oxidizing gases such as ordinary steam, carbon dioxide, or oxygen, which are applied to Nano biochar at temperatures above 700 to 1200 ° C. The basis of the chemical activation method is the combination of biomass with acids, bases, or salts before carbonization [29-30]. Chemically activated Nano biochemistry is carbonized at lower temperatures than physical processes, but the amount of specific surface area created by both processes is almost the same [2, 3].

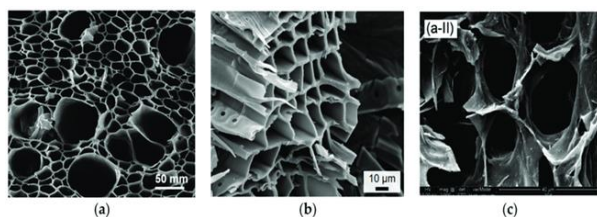


Figure 3. SEM images of biochar from the pyrolysis of (a), (b) wood sawdust, and (c) sisal leaves [2].

3. Results and Discussion

3.1. Effect of Nano biochar on soil organic carbon content

As mentioned, soil organic carbon (SOC) decomposes over time and is released into the

atmosphere as carbon dioxide gas. Based on the results, adding Nano biochar to the soil significantly increases the soil's organic carbon[104-106]. For example, by adding 8% Nano biochar to the soil, the amount of organic carbon increases by about 41%, and after 210 days, the Nano biochar added to the soil does not decrease. Based on the results, it is hypothesized that Nano biochar increases the stability of soil organic carbon and reduces its mineralization. Soil organic carbon stability can be increased in the following three ways [31-33]:

(1) physical stabilization of organic carbon by aggregation, (2) fusion of organic carbon with clay and silt particles (silt or fine-grained soil), And (3) soil biochemical stabilization through the formation of degradable SOC compounds[105-107]. Among the mentioned factors, the uptake of soil organic carbon into the biochar is the most likely cause of increasing SOC stability. In most studies, SOC decomposition is reduced by adding biochar to the soil (see Figure 4) [1].

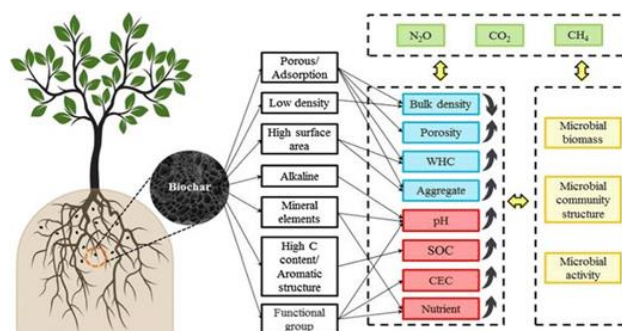


Figure4. Effect of Nano biochar on soil organic carbon content [34].

3.2. Effect of Nano biochar on carbon dioxide emissions from soil

Initially, carbon dioxide emissions are increased by adding biochar to the soil. For example, adding 8% biochar to the soil increases carbon dioxide emissions into the soil containing biochar during the first 20 days; But after 120 days, gas emissions are much lower. In other words, carbon dioxide emissions are reduced by increasing soil biochar over long periods of time. In general, the emission of carbon dioxide from the soil depends on soil conditions, soil microbial population, and physicochemical properties of biochar [34-36]. However, by adding biochar to the soil, its unstable part may stimulate and increase the growth of microorganisms[108-110]. Biochar micrometric porosity increases the soil moisture-holding capacity, and increasing moisture means reducing the decomposition of SOC. Therefore, biochar indirectly

reduces carbon dioxide emissions by increasing soil moisture (See Figure 4) [1].

3.3. Effect of Nano biochar on soil physical properties

The difference in physical structure between soil and biochar leads to changes in tensile strength, hydrodynamics, and gas flow in the soil. These events can also affect the lives of soil animals. All of these effects depend on the type and characteristics of the biochar used (raw material and heat). When the tensile strength of biochar is lower than the soil (clay-rich soil), the addition of biochar reduces the tensile strength of the soil. Typically, in a study performed on Alf soils (soils specific to coniferous and deciduous forest areas (Alf soils)), it was found that with the addition of biochar, the tensile strength was reduced from 4.64 to 31 kPa. Mechanical impedance reduction is a very important factor that affects root growth [37-39]. At this time, the roots are less resistant to soil and the plant can easily develop its roots, but this is only one of the factors that increase the growth and development of roots in the culture medium [111-113]. In one study, the root of the plant developed well when 10% of the culture medium was biochar, and when this ratio increased to 15% or more, no significant change in root growth was observed (Figure 5). Root growth and mycorrhizae (fungi coexisting with plant roots: Mycorrhiza), soil mineral elements have also increased, which is one of the factors increasing the seed germination rate in soils containing biochar. Decreased tensile strength may increase the mobility and displacement of invertebrates in the soil. Invertebrates move through the soil and feed on substances that contain a variety of vitamins and nutrients, which in turn increases soil fertility. By reducing the bulk density of the soil, Biochar increases the porosity and porosity of the soil, which affects the amount of water retention in the soil, the model of root development, and soil organisms. This event can be explained by the low density of biochar bulk relative to soil minerals [40-41]. Biochar has macro and micropores (diameter about 1 to more than 50 nm) that can withstand the weather well, thus reducing the density of Biochar bulk in the soil significantly. According to studies, the density of biochar bulbs varies between 0.09 to 0.5 grams per cubic centimeter, depending on the type of raw material. This amount is much less than the bulk density of soils. In one study, by adding 60 tons per hectare of biochar to the soil (with a bulk density of 56.1 g / cubic centimeter), the bulk density of soil decreased by about 5.8% [2].

3.4. The effect of Nano biochar on soil chemical properties

The properties of known and unknown organic matter in Biochar change over time due to processes such as

aeration, reaction with organic matter and soil minerals, and oxidation by microorganisms. The addition of biochar causes changes in pH, electrical conductivity (EC), cation exchange capacity (CEC), and soil nutrient content. Depending on the raw material from which the biochar is formed, the pH of the biochar is very variable and is around 4 to 12. The higher the temperature when biochar is formed, the higher its final pH, which changes over time and can increase or decrease [114-117].

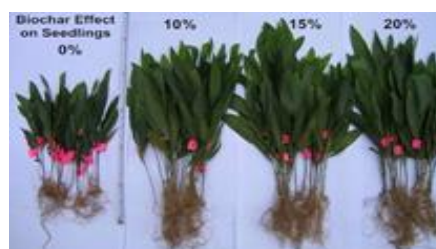


Figure 5. The effect of biochar on increasing root and stem growth - from left to right soil containing zero, 10, 15, and 20% of biochar [42].

This property has also been attributed to that raw material. Observations show that the pH of oak biochar decreased from 9.4 to 7.4 after one year and in contrast, the pH of biochar from corn forage decreased from 7.6 to 1.8 during the same period. This increase and decrease in biochar have been attributed to the functional groups in it. Researchers believe that the reason for the decrease in pH is more in the oxidation of carbon to carboxylic acid groups. While the cause of the increase in pH is attributed to the dissolution of alkaline compounds [42-43]. Therefore, the biochar in the soil can change the pH of the soil with its changes over time. Biochar can have a positive or negative net charge and initially has a lower cation exchange capacity than soil organic matter [118-120]. The higher the ash content of the raw material from which the biochar is formed, the higher the CEC and charge density in the final product. Of course, the amount of CEC biochar also depends on the temperature during its formation. The CEC in biochar is mostly related to the functional groups of organic acids such as humic acid, and such compounds are destroyed when the formation temperature rises too high. As a result, the final CEC rate of the biochar is reduced (Figure 6). For example, biochar consisting of corn forage at 350 ° C has a CEC of 3.419 mmol/kg, which decreases to about 1.252 mmol/kg at a temperature of more than 600 ° C. Adding high CEC biochar improves soil conditions and can prevent nutrient wastage (due to sedimentation, adsorption to soil minerals and leaching). As a result, the efficiency of the fertilizer increases, and more nutrients are provided to the

plant during the growing season. According to research, biochar can reduce the leaching rate of nitrogen fertilizers (ammonium compounds) by about 60%. On the other hand, this property causes the adsorption of heavy metals and organic soil contaminants (such as pesticides, etc.) and reduces the level of pollution in the soil. Biochar can also absorb soil organic matter, thus not only increasing its CEC but also protecting soil organic carbon. As a result, soil organic carbon is not decomposed and the amount of soil organic matter increases over time [121-123]. Biochar cation exchange capacity allows it to absorb elements such as sodium, calcium, and magnesium and thus play an effective role in reducing the salinity (EC) and osmotic potential of the soil solution [44-46]. As a result, the plant is under less salinity stress, and plant yield increases. Biochar can also reduce the concentration of soluble compounds such as phenol in soil solution. In acidic soils, the concentration of elements such as aluminum and manganese in the soil solution increases [47-49]. The presence of these elements, in addition to causing poisoning, also interferes with the absorption of other nutrients by the plant, which Biochar can reduce their toxicity by reducing the concentration of these elements [50]. The combination of biochar with acidic solutions causes some elements such as Si, Fe, S, P, K, Mg and Ca to be released from it and enter the soil solution, as a result of which plants and microorganisms can use it [2, 3, 4].

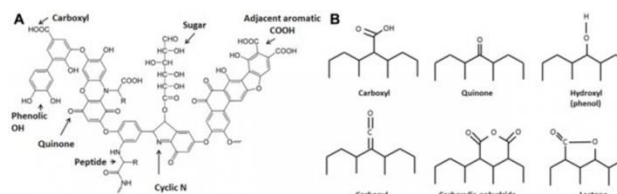


Figure 6. Schematic of the chemical composition of biochar and its types of functional groups [50].

4. Conclusion

1. Addition of Nano biochar to the soil increases the stability of soil organic carbon against environmental factors and reduces its mineralization. This significantly reduces carbon dioxide emissions. Increasing organic carbon also has effects such as improving soil structure, increasing water holding capacity in the soil, increasing the activity of microorganisms, and increasing the bioavailability of nutrients for the soil. Therefore, as the amount of soil biochar increases, its positive effects on the environment will increase.

2. In general, Nano biochar produced from different plant materials and different thermal decomposition

conditions have unique physicochemical properties. This material with different absorption properties can have positive effects on a variety of soils. Nano biochar production is an effective and green technology that can increase the efficiency of water and fertilizer use in the soil. It can also be used as a substrate for macro and micronutrients so that the nutrients in the substrate absorb all the fertilizer of frankincense. Nano biochar with several properties can improve plant growth in saline soil conditions. The ability to remove a variety of organic and inorganic contaminants from the soil is another advantage of Nano biochar. It is hoped that by using such materials, fertile agricultural soils will be free from the risk of destruction and erosion and the production of agricultural products per unit area will increase.

abbreviations

WHC water holding capacity
SOC Soil organic carbon

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