Technology of Acid Soil Improvement with Biochar: A Review

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Abstract. This paper comprehensively analyzed and summarized the main research progress of biochar in improving acid soil technology at home and abroad. In this paper, the distribution, cause of formation and harm of acid soil were introduced, the differences between biochar improver and traditional improver were compared, the structure and functional basis of biochar were expounded, and the improvement of physical and chemical properties of acid soil was analyzed. Finally, combining with the current situation of China's agricultural development, the paper puts forward the prospect of the problems that need to be paid attention to in the process of biochar research, in order to provide reference for the application and industrial development of biochar.

1. Introduction

Since the beginning of the 21st century, the impact of food, environment and energy crisis on the human being has become more and more serious, and the governments, experts, and other parties concerned have been searching for the ways to cope with such crises, but producing little effect. In such case, with its unique structure, physical and chemical characteristics, abundant sources of materials, and extensive application value, biochar has become known as the “black gold” to the public and recognized by the academic circle, and also become one of the hot research areas.

With regard to the agricultural production, we must become soberly aware of the importance of agro-ecological environment. The “soil, crop, and environment” are interdependent and inseparable to each other. Especially in China, it is an indisputable fact that higher degree of soil acidification is affecting the crop yield. The biochar technology conforms to modern agricultural development concepts such as “low carbon, environmental protection, and sustainable development”, so that it will exert an important effect and significance in control of soil acidification, promotion of the virtuous cycle of agricultural environment, and sustainable development [1].
2. Overview of acidified soil

Soil acidification means the process of leaching loss after the calcium, magnesium and other salt-based ions in the soil are substituted by exchangeable hydrogen and aluminum ions, which is a relatively slow process [2]. As an important chemical property of soil, soil acidity or alkalinity has the direct effect on the nutrient content of soil, nutrient availability, and soil microbial activity, and then affects the growth process of the crops. Due to the imbalance of H+ and OH- in the soil solution, the soil with pH value less than 6.5 is called the acid soil. As an important form of soil degradation, soil acidification has become a focus of common concern in the fields of agricultural production and ecological environmental protection at home and abroad [3].

2.1. Distribution of acidified soil

The research shows that 30% of the global land area not covered by glacier is the acidified soil. In the whole world, the acid soil is distributed mainly in temperate, tropical, and subtropical regions, while the acidified soil in North America and Northern Europe mainly consists of the podzolic soil [4]. At present, the problem of soil acidification in China is also extremely severe. Statistics show that from the 1980s to the 21st century, the pH value of farmland soil in China decreased by 0.5 units on average, and the area of acidified land accounted for more than 40% of arable land area in China. The acid soil in China is characterized by high strength, large area, and wide distribution [5].

According to statistics, the total area of the acidified soil in China has reached as high as 226,000,000mu, accounting for about 24.9% of the area in China. At present, the acidified soil is mainly distributed in the tropical and subtropical regions in the southwest region and the south of the Yangtze River in China; in addition, the facilities land, vegetable land, and dry farmland in northern region of China are also acidified. Most of the acidified soil has the pH value lower than 5.5, some of the acidified soil has the pH value lower than 5.0, and the severely acidified soil has the pH value lower than 4.5 [6]. At present, both the natural vegetation such as forest and grassland, and the anthropogenic soil in orchards and tea gardens, are presenting a trend of intensified acidification. Therefore, it is of great significance to take effective protection and control measures to reduce the damage of acidification to soil quality [7].

2.2. Causes for soil acidification

There are natural causes and human causes for soil acidification. The natural acidification is universal and inevitable in nature. The human factors have accelerated this process to a great extent.

The natural acidification mainly refers to the phenomenon that a large number of salt-based ions are leached in soil, and the exchangeable hydrogen and aluminum ions are increased in large quantities in some regions due to the heavy precipitation, and such process of acidification is relatively slow. Human factors mainly include acid deposition, improper application of nitrogen fertilizer, continuous cropping, and plantation of acid-producing crops. Acid deposition means the phenomenon that the sulfur and nitrogen compounds produced from the combustion of fossil fuel and the emission of automobile exhaust fall onto the ground after the processes such as diffusion, precipitation, or action of gravity. When applying the acidic fertilizers such as ammonium chloride, the ammonium ions are oxidized, and then absorbed and taken away by crops, while the content of hydrogen ions and aluminum ions increases, leading to the decrease of soil pH. Continuous cropping and plantation of acid-producing crops are also the important causes for soil acidification [6].

2.3. Hazards of soil acidification

2.3.1. Massive leaching loss of salt-based ions. Soil acidification leads to accelerated leaching loss of salt-based ions, and the amount of such leaching loss is affected by pH value of soil. If the pH value of soil decreases, the positive charge in the soil increases and the negative charge decreases, and the adsorption amount of calcium, magnesium, potassium and other nutrient ions decreases significantly. The ability of such ions to integrate the soil is proportional to the pH value, so that such ions are more
likely to be leached with water. The experiments confirm that some minerals in the soil will be weathered after the leaching by acid rain and then release salt-based ions [8], indicating that the long-term leaching by acid rain will lead to the loss of soil nutrient pool, resulting in the impoverishment of soil nutrients.

2.3.2. Release of metallic ions. Due to the soil acidification, a large number of aluminum ions will be released from the aluminum minerals in the soil, leading to aluminum poisoning of plants. Studies have shown that under the influence of aluminum toxicity, the growth of the plant root is inhibited, and the absorption and transport function of the root and the enzyme activity of the root decrease rapidly. The excessively high concentration of aluminum in the plants will also inhibit the cell mitosis and DNA synthesis, affect enzyme activity, destroy structure of cell membrane, and inhibit nutrient absorption [9]. In the condition of low pH value, the solubility and activity of heavy metal ions such as manganese, copper and zinc in the soil will increase. When their concentration exceeds a certain limit, heavy metal poisoning will occur in crops, affecting the growth and development of crops, and posing a potential threat to agricultural production and ecological environment. The release of heavy metals not only affects the growth of crops, but also enters the food chain through absorption and enrichment by plants. However, most heavy metals cannot be metabolized normally in animals, nor can they be eliminated, so heavy metal poisoning will occur if humans and animals eat more than a certain amount [10].

2.3.3. Decreased microbial activity. There are a large number of beneficial microorganisms in the soil, which play an important role in the growth of crops. Most beneficial microorganisms, on the other hand, thrive in neutral environments with a pH value ranging from 6.5 to 7.5. According to research, with the decrease of pH value of soil, the species and activities of such microorganisms will decrease, so as to further affect the fixation of nitrogen and mineralization of organic matters in soil, and affect the conversion of nutrients seriously, resulting in a lower crop yield [11]. In general, in case of the higher microbial diversity of the soil, it is difficult for pathogens to breed, and the ratio of bacteria to fungi decreases with the extension of continuous cropping years, so the soil fertility evolves from “bacterial” to “fungal” on the basis of the mechanism is that some microbial populations, especially the pathogenic fungi, will accumulate in large quantities during the process of continuous cropping process, leading to the occurrence of serious plant diseases and insect pests, which cannot be controlled and have a serious impact on crop production [9].

2.3.4. Decreased nutrient availability. The adsorption of potassium, calcium, magnesium and other cations by soil colloid will be weakened with the aggravation of soil acidification. As a result, aluminum ions in soil solution will constantly crowd out salt-based ions, resulting in the decrease of salt-based saturation and cation exchange capacity. The diversity and quantity of soil microorganisms will also be affected by soil acidification. In highly acidic soil, almost all microorganisms will be affected by aluminum toxicity, and the low pH value of soil will inhibit the activity and quantity of soil microorganisms. Because soil microorganisms are directly involved in the decomposition of organic matters in the soil, the balance of carbon, nitrogen, phosphorus and sulfur in the circulation of such elements in the soil is indirectly affected while the microbial activity is affected. The absorption of calcium and magnesium ions by plant roots is also inhibited by competitive cations with higher concentrations in acid soil [12]. The contents of calcium and magnesium in the leaves also decrease significantly with the increase of hydrogen ions in the soil [13].

3. Traditional restoration methods

Iming at the phenomenon of soil acidification, the experts and scholars from all over the world are trying to find effective soil improvers. Currently, there are three major categories of traditional acid soil improvers including lime, industrial by-products and organic materials [14]. The studies show that all such three categories of improvers have certain effect on the improvement of acid soil, and can increase the content of salt-based ions in soil and reduce the aluminum toxicity and acidity of soil. However,
such improvers are used for a single purpose of improvement, and need to be applied frequently with certain side effects.

3.1. Lime Improver
Limestone mines are widely distributed in China, and the lime is featured by simple production process and low price; therefore, the lime improver is often used in agricultural production. The lime-like substances mainly include limestone, quicklime, and slaked lime. At present, the most commonly used method for soil improvement is the application of lime.

Lime is rich in elements such as calcium and magnesium, and can increase the content of exchangeable calcium and magnesium in soil after application. Due to the strong flocculation of calcium ions and the formation of hydroxides with some amorphous aluminum and iron in the soil, the application of lime can reduce the acting force between soil particles and improve the soil structure [15]. The application of such improver can reduce the acidity of topsoil easily and increase the concentration of exchangeable calcium ions in topsoil; such improver can neutralize hydrogen ions in soil quickly and effectively, increase the pH value of soil, and neutralize potential acids in soil; such improver can improve the soil structure, reduce the toxic effect of heavy metals on crops, and improve the quality and yield of crops; such improver can also reduce the content of exchangeable aluminum in soil solution and supplement the calcium element which is lacking in acid soil [16].

However, there are also some deficiencies in the application of lime in acid soil. The long-term application of lime in soil will accelerate the leaching of potassium and magnesium ions, and the cessation of application of lime will lead to a stronger re-acidification process. In addition, the application of lime in a large amount or for a longterm will not only lead to the soil hardening to form the “lime hardening field”, but also lead to the imbalance of calcium, potassium and magnesium in the soil, resulting in reduced production. Application of lime may also cause the precipitation of hydrate oxides of magnesium and aluminum, reducing the concentration of magnesium ions in soil solution and plant availability [17]. Therefore, the improvement of acidized soil with lime is not satisfactory.

3.2. Industrial and Mining By-products
The research shows that there are alkaline in dolomite, fly ash, phosphorous gypsum, alkali slag and other minerals, silt, pulping wastewater, and other substances, which can be used to neutralize the acid components in the soil and improve the soil acidity or alkalinity. Therefore, such industrial and mining by-products are often used as raw materials to improve soil acidity [18].

Dolomite is mainly composed of crystalline calcium carbonate and magnesium carbonate. The content of exchangeable aluminum and manganese in the soil decreases significantly after application of dolomite, and with the increased amount of dolomite powder, the content of available phosphorus and available potassium in the soil presents an increasing trend, and the re-acidification phenomenon is not liable to occur. Characterized by small density and large porosity, the fly ash can improve the soil structure and promote the metabolism of crops. With the content of alkaline substances such as calcium oxide and magnesium oxide, it can neutralize hydrogen ions in the soil, improve the nitrate reductase activity of crops, enhance the nitrification of organic matters, promote protein synthesis, and improve yield and quality of crops. Phosphorous gypsum, as an improver of highly acidic soil, can promote crop growth and improve the balance of nitrogen, phosphorus, potassium and calcium in crops, which is very important for achieving high yield and high quality, and can play a dual role of soil improvement and fertilizer cultivation [19].

This kind of improver has certain improvement effect on acid soil; most of such improvers are sourced from some industrial by-products, which are relatively cheap. But most of such improvers contain a certain amount of toxic metal. For example, phosphorous gypsum and phosphate ore powder contain a small amount of lead, cadmium, mercury, arsenic and chromium [20]. Despite of the small content, such improvers can cause pollution to the environment.
3.3. Organic materials

In addition to the above soil improvers, some organic materials such as crop stalks, green manure, and plant ash are also used in the improvement of acid soil. Since the ancient times, the people have been purposefully applying organic materials to the soil to fertilize and improve the soil. Microorganisms in soil can decompose organic matters, produce a variety of organic complexes to enrich soil nutrients, and raise the availability of soil nutrients while enhancing the buffering power of soil against acid and alkali. The application of organic matters can enhance the agglomeration of soil particles, improve the pore structure of soil, and intensify the aggregate structure of soil [21]. Such organic material contains a large number of nutrients, so it can improve the soil fertility, increase the types and activities of soil microorganisms, change the population distribution density, reduce the content of exchangeable aluminum in the soil, and reduce the toxic effect on crops.

The application of organic materials can increase the pH value of soil, but the duration of time is limited, requiring multiple applications. Moreover, the organic materials will release a large amount of CO2 in the process of mineralization, so as not to play the role of soil carbon sequestration. The ammonium ions produced in the process of mineralization will also undergo nitrification and even lead to the decrease in pH value of soil again [22].

4. Structure and characteristics of biochar

4.1. Biochar improver

The pyrolysis of biomass materials in anaerobic or anoxic conditions can generate CO2, flammable gas, volatile oil, and tar substances, and a solid substance rich in carbon, which is commonly known as biochar [23]. The biomass materials used to prepare biochar may be the cheap household garbage and wastes. The conversion of agricultural wastes into biochar through pyrolysis process can reduce the environmental pollution caused by agricultural wastes and replace non-renewable energy with renewable energy. Therefore, in recent years, biomass carbon has attracted extensive attention from academia, enterprises and government departments.

If the biochar is used as the soil improver, a number of beneficial effects will poses on soil. The biochar can improve the physical property of soil, enhance the water retention capacity of soil, promote the development of microbial population in soil, enhance the activity of microorganism, reduce the nutrient leaching of soil, promote nutrient cycling, and increase the content of organic carbon in soil, so as to promote the growth of plants. On the surface of biomass carbon, there are negative charges with the high cation exchange capacity, which can improve the soil’s ability to hold and retain calcium, potassium, magnesium, NH4+ and other nutrient ions, and improve the soil fertility [24]. Another important feature of biochar is that such biochar is alkaline and has a high pH value, so the biochar can be used for improvement of acid soil. Due to the stability, biochar can overcome the deficiency in direct application of lime improver, and avoid the phenomenon of re-acidification. In addition, the raw materials of biochar are sourced from biomass, reducing the risk of heavy metals to a great extent. Second, the application of biochar can also better inhibit the nitrification of soil without repeated application.

4.2. Composition and functionality basis of biochar

The function of biochar mainly depends on its physical and chemical properties. The physical and chemical properties of biochar depend on the materials and conditions for preparation of biochar, such as temperature, oxygen content, and time. Therefore, different raw materials for biochar preparation and different preparation conditions will lead to great differences in the properties of biochar obtained. However, biochar also has certain commonalities, and the utilization of such commonalities is the hotspot and focus in research of biochar at present.

Biochar contains a certain amount of alkaline substances, so it is generally alkaline. The research shows that the organic functional groups such as -COO- and -O- on the surface of biochar and the carbonates in biochar are the main forms of alkali [25]. The contribution of carbonates to the alkalinity
of biochar increases with the rise in the preparation temperature, while the contribution of organic functional groups shows an opposite trend.

Mainly composed of aromatic hydrocarbons and elemental carbon or carbon with graphite structure, biochar is stable in nature with the carbon content more than 60%. It is not only highly aromatic, but also has strong anti-decomposition ability and thermal stability, so it is not easy to be decomposed by microorganisms. Biochar ash is mainly composed of oxides or salts of mineral elements such as potassium, sodium, calcium and magnesium, which are alkaline when dissolved in water. Therefore, biochar can increase the pH value of soil and improve the acidity or alkalinity of soil [26], and some of the mineral elements (nitrogen, phosphorus, potassium, etc.) contained in biochar are important nutrients in the soil. In addition, due to the high organic carbon content of biochar [27] and the abundance of organic functional groups (carboxyl group, hydroxyl group, aldehyde group, etc.), biochar can also increase the content of organic matters in soil.

With a higher porosity, the biochar can be applied into soil to reduce the soil bulk density, improve water, gas, and heat conditions of soil, and facilitate the growth of soil microorganisms and crops as well as the degradation of organic pollutants in soil [24]. The large specific surface area of biochar can increase the ability of soil to hold water and fertilize, and reduce the effectiveness of heavy metals and organic pollutants in soil. Based on such fundamental properties, biochar has the adsorption capacity, antioxidant capacity, and strong anti-biological decomposition ability, so it can be widely used in industry, agriculture, energy, environment, and other fields.

4.3. Modified biochar

In order to further improve the performance of biochar, the researchers modified biochar. The modification techniques for biochar include the change in properties of the biochar in different conditions, or addition of elements or compounds inside the structure or on the surface of the biochar. The introduction of such elements or compounds will lead to specific behaviors of the biochar or enhance their efficacy. Such modified biochar with specific functions is known as the modified biochar [28]. There are five modification methods for biochar including chemical modification method, physical modification method, surface covering method for immersing in mineral or inorganic adsorbent, biological method, and magnetic modification method.

With regard to chemical modification, acid, alkali, hydrogen peroxide, and other activators are used to modify biochar, so as to change the surface chemical structure of biochar, so that biochar has more functional groups and microporous structures, larger specific surface area, and cation exchange capacity, and then enhance its adsorption capacity of heavy metals, nutrient elements and organic pollutants. Ding et al [29] modifies biochar with sodium hydroxide solution, removes a variety of metal ions such as Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, and Ni^{2+} in aqueous solution; after such modification, the specific surface area, surface oxygen containing functional groups, cation exchange capacity, and thermal stability of the biochar are improved, and the adsorption capacity of modified biochar to all kinds of ions is 2.6-5.8 times as much as that of the raw charcoal.

With regard to physical modification, the performance of biochar is enhanced by improving the pore structure of biochar, increasing the number of micro-pores and mesopores, increasing the specific surface area of biochar, introducing the oxygen-containing functional groups, and improving the surface variable chemical properties; compared with chemical modification, physical modification is cleaner and easier to control. In the traditional biochar pyrolysis, the energy is first converted into heat, which is then transferred from the biomass surface to the interior along a temperature gradient. However, microwave-assisted pyrolysis biochar [30] directly converts electromagnetic energy into heat at the molecular level, and the heat is transferred from the inside of the biomass to the surface. During the process of pyrolysis, the larger molecules volatilizes first. With the rise in pyrolysis temperature, the size of volatile molecules gradually decreases, among which the volatilization of smaller molecules will increase the micro-pores of biochar, and decrease the number of basic groups.

Biochar composite is a method to modify biochar by coating or impregnating different metal oxides, clay minerals and carbonaceous materials on the surface of biochar during different pyrolysis periods.
Bing Li et al. [31] adopt manganese oxide loading modification, and the adsorption capacity of modified biochar to Cd²⁺ is 81.10 mg/g, while that of the raw biochar is 32.74 mg/g, which is attributable to the developed pore structure and large specific surface area after modification. The magnetic modification of biochar is similar to the loading of carbon material onto the surface of biochar. By loading the magnetic material onto the biochar, it is possible to not only improve the adsorption capacity of biochar, but also magnetize the biochar, so that the biochar can be recycled.

By biological method, the anaerobic bacteria are used to convert organic matters into biogas and digesters, so as to obtain biochar from digestive residues. The digested biochar has the higher specific surface area and pH value, stronger anion exchange capacity, and other excellent properties. Aránet al. [32] make bagasse into biochar by means of anaerobic digestion; although less methane is produced in anaerobic digestion, and the preparation rate of biochar with bagasse subject to anaerobic digestion is similar to that with bagasse not subject to anaerobic digestion, the biochar made of bagasse subject to anaerobic digestion has the higher pH value and specific surface area, larger ion exchange capacity, stronger hydrophobicity, and more negative surface charges.

5. Improvement of acidified soil by biochar

5.1. Improvement of physical properties of soil by biochar

5.1.1. Improvement of water holding capacity of soil. The water holding capacity of soil mainly depends on the pore content, size distribution and continuity of soil. The biochar has a porous structure, so its pore distribution, particle size, mechanical strength, and connectivity have the effect on the pore structure of soil; when applied into soil, the biochar can increase the soil porosity and promote the microbial activity. After the application of biochar, due to its large specific surface area and the characteristics of loosening and porosity, the number of soil pores, the content and stability of soil aggregates can be improved, and the improvement of soil pore structure will affect the water holding capacity of soil. Studies show that with the increase in added amount of biochar, the water content of biochar will increase gradually due to the increase of pores, but when the added amount of biochar continues to increase, the water content of biochar will decrease, which is mainly related to the water repellency on the surface of the biochar [33].

5.1.2. Reduction of soil bulk density. The agricultural effect of soil varies with the bulk density. The soil with low bulk density and high content of organic matter content is more conducive to the release and maintenance of soil nutrients and the reduction of soil hardening degree, and beneficial to seed germination and saving of planting cost. Zhang Meng et al. [34] apply 25g/kg biochar to silty soil, and the soil bulk density decreases significantly from 1.52g/cm³ to 1.33g/cm³. There are three possible reasons for decrease of soil bulk density after the application of biochar. One is the “dilution effect”, that is, the bulk density of biochar is smaller than that of soil, and the total bulk density of soil decreases after the addition of biochar [12]. The second is the effect on the charge of soil colloid. The solution or suspension of organic compounds causes the clay particles to move with each other by changing the charges of such clay particles, so as to increase the permeability coefficient of the clay, increase the cracks of the clay particles, and increase the secondary porosity of the soil. This is the mechanism on the basis of which the soil compactness is reduced after the organic matters are added to soil, and the ash content in biochar may play the same role [27]. The last one is that after added to the soil, the biochar increases the friction between soil particles, thus reducing the compactness of the soil and decreasing the bulk density of the soil.

5.1.3. Promotion of carbon cycling. Nowadays, biochar has become a hotspot in research in the world, and has become recognized by the people in application potential in soil improvement. With the highly stable carbon structure, biochar can be retained in soil for hundreds to thousands of years, so that it cannot only improve the organic matter in soil for a long time, but also alleviate the greenhouse effect.
As a kind of carbon source, biochar can increase the total carbon content of the soil, giving microorganisms more carbon sources. Studies show that the soluble organic carbon in biochar can be utilized by microorganisms, and biochar, as a potent carbon source, can provide microorganisms with a continuous supply of soluble organic carbon. Adding biochar to soil is a process in which the greenhouse gases in the atmosphere are fixed into the soil directly or indirectly, so as not only to improve soil structure, but also to increase nutrient utilization rate and reduce greenhouse gas emissions [35]. Furthermore, due to the very slow decomposition, biochar can be used as a sustainable method for carbon sequestration, or used as a material for carbon emission reduction. The carbon content of biochar is very high, so the biochar added into soil can increase the organic carbon content of soil, reduce the mineralized amount of organic carbon, and improve the stability of organic carbon. As a renewable resource, biochar will become a green soil improver in substitution for fossil materials, and improve soil properties.

5.2. Improvement of chemical properties of soil by biochar

5.2.1. Increase of pH value of acid soil. The chemical properties and nutrient composition of biochar are the main factors affecting soil improvement and promoting increase in crop yield. During the preparation process of biochar, biochar is becoming alkaline with the continuous pyrolysis of organic matter and the continuous generation of ash, and the pH value of biochar increases with the rise in pyrolysis temperature and extension of pyrolysis time. Biochar is mainly composed of aromatic carbon structure, and is alkaline due to the higher alkalinity; biochar has large porosity and specific surface area, as well as contains a certain amount of nutrient elements. The pH value of biochar ranges from 7.5 to 7.8 [36]. Most of the substances contained in biochar itself are alkaline, and it is found that such alkaline substances can enter and change soil components easily, so that it is possible to increase pH value of soil and reduce acidity of soil when biochar is applied to acid soil [37]. The experiment confirms that the biochar manifests the improvement effect of sawdust biochar > sludge biochar > wheat straw biochar while increasing pH value of red soil. This rule is related to the alkalinity of biochar itself. Due to the high content of alkaline substances, sawdust biochar can achieve the most significant effect on increase of pH value of soil [38], and the effect on decrease of soil acidity within a certain range is positively correlated with the applied amount of biochar [39,40]. When studying the effect of different wheat straw biochar on soil of red soil orchard, the foreign laboratory finds that compared with the situation that the biochar is not applied, the application of biochar in the amount of 40t/hm² can reduce the capacity of orchard soil significantly, and increase the pH value of soil by 0.88 units; the biochar made at the carbonizing temperature of 700ºC can achieve the most significant effect on remediation of acid soil [41].

5.2.2. Reduction of exchangeable aluminum in acid soil. The essence of soil acidification is the process in which the hydrogen ion is increased, the aluminum ion is hydrolyzed, and the salt-base cation is decreased. Aluminum toxicity is the most important factor restricting the crop growth in acid soil. When the concentration of soluble aluminum ions in soil solution exceeds a certain limit, it will produce toxic effect on crops. Exchangeable aluminum is the main active form of aluminum in acidic soil. Adding biochar to the soil can reduce its content and mitigates its toxic effect on plants significantly [42].

Biochar contains a certain amount of salt-base cations such as calcium, magnesium and potassium. If biochar is applied into soil, such salt-base cations will exchange with exchangeable aluminum in soil so as to reduce the content of exchangeable aluminum in soil. The increase incontent of exchangeable salt-based cation will result in the increase in content of salt-based nutrients in soil and improve the fertility level of soil, especially the significant increase in exchangeable calcium and potassium [43]. The increase in content of calcium and magnesium in soil can also alleviate the toxic effect of aluminum on plants effectively, because calcium and magnesium can compete with aluminum ions for the adsorption potential on surface of plant root, and reduce the amount of aluminum ions on surface of root. Experiment confirms that the effect of biochar on exchangeable aluminum in acid soil is realized mainly by changing the pH value of soil [44]. With the increase in pH value of soil, exchangeable aluminum is
hydrolyzed into hydroxyl aluminum and partially forms aluminum hydroxide or oxide precipitation. The surface of biochar is rich in oxygen-containing functional groups. These organic functional groups can form stable chelates with aluminum, which can transform exchangeable aluminum in soil into organic complexed aluminum with low activity.

5.2.3. Inhibition of soil nitrification. Nitrification is a process in which ammonia in soil is oxidized to nitrate nitrogen under the action of microorganisms, and composed of two continuous processes completed by ammonia-oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB). In suitable environmental conditions, ammonium in soil can undergo rapid nitrification. Nitrate, the nitrification product, is not easy to be absorbed by soil colloid, so nitrification is liable to cause serious threat to the environment. Some scholars also believe that nitrification in soil will release protons, resulting in decrease of pH value [45].

Studies show that biochar can improve acid resistance of soil by inhibiting nitrification of soil [46]. Due to the large specific surface area, biochar can absorb NH$_4^+$ from soil, leading to the reduction of available NH$_4^+$ in soil, thus inhibiting nitrification [47]. In addition, biochar has a significant inhibitory effect on AOB, and the amount of AOB is positively correlated with content of nitrate nitrogen, but has nothing to do with the added amount of biochar. It is further demonstrated that biochar can inhibit AOB abundance and thus reduce nitrification in soil [48]. Biochar plays a dual role in inhibiting soil nitrification. On the one hand, the application of biochar reduces nitrification capacity and rate by inhibiting the activity of AOB and NOB, and reduces the release of protons during the process of nitrification. On the other hand, the protonation of carboxyl groups on the surface of biochar can improve the acidity resistance of soil and improve the pH buffer capacity of soil [49]. Yong et al. [50] prepare biochar without phenolic substances and conducted a control test with the untreated control group to observe the effect on AOB abundance. It is found that untreated biochar could reduce AOB abundance by 3 orders of magnitude. It is proved that the inhibition of nitrification by biochar is caused by the phenolic substances contained in biochar, and the biochar containing phenolic substances can reduce the diversity of AOB in soil.

5.2.4. Increase of nitrogen and phosphorus in soil. Nitrogen, as the most important limiting factor of crop yield, has attracted much attention in agriculture. In order to increase crop yield, a large amount of nitrogen fertilizer is used in agricultural production. However, excessive application of nitrogen fertilizer arouses a series of environmental problems. In addition, leaching loss of nitrogen is also an important reason for limiting the utilization rate of fertilizer. How to reduce leaching loss of nitrogen and increases the utilization rate of nitrogen fertilizer have attracted people’s attention [51]. In addition to nitrogen, phosphorus in the soil is characterized by easy fixation and poor mobility. Especially in acid soil, iron and aluminum have the high activity and are easy to form insoluble iron and aluminum phosphorus with phosphorus, and even occluded phosphorus with less effectiveness. Therefore, there are also the problems in acid soil such that the total phosphorus content in acid soil is not low, but the phosphorus availability is not high [52].

Biochar increases the ability of soil to hold nitrogen mainly by the following ways. One is to increase the adsorption and holding capacity of the soil to ammonium ions; due to abundant oxygen-containing functional groups on the surface of biochar, a large number of negative charges, porous structure, and large specific surface area, biochar has a strong adsorption capacity to ammonium so as to reduce nitrogen loss [53]. The second is that the increase of soil’s capacity to hold ammonium reduces the rate of soil nitrification. The third is that biochar increases the water retention capacity of soil and reduces leaching loss of nitrate nitrogen. The fourth is that the porous structure of biochar provides an activity place for microorganisms, which is conducive to the development of nitrogen-fixing microbial communities and enhances the biological nitrogen fixation capacity of soil [54]. Biochar can increase the ability of soil to retain nitrogen and improve the effectiveness of soil nitrogen. This will not only reduce the applied amount of fertilizer, but also reduce the pollution of nitrogen leaching loss to the water environment, and reduce emissions of NO$_2$ and other greenhouse gases.
In addition, biochar can also fix phosphorus by means of soil exchange sites, thus reducing the formation of Fe-P and Al-P. Also, by changing the pH value of soil, metal ions in the soil solution can be adsorbed and fixed so as to reduce the precipitation of phosphorus [55]. The increase of alkaline metal oxides in soil and the decrease of soluble aluminum in soil solution are considered to be the most important reasons for biochar to increase soluble phosphorus in soil [56]. In addition, biochar itself is also high in phosphorus content, which can be used by crops to improve the phosphorus level of soil and increase crop yield.

5.2.5. Improvement of microbial activity in soil. Biochar keeps the micro-pore structure of raw materials, provides a good “refuge” place for microbial habitat and reproduction, reduces the survival competition among microorganisms, and provides them with different sources of carbon, energies and mineral nutrients, so that they can survive and reproduce vigorously. Mahmood et al. [57] find that after applying tree ash into the soil, the activity of bacteria increases with the change of bacterial community structure, and biochar can promote the growth of bacteria. In addition, the application of biochar into soil can also change the community structure and activity of fungi in soil, and increase the number and improve the activity of soil microorganisms as a whole. With the microporous characteristics, biochar also has a good connectivity, on the basis of which it is possible to preserve water and air for a long time, and provide good environmental conditions for the growth and reproduction of microorganisms.

6. Conclusions and prospects
At present, the soil acidification phenomenon for different reasons is becoming more obvious in the whole world, so the R&D and use of soil improver is particularly important. Compared with other traditional restoration methods, biochar improver achieves the significant effect on acid reduction. The main reason is that biochar itself is alkaline, the acidity of soil can be reduced after application of biochar, and the degree of improvement is positively correlated with the applied amount of biochar. Biochar has significant effect on chemical properties of soil such as inhibiting soil nitrification, increasing nitrogen and phosphorus in soil, reducing exchangeable aluminum in soil, and alleviating aluminum toxicity. In addition, biochar improver can improve physical properties of soil to a certain extent, such as water holding capacity of soil, soil bulk density, and carbon cycling.

However, we shall not lose sight of the existing problems. At present, the application of biochar in soil is not universal, and the comprehensive consideration shall be given to the relevant characteristics of raw carbonizing materials and how such characteristics can make up for the specific defects of soil. Obviously, further research is needed to fully realize the potential of biochar as a high quality soil improver [58]. At present, the research prospect of biochar and the problems to be solved are shown as follows: First, there are many kinds of raw materials of biochar distributed widely, and there are few studies on the characteristics, environmental effects and influencing factors of biochar in different preparation conditions. Most of the studies are limited to the stage of short-term small-scale farmland and laboratory simulation, with large errors compared with actual applications, resulting in the lack of systematic and comprehensive understanding [59]. Second, in the actual soil environment, there are many factors leading to soil acidification, while most scientific experiments are conducted only for study on the single-cause restoration mechanism and the effect of biochar, showing a poor reliability of conclusion. If there are multiple factors coexisting, it is still unknown whether the restoration mechanism and effect of biochar will change [60]. Third, the current studies on soil improvement by biochar as an improver lay the emphasis on the response to the external environment, and there are less studies on the change of biochar itself; for example, whether there is any change in the physical and chemical properties of biochar as improver during the restoration and remediation process of acid soil environment [61]; in the future, it is necessary to conduct more researches on this aspect.

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