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Study on Improvement Effect of Saline-alkali Soil by Cationic Modified Biochar

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Abstract. The severe soda-alkali soil in the western Songnen Plain was used as the experimental object. Compared with the application of common biochar, the effects of modified biochar on the basic physical and chemical properties, agglomerate distribution, organic carbon and total nitrogen distribution of saline-alkali soil were analyzed. The experiment adopts the indoor culture method, and the use of common biochar (B) and iron modified biochar and calcium modified biochar is 0, 1.5%, 5% . A total of 7 treatments: CK, B1.5, B5, FBS1.5, FBS5, CBS1.5, CBS5. The results show: 1. Modified biochar significantly reduced soil pH with a maximum reduction of 12.2%. Both biochar and modified biochar significantly reduce soil ESP. The reduction effect of FB5 was the most significant in each treatment, which was 58.2% lower than CK, followed by FB5, which was 41.8% lower than CK. The introduction of cations and the significant reduction of ESP showed strong Na+ substitution and adsorption capacity, thereby alleviating soil salt accumulation and improving soil basic physical and chemical properties. 2. Both modified biochar and ordinary biochar increased the content of soil microaggregates (0.053-0.25mm). The modified biochar was significantly higher than ordinary biochar, and the function of improving soil structural stability was stronger. Among them, CBS improvement effect is better than FBS. The ratio of CBS5 treatment increased the microaggregate to the highest, with an increase of 66.4%; the increase of CBS1.5 treatment was 56.2%; the proportion of FBS5 and FBS1.5 microaggregates increased by 51.1% and 32.2% respectively. The geometric mean diameter (GMD) of all treatments was higher than that of CK treatment, in which CBS5 treatment significantly increased GMD by 18.6%; modified biochar treatment increased mean weight diameter (MWD), of which CBS5 significantly improved MWD. The increase was 8.8%.

1. Introduction

Saline-alkali soil is a general term for various types of soils with different degrees of salinization and alkalization. It is heavily influenced by the saline-alkali composition in the soil, and is formed by the combination of different natural environmental factors and human activities. Salt Alkaline soil is widely distributed in more than 100 countries and regions around the world, widely distributed, and difficult to repair and use. The Songnen Plain is located in the northeastern part of China. The salt composition in the soil is dominated by Na_2CO_3 and $NaHCO_3$, with an area of more than 3 million hm^2. It is the largest distribution area of soda-type saline-alkali soil in China. At present, biochar is more and more widely used in the field of saline-alkali land restoration. Studies have shown that biochar can reduce the soil bulk density of saline-alkaline soil and improve soil structure[1]. However, the effect of biochar on improving soil structure is not significant for soda ash soil, because biochar cannot fundamentally reduce soil exchangeable Na^+ content. The degree of alkalization of soda-alkali soil is too high, resulting in the dispersion of soil particles and the formation of a good agglomerate structure. According to research, biochar application increases salt saturation and increases soil pH value [2], and its cation exchange capacity is limited in soda alkaline soils with high salinity. The multivalent cations on the surface of biochar (such as Ca^{2+}) can replace the Na+ on the surface of soil clay, reduce the dispersibility of soil clay, promote the flocculation of mineral colloids and agglomeration of cosmids to form micelles or microaggregates. In this project, the biochar modification preparation method was designed from the perspective of enhancing the negative load capacity of biochar cations and verified its improvement effect on saline-alkaline soil.

2. Materials and methods

2.1 Test materials
The soil used in the experiment was paddy soil sampled from Jilin Songyuan, and the planting period was ten years. The soil sample has a pH value of 8.86, an EC value of 0.453 mS/cm, and a maximum moisture content of 48.70%.

2.2 experimental design

2.2.1 Preparation of biochar
The biochar used in the experiment was prepared from corn stover. After washing a certain amount of corn stover, the oven was dried at 75°C, dried, and weighed. The plant sample was pulverized by a pulverizer and passed through a 20 mesh sieve for use. The corn stover powder was pyrolyzed in a vacuum muffle furnace at 400°C for 4 h, cooled and weighed, and the biochar was crushed and sieved for use. The straw biochar has a pH value of 8.31 and an EC value of 2.23 ms/cm. The biochar used in the test was air-dried, ground, and passed through a 0.15 mm sieve.

2.2.2 Preparation of modified biochar
Biochar made from corn stover was selected as raw material, and acidified in a 1 mol/L hydrochloric acid solution at a solid-liquid ratio of 1:10 for 2 h, filtered and dried. The mass ratio of Fe^{3+}/Ca^{2+} to biochar was 0.8, and it was soaked in a salt solution of Ca^{2+} and Fe^{3+} for 2 hours, dried at 80°C, and placed in a muffle furnace at 400°C for 4 hours. Composite biochar modified material. After natural cooling, it was ground and passed through a 0.15 mm sieve for use.

2.2.3 Culture test of soda saline-alkali soil
Through indoor culture experiments, the improvement effect of loaded cationic bio-modified carbon materials on heavy saline-alkali soil was studied. The culture experiment consisted of 7 treatments, without adding any material control (CK), adding 1.5% of ordinary biochar (B1.5), adding 5% of ordinary biochar (B5), the amount added was 1.5% iron modified biochar (FBS1.5), 5% iron modified biochar (FBS5), 1.5% calcium modified biochar (CBS1.5), added A 5% calcium modified biochar treatment (CBS5). Each treatment was repeated 3 times. After the biochar 1 mm sieve, mix with the 2 mm sieve dry soil in the above ratio. The amount of mixed soil sample added to each flask is 200 g (total weight of air-dried soil and added materials), distilled water is added to 60% of the maximum water holding capacity in the field, and the cap is covered, but not completely sealed for gas exchange. . The culture was carried out under the constant temperature of (25±1) °C, and the water was supplemented by the weighing method during the cultivation to keep the soil water content constant. The pH and EC of the cultured soil samples of the 2nd, 7th, 18th, 35th and 54th day were measured after air drying. The water-stabilized agglomerate distribution, carbon-nitrogen content of each fraction-level agglomerate, and CEC were determined on the 54th day.

2.3. Analytical methods
pH, EC value: solid-liquid ratio 1:5, shaking for 3 min, standing for half an hour, using a multi-parameter conductivity meter (Mettler Toledo S479 SevenExcellence, SUI) measuring instrument to determine the pH and EC of the extract.

Grading and calculation of soil aggregates: The soil agglomerates were classified by wet sieve method [3]. Three soil samples were taken for each treatment, 100 g each, and the soil samples were soaked in deionized water for 20 min and then poured into a sieve. The sieve pore size is 2, 0.25 and 0.053 mm from top to bottom, respectively. It is sieved at a frequency of 20 r/min for 15 min with agglomerate analyzer, and the soil sample is classified into <0.053 mm, 0.053~0.25 mm, 0.25 mm~2 mm and >2 mm four-grain grade, the obtained agglomerates are transferred to an aluminum box, dried at 50℃, The average weight diameter (MWD) and the geometric mean diameter (GMD) were calculated according to the formula (1) and formula (2) using the particle size aggregate data obtained after the wet sieve.

$$MWD = \sum_{i=1}^{n} X_i W_i \quad (1)$$

$$GMD = \sum_{i=1}^{n} (\ln X_i) W_i \quad (2)$$

Soil cation exchange capacity (CEC): Determination of soil cation exchange capacity using sodium acetate-flame photometry.

Calculation of soil alkalization degree: alkalization degree = (exchangeable sodium ion content / cation exchange amount) ×100%, wherein the amount of cation exchange is determined by ammonium acetate-centrifugal exchange method [4].

Soil total carbon total nitrogen: 3.00 g of soil sample was weighed into the small mash from each treatment grade, the inorganic carbon in the soil sample was removed with 1 mol/L hydrochloric acid solution, and the soil sample was baked at 60°C. It is slightly moistened and dried in a vacuum drying oven at 100°C for 10 h. The soil sample is dried by ball milling, and the whole carbon all nitrogen is determined by a fully automatic carbon and nitrogen analyzer.

2.4 Data Processing
The test data were recorded and sorted by Excel. The data were analyzed by ANOVA using SPSS 22, and multiple comparisons were performed by LSD method (α=0.05). The data was compiled using Origin8.0 software.

3. results and analysis

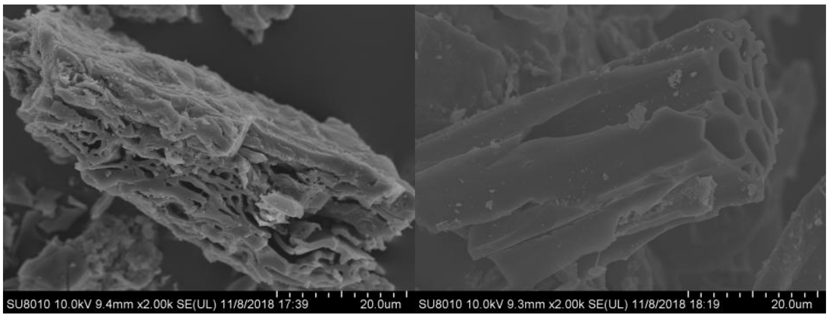
3.1 Performance parameters of modified biochar
Table 1 pH and EC of Modified biochar

	pH	EC(mS/cm)
Unmodified	8.10	2.23
Iron modification	1.76	6.29
Calcium modification	5.56	12.06

The performance of cationic biochar modified materials was characterized. The characterization indexes mainly include pH, EC and SEM. It can be seen from Table 1 that the pH of the original biochar is alkaline, the pH becomes acidic after modification, and the EC value is greatly improved.

3.1.1 SEM figures

It can be seen from the electron micrograph of Fig. 1 that the surface of the biochar before modification is smooth, and the surface is roughened by chemical etching after modification, and contains a large amount of particulate matter, indicating that the cation is successfully loaded. The surface of the unmodified biochar is mainly microporous, and the surface pore diameter of the modified biochar is obviously increased, which may be due to the dissolution and erosion of hydrochloric acid.



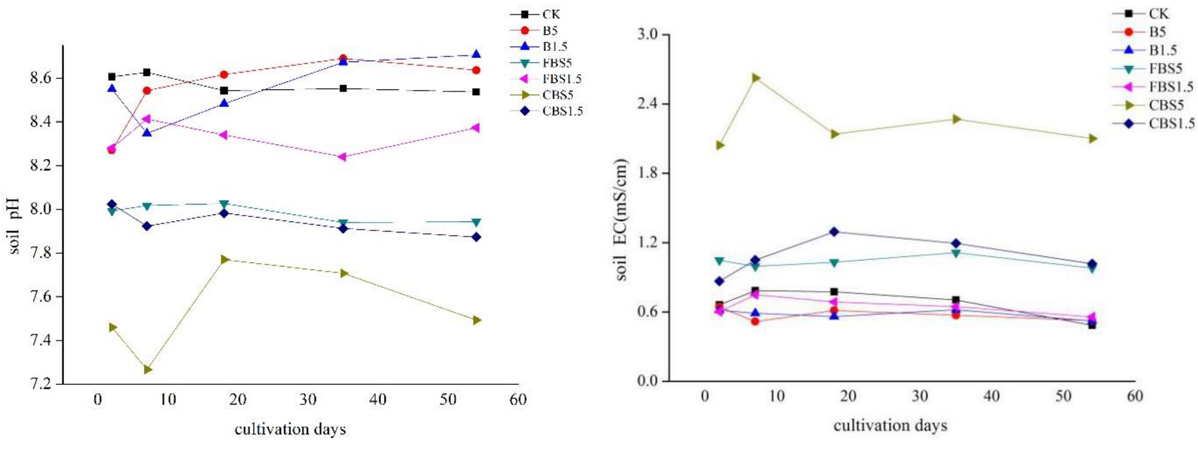
(A) (B)

Figure 1 Scanning electron microscopy image of biochar (A) and modified biochar (B)

3.2 Effects of different treatments on saline-alkaline soil

3.2.1 Effects on pH

The pH of the soil can reflect the degree of alkalization of the saline-alkali soil to some extent. As shown in Fig. 2, the pH of the CK treatment became stable at 18 days, and the subsequent pH fluctuated around 8.5. Conventional biochar treatment increased pH of the soil. Concretely, pH of the soil treated with conventional biochar gradually increased with time. When it became stable, the pH of the soil was between 8.6 and 8.8. The modified biochar treatment significantly reduced pH (P <0.05, the same below), in which the CBS5 treatment decreased the most, with a decrease of 12.2%; then became the CBS1.5 treatment and the FBS5 treatment, with the decrease of 7.8% and 7.0% respectively; FBS1.5 treatment had the smallest reduction, with a decrease of 1.9%.



(A) (B)

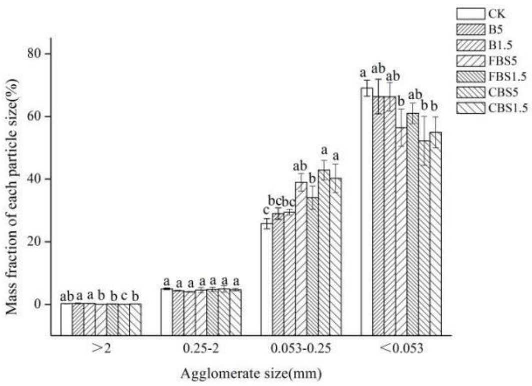
Figure 2 (A) Trends in pH of different treated soils (B) EC trend of different treated soils

3.2.2Effects on EC

Electrical Conductivity (EC) is an indicator of the amount of soluble salts in the soil to assess the extent of soil salinity stress on plants. As shown in Fig. 2, both the conventional biochar treatment and modified biochar treatment significantly increased the EC value of the soil at first of incubation. This is because the modified biochar used in CBS and FBS treatment carried more Ca^{2+} and Fe^{3+}, which increased the content of polyvalent metal cations in the soil. As the number of culture days increased, the EC of the modified biochar group showed a downward trend.

3.2.3Effects on soil water-stable aggregates

Agglomerates are the basic unit of soil structure and are closely related to soil nutrient maintenance and supply. As shown in Fig. 3, compared with CK treatment, the content of microaggregates (0.053~0.25 mm) in other treatments was significantly higher than that in CK treatment, and the effect of modified biochar on microaggregate formation was better than that of common biochar. Among them, the increase of CBS5 was the highest, with an increase of 66.4%; the increase of CBS1.5 was the second, the proportion of micro-aggregates increased by 56.2%; the proportion of treated micro-aggregates of FBS5 and FBS1.55 increased by 51.1%, 32.2%, respectively; ordinary biochar treatment was not significantly different from CK-treated cohesive particles (<0.053 mm); Except FBS1.5 treatment, the modified biochar-treated cohesive particles (<0.053 mm) were significantly decreased compared to CK, in which CBS5 had the highest proportion of sticky powder (<0.053 mm), which was 24.4%. The geometric mean diameter (GMD) of all treatments was higher than that of CK treatment, in which CBS5 treatment significantly increased GMD by 18.6%; except for B1.5, the other treatments increased the average weight diameter (MWD), of which only CBS5 was significant. The MWD was upgraded by 8.8%. The ordinary biochar reduces MWD, but it is not significantly different from CK.



Note: Different letters on the same-grained aggregate column represent the difference between treatments (P<0.05), the same below.

Figure 3 Composition of soil water-stable aggregates in different treatments

Table 2 Geometric mean diameter (GMD) and mean weight diameter (MWD) of different treated soils

Treatment	MWD/mm	GMD/mm
CK	0.136±0.007b	0.082±0.003b
B1.5	0.131±0.010b	0.083±0.008ab
B5	0.135±0.002b	0.083±0.008ab
FBS1.5	0.141±0.010b	0.088±0.005ab
FBS5	0.141±0.011b	0.092±0.008ab
CBS1.5	0.145±0.009b	0.094±0.006ab

CBS5	0.148±0.005ab	0.097±0.009a

Note: Different letters in the same column represent the difference in significance level (P<0.05).

3.2.4. Effect of ESP

The degree of sodium alkalinity (ESP) is the percentage of exchangeable Na^+ adsorbed on the soil colloid, which is the percentage of cation exchange. It is the method for judging the degree of soil salinization. As shown in the data in Table 3, both modified biochar treatment and biochar treatment significantly reduced soil alkalinity compared to CK treatment. FB5 had the best effect on ESP reduction in each treatment, which was 58.2% lower than CK, followed by FB5, which was 41.8% lower than CK.

Table 3 Degree of alkalization of different treated soils

Treatment	CK	B1.5	B5	FB1.5	FB5	CBS1.5	CBS5
ESP（%）	20.6 ±0.6a	14.7 ±0.4e	12.1 ±0.3c	13.7 ±0.2b	8.6 ±0.3d	13.1 ±0.5b	12.0 ±0.4c

3.2.5 Effect of carbon content and contribution rate of each grade

Soil organic carbon (SOC) is an important indicator for evaluating soil fertility. As shown in Table 4, both the common biochar treatment and the modified biochar treatment significantly increased the organic carbon content in the soil, and the higher the applied amount, the higher the increase of the organic carbon content in the soil. Among them, the increase of B5 and FBS5 was the most prominent, with an increase of 175.0% and 165.6%, respectively.

Table 4 Total soil organic carbon and total nitrogen content of different treated soils

Treatment	CK	B1.5	B5	FBS1.5	FBS5	CBS1.5	CBS5
SOC(g/kg)	12.852 ±0.814d	18.375 ±1.264c	35.345 ±3.165a	23.971 ±0.651bc	34.135 ±1.213a	19.314 ±1.046c	25.149 ±3.940b
TN(g/kg)	1.917 ±0.050a	1.608 ±0.068b	1.857 ±0.097a	1.510 ±0.014b	1.804 ±0.062a	1.535 ±0.064b	1.510 ±0.069b

Each treatment significantly increased the SOC content of microaggregates (0.053~0.25 mm) and sticky particles (<0.053 mm). Except for FBS5 the SOC content of the granular aggregates of sticky powder (<0.053 mm) was the highest compared to the SOC content of different treated agglomerates, and the remaining treatments had the highest SOC content of large agglomerates (>0.25 mm). Among them, compared with the CK group, CBS5 and B5 significantly increased the SOC content of large agglomerates (>0.25 mm); the increase of CBS5 was 25.9%; the increase of B5 was 19.9%. As shown in Fig. 5, each treatment is that the cohesive particles (<0.053 mm) have the highest contribution rate to SOC, ranging from 69% to 85%. Among them, the common biochar treatment group increased the contribution rate of viscous particles (<0.053 mm) to SOC; the modified biochar treatment reduced the contribution rate of viscous particles (<0.053 mm) to SOC.

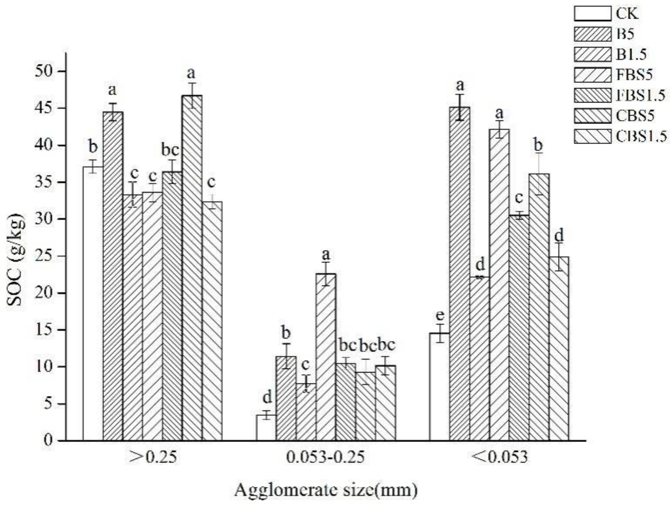


Figure 4 Different grades of soil carbon content in different treatments

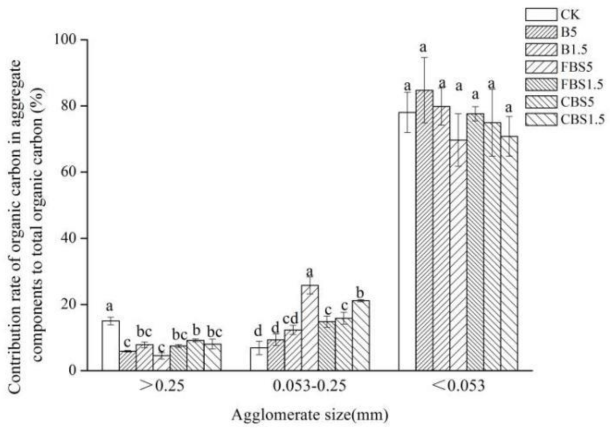


Fig.5 Contribution rate of organic carbon (SOC) of all aggregates in different soils to total organic carbon

3.2.6Effect on nitrogen content and contribution rate of each grain size

Each treatment significantly reduced the total nitrogen content of the soil. Compared with different size aggregates, the total nitrogen (TN) content of the large agglomerates (>0.25 mm) was the highest, and the microaggregates (0.053~0.25 mm) had the lowest TN content; each treatment reduced the large agglomerates (The TN content of >0.25 mm), and microaggregates (0.053~0.25 mm) was significantly lower except B5 and FBS5. The microaggregate (<0.25 mm) TN content increases with the amount of biochar or modified biochar applied.

The contribution rate of the different agglomerate size fractions to TN of all treatments showed a decrease with increasing grain size. Only FBS5 significantly increased the contribution rate of microaggregates (0.053~0.25 mm) to TN in whole soil, increasing by 53.9%; B5 and CBS5 significantly reduced the contribution rate of microaggregates (0.053~0.25 mm) TN, reducing by 4.0%, 2.5%, respectively. The contribution rate of the large agglomerates (>0.25 mm) to the whole soil TN was significantly reduced, and the FBS5 decreased the most, which was 42.3%

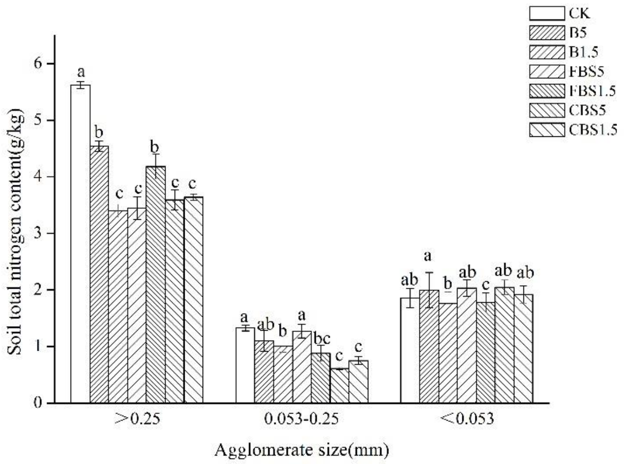


Figure 6 Different levels of nitrogen in different treatment soils

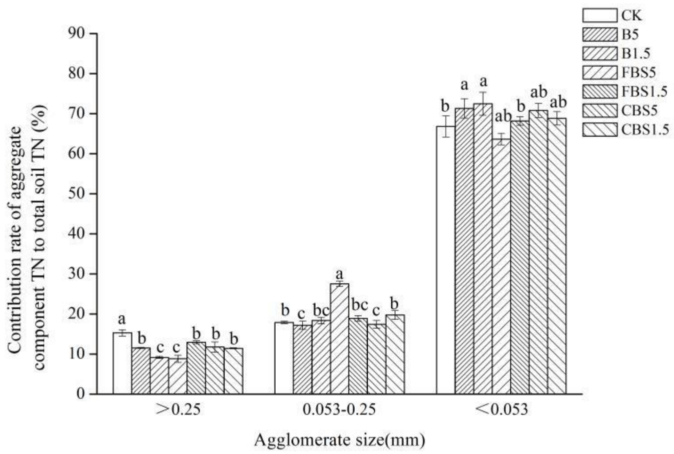


Fig.7 Contribution rate of total nitrogen (TN) to the total soil TN of different aggregates in different treatments

4. discussion

4.1. Effect on basic physicochemical properties of saline-alkali soil

pH in the range of 5.5-8 is more conducive to the accumulation of soil nutrients and the growth of microbial communities [5], reducing the pH of saline-alkali soil is the key to improving saline-alkali soil. In this test, the pH of CK was basically stable at 18 days and was maintained at around 8.5. Ordinary biochar treatment increases the pH of the soil because of the presence of alkaline substances such as potassium carbonate, sodium carbonate, calcium oxide, and basic functional groups in ordinary biochar[6]. The modified biochar treatment significantly reduced the pH of the soil, and the CBS5 treatment decreased the most. This is because biochar is modified with hydrochloric acid, so it is acidic after modification, so the pH will drop significantly after being applied to the soil.

A large amount of Na+ adsorbed by soil colloids in saline-alkaline soils produces salt stress, which is an important factor affecting the normal growth of crops [7]. EC is an indicator reflecting the content of soluble salts in the soil. The Fe^{3+} and Ca^{2+} introduced by the modified biochar treatment group increase the soil EC value. Compared with CK treatment, both modified biochar treatment and biochar treatment significantly reduced soil alkalization (ESP), and the effect of modified biochar reduction was more obvious at the same concentration. This is because the large amount of cations introduced by modified biochar can be used as a source of nutrients for crop minerals. On the other hand, it can exchange Na^+ adsorbed by salinized soil colloids, reduce soil salt stress and reduce ESP. In summary, FBS and CBS increased the EC value to a certain extent, and fully exchanged Na^+ in saline-alkali soil, which improved the soil properties and crop growth.

4.2. Effect on alkaloid aggregates of saline-alkali soil

In this experiment, the addition of biochar significantly increased the content of soil microaggregates (0.053-0.25 mm), and the modified biochar effect was better than ordinary biochar, and the modified biochar treated sticky powder (<0.053 mm) The content is significantly lower than that of CK. This is consistent with previous studies [8], that is, "multi-level agglomeration theory", indicating that the application of biochar promotes the aggregation of soil colloidal particles to form micro-agglomerates, and the single-grained and micro-agglomerates are gradually stepped through various bonding effects. Formation of sticky particles, microaggregates and large agglomerates. The formation of soil agglomerates requires appropriate time. In this experiment, most of the clay particles (<0.053 mm) agglomerate each other to form soil microaggregates (0.053-0.25 mm). Modified biochar promotes the formation of soil aggregates better, which may be due to the formation of a more suitable pH after the addition of modified biochar, while significantly reducing ESP, improving soil properties[9,10]; at the same time, studies have found that biomass carbon will form a "cation bridge" from aromatics and cations[11]. In this test, the modified biochar enhances the multivalent cation-biochar-soil clay due to the introduction of cations. The bridging effect is better than ordinary biochar. The specific mechanism needs further research.

MWD and GMD are commonly used indicators to reflect the size distribution of soil aggregates. The addition of biochar significantly increased the geometric mean diameter (GMD) of the soil, and the effect of CBS5 was the most significant. Except that the difference between B5 treatment and CK was not significant, the groups added with biochar also increased the average weight diameter (MWD) of the soil, and the effect of CBS5 was significant. At the same time, MWD and GWD increase with the addition of modified biochar after the addition of modified biochar, which is consistent with previous studies[12], which is the cementation of organic macromolecules contained in biochar itself. For reasons of agglomeration, modified biochar-supported cations enhance this effect. The test results show that the addition of biochar improves the stability of soil structure, and CBS5 has the best effect.

4.3 Effect of biochar on carbon and nitrogen contents and contribution rate of aggregates with different particle sizes in saline-alkaline soil

In this experiment, both the common biochar treatment and the modified biochar treatment significantly increased the organic carbon content in the soil, and the organic carbon content increased with the increase of biochar addition. The organic carbon content of the cohesive particles (<0.053 mm) increased the most in each treatment compared with the change of each particle size. The contribution rate of organic carbon of modified biochar sticky powder (<0.053 mm) was significantly lower than that of common biochar and granular aggregate.Some biochars may still be in microaggregates in this experiment. The process of cementation, so the addition of biochar increased the organic carbon content of the sticky powder (<0.053 mm). At the same time, the modified biochar promoted the conversion of sticky powder particles (<0.053 mm) to soil microaggregates (0.053-0.25 mm), resulting in a significant increase in the content of microaggregates (0.053-0.25 mm), Therefore, the contribution rate of organic carbon of the sticky powder (<0.053 mm) is lowered.

The results showed that the organic carbon and total nitrogen in the soil had the same trend with the particle size of the agglomerates, that is, the SOC content in each particle size was satisfied: sticky powder > microaggregates > large agglomerates; the total nitrogen content in each grain level was also Sticky powder > microaggregates > large agglomerates. and the ammonium nitrogen in the alkaline nitrogen is hydrolyzed to ammonia gas under alkaline conditions, and the modified biochar creates more The proper soil environment, so the loss of nitrogen is also greater.

5. Conclusion

In this experiment, the modified biochar loaded with Fe^{3+} and Ca^{2+} was designed and compared with ordinary biochar. The indoor saline-alkaline soil culture experiment was carried out with different application rates. The test results showed:

1.Compared with ordinary biochar, modified biochar significantly reduces the pH value of saline-alkaline soil, exhibits strong Na+ substitution and adsorption capacity, alleviates soil salt accumulation, and reduces high salinity in saline-alkaline soil to soil structure. The destruction has improved the basic physical and chemical properties of the soil.

2.Both modified biochar and ordinary biochar increased the content of soil microaggregates (0.053-0.25 mm). The modified biochar was significantly higher than ordinary biochar, and the function of improving soil structural stability was stronger.

3. The application of modified biochar and common biochar increased soil organic carbon and reduced soil total nitrogen, but the effect on the contribution rate of organic carbon and total nitrogen at each grain level was different. The specific mechanism needs further the study.

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