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Remediation Effects in Maize-straw-derived Biochar of Cadmium-contaminated Soil

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Abstract

To clarify the effects and the application value of biochar on remediation of cadmium (Cd)-contaminated soil, a pot experiment was conducted with the typical farmland soil suffering from Cd-contamination derived from the contaminated irrigation area at countryside of Shenyang in China. The results showed that maize-straw-derived biochar which used dry distillation of carbonization technology under deficient oxygen and low temperature (400-450℃) had well characteristic of structure and physical and chemical properties. It could reduce the available cadmium ion enrichment of Cd-contaminated soil to a certain extent that with the “passivation or inhibitory” effect related the time-lapse. The Soil pH had fluctuation for the biochar amendment, but did not appear the “continuously higher or lower” phenomenon. And also, the biochar significantly improved the soil organic matter and available nutrient with additive effect performed as time-lapse. As the same time, the biochar amendment significantly reduced the cadmium content of rice grain by an average of 33.01% decreased than that of control (CK). This result suggests that maize-straw-derived biochar is a kind of deal adsorption material for Cd-contaminated soil remediation which has good application prospect.

Keywords: Biochar, Cadmium-contaminated, Rice yield.

1. Introduction

With the rapid development of modern industrialization, urbanization, and industrial emissions, the city life sewage and garbage pollution gradually intensified especially the unreasonable use of pesticides and chemical fertilizer, causing the farmland quality gradually declined [1]. In particular, the heavy metal pollution of farmland, have become one of the important problems of the government, experts and the public's attention. According to incomplete statistics, china's heavy metal pollution of current farmland has been more than 2×107hm2 [2], resulting in the crop production reduced up to 1×107t. According to statistic, the cadmium-contaminated farmland in China has more than 2×105 hm2, with an annual output of crop grain with cadmium content exceeding standard has reached 14.6×108 kg. Heavy metal pollution not only reduce crop yield, but also threaten human health through the “food-health” chain, becoming “invisible-killer” affect national grain production security, food safety and society sustainable development. At present, the main method to deal with the heavy metal pollution by precipitation, complexation, irrigation, antagonistic, and electro- chemical method, etc. But there are generally exist outstanding problems such as high cost, get effective slowly, and has ecological security risks. Therefore, to explore effective remediation ways of heavy metal polluted farmland, new comprehensive remediation technology which have low cost, ecological security, and environment-friendly has become urgent problems to be solved. Highly aromatic carboxylic acid esterification, rich micropore structure, large

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specific surface area and strongly adsorption ability [3, 4] was the biochar obvious characteristic that made it become an ideal material for agriculture and environmental protection. Therefore, the biochar technology and its application in recent years has become one of the hot topics, maybe provide a new way for heavy metal pollution remediation [5]. At present, domestic and international researches showed that biochar as an adsorbent, had a certain inhibitory or adsorption effects on heavy metal ions, chlorobenzenes organic pollutants, and pesticide residues, thereby reducing the pollutant concentration and bioavailability [6-10]. But the current research of biochar to the heavy metal pollution were centralized under the laboratory condition, so there was less relevant reports on the effects of biohcar in heavy metal pollution contaminated-farmland.

In this paper, the maize-straw-derived biochar which used as input material by outer source was conducted to clarify the remediation effects of biochar on the typical farmland of heavy metal contaminated, and explore the possibility of biochar application on heavy metal contaminated- farmland remediation.

2. Experimental Procedure

The soil used come from the Cd-contaminated area where by contaminated area at the countryside of Shenyang in China, which was undisturbed topsoil of the layer 0-20cm, the physical and chemical properties were shown in Table.1

Table.1 The experimental soil physics and chemistry property

pH	Organic matter ($g·kg^{-1}$)	Total nitrogen ($g·kg^{-1}$)	Available nitrogen ($mg·kg^{-1}$)	Available phosphorus ($mg·kg^{-1}$)	Available potassium ($mg·kg^{-1}$)	Cation exchange capacity ($cmol·kg^{-1}$)	Total cadium ($mg·kg^{-1}$)
6.82	13.16	3.28	149.81	82.86	304.47	21.78	1.76

The rice variety used for experiment was japonica rice. Maize-straw-derived biochar made by dry distillation of carbonization technology under oxygen deficient and low temperature (400-450℃) with diameter of 0.15-0.18mm. The biochar physical and chemical properties were set in Table.2

Table.2 Main physics and chemistry property of maize-straw-derived biochar

pH	Fixed carbon (%)	Ash (%)	Volatile (%)	BET measurement surface area ($m^2 • g^{-1}$)	Langmuir measurement surface area ($m^2 • g^{-1}$)	Total pore volume ($ml • g^{-1}× 10^{-3}$)	Barrett-Joiner-Halenda pore ($ml • g^{-1} ×10^{-3}$)	MK-Plate pore ($ml • g^{-1}× 10^{-3}$)	Micro porous pore ($ml • g^{-1}×10^{-3}$)	Average pore diameter (nm)
9.28	60.18	13.46	26.36	1.46	2.41	6.88	5.36	4.75	0.98	21.58

The experiment was carried out in Shenyang Agricultural University, adopted pot experiment method and randomized block arrangement. It was set for 4 treatments with 3 repeats of 10 pots for each treatment, shown as follows. The treatment was set as CK (no biochar), C1 (5g•kg-1 of biochar application), C2 (10g•kg-1 of biochar application). According to the standard amount of biochar application, each pot was filled with Cd-contaminated soil of 8kg (only for dry soil), which would be blended fully and prepared for use before 1 month of rice transplanting stage. Rice seedlings were transplanted respectively in May 27 with one plant per hill. Equipped with defend canopy, which would prevent the water outflow in pot. Date statistical analysis was conducted using SPSS17.0. The difference among means of experimental data was determined by Duncan's multiple range tests using analysis of variance (one-way ANOVA) with a significant level of 0.05.

3. Results and discussion

3.1 Maize-straw-derived biochar microstructure and physicochemical properties

We could see the main bundle of maize-straw integrated organizational structure was complete before carbonization (Fig.1).But after heating, pyrolysis, and charring carbonization process, could obviously see that some original organization (unstable or volatile parts) of maize-straw disappeared, which formed charring-lignin to prop up the porous frame with microstructure clearly and abundantly (Fig. 2). This structure was an important basic physicochemical of biochar which had large specific surface area and strong absorbability. Therefore, maize-straw-derived biochar in soil could adsorb more organic matter, nutrient or heavy metal ions, which would play an important role on soil physicochemical properties, nutrients and environmental pollution.

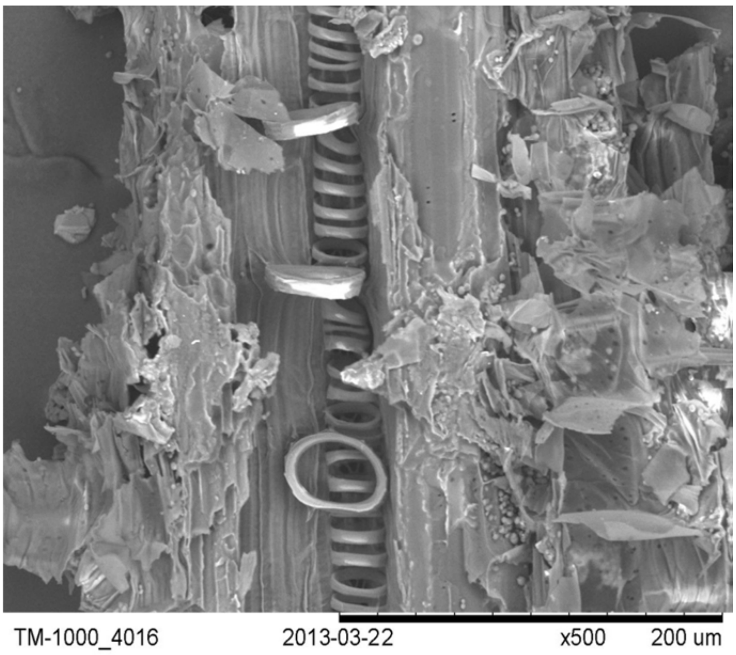

Fig.1 SEM micrographs of the maize straw (Before carbonized)

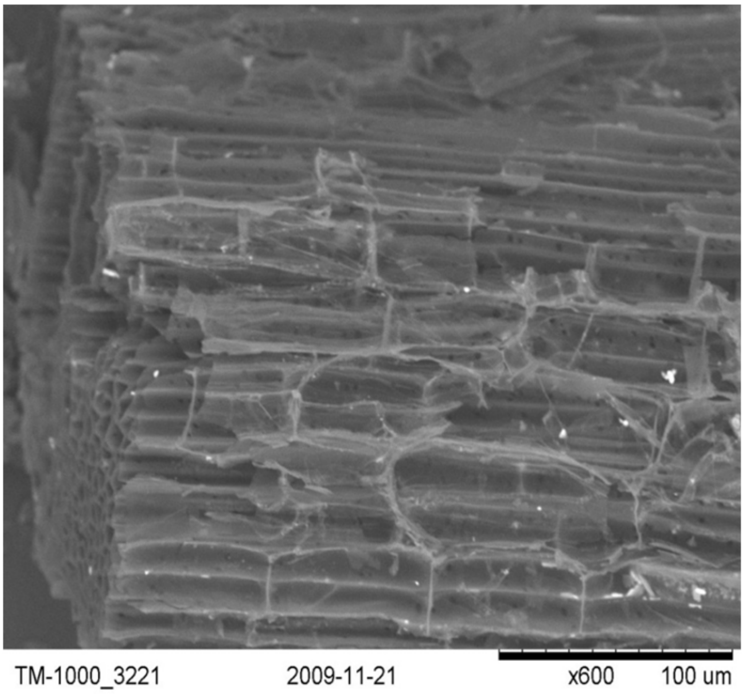

Fig.2 SEM micrographs of the maize-straw-biochar (After carbonized)

Maize-straw-derived biochar was presented alkaline, with large specific surface area, fixed carbon and ash content, especially had micropore richly. In particular, it had higher C element content which was not to be decomposed in soil, and also contained essential elements (N, P, K, S) and others mineral elements (e.g. Ca, Mg, Fe) which crop needed. Therefore, it would play a stable support role in soil, and provided more nutrition for crop. To sum up, the maize-straw-derived biochar had good structure and physicochemical properties that would play important role in soil amendment, reducing heavy metal pollution, and increasing crop yield.

Table.3 Main physics and chemistry quality of maize-straw-derived biochar

pH	Fixed carbon (%)	Ash (%)	Volatile (%)	BET surface area ($m^2 \cdot g^{-1}$)	Total pore volume ($ml \cdot g^{-1} \times 10^{-3}$)	Barrett-Joiner-Halenda pore ($ml \cdot g^{-1} \times 10^{-3}$)	Microporous pore ($ml \cdot g^{-1} \times 10^{-3}$)	Average pore diameter (nm)
9.28	60.18	13.46	26.36	1.46	6.88	5.36	0.98	21.58

Table.4 Main element composition of maize-straw-derived biocharr

Elements	C	N	P	K	S	Na	Mg	Ca	Fe	Al
Maize-straw-derived biochar content (%)	70.48	1.55	0.81	1.78	0.66	0.02	1.26	0.59	0.12	0.21

3.2 Effect of biochar on pH of Cd-contamination soil

With biochar amendment, the differences of soil pH at rice tillering stage was small. But at the jointing stage, soil pH of treatment C2 had improved that had significant difference with other treatments. The results indicated that high rates of biochar amendment had obvious enhancing effect on the soil pH. To the heading stage, the soil pH of biochar treatments were decreased compared to the control, shown as C2<C1<CK. But with the time prolonged, to the filling stage, the biochar treatments increased that were higher than control and shown as with biochar amendment increased the effect strongly. In general, the soil pH of biochar amendment showed different in each rice growth period, showing wave-motion trend while the control was relatively smooth which had no large fluctuations. Obviously, the biochar had strongly effect on soil pH, but the phenomenon did not show continued increase or decrease (Fig.3).

The biochar was alkaline, so it applied into soil could have a direct effect on soil pH. In the rice early growth stage, biochar presented enhance effect to soil pH that was consistent with the result of Glaser, et al research [11]. For the other stages, the fluctuation of soil pH showed "reducing first and increasing later" but did not show sustained increase or decrease trend. This may be related to the biochar adsorption for different organic substances and base cations, changed the amount of soil cationic and its "activity degree". The biochar surface active sites also maybe generate competitive adsorption with organic matter and base cations, its adsorption amount and intensity was related to the soil ecological environment changed, thus resulting in soil pH fluctuated.

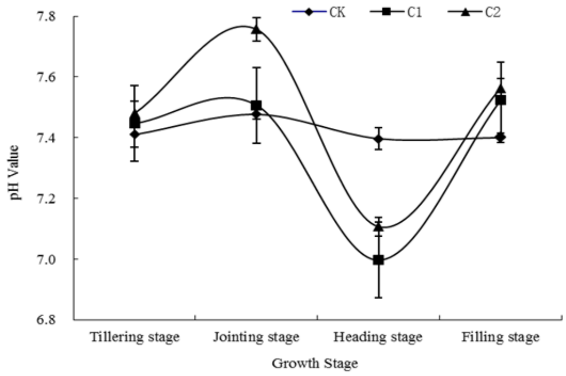

Fig.3 Maize-straw-derived biochar affected on soil pH at different rice growth stages

3.3 Effects of biochar on available nutrient of Cd-contamination soil

3.3.1 Effect of biochar on available nitrogen

At the tillering stage, the soil available nitrogen content of biochar treatments were obviously higher than that of control that shown decreased with the increased of biochar amendment. At the jointing stage, the treatment C2 was lower than that of control, but the difference was not significant. At the heading stage, biochar treatments were shown the same as tillering stage. But with the time lapsed, to the filling stage, the available nitrogen content of treatment C1 and C2 were greatly improved, shown as C2>C1>CK. Among them, the higher rate of biochar amendment (C2) which had obviously effect on soil available nitrogen that was significant difference with control. In addition to the jointing stage, the low biochar amendment (C1) could obviously improve soil available nitrogen in the rice early growth stage, but the higher rate of biochar amendment (C2) was effect more strongly in the later growth stage (Fig.3).

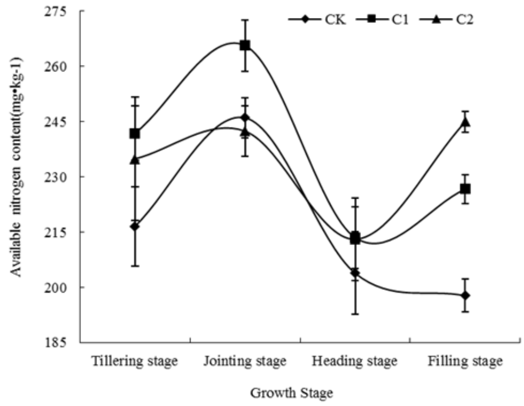

Fig.3 Maize-straw-derived biochar affected on soil available nitrogen at different rice growth stages

3.3.2 Effect of biochar on available phosphorus

At the tillering stage, biochar treatments (C1, C2) were significantly higher than that for the control by 12.79%, 10.9%, respectively, shown as with C1>C2>CK. At the jointing stage, the difference of biochar treatments with control was further increased, The biochar treatment of C2, C1 was higher than that of control by 12.12%, 16.74%, respectively, thereby marking an average increase of 14.43%. To the heading and grain filling stage, the biochar treatments were had continued increase which reduced the difference with control. On the whole, biochar amendment had continuous and obvious effects on the soil available phosphorus content. In the early growth stage, low biochar amendment had relatively obvious effect. But with time lapsed, the high rate of biochar amendment gradually effect strongly that shown a cumulative effect to some extent (Fig. 4).

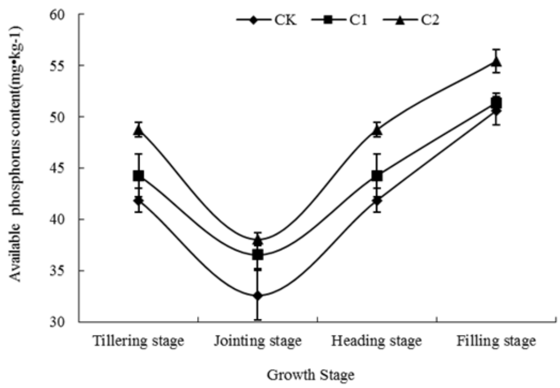

Fig.4 Maize-straw-derived biochar affected on soil available phosphorus at different rice growth stages

4. Conclusions

The maize-straw-derived biochar which used dry distillation of carbonization technology under oxygen deficient and low temperature (400-450℃) had well basic characteristic of structure and physicochemical properties. The maize-straw-derived biochar which was used into the Cd-contaminated soil could significantly improve the soil physicochemical properties that had leading regulatory effect on soil pH, and increased the soil available nutrients and organic matter content, the soil overall production capacity improved. Especially, the biochar had a certain "passivation or inhibitory" effects on reducing the soil cadmium ion concentration in the late rice growth stage, and also significantly reduced the cadmium content of rice grain that increased food safety. To sum up, maize-straw-derived biochar is a kind of deal adsorption material for the environmental pollution and other fields which has good application prospect.

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