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Composition, Property Characterization and Application of Agricultural and Forest Biomass Carbon

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Abstract We analyzed the compositions and basic properties of agricultural and forest biomass carbon, and used the pot method to study the influence of such element on the remediation of contaminated soils and growth of crops. Results show that agricultural and forest biomass carbon contains various nutrients that are necessary for crop growth, high specific surface area, and pore structure development. Cotton stalk charcoal can reduce bioavailability of Cadmium (Cd) in soil. Under mild Cd pollution, soil treated with cotton stalk charcoal adsorbs Cd at a rapid rate. With increasing extent of Cd pollution, Cd adsorption rate gradually slows down and Cd adsorption amount gradually increases. In soil treated with cotton stalk charcoal, the amount of Cd accumulated in the edible portions and roots of *Brassica chinensis* significantly decrease. The Cd mass fraction of the edible portions and roots are reduced by 49.43% – 68.29%, 64.14% – 77.66% respectively. Appropriately adding carbon cotton stalks increases crop biomass. At a certain range, increasing cotton stalk charcoal also promotes the absorption of major nutrients in *Brassica chinensis*.

Key words Agricultural and forest biomass carbon, Cd-contaminated soil, Remediation

1 Introduction

Plant biomass refers to any organic material that uses solar energy produced by photosynthesis; it is the direct or indirect product of plant growth[3]. Biomass is classified into two types: agricultural and forest biomass[8]. Agricultural biomass comprises crop stalks (such as rice, corn, and wheat straw) and agro-processing litter (such as rice husk, corn core, peanut shells, and cane bagasse)[5, 10, 12]. Forest biomass principally includes the biomass resources created during forest growth and forest production (*e.g.*, branch residues from firewood forest and tending of forest), as well as litter from forestry by-products (*e.g.*, nutshells and nutstones)[7, 16]. Agricultural and forest biomass resources are currently used in many ways, including biochemical conversion through direct combustion, gasification, liquefaction, carbonization, compression molding or forage and artificial board processing. The biomass carbon using biomass as raw materials is non-polluting, high reserve, and renewable; it has become one of the new materials and energy sources with high potential for development[4, 6, 14]. In fully or partly hypoxic conditions and pyrolysis carbonization at relatively low temperatures (≤ 700 ℃), agricultural and forest biomass can be converted into stable agricultural and forest biomass carbon that is extremely rich in carbon content. Agricultural and forest biomass carbon is characterized by a developed pore structure and high specific surface area with a high negative charge; it therefore lends itself to strong adsorption[1]. Biochar can be used as a modifier that improves soil environments, promotes nutrient absorption in plants, enhances soil fertility, and purifies and remediates contaminated soil[2, 9]. Extensive international and domestic research has been carried out on biochar for the remediation of polluted soil and crop growth; significant progress has also been made under such initiatives[11, 13, 15]. However, agricultural biomass carbon for application in agriculture remains a controversial issue. Only the specific analysis of the characteristics of soil, crops, and biomass carbon can promote the rational use of biomass carbon in agriculture. To resolve this issue, the current study uses the analysis of the composition and characteristics of agricultural and forest biomass carbon as bases for determining recommendations on the remediation of polluted soil and crop growth/yield.

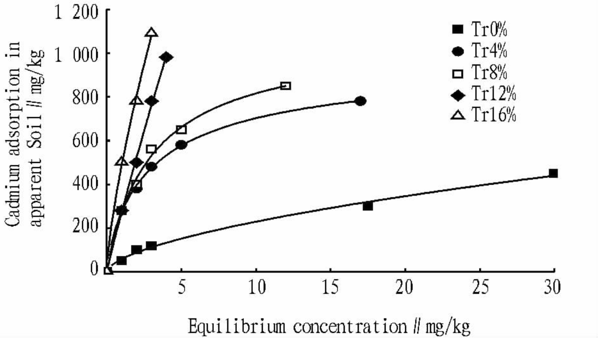

Fig. 1 **Adsorption isotherms of the treated soil samples adsorbing different concentrations of Cd until reaching equilibrium**

2 Experimental protocols and results

2.1 Composition and characterization of agricultural and forest biomass carbon

2.1.1 Elemental content of agricultural and forest biomass carbon. The elemental contents of agricultural and forest biomass carbon differ depending on type and origin of raw materials. The ele-

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mental composition of rice straw charcoal was determined using an elemental analyzer (Vario EL III, Germany Elementar, Inc.) (Table 1).

The rice straw charcoal contains potassium, calcium, manganese, aluminum, iron, and other nutrients that are necessary for crop growth. Thus, this material can be made into an organic fertilizer.

2.1.2 Specific surface area and pore volume of agricultural and forest biomass carbon. Adsorption performance is an important indicator of the effective use and development of agricultural and forest biomass carbon. Surface area and aperture-pore volume distribution are two important factors that affect the adsorption properties of agricultural and forest biomass carbon. The biochar surface areas and pore sizes of cotton stalk charcoal, rice straw charcoal, wheat straw charcoal, and corn straw carbon were determined using a full-automatic specific surface area and micropore analyzer (ASAP2020, United States Mike Instruments, Inc.). The specific surface areas and aperture-pore volume distribution are shown in Tables 2 and 3, respectively.

Table 1 Rice straw charcoal elements

Element	Content/(mg/kg)	Element	Content/(mg/kg)	Element	Content/(mg/kg)	Element	Content/(mg/kg)
C	3.70×10^5	N	8.18×10^3	Mn	1.17×10^3	B	60.42
Si	2.85×10^5	P	3.96×10^3	Al	833.41	Zn	39.18
K	3.10×10^4	Mg	2.87×10^3	Fe	818.42	Cu	23.39
Ca	1.30×10^4	Na	2.72×10^3	Ba	100.83	Ni	16.64

Table 2 Specific surface areas of several types of agricultural and forest biomass carbon

	Cotton stalk charcoal	Rice straw charcoal	Wheat straw charcoal	Corn straw carbon
$\sum\Delta S/(m^2/g)$	190	157	65	158

The experiments on four types of agricultural and forest biomass carbon show that cotton stalk charcoal exhibits the largest specific surface area, *i.e.*, 190 m^2/g (Table 2). The specific surface areas of rice straw charcoal and corn straw carbon are 157 and 158 m^2/g, respectively. Wheat straw charcoal has the lowest specific surface area, at 65 m^2/g. Cotton stalk charcoal exhibits maximal adsorption performance, and it can be made into different products, including an organic fertilizer and slow release agent.

Table 3 Pore volume distributions of several types of agricultural and forest biomass carbon

Rn (0.1 nm)	Cotton stalk charcoal		Rice straw charcoal		Wheat straw charcoal		Corn straw carbon	
	ΔV_i // μL/g	$\Delta V_i/V_n$ // %	ΔV_i // μL/g	$\Delta V_i/V_n$ // %	ΔV_i // μL/g	$\Delta V_i/V_n$ // %	ΔV_i // μL/g	$\Delta V_i/V_n$ // %
90 – 110	0.4	0.4	0.6	0.7	0.2	0.6	0.3	0.4
70 – 90	0.7	0.7	1.2	1.3	0.4	1.0	0.6	0.8
50 – 70	1.4	1.3	2.1	2.2	0.8	1.9	1.1	1.4
42 – 50	0.6	0.6	0.9	1.0	0.4	0.8	0.5	0.6
34 – 42	1.1	1.1	1.6	1.7	0.6	1.5	0.8	1.0
30 – 34	0.5	0.5	0.9	0.9	0.2	0.4	0.4	0.4
26 – 30	0.4	0.4	0.6	0.6	0.1	0.3	0.3	0.3
22 – 26	0.8	0.8	0.8	0.8	0.4	0.8	0.4	0.4
18 – 22	2.4	2.3	1.4	1.5	1.3	3.2	0.4	0.5
16 – 18	2.9	2.8	1.8	1.9	1.9	4.6	0.4	0.5
14 – 16	4.0	3.8	2.5	2.6	2.9	7.0	0.8	0.9
12 – 14	4.3	4.1	2.0	2.1	4.4	10.6	2.0	2.4
10 – 12	3.9	3.7	11.0	11.7	1.0	2.3	7.9	9.7
9 – 10	6.0	5.8	22.0	23.5	2.7	6.5	4.1	5.0
<9	74.6	71.8	44.4	47.4	24.5	58.6	61.9	75.6

The pore structure of the four types of agricultural and forest biomass carbon consist primarily of micropores, and minimal amounts of mesopores and macropores. In the adsorption process, micropores are the main adsorption sites. They can come into direct contact with adsorbates and exhibit good adsorption capacity even under low adsorbate concentrations. In the remediation of metal-polluted soil, therefore, agricultural and forest biomass carbon can efficiently reduce the bioavailability of heavy metals in soil by adsorption or coprecipitation.

2.1.3 Determination of agriculture and forest biomass charcoal ash, volatiles, fixed carbon, and calorific value. Rice husk from Xuancheng, Anhui Province and wood chips from Daxinganling were taken as raw materials made into rice husk charcoal and Daxinganling charcoal. Agricultural and forest biomass carbon ash, volatile matter, and fixed carbon were measured in accordance with the China National Standards for Charcoal and Charcoal Testing (GB/T17664 – 1999). The calorific value was determined using a digital oxygen bomb calorimeter (XRY – 1A, Changji Geological Instruments, Inc., Shanghai, China). The test results are shown in Table 4.

The calorific value of rice husk charcoal is low because the ash of that is numerous. This biomass is used to make organic fertilizers or insulation materials for application in iron and steel industries. The heating value of Daxinganling charcoal is high because this biomass has a small amount of ash. It is made into a reducing agent and activated carbon material for fuel, or used in the metallurgical industry.

Table 4 Agricultural and forest biomass charcoal gray stars, volatiles, fixed carbon and calorific value

Carbon type	Ash//%	Volatile//%	Fixed carbon//%	Calorific value//kJ/kg	Calorific value//kcal/kg
Rice husk charcoal	45.35	5.21	49.44	18530	4433
Daxinganling charcoal	6.52	9.34	84.14	30740	7354

2.2 Effect of agricultural and forest biomass carbon on the remediation of contaminated soil and crop growth

2.2.1 Effect of agricultural and forest biomass carbon on the remediation of contaminated soil. Cotton stalk charcoal was using the cotton stalk from the suburbs of Changzhou as raw material. It is the solid product obtained under the following testing conditions: carbonization temperature, 450 ℃; heating rate, 150 ℃/h; holding time, 1 h. The test soil is from a pollution-free agricultural production plant base in Changzhou Wujin District. $CdCl_2 \cdot 2.5H_2O$ is AR grade, and the *Brassica chinensis*s are Chia Tai 3 heat-resistant green seedlings. Soil was cultured in the preparation phase of the test. Soil samples (1000 g) were added with different proportions of cotton stalk charcoal in a 30 ℃ incubator. The samples were regularly weighed, watered, and cultured for 60 days to ensure that the soil samples exhibit an adequate response to cotton stalk charcoal. There were five treatments as follows: (1) soil samples added no cotton stalk charcoal, Tr0%; (2) soil samples added with 40 g of cotton stalk charcoal, Tr4%; (3) soil samples added with 80 g of cotton stalk charcoal, Tr8%; (4) soil samples added with 120 g of cotton stalk charcoal, Tr12%; (5) soil samples added with 160 g of cotton stalk charcoal, Tr16%.

(i) Effect of agricultural and forest biomass carbon on the apparent adsorption of Cd^{2+} in soil. Weighed cultured soil samples treated with Tr0%, Tr4%, Tr8%, Tr12%, and Tr16% 5.000 g, respectively, and then put them into 100 mL centrifuge tube. To these samples, cadmium (Cd) ion series solution ($CdCl_2 \cdot 2.5H_2O$ preparation) using 0.01 mol/L $CaCl_2 \cdot 6H_2O$ as background solution was added with 50.0 mL. The mass concentrations were 0, 0.5, 1.0, 5.0, 10, 50, and 100 mg/L. The aforementioned procedure was repeated twice. The soil samples were subjected to intermittent oscillation (oscillated once every 4 h, and each time 20 min) at (25 ± 1) ℃ until they reached adsorption equilibrium. The samples were then centrifuged and filtrated. The concentration of Cd^{2+} was measured using an Elan DRC-e inductor coupled plasma mass spectrometer (ICP – MS) (Perkin Elmer, US).

Fig. 1 shows the adsorption isotherms of the soil samples treated with Tr0%, Tr4%, Tr8%, Tr12%, and Tr16% adsorbing different concentrations of Cd until reaching equilibrium.

With increasing Cd concentration, the amount of Cd adsorbed in each treated soil sample gradually increases (Fig. 1). At low concentrations, the soil samples treated with cotton stalk charcoal exhibits rapid Cd adsorption, and the adsorption rate trends downward increasing Cd concentration. Cotton stalk charcoal promotes Cd adsorption in soil and therefore reduces bioavailability of Cd. On one hand, cotton stalk charcoal has a large specific surface area and an abundant microporous structure. On the other hand, cotton stalk charcoal is an alkaline substance. With increasing amount of cotton stalk charcoal added, the pH of the soil samples increases, thereby increasing the number of negative charge in soil colloids and weakening the competitiveness of H^+. Heavy metals exist in the form of insoluble hydrogen oxide, carbonate, or phosphate. Thus, treating soil with cotton stalk charcoal reduces bioavailability of Cd in Cd-contaminated soil.

(ii) Effect of agricultural and forest biomass carbon on Cd absorption in *Brassica chinensis*. To further examine the capacity of straw carbon to remediate Cd-contaminated soil, we studied how soil treated with cotton stalk carbon affects the Cd absorption in *Brassica chinensis* by pot experimentation in an artificial climate chamber. The soil samples treated with Tr0%, Tr4%, Tr8%, Tr12%, and Tr16% were thoroughly mixed with exogenetic Cd pollution. Cd was then added as the $CdCl_2$ solution. The added amount was the same for each treatment, i.e., 1.0 mg/kg. Field water capacity was maintained and the samples were placed in pots after 1 month. Each pot had soil samples (3 kg) that were air-dried and passed through a 5 mm sieve. And with the same amount of N (150 mg/kg), P_2O_5 (100 mg/kg), and K_2O fertilizers (150 mg/kg), the soil was allowed to age for a week and then planted with consistent age and similar growth vigor seedlings of 10 strains. The plants were watered with deionized water and harvested after 40 days of growth. The harvested plants were washed with tap water, rinsed with deionized water, and dried. The ground parts and roots were then weighed. The samples were de-enzymed at 95 ℃ for 15 min, dried at 65 ℃, and weighed. The samples were ground to be passed through a 0.85 mm sieve and then digested using $HNO_3 - HClO_4$. The Cd mass fractions of the ground edible parts and roots of the plants were determined by atomic absorption spectrophotometer. The results are shown in Table 5.

The addition of cotton stalk carbon decreases the accumulated Cd in the edible portions and roots of the tested *Brassica chinensis*. The Cd content of the various parts of the plant declines in the soil samples treated with Tr4%, Tr8%, Tr12%, and Tr16% compared with the soil samples that were not treated with cotton stalk charcoal. The Cd content in the edible parts decreases by 49.43% – 68.29%, while that in the roots of the *Brassica chinensis* declines by 64.14% – 77.66%. This result indicates that the soil samples treated with cotton stalk charcoal slows down the release of Cd. However, the Cd contents in the parts of the *Brassica chinensis* planted in the Tr12% – and Tr16%-treated soil samples are higher than that in the Tr8%-treated soil sample. *Brassica chinensis growth is suppressed when the amount of cotton stalk carbon added exceeds a certain value, thereby increasing the relative* Cd content in various parts of the *Brassica chinensis*. In practical application, a necessary requirement is to add an appropriate amount of Cd in accordance with the differences among crops and degree of soil contamination.

2.2.2 Effect of agricultural and forest biomass carbon on crop growth.

(i) Effect of agricultural and forest biomass carbon on *Brassica chinensis* biomass. We studied how cotton stalk carbon-treated soil affects *Brassica chinensis* biomass by pot experimentation in an artificial climate chamber. The samples treated with Tr0%, Tr4%, Tr8%, Tr12%, and Tr16% were passed through a 5 mm sieve, air dried (3 kg), and then separately placed in pots with the same amount of N (150 mg/kg), P_2O_5 (100 mg/kg), and K_2O fertilizers (150 mg/kg). The soil was allowed to age for a week and then planted with consistent age and similar growth vigor seedlings of 10 strains. The plants were watered using deionized water and harvested after 40 days of growth. The harvested plants were washed with tap water, rinsed with deionized water, and dried. The ground parts and roots were then weighed. The samples were de-enzymed at 95 ℃ for 15 min, dried at 65 ℃, and weighed.

Table 5 Comparison of Cd absorption in various parts of *Brassica chinensis* planted in soils subjected to different treatments

Treatment mode	Cd content in the edible portions//mg/kg	Increase (±%)	Cd content in the roots//mg/kg	Increase (±%)
Tr0%	0.386A	–	1.024a	–
Tr4%	0.196B	–49.43	0.474b	–73.61
Tr8%	0.163C	–67.60	0.230e	–77.66
Tr12%	0.146C	–62.29	0.468c	–66.32
Tr16%	0.160C	–68.29	0.367	–64.14

Note: Capital letters indicate significance at level $P < 0.01$; lowercase letters indicate significance at level $P < 0.05$.

Table 6 Effect of agricultural and forest biomass carbon on *Brassica chinensis* biomass

Treatment	Root length cm	Plant height cm	Above-ground fresh weight//g/plant	Under-ground fresh weight//g/Plant)	Total biomass g/ plant	Biomass increase over that in Tr0% (±%)
Tr0%	10.6	28	142	10.36	162.36	–
Tr4%	12.16	32	164	11.16	176.16	14.97
Tr8%	13.8	33.2	172.4	11.746	184.146	20.87
Tr12%	9.76	26.6	120	9.36	129.36	–16.10
Tr16%	9.61	24	90.2	8.73	98.93	–36.06

The influence of biochar on root length, plant height, above-ground and under-ground fresh weight, and total biomass show a similar trends;, that is, various indicators tend to increase but then decrease with the addition of biomass carbon (Table 6). Under different biomass carbon treatments, the *Brassica chinensis* growth conditions are better in Tr8%-treated soils, which exhibit an increase in *Brassica chinensis* biomass by 20.87% over the levels observed in the Tr0%-treated samples. *Brassica chinensis* growth worsens in the Tr16%-treated soils, which exhibits a reduction in XXX by 36.06% over the levels observed in the Tr0%-treated samples. Thus, adding a moderate amount of agricultural and forest biomass carbon promotes *Brassica chinensis* growth.

(ii) Effect of agricultural and forest biomass carbon on the absorption of primary nutrients in *Brassica chinensis*. Similarly, we studied how cotton stalk carbon-treated soil affects the absorption of primary nutrients in *Brassica chinensis* by pot experimentation in an artificial climate chamber. The soil samples treated with Tr0%, Tr4%, Tr8%, Tr12%, and Tr16% were passed through a 5 mm sieve, air dried (3 kg), and separately placed in pots with the same amount of N (150 mg/kg), P_2O_5 (100 mg/kg), and K_2O fertilizers (150 mg/kg). The soil was aged for a week and planted with consistent age and similar growth vigor seedlings of 10 strains. The plants were washed using deionized water and harvested after 40 days of growth. The harvested plants were washed with tap water, rinsed with deionized water, and dried. The ground parts and roots were then weighed. The samples were de-enzymed at 95 ℃ for 15 min, dried at 65 ℃, and weighed. The samples were then ground to be passed through a 0.85 mm sieve and then digested using H_2SO_4 and H_2O_2. The nitrogen, phosphorus, and potassium contents of the plant samples were measured by the Kjeldahl method, molybdenum blue colorimetric method, and flame photometry method, respectively.

With the addition of biomass carbon, nitrogen uptake in the *Brassica chinensis* first increases and then decreases (Table 7). Within a certain range, biochar can promote nitrogen uptake in *Brassica chinensis*. However, nitrogen uptake tends to decrease when biochar is sequentially added. Therefore, adding a large amount of biochar does not translate to high efficiency. The increase and subsequent decrease in the nitrogen content of *Brassica chinensis* is attributed to the fact that *Brassica chinensis* production first increases then decreases, because the dilution effect decreases nitrogen content when *Brassica chinensis* production increases. The increase in phosphorus content in *Brassica chinensis* is associated with the increase in the absorption of available phosphorus absorption in the biomass charcoal treated soil samples; this increase contributed to the activation of phosphorus. P uptake does not increase with increasing phosphorus content because *Brassica chinensis yield first increases and then decreases, but Brassica chinensis* yield is more in biomass charcoal treated soil than no biomass charcoal (Tr0%) soil. The K and P contents and concentration in *Brassica chinensis* show similar regularity. Increasing K absorption in *Brassica chinensis* improves its nutritional quality.

Table 7 Effect of biomass carbon on major nutrient content and concentration in *Brassica chinensis*

Treatment	N uptake mg/plant	N content mg/kg	P uptake mg/plant	P content mg/kg	K uptake g/plant	K content g/kg
Tr0%	50.06	328.61	1.44	9.45	45.51	298.75
Tr4%	55.59	317.37	1.76	10.05	70.27	401.16
Tr8%	56.72	308.00	1.93	10.49	69.76	378.85
Tr12%	34.35	265.59	1.52	11.73	68.66	530.83
Tr16%	36.97	373.71	1.53	15.43	54.49	550.83

3 Conclusions

(i) Agricultural and forest biomass carbon is rich in potassium, calcium, manganese, aluminum, iron, and other nutrients necessary for crop growth. These types of carbon are also characterized by high specific surface areas and developed pore structures (abundant microporous structure), making for strong adsorption capacity.

(ii) Agricultural and forest biomass carbon can remediate soil that is heavily contaminated by metals. Treating soil with cotton stalk charcoal diminishes bioavailability of Cd. Under mild Cd pollution, soil treated with cotton stalk charcoal treated exhibits rapid Cd adsorption. As Cd pollution increases, the adsorption rate gradually slows down, but the amount adsorbed gradually increases. Treating soil with cotton stalk charcoal (Tr4%, TR8%, Tr12%, Tr16%) significantly reduces the accumulated Cd in the edible parts and roots of *Brassica chinensis*. The Cd mass fraction of the edible portions of *Brassica chinensis* declines by 49.43% – 68.29%, and that of the roots drops by 64.14% – 77.66%.

(iii) Adding an appropriate amount of agricultural and forest biomass carbon can increase crop biomass. The *Brassica chinensis* biomass in the Tr8%-treated soil increases to 20.87%, whereas that in the Tr16%-treated soil decreases to 36.06%. Within a certain range, increasing agricultural and forest biomass carbon promotes the absorption of major nutrients in *Brassica chinensis*. When a certain amount of biochar is added, the absorption nutritional elements in *Brassica chinensis* tends to decrease.

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(From page 68)

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