Marked Changes in Biochar's Ability to Directly Immobilize Cd in Soil: Implication for Biochar Remediation of Cd Contaminated Soil

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Abstract

To investigate the change in biochar's ability to directly immobilize Cd in soil a successive wheat cultivation with experiment was conducted. Three biochar with different Cd adsorption mechanisms were added into soils and a mesh bag was used to separate the soil particles (> 1 μm) from biochar. The results showed that the ash contents and anionic contents (CO_3^{2-} and PO_4^{3-}) of the biochar decreased with the cultivation time, while the oxygen-containing functional groups content and CEC of the biochar increased. Resultly, the Cd concentration on biochar decreased, highly decreased by 68.9% for WBC300, while unstable Cd species (acid soluble and reducible fraction of Cd) on biochar increased with successive cultivation, increasing from 3% to 17% for WBC300 in FS. Correspondingly, the ability of biochar to inhibit Cd accumulation in wheat decreased. The results of this study illustrated that the ability of biochar to directly immobilize Cd in soil is not permanent, it gradually decreases with aging in soil. The adsorption mechanism of Cd on biochar changed from precipitation to complexation and ion exchange processes could be the main reason.

1. Introduction

It is widely reported that farmland contaminated with heavy metals can pose a serious threat to the food security and human health due to their non-degradability, high toxicity, and bioaccumulation (Xu et al., 2016; Hamid et al., 2019). Among the remediation methods of heavy metal polluted soil, passivation is considered as an efficient, low-cost, and environmental-friendly method (Brendova et al., 2016;Yousaf et al., 2016; Hamid et al., 2019). The passivators (e.g., biochar, sepiolite, and lime) added to soil can interact with the heavy metals in soil and convert them to less soluble and non-bioavailable forms (Zhang et al., 2016; Lahori et al., 2020).

Biochar is a carbon-rich solid product obtained by pyrolysis of biomass materials under oxygen-limited condition(Yuan et al., 2021). Due to its special physical-chemical properties, biochar has been widely used to immobilize soil heavy metals in recent years (Hamid et al., 2019; Yuan et al., 2021). Biochar can immobilize heavy metals in soil by direct and indirect interaction. First, biochar can interact with heavy metals in soil solution through complexation, precipitation, and cation exchange processes (Liu and Fan, 2018). Second, biochar can also change soil's properties, such as increasing the soil pH, changing the soil redox potential, microbiological compositions, and indirectly decrease the bioavailability of heavy metals (BHM) in soil (Cai et al., 2020; Cheng et al., 2020; Yuan et al., 2021). Hence, the efficiency of biochar on heavy metal immobilization in soil is closely related to the properties of biochar. However, the properties of biochar vary inconsistently after it was added in soil, especially when it closely contact with soil or exposure to changing environmental conditions (Yang et al., 2021). It has been reported that biochar's CEC, pH, specific surface area, and oxygen-containing functional groups would be changed significantly during the biochar aging process (Sorrenti et al., 2016; de la Rosa et al., 2018). Normally, the BHM in soil would be varied based on the increase or reduction of the active sites in biochar. The increase of biochar's CEC, oxygen-containing functional groups and specific surface area can decrease the BHM through increasing adsorption sites, while the decrease of biochar's pH and specific surface area can lead to the opposite effects due to the reduction of active sites(Yuan et al., 2021).

It showed be noted that a prerequisite for successful biochar application in the remediation of contaminated soils is that the immobilized heavy metals are not easy to release over a long period of time. However, the stability of these heavy metals is affected by biochar's properties and aging conditions (e.g., soil properties, aging time, agricultural measures, etc.). Many previous scholars have investigated the BHM changes in biochar amended soil with aging and the influence factors, however contradictory results were obtained regarding this scientific problem (Kumar et al., 2018, Gonzaga et al., 2020; Zhong et al., 2020). Additionally, the existing researches only focused on the changes of the bioavailability or speciation of heavy metals in soils. It remains unclear that how does the speciation of heavy metals in biochar change with aging process. Besides acid soil, biochar can also reduce the BHM in alkaline soils, where increasing soil pH is not the main mechanism(Zhang et al., 2016; Janus et al., 2018). There is also no clear understanding that the immobilized heavy metals in alkaline soils by biochar were at risk of release or not. Thus, the major objectives of this work were (i) to investigate the alteration in biochar properties with increasing aging time in both an acid soil and an alkaline soil; (ii) to explore the species changes of cadium (Cd) on biochar with aging time; (iii) to explore the long-term effect of biochar on directly immobilization Cd.

2. Materials And Methods

2.1 Soil and biochar

Three kinds of biochar were used in this work, which were obtained by pyrolyzing pig manure at 700°C and wheat straw at 300°C or 700°C under limited air. A more detailed description of this method was provided in our previous study (Ren et al., 2016; Chen et al., 2021). These biochar were referred to as PBC700 derived from the pig manure, WBC300 and WBC700 derived from the wheat straw based on their pyrolysis temperature. PBC700 adsorbed Cd mainly through precipitation(>90%), WBC700 adsorbed Cd through precipitation (>50%) and ion exchange (>30%), and WBC300 bond Cd via complexation (>39%) and ion exchange (>38%)(Chen et al., 2021).

Two soil samples polluted by Cd with different properties were collected from different regions in China, an acid soil (GS) and an alkaline soil (FS). GS (red soil) was collected in Guangxi Zhuang Autonomous region, and FS (calcareous soil) was collected in Shaanxi province. The pH of GS and FS was 5.6 and 8.9, respectively. The total Cd content in GS and FS was 3.2 mg kg^{-1} and 4.7 mg kg^{-1}, respectively. The soil samples were air-dried, sieve through a 2-mm sieve, and then stored in polyethylene Ziploc bags for further analysis.

2.2 Experiment design

A successive wheat cultivation experiment was conducted to investigate the changes of biochar' properties and Cd species in biochar with different cultivation time in two types of soil (GS and FS). The cultivation experiments were carried out in a customized plastic container (30 cm × 10 cm × 20 cm) filled with growth substrate and soil. The mixture of quartz sand and biochar (WBC300, WBC700 or PBC700) was served as the growth substrate and placed in a polyamide mesh bag (20 cm × 5 cm × 15 cm) with a mesh size of 1 μm to ensure the separation between soil and biochar particles. The quartz sand (0.45~1 mm) was pretreated with dilute hydrochloric acid (1:1) for 24 h to remove heavy metals. The percentage ratio of biochar in the mixture was 3% by weight in accordance with the mediate agronomic addition rate (Ren et al., 2016;Ren et al., 2021). The polyamide mesh bag was placed in the middle of the container, surrounded by soil. About 2000 g air-dried soil samples and 20 g biochar samples were placed into one container.

Deionized water was added to the soil samples in the containers to adjust water content, which would seep into the biochar samples in the mesh bag. Ultimately, the soil and biochar samples were moistened to 50% of water holding capacity (WHC). Wheat was chosen as the test crop to study the influence of being cultured with plant on the properties of biochar, because it is a common crop in China. The sterilized wheat seeds were evenly scattered in the growth substrate. The containers with different biochar were placed in an artificial climate chamber to conduct the cultivation experiment.

After 30 d of cultivation, a destructive harvest was performed to end the first stage of aging process. A small portion of biochar was collected and freeze-dried for further analysis. The soil samples and the growth substrate were air-dried and mixed evenly, respectively, then added again into the container and conducted the wheat cultivation again. Eventually, the cultivation experiment was repeated three times, and each cultivation period lasted for 30 d. A pot experiment without wheat was served as the control treatment.

2.3 Biochar analysis

The pH value, ash content, CEC, $CO_3^{2-}$and PO_4^{3-} content, and surface organic elemental composition of the biochar with different aging times were analyzed. The pH value was measured with a pH meter in 1:5 (w/v) suspension of a 0.01 mol L^{-1} $CaCl_2$ solution. The ash content was measured by the thermo–gravimetric method (Ren et al., 2016). The CEC was analyzed using the hexaamminecobalt (Ⅲ) chloride extraction method (Kazak, 2020). The CO_3^{2-} and PO_4^{3-} contents in biochar were measured by the acid base titration and ascorbic acid method, respectively. The surface elemental compositions were determined using an X-ray photoelectronic spectrometer (XPS) (ULVAC–PHI PHI 5000 VersaProbe, Japan).

The total Cd in the biochar were measured by atomic absorption spectrometry (Zeenit 700P, Analytikjena, Germany) after being digested by the HNO_3-HCl-HF solution. The sequential extraction procedure method was used to separate Cd in biochar into four fractions, i.e., acid soluble (F1), reducible state (F2), oxidizable state (F3) and residual state (F4)(Wang et al., 2017).

2.4 Desorption experiment

To investigate the effects of root exudates on Cd desorption from biochar during the wheat cultivation, oxalic acid and malic acid, the main components of wheat root exudates, were used to perform a sorption-desorption experiment. After the Cd (initial concentration was 100 mg· L^{-1}) was adsorbed by biochar (WBC300, WBC700 and PBC700), the desorption dynamic experiment was conducted by replacing 90% of the supernatant with the oxalic acid or malic acid solution. The tubes were resealed and shaken for different time (1 min, 3 min, 5 min, 7 min, 10 min, 30 min, 60 min, 180 min, 300 min, 540 min, 15 h, 24 h, 48 h, 72 h), and then centrifuged, the Cd concentration in the supernatants was determined by AAS.

2.5 Effect of biochar on wheat growth

The harvested wheat plants were first fixed at 105 °C for 30 min and then dried to constant weight at 80 °C. The above-ground biomass of wheat plant was weighed. Cd content in wheat plant was determined with the method described in our previous literature (Wei et al., 2018).

2.6 Data analysis

The Elovich model was used to fit the desorption dynamic curves. Statistical analysis was performed using one-way ANOVA (SPSS Inc, Chicago, IL, USA). Significant differences between treatments were calculated at 5% probability levels ($p<0.05$).

3. Results And Discussion

3.1 Characterization of fresh and aged biochar

The pyrolyzing temperature and biomass materials are the main factors that affect biochar’s properties. As shown in Table 1, the ash content of PBC700 (manure-derived biochar) is significantly greater than that of WBC (derived from wheat straw). Because the ash content of the manure was significantly higher than that of the plant materials. In addition, the inorganic fraction commonly included K, Na, Ca, Mg, PO_4^{3-} and CO_3^{2-}, which can not be easy to loss during the pyrolyzing period and preserved in the biochar(Xiao et al., 2018). The PO_4^{3-} contents of PBC700 and WBC700 were 2538 mg kg^{-1} and 119 mg kg^{-1}, respectively, which was markedly higher than that in WBC300 (Shown in Table 1). With the pyrolytic temperature increasing, the organic C content in WBC increased based on a dry-ash-free basis, while the H, N and O contents decreased (Table 1). As a result, the O/C and (O+N)/C ratios of WBC300 were larger than that of WBC700. Since the atomic ratios of O/C and (O+N)/C are commonly used to characterize the polarity of materials(Ren et al., 2016). The higher O/C and (O+N)/C ratios of WBC300 suggested that WBC300 contained more oxygen-containing polar functional groups.

Table 1
Physicochemical properties of the fresh biochar

	Unit	WBC300	WBC700	PBC700
Ash	%	17.1±1.1	21.2±1.0	71.7±2.3
Total C [1)]	%	70.3±2.2	81.3±1.9	75.4±2.1
Total H [1)]	%	5.93±0.8	3.75±1.0	3.7±0.3
Total N [1)]	%	0.9±0.05	\ [3)]	\
Total O [1)]	%	24.0±0.9	16.5±0.8	13.9±1.1
H/C [2)]	-	1.01	0.553	0.539
(O+N)/C [2)]	-	0.268	0.152	0.126
PO_4^{3-}	mg kg^{-1}	9.88±0.36	119.04±8.57	2538±78
CO_3^{2-}	g kg^{-1}	3.57±0.51	5.84±0.89	5.67±0.36
pH	-	9.2	10.0	10.4

Note: [1)] the elemental compositions are on a dry-ash-free basis, [2)] H/C is the atomic ratio of hydrogen to carbon, (O+N)/C is the atomic ratio of oxygen and nitrogen to carbon;[3)] \ :not determined.

Both the inorganic and organic fraction in biochar contain the adsorption sites of heavy metals. For example, the inorganic fraction in biochar can promote the adsorption of Cd by ion exchange and precipitation, and the oxygen-containing functional groups in biochar can bind Cd via forming complex compounds (Liu and Fan, 2018; Chen et al., 2021). Hence the physico-chemical properties of biochar markedly affect the adsorption and fixation of Cd on biochar. Since the contents and fractions of inorganic and organic fraction in WBC300, WBC700 and PBC700 are different, the adsorption mechanisms of Cd on the three biochar are significantly different. As reported in our previous literature, WBC300 mainly bind with Cd via ion exchange and complexation action, WBC700 and PBC700 mainly adsorbed Cd with precipitation action(Chen et al., 2021).

In all treatments, significant changes in biochar’s properties occurred during the successive cultivation process (Table 2), and further, a significant soil effect on almost all properties of biochar could also be noted (Table 2). The ash content and pH value of the three biochar decreased compared to those of the corresponding fresh biochar during the aging process. Among the three biochar, the ash content of WBC700 and PBC700 decreased more obviously than WBC300. 74.1%-44.1% and 43.4%-30.0% of the ash in WBC700 and PBC700 were lost during the successive cultivation process in FS or GS, respectively. While only 16.3%-11.1% of the ash disappeared in WBC300. Previous studies have shown that inorganic fraction can be released from biochar and uptaked by plants (Wu et al., 2015; Ren et al., 2016). As shown in Table 2, the PO_4^{3-} content of the three biochar also decreased during the aging process. Therefore, it is reasonable that the uptake of inorganic elements by the wheat roots led to the decrease in the ash content of the aged biochar. The ash component in biochar obtained at higher temperature (WBC700 and PBC700 in the present study) is more easily released. In addition, the aging effect of alkaline soil (FS) on biochar' ash content was more significant than acid soil (GS). The reduced ash contents of WBC700 and PBC700 during the aging period in FS were higher than those in GS. Since the FS is alkaline soil with many carbonates, the inorganic cations such as Ca^{2+}, Mg^{2+} could precipitate with CO_3^{2-} and released from biochar, which maybe contribute to explain the soil effect.

Table 2
Properties of biochars with different aging time

Biochar	Soil	Planting times	Ash content (%)	pH	CEC (cmol(+) kg^{-1})	PO_4^{3-} (mg kg^{-1})	CO_3^{2-} (g kg^{-1})
WBC300	/	/	17.1±1.10	9.20	26.1±1.12	9.88±0.36	3.57±0.51
	FS	1	18.0±0.50	9.27	42.1±0.10	8.01±0.13	3.58±0.2
		2	15.0±0.40	8.02	43.4±0.23	/[1)]	3.41±0.21
		3	14.3±0.12	7.96	43.4±0.52	/	3.17±0.18
	GS	1	16.7±0.30	9.20	34.6±0.17	/	3.49±0.13
		2	17.0±0.70	8.96	37.5 ±0.19	/	3.81±0.23
		3	15.2±0.54	8.42	41.0±0.52	/	3.67±0.23
WBC700	/	/	21.2±1.00	10.0	22.8±2.31	119±8	5.84±0.89
	FS	1	11.9±0.70	9.28	29.4±0.53	85.0±0.3	6.54±0.1
		2	7.4±0.20	8.45	36.4±0.12	54.2±1.3	7.04±0.18
		3	5.5±0.10	8.57	36.5±0.25	31.0±2.6	6.37±0.15
	GS	1	17.4±0.43	9.71	32.4 ±0.17	75.2±1.4	5.75±0.10
		2	12.8±0.12	8.52	30.4±0.19	62.3±4.8	6.94±0.21
		3	11.9±0.40	8.60	31.6 ±0.17	63.35±3.59	6.25±0.18
PBC700	/	/	71.7±2.30	10.4	28.9±2.50	2.54E3±78	5.67±0.36
	FS	1	43.0±0.10	9.41	29.4±0.53	2.00E3±60	5.99±0.11
		2	44.6±0.68	8.71	36.4±0.12	1.24E3±40	6.90±0.15
		3	40.6±0.14	8.96	36.5±0.25	1.73E3±51	6.21±0.21
	GS	1	57.2±0.45	9.75	30.5±0.16	1.46E3±57	6.67±0.14
		2	53.0±0.65	8.90	32.0±0.18	1.07E3±50	6.33±0.22
		3	50.2±0.70	8.68	32.36 ±0.53	1.13E3±61	6.41±0.11

Note: [1)]\ :not determined.

As listed in Table 1s (supplied in the supporting information, SI), significant differences in the surface chemistry were observed between the fresh and aged WBC700. Although the −CH/-C-C/−C=C was the major component in the fresh WBC700, its relative content significantly decreased with the aging time.

And the polar groups (-COOR, -C=O, -COR) sharply increased in the aged WBC700. These alterations could be attributed to soil organic matter (SOM) adsorption on biochar or oxidation of biochar surface either via biotic or abiotic processes as reported in many previous literatures. The increase in the oxygen-containing functional groups on the aged biochar can increase CEC of biochar. And this could be the main reason that the CEC of the aged WBC300 in FS and GS increased.

3.2 Changes in total Cd concentration in biochar

The total concentration of Cd in biochar was determined to measure the transport of Cd from soil to biochar (Figure 1). After the first cultivation period, the total Cd concentration in WBC300, WBC700 and PBC700 in FS were 1.26,1.31, and 1.51 mg kg^{-1}, respectively, which was significantly lower than that of biochar aged in FS without wheat. Although the total Cd concentration in FS (4.7 mg kg^{-1}) was higher than that in GS (3.2 mg kg^{-1}), the total Cd concentration in the three biochar in FS were lower compared with the biochar in FS. This phenomenon could be attributed to that Cd is more active in acid soil than in alkaline soil. However, the total Cd concentrations in the three biochar decreased with prolonging aging time, especially for the three biochar aged with wheat. After being cultured with wheat for three times, the total Cd concentration in WBC30, WBC700, and PBC700 in FS decreased by 63.5%, 44.2%, 68.0%, respectively, when compared with those biochar cultivated with wheat once. And the same variation trend was also observed on biochar aged in FS with wheat.

The transport of Cd from soil to biochar is affected by the mobility of Cd in soil and the immobilization of Cd by biochar. The soil pH affected the mobility of Cd greatly, and Cd in acidic soil is more migratory than in alkaline soil (Liu et al., 2018). The biochar can directly immobilize Cd through complexation, precipitation, and cation exchange processes, depending on biochar's properties. WBC300 contains more oxygen-containing functional groups and mainly immobilize Cd via ion exchange and complexation action. With higher ash content, WBC700 and PBC700 mainly bound Cd via precipitation, and the inorganic fraction in the biochar played an important role in immobilizing Cd, as reported in our previous study (Chen et al., 2021). During the aging process, the ash contents of the three biochar all decreased as shown in Table 1, which could result in the decrease of total Cd concentration in the three biochar during the aging process.

In addition, it is well documented that plant roots release many exudates, including low molecular organic acids, polymer degrading enzymes, saccharides and amino acids (Vranova et al., 2013; Hou et al., 2015). These exudates could not only affect the properties of biochar but also enhance the mobility of immobilized Cd (Lefevre et al., 2013; Ren et al., 2018). To investigate the effects of wheat root exudates on Cd desorption from biochar, we chose oxalic acid and malic acid as the representative low molecular organic acids of the wheat root exudates and conducted a sorption-desorption experiment. The desorption kinetic curves were shown in Figure 2, and the fitting parameters were listed in Table 2s. As shown in Figure 2, compared to the desorption solution of $CaCl_2$, both the desorption solution of oxalic acid and malic acid significantly increased the total desorption rate of Cd from WBC300 and WBC700. For PBC700, the malic acid solution promoted the desorption of Cd, while the oxalic acid solution inhibited the desorption of Cd. The total Cd desorption amount of WBC300 were higher than those of WBC700 and PBC700, indicating that the adsorbed Cd on WBC300 was more easily desorbed than on WBC700 and PBC700. However, the desorption rate of Cd from WBC300 was significantly lower than those from WBC700 and PBC700 (as shown in Table 2s).

To analyze the desorption mechanism of Cd by organic acids, the contents of PO_4^{3-} and HCO_3^- in solution before and after desorption were determined, and the results were listed in Table 3s. The contents of PO_4^{3-} and HCO_3^- in biochar solution increased significantly after desorption by organic acid (Table 3s), indicating that both oxalic acid and malic acid could promote PO_4^{3-} and HCO_3^- release from biochar. Since the precipitation of Cd with PO_4^{3-} and HCO_3^- on biochar is the main adsorption mechanism of Cd on WBC700 and PBC700, the desorption of Cd from WBC700 and PBC700 is accompanied by the release of PO_4^{3-} and HCO_3^-. As shown in Table 2s and Figure 2, the desorption rate and amount of Cd from PBC700 were greater than that of WBC700, which was consist with the increasing trend of HCO_3^- content in the biochar solution after desorption. In addition, for the same biochar (WBC700 or PBC700), the desorption amount of Cd from the biochar by malic acid was higher than that by oxalic acid (Figure 2), and the contents of PO_4^{3-} and HCO_3^- in the malic acid solution were significantly higher than in the oxalic acid solution after desorption (Table 3s). Therefore, organic acids in root exudates could promote the dissolution of Cd adsorbed on biochar by precipitation.

3.3 Changes in Cd species on biochar

Four fractions of Cd were determined using the BCR sequential extraction procedure to characterize the Cd species on the aged biochar. As shown in Figure 3, the oxidizable and residual fraction were the main species of Cd on the aged biochar. Both the content and the ratio of each fraction changed significantly. The ratio of acid soluble (F1) and reducible Cd (F2) on the biochar showed an obvious increase with aging time, while the oxidizable Cd (F3) decreased markedly. The PBC700 aged in GS with wheat showed the largest changes in the ratio of F1, which increased 0.67% from to 32.4%. For the same biochar, although the ratio of each fraction of Cd on the biochar aged in different soil was different, the variational trend was consistent (Figure 1s).

It has been reported that the application of biochar to soil could lead to Cd transformation and influence the bioavailability of Cd in soil (Hamid et al., 2019; Yuan et al., 2021). However, there was little research about the influence of soil aging on changes of Cd species on biochar. In this study, we found that the four fractions of Cd on biochar were significantly influenced by wheat. During the aging process, the F1 and F2 of Cd increased. The toxicity of Cd mostly depends on the F1, which is mobile and labile and consists of soluble, exchangeable and carbonate-bound metals (Wang et al., 2017). The F2 of Cd is also labile and has potential environmental impacts. Once the soil condition changed, such as the reductive conditions, the bound-ion will be easily released and available for the plants (de Livera et al., 2011). The properties of biochar changed obviously during the aging process, as we discussed above. The changes in biochar's properties can influence the adsorption between Cd and biochar. Both the organic fraction with oxygen-containing functional groups and inorganic fraction, such as carbonates and phosphates are the main adsorption sites, which can bind with Cd through complexation, cation exchange and precipitation, respectively (Chen et al., 2021). During the biochar aging process, as shown in Table 1s, biochar surface generated more oxygen-containing functional groups. Afterwards, the new active sites were available for biochar to complex with Cd. Typically, the increase of biochar CEC was conductive to the cation exchange process. While the decrease of biochar pH and ash content would count against the precipitation process. Therefore, the mechanism of Cd immobilization by biochar changed during the successive cultivation process, which may result in the transformation of Cd species.

3.4 Effect of biochar aging on Cd accumulation in wheat plants

The Cd accumulation in wheat plants from biochar with different aging time was determined and shown in Figure 4. The application of biochar significantly decreased the accumulation of Cd in wheat. For FS, compared with the treatment without biochar, the Cd content in wheat decreased by 9.1%,62.2% and 83.4% with the treatment of WBC300, WBC700 and PBC700, respectively. While for GS, the Cd content in wheat decreased by 38.3%,81.1%, and 81.7% with the treatment of WBC300, WBC700 and PBC700, respectively, when compared with the treatment without biochar. Hence, the biochar can immobilize Cd and reduce the bioavailability, which is consist with previous literatures. The Cd accumulation in wheat from FS was lower than that from GS, and the reduction of Cd content in wheat by biochar added to GS was higher than that by biochar added to FS. This could be attributed to the different bioavailability of Cd in FS and GS.

In this experiment, the wheat was planted in the mixture of biochar and quartz sand not in the soil directly. Hence, the bioavailability of Cd in the mixture of biochar and quartz sand directly influence the Cd content accumulated in the wheat. With the increase of the cultivation times, the accumulation of Cd in wheat in most treatments gradually reduced (Figure 4). It should be noticed that in the control groups (FS and GS without adding biochar), the Cd content accumulated in wheat also reduced with the cultivation times (shown in Figure 4). In the FS, the Cd content in wheat plants decreased from 1.46 mg kg^{-1} in the first cultivation to 1.28 mg kg^{-1} in the third cultivation, which decreased by 12.3%. In the GS, the Cd content in the wheat plants in the third cultivation decreased by 66.6%, compared with that of the first cultivation. Hence, the decreased accumulation of Cd in wheat can not directly indicate the reduce of Cd bioavailability in biochar.

To analysis the changes of the bioavailability of Cd in biochar during the successive cultivation, we compared the Cd contents in wheat between in the control groups and the treatment groups during each cultivation time. During each cultivation time, the addition of biochar can reduce the Cd accumulation in wheat. The reduce degree varied with the biochar and soil types. The reduce degree caused by WBC300 in both FS and GS first increased obviously and then decreased. While the reduce degree in the first and second cultivation time caused by WBC700 and PBC700 in both soils varied slightly, but decreased markedly in the third cultivation time, except WBC700 in FS. Compared the two soils, the reduce degrees caused by WBC300, WBC700 and PBC700 in GS (acid soil) were lower than those in FS (alkaline soil), indicating that the bioavailability of Cd in the biochar aged in acid soil was higher than that in the biochar aged in alkaline soil.

Biochar can not only reduce the Cd accumulation in wheat, but also promote the wheat growth. Data for the aboveground biomass of wheat were given in Figure 5. the aboveground biomass of wheat in FS and GS with biochar treatment significantly increased, compared with those in FS and GS without biochar in the first cultivation, especially in FS-WBC700 and GS-WBC700, which increased by 45.3% and 43.5%, respectively. In addition, the biomass of wheat in FS-WBC700 and GS-WBC700 increased with the increasing of cultivation times.

Bochar can directly immobilize Cd in soil solution through adsorption, such as complexation, cation exchange and precipitation processes. In addition, the biochar can affect the properties of soil particles, resulting in the release of Cd from soil particles into soil solution and redistribution, which could be the indirect way by which the biochar influences Cd species in soil (Hamid et al., 2019). In this research, the wheat was planted in the mixture of biochar and quartz sand not in the soil directly. The Cd accumulated in wheat plant mainly come from the Cd existed in the biochar solution or desorbed from the biochar. Therefore, the accumulated content of Cd in wheat can be used to characterize the ability of biochar to directly immobilize Cd. As discussed above, the reduce degrees of the Cd accumulation in wheat caused by the biochar were all decreased with the aging time, which means that the ability of biochar to directly immobilize Cd gradually reduced with the biochar aging.

4. Conclusion

Our results indicated that the properties and immobilization ability of biochar applied to rhizospheric environment were significantly affected by wheat growth. The changes of biochar’s properties significantly influence the direct immobilization mechanism of Cd on biochar. The ash contents and anionic contents (CO_3^{2-} and PO_4^{3-}) of all the biochar decreased with the aging time, while the oxygen-containing functional group content and CEC both increased. The direct immobilization mechanism of Cd on biochar changed from precipitation to complexation and ion exchange processes, and the bioavailability of Cd on the biochar increased with aging process. Therefore, the ability of biochar to directly immobilize Cd in soil is not permanent but gradually decreases with aging in soil.

Declarations

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Competing Interests

We declare that there are no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. **Author Contributions**

Xinhao Ren：Conceptualization,，Project administration，Funding acquisition, Writing - Review & Editing. Jiayi He：Investigation，Methodology，Writing- Original draft preparation. Qiao Chen：Methodology, Software, Validation，Data curation. Fei He：Formal analysis. Ting Wei：Resources. Honglei Jia：Visualization. Junkang Guo：Review & Editing.

All authors read and approved the final manuscript.

Data availability

The datasets used or analyzed during the current study are available from the corresponding author on reasonable request.

Ethical approval

This manuscript was only submitted on Environmental Science and Pollution Research. The authors make sure they have permissions for the use of software, questionnaires/(webs) surveys and scales in their studies (if appropriate). This research may not be misapplied to pose a threat to public health or national security. There was no animal experiment in this manuscript.

Consent to participate and publish

Results in this manuscript were presented clearly, honestly, and without fabrication, falsification or inappropriate data manipulation (including image based manipulation).

All co-authors have seen and approved the manuscript and have agreed to its submissions for publication.

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Figures

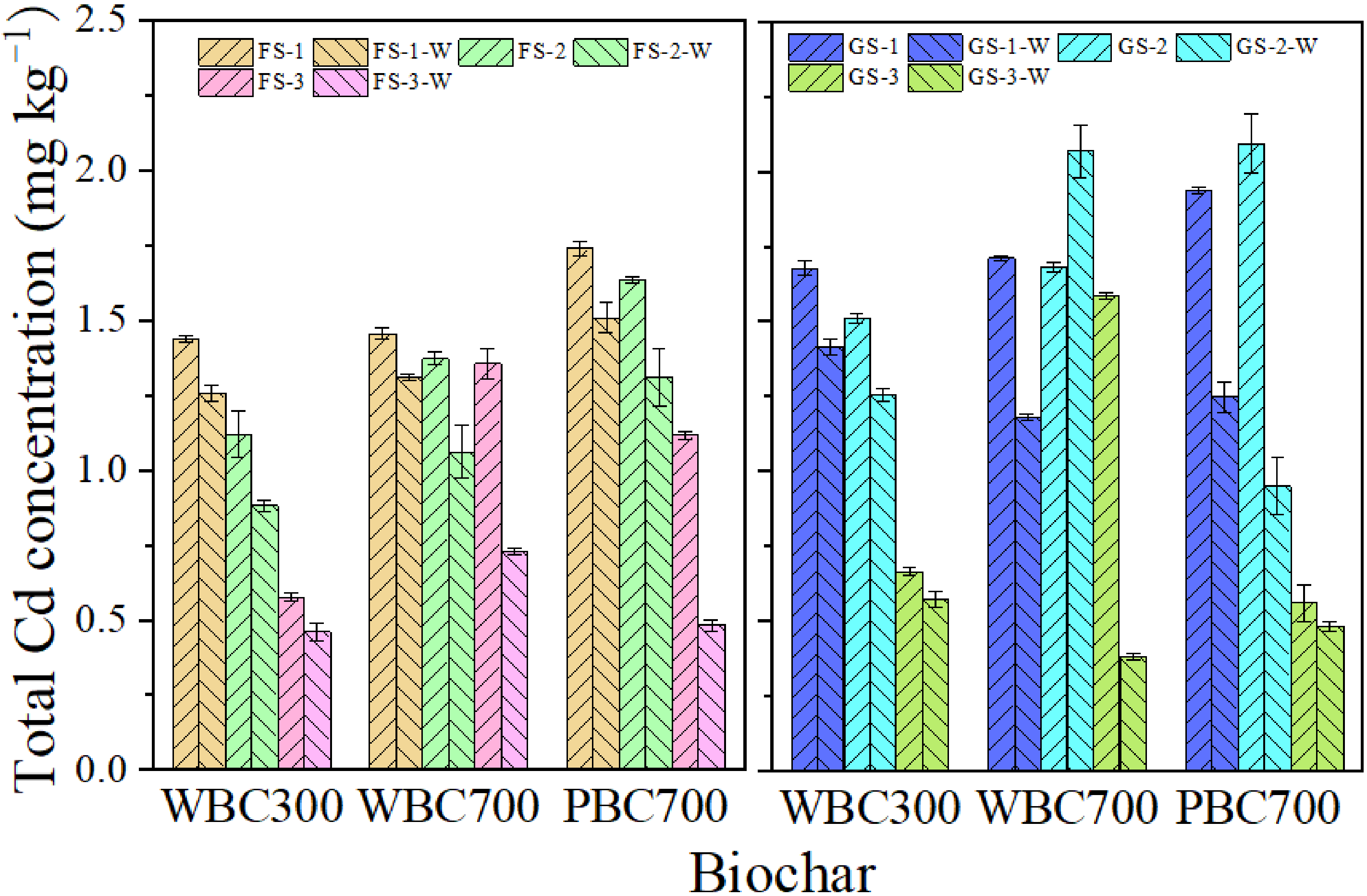

Figure 1

Total Cd concentration in biochar with different culturation time in two soils. FS/GS-1, FS/GS-2, FS/GS-3 refers to biochar cultured in FS or GS without wheat for the first time, successive two times, and successive three times, respectively; FS/GS-1-W, FS/GS-2-W, FS/GS-3-W refers to biochar cultured in FS or GS with wheat for the first time, successive two times, and successive three times, respectively.

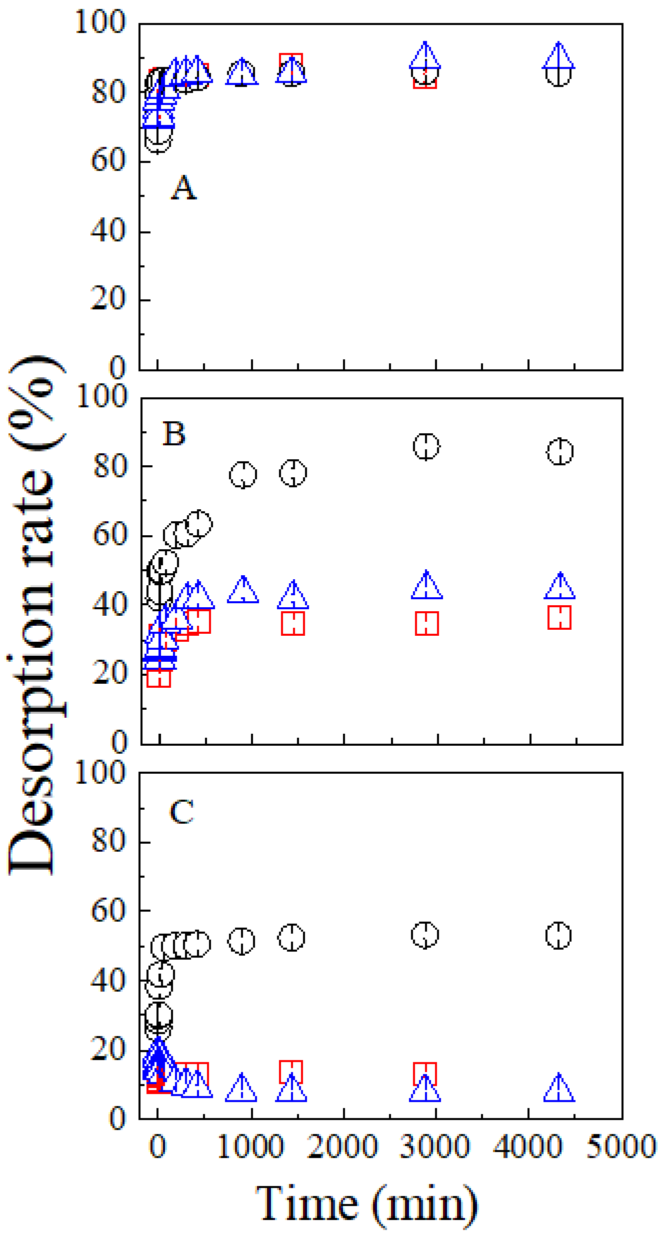

Figure 2

Desorption kinetics of Cd from biochar (A: WBC300; B: WBC700; C: PBC700) by $CaCl_2$ solution (□), oxalic acid (Δ) and malic acid (⬤)solution.

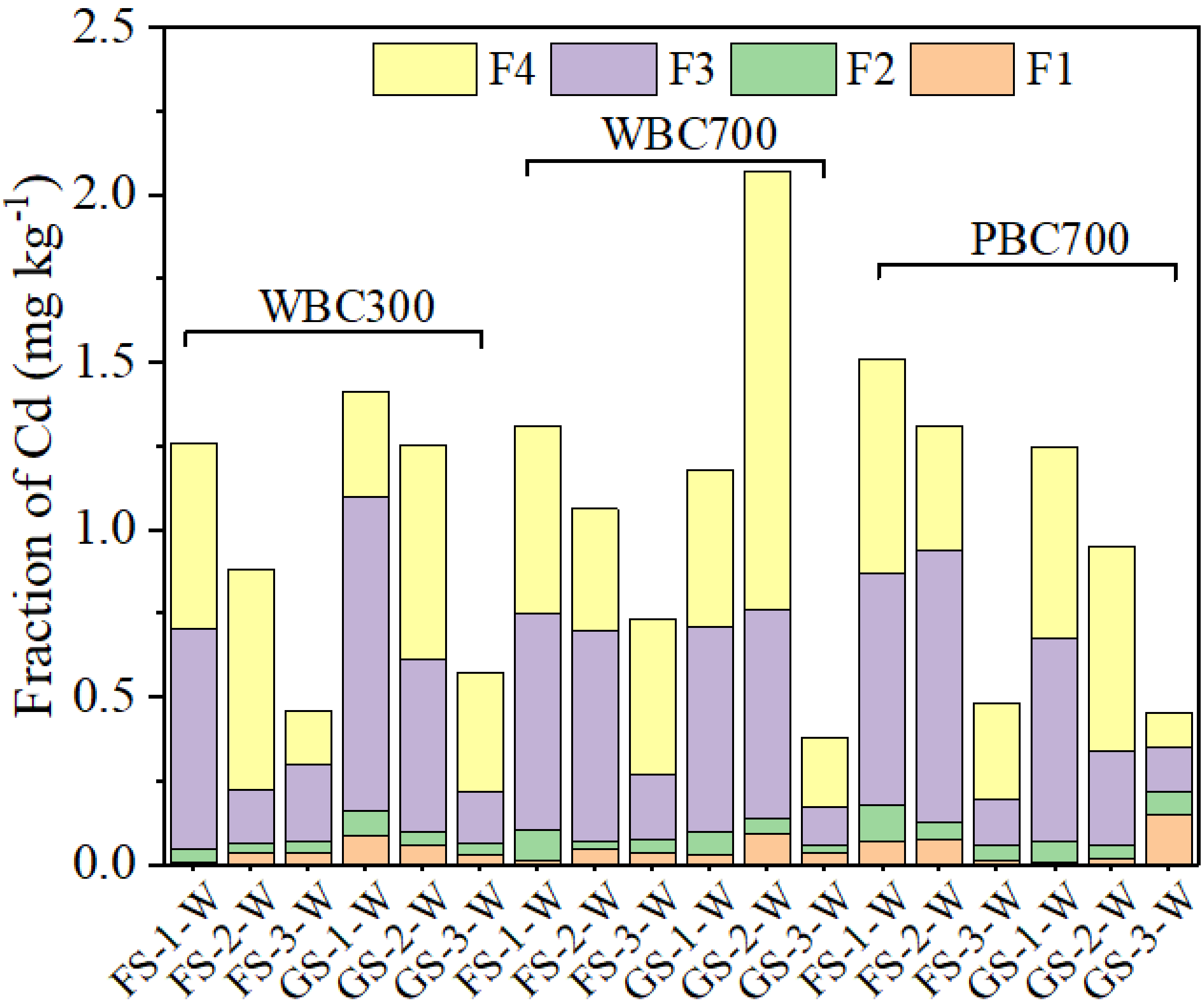

Figure 3

Fraction of Cd in biochar with different cultivation time in two soils. F1, F2, F3, and F4 represent acid-soluble fraction, reducible fraction, oxidizable fraction, and residual fraction, respectively; FS/GS-1, FS/GS-2, FS/GS-3 refers to biochar cultured in FS or GS without wheat for the first time, successive two times, and successive three times, respectively; FS/GS-1-W, FS/GS-2-W, FS/GS-3-W refers to biochar cultured in FS or GS with wheat for the first time, successive two times, and successive three times, respectively.

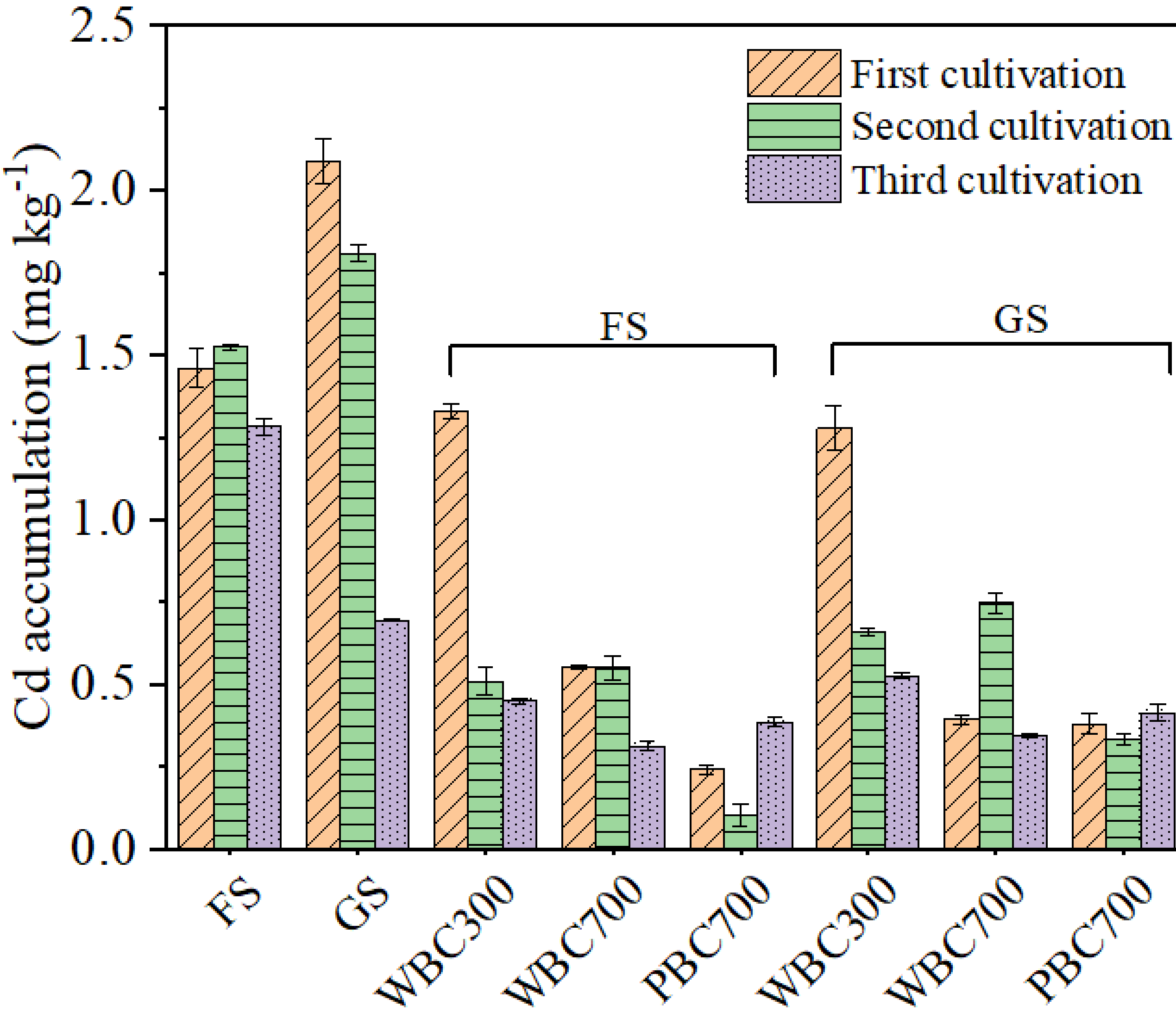

Figure 4

Content of Cd accumulation in wheat from biochar in each cultivation time.

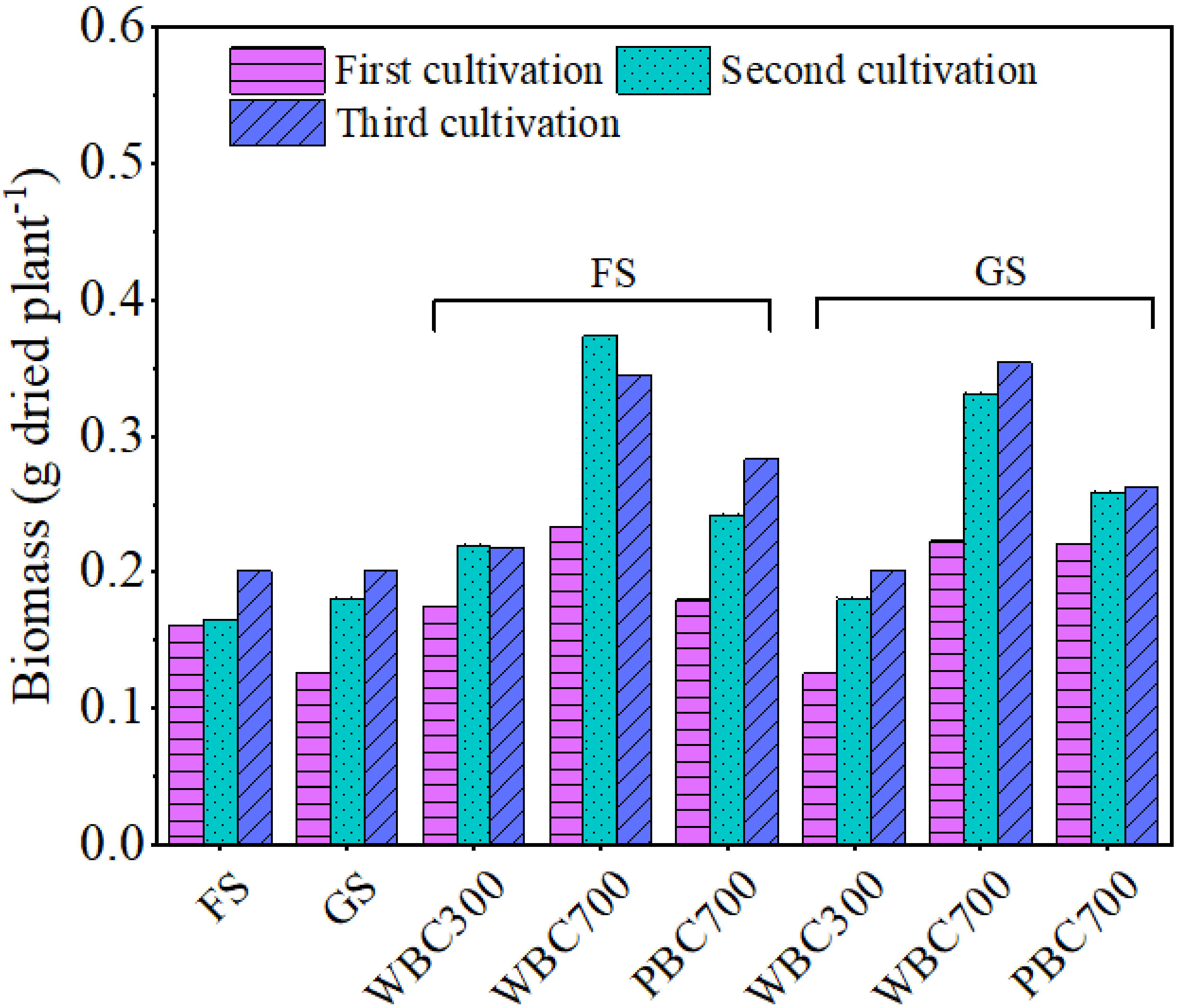

Figure 5

Aboveground biomass of wheat plant in each cultivation time in different treatments.

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