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Original Research

Effects of Hybrid Giant Napier Biochar on Cadmium Migration in a Cabbage-Soil System Contaminated with Cadmium and Butachlor

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Abstract

We investigated the effects of high-productivity plant hybrid giant Napier (HGN)-derived biochars prepared at different pyrolysis temperatures on Cd migration in a soil-cabbage system contaminated with Cd and butachlor. The results showed that with the enhancement amount of biochar applied, soil pH and electrical conductivity (EC) increased, whereas the available Cd content dropped significantly ($P<0.05$). The maximum decreasing value (66.08%) of the available Cd content was observed, while with 5% biochar prepared at 400ºC. Further application of this biochar caused a significant biomass increase and a Cd content decrease of cabbage ($P<0.05$). Notably, the cabbage biomass even increased to 573.58%. The application inhibited Cd migrations from the soil to the underground part and, successively, the overground part of the cabbage, leading to reduced bioaccumulation of Cd. With 5% biochar prepared at 400ºC, the maximum decrease of the Cd content reached up to 90% in the aboveground part and 70% in the underground part of cabbage, respectively. Hence, the investigation demonstrates that high-productivity HGN-derived biochar can be a good candidate for immobilizing Cd and reducing its bioaccumulation.

Keywords: cadmium, butachlor, *Pennisetum hybridum*, bioavailability

Introduction

Butachlor is an important chloroacetanilide herbicide applied in agriculture all over the world. In China, butachlor is now one of the three most widely utilized herbicides, with a yield of 1×10^4 t per year [1]. The application of butachlor in large quantities IES may cause the contamination of underground water, surface-water, and paddy soil in China, leading to disruption of the environment and ecosystems [2]. At the same time, anthropogenic activities result in increasing pollution of heavy metals that cannot be degraded and hence accumulate in the environment. Heavy metals threaten soil quality, plant survival, and human health, and their mobility are of global concern [3]. Cadmium (Cd) is a non-essential metal element that may cause damage even at very low levels. Cd in croplands can result in enhanced dietary exposure through

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soil-plant-food chain transfer, causing elevated levels of Cd in human organs [4]. Heavy metals and herbicides are frequently found together as contaminants in soils in China [5]. Therefore, it would be desirable to develop restoration agents to dispose of both contaminants in soil.

Biosorption is emerging as a technique offering the utilization of economical alternate biological materials such as biochars, which are produced by heating biological materials in a low-oxygen chamber (pyrolysis) [6]. Biochars demonstrate clear potential for the remediation of a variety of organic and inorganic pollutants in soils, and many studies have also affirmed that biochars are good agents for immobilizing soil heavy metals and reducing their accumulation in plants [7]. Biomass such as woody material, green wastes, and animal manures can be used for biochar production. Hybrid giant Napier grass (HGN) is a high-productivity perennial grass plant with a rapid growth rate and high photosynthetic efficiency [8]. And it should be able to be applied as feedstock for bio-oil production through pyrolysis with biochar as an important byproduct [9]. The main objective of this study is to assess the effects of HGN-derived biochar application on the availability of Cd in soil as well as its migration in a soil-cabbage system contaminated with Cd and butachlor.

Materials and Methods

Experimental Materials

The subsoil sample (0-15 cm deep) was collected from the Experiment Teaching Base, South China Agricultural University, Guangzhou, China. The samples were air-dried and ground to pass a 60-mesh sieve. Selected soil properties were pH 6.0, EC 483 μS/m, organic matter 19.87 g/kg, TN 1.048 g/kg, TP 0.863 g/kg, TK 23.34 g/kg, alkali-hydrolysable N 209.99 mg/kg, available P 39.36 mg/kg, and available K 139.19 mg/kg. After six months planting, the stem of HGN (*Pennisetum hybridum*) was collected and cut into 1×5 cm pieces. After drying at 60ºC for 24h, it was pyrolyzed under oxygen-limited conditions in a furnace (Shanghai Yizhong Electricity Furnace Inc., Shanghai, China). The temperature was raised at a rate of 10ºC/min up to 300ºC, 400ºC, or 500ºC. And the residence time in peak temperature was 2 h. The biochar was cooled to room temperature and ground to pass a 60-mesh sieve before use. Chinese flowering cabbage Sijiu-19 (*Brassica parachinensis*) seeds were brought from Guangzhou Academy of Agricultural Sciences, China.

Experimental Design

A series of single-factor experiments were conducted to assess the effects of different concentrations (0, 5, 10, 20, and 50 mg/kg) of butachlor on the available Cd content in the soil treated with different concentrations of Cd (1, 5, 10, and 20 mg/kg). Each treatment was performed with three replicates. Experiments were carried out in polythene cups with 0.1 kg soil (caliber 15 cm, bottom diameter 10 cm, and high 10 cm) and all cups were placed in an incubator with 85% humidity at 23ºC in dark. After 15d, 3 g of soil was collected for Cd determination.

For treatment of soil with biochar, the concentration of both Cd and butachlor was set at 10 mg/kg. Experiments were carried out in polythene cups with 0.5 kg soil (caliber 22 cm, bottom diameter 20 cm, and high 12 cm) and cups without biochar were set as control group (CK). Biochars prepared at different temperatures were applied in the soil at 1%, 3%, and 5% (w/w), respectively. Three replicates were set for each treatment. PT300, PT400, and PT500 represented treatments applied with biochar prepared at 300ºC, 400ºC, and 500ºC, respectively. All cups were placed in an incubator with 85% humidity at 23ºC during daytime and 20ºC for night with 300 $\mu Em^{-2}s^{-1}$ light intensity. After 30d, 3 g of soil was collected for physico-chemistry properties (pH, EC, Cd content, etc.) determination and subsequently 20 cabbage seeds were sowed into the soil. After another 30d, the plant was collected for biomass and Cd content detection and 3 g of soil was collected for Cd determination.

Sampling and Measurements

The collected soil was air-dried, crushed, and sieved through a 2 mm mesh before analysis. The biochar pH, soil pH, and EC were determined at a soil:water ratio of 1:2.5 (g/mL) using a sensION-156 meter (Hach). The shoots of cabbage were removed just above the soil surface, and successively washed with running tapwater over a mesh, and rinsed with deionized water three times. After being dried to constant weight at 70ºC in a forced-air cabinet, the samples were weighed and ground to pass a 0.75 mm mesh. The Cd content in plant was detected with an atomic absorption spectrophotometer (AA-6300, Shimazu) after digesting with nitric and perchloric acids. The Cd forms in soil were determined according to the method established by Tessier et al. [10]. For available Cd detection, soil was extracted with a mixture of 0.005 mol L^{-1} diethylene triamine pentaacetic acid, 0.1 mol L^{-1} triethylamine, and 0.01 mol L^{-1} $CaCl_2$.

Data Analysis

All data were presented as mean ±standard error. Statistical analysis was performed with SPSS13.0 statistical package (SPSS Inc., Chicago, IL, USA).

Table 1. pH and yield of *Pennisetum hydridum*-derived biochar.

	Biochar yield	pH
L300	37.13%	7.28
L400	33.14%	8.89
L500	28.60%	8.46

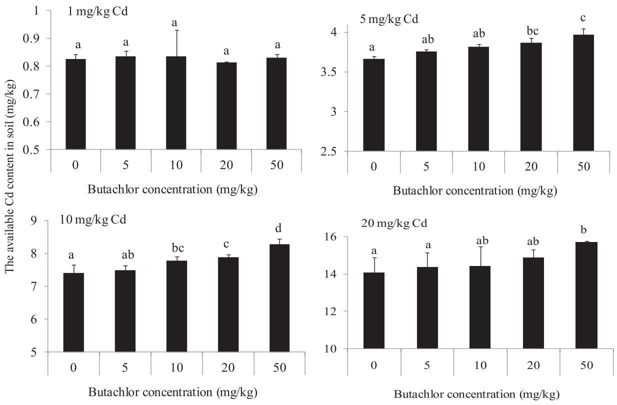

Fig. 1. Effects of different concentrations of butachlor on the available Cd content in soil polluted with different concentrations of Cd. Different lowercase letters in the same column indicated significant differences (Duncan's multiple range test method, $p<0.05$; the same below).

Duncan's multiple range tests were applied after the analysis of variance (ANOVA) ($P<0.05$). Biochar yield was calculated by the percentage of the ultimate weight to the raw material weight. Bioaccumulation factor (BF) was calculated by Cd content in plant vs. that in soil, and translocation factor (TF) was calculated by Cd content in aboveground vs. underground parts.

Results and Discussion

Effects of Pyrolysis Temperature on Biochar Yield and pH

As shown in Table 1, biochar yield dropped with increasing pyrolysis temperature. And the biochar that was prepared at 300ºC showed the highest yield (37.13%). HGN-derived biochar was alkaline and the pH values of biochar prepared at 400 and 500ºC were higher than that

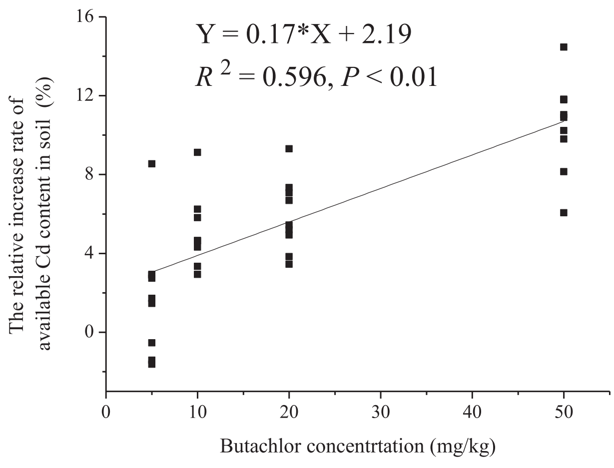

Fig. 2. The relationship between butachlor concentration-treated and the relative increase rate of the available Cd content in soil contaminated with Cd.

of biochar prepared at 300ºC. When prepared at 400ºC, the biochar showed the highest pH value (8.89) and was consistent with the results documented by other authors [11-13].

Méndez et al. [12] addressed the fact that pyrolysis promoted the pH value of the sewage sludge by more than 2.5 units, from 6.98 to 9.54. Park et al. [13] also documented that the pH value of black carbon prepared at 300°C was much lower than that of chicken manure and green waste-derived biochar prepared at 550ºC. Ashleigh et al. [14] recorded that the willow-derived biochar prepared at 350ºC showed low acidity to neutrality with a shift to basic character when pyrolysis temperature was higher than 450ºC. The probable cause is that some

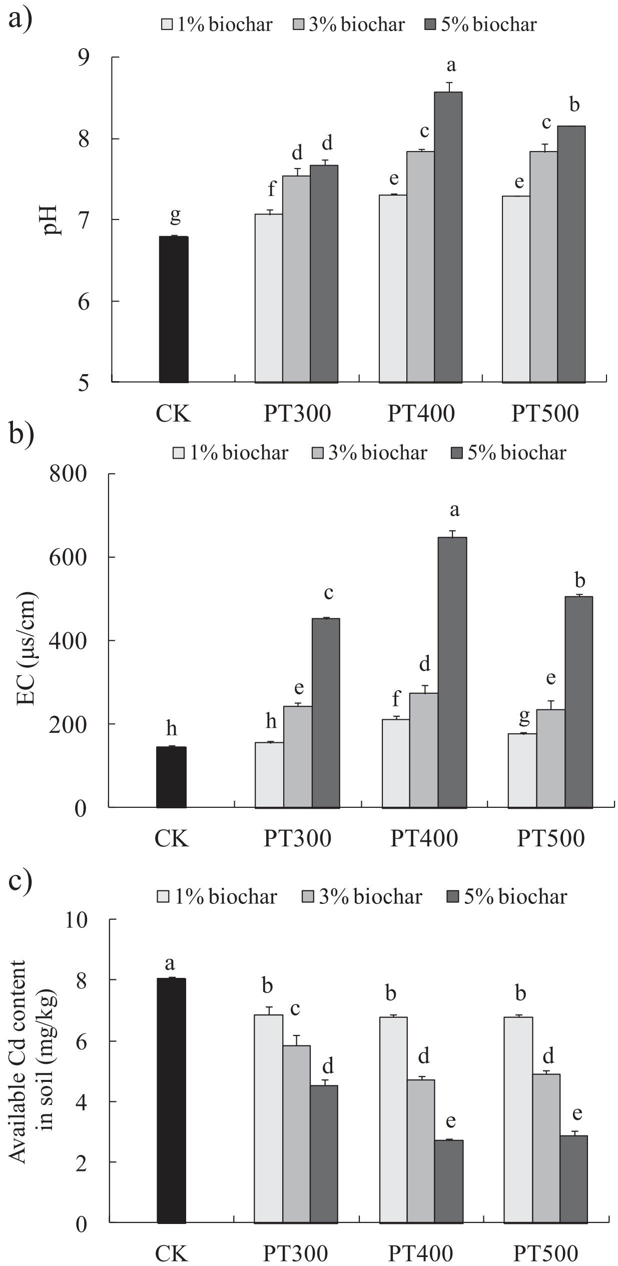

Fig. 3. Effects of biochar on pH a) and EC b), and the available Cd c) in soil polluted with Cd and butachlor.

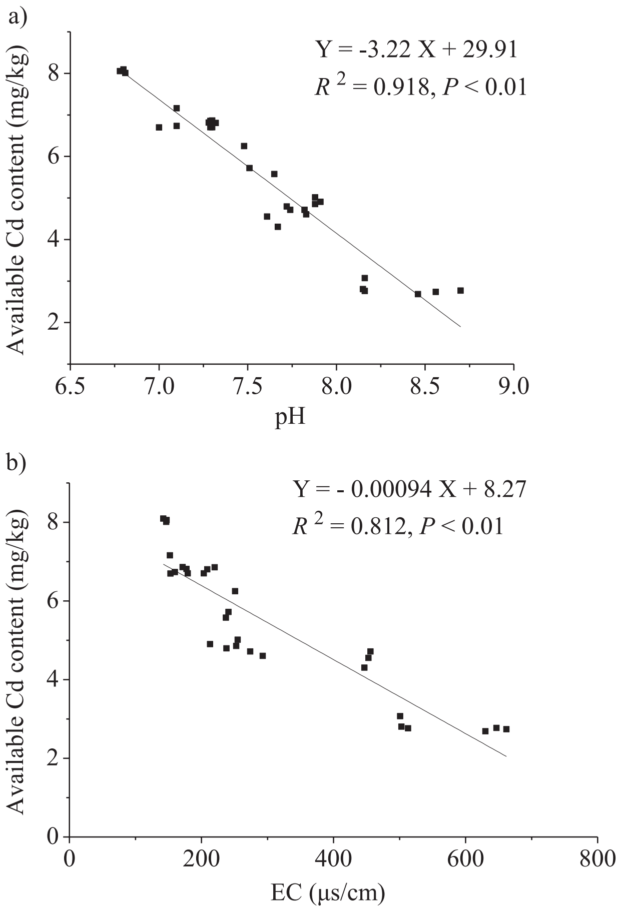

Fig. 4. Correlation of soil pH a) and EC b) with the available Cd content in soil contaminated with Cd and butachlor.

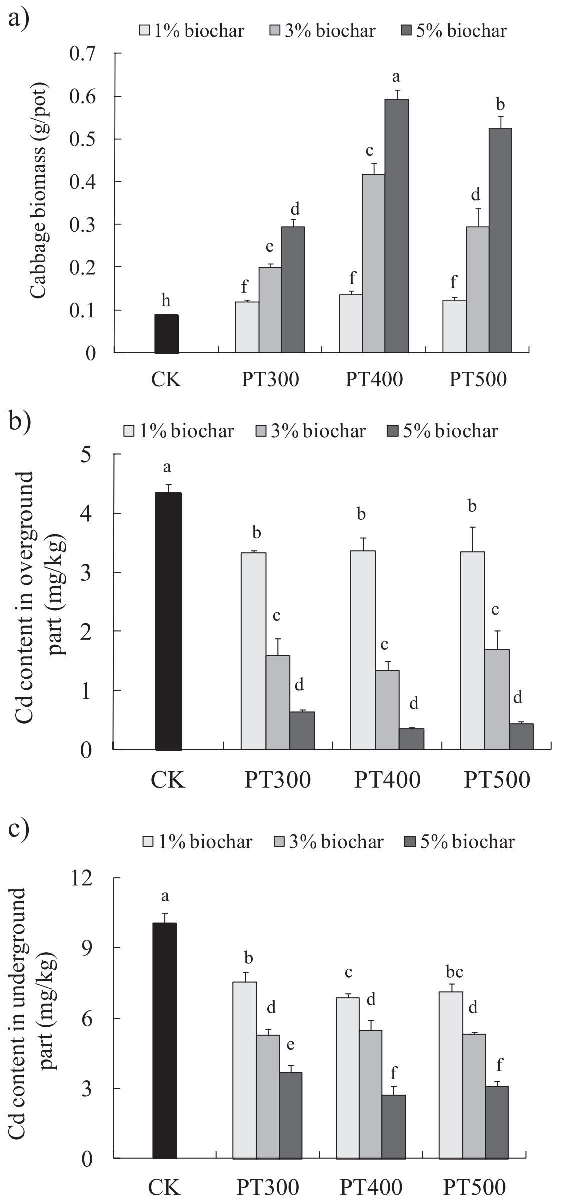

Fig. 5. Effects of biochar on biomass a), Cd content in the aboveground part b), and the underground part c) of Chinese flowering cabbage planted in soil polluted with Cd and butachlor.

mass (such as acidic surface moieties) lost as a result of the removal of volatile constituents and surface oxygen moieties [14].

Effects of Butachlor on Cd Availability in Soil

As shown in Fig. 1, compared with CK, the highest level (50 mg/kg) of butachlor treatment promoted the available Cd content in soil contaminated with 5, 10, and 20 mg/kg Cd significantly (P<0.05). Moreover, a significant positive relationship (P<0.01) between the relative increase rate of the available Cd content and the concentration of butachlor applied in soil was observed (Fig. 2). The highest increase rate (>11%) was observed when treated with 20 mg/kg butachlor and 50 mg/kg Cd, which demonstrated that butachlor may improve the availability of Cd in soil when the concentration of Cd applied was higher than 5 mg/kg. To our knowledge, this is the first time assessing the effects of the herbicide butachlor on Cd availability in soil directly, although the indirect effects have been documented by Yu and Zhu [15], who found that butachlor aggravated the cadmium-induced inhibition of growth and promoted the accumulation of Cd in rice significantly. It seems that organic matters can promote the available Cd in soil. Zhou et al. [16] found that glyphosate can decreased the adsorption of Cd in soils and increase the movement of Cd in the soil-water system. Yuan et al. [17] recorded that organic acids could promote Cd desorption from soils. Li et al. [18] also addressed the idea that the application of EDTA combined with a low dosage of ethyl lactate significantly enhanced the efficiency of willow in removing Cd (promoting bioavailability) from soil.

Effects of Biochar on Soil pH, EC, and Bioavailable Cd

As shown in Fig. 3a, compared with CK, soil pH increased with rising biochar applied in soil with PT400 and PT500. The highest increase in soil pH showed in PT400. And the increase in soil pH was consistent with the promotion in alkalinity of biochar prepared. Khan et al. [19] found that soil pH increased after applying sewage sludge biochar (SSBC). Moreover, a similar result was also available from paddy field study [7]. As shown in Fig. 3b, soil EC increased significantly ($P<0.05$) compared to CK. With 5% biochar prepared at 400ºC, the highest EC increase rate (4.44 fold) showed. It is similar to the results addressed by Hossain et al. [11].

The available Cd in soil dropped significantly ($P<0.05$) with increasing amounts of biochar (Fig. 3c). When treated with 5% biochar prepared at 400ºC, the highest fall of the available Cd was observed and the available Cd content under these conditions was only 66.08% of that in CK. Inverse correlations ($P<0.01$) between soil pH or EC and the available Cd content showed in Figs 4a and 4b, respectively, and this relevance between pH and the available Cd content was relatively high ($R^2 = 0.918$). It is similar to results recorded by many other authors. Zhang et al. [20] recorded that biochar significantly promoted soil pH and EC, whereas it reduced the $CaCl_2$-extractable Cd. Khan et al. [19] also documented that with SSBC, soil pH changed to a range associated with the maximum adsorption of metals and precipitation of insoluble species. Possible mechanisms for heavy metal retention by biochar include the formation of metal (hydr) oxide, carbonate, and specific metal-ligand complexation involving surface functional groups of biochar [13]. In addition, large surface area, good ion exchange capacity, and a range in chemical compositions of biochar may also be key characteristics [3]. The present study demonstrates that Cd deactivation ability of biochar could be related highly to the increase of alkaline functional groups of biochar.

Effect of Biochar on Cabbage Biomass and Cd Content in Cabbage

As shown in Fig. 5a, in all biochar treatments, the growth of cabbage planted in soil improved significantly ($P<0.05$) in contrast to CK. Moreover, this promotion increased when increasing the amount of biochar. Especially when treated with 5% biochar prepared at 400°C, the highest percentage of biomass increase (573.58%) was shown. As shown in Fig. 6a, a significant negative correlation between cabbage biomass and available Cd content was observed ($P<0.01$). Many studies have addressed biochar promoting biomass and productivity of plants in soil with Cd [7, 19]. However, Zhang et al. [20] found that although biochar could immobilize soil Cd, it did not improve plant growth. Moreover, Marks et al. [21] documented that some biochars stimulated plant growth, whereas others showed strong inhibition. Prapagdee et al. [22] also found that 10% biochar could promote plant growth, whereas 15% biochar treatment caused adverse effects. It seems that the effects of biochar on plant biomass or crop production are closely related to plant species, biochar types, amount applied, and soil properties.

As shown in Figs 5b and 5c, the Cd content in different parts of cabbage was reduced significantly after applying biochar. With increases in the amounts of biochar applied, the Cd content in the aboveground part of cabbage was reduced dramatically. With 5% biochar prepared at 400ºC, the highest drop (91.86%) of Cd content in the aboveground part was exhibited. A decrease in the underground part was also observed, although it was lower than that in the aboveground part. Moreover, when treated with 5% biochar prepared at 400ºC, the highest drop of Cd content in cabbage was also shown.

As shown in Table 2, with increasing amounts of biochar applied, the BF values of the aboveground and underground parts of cabbage were reduced gradually. And when treated with 5% biochar prepared at 400ºC, the highest decrease (91.97%) was observed (Table 2). As shown in Figs 6b and 6c, the positive correlations between Cd content in aboveground part or that in underground part and the available Cd content in soil was

Table 2. Effects of biochar on Cd accumulation in the aboveground and the underground parts of Chinese flowering cabbage.

Treatment		Bioaccumulation factor (BF)		Translocation factor (TF)
		Overground part	Underground part	
CK		0.436±0.011d	1.007±0.036f	0.434±0.026d
300ºC	1% biochar	0.334±0.003c	0.756±0.034e	0.442±0.017d
	3% biochar	0.159±0.024b	0.527±0.021c	0.303±0.048bc
	5% biochar	0.064±0.003a	0.368±0.025b	0.174±0.014a
400ºC	1% biochar	0.337±0.018c	0.688±0.015d	0.489±0.015d
	3% biochar	0.134±0.013b	0.55±0.033c	0.244±0.013b
	5% biochar	0.035±0.001a	0.271±0.033a	0.132±0.016a
500 °C	1% biochar	0.336±0.034c	0.715±0.025de	0.469±0.036d
	3% biochar	0.169±0.026b	0.531±0.009c	0.32±0.054c
	5% biochar	0.044±0.002a	0.309±0.017a	0.142±0.014a

The data were presented as mean ± standard error (n = 3). Different lowercase letters in the same column indicated significant differences (Duncan's multiple range test method, p<0.05).

shown (R^2 were 0.886 and 0.876, respectively, P<0.01). It demonstrates that biochar application can reduce the bioavailability of Cd in soil and the bioaccumulation of Cd in cabbage. The BF value of the underground part was far higher than that of the aboveground part – with or without biochar. Moreover, the decrease in bioaccumulation of Cd in the underground part was much higher than that in the aboveground part. At the same time, for CK the BF value of the underground part was 2.31-fold of that of the aboveground part.

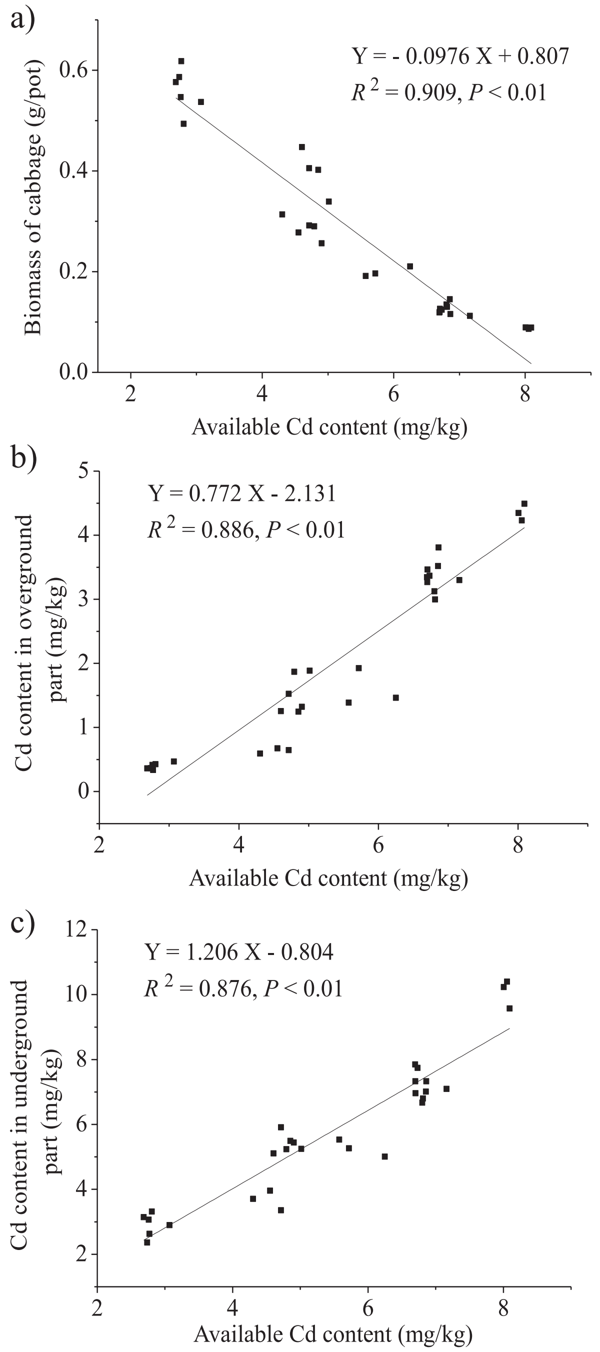

Fig. 6. Correlation of cabbage biomass a), Cd content in the aboveground part of cabbage b), and the underground part of cabbage c) with the available Cd content in soil contaminated with Cd and butachlor.

Contrasted with CK, no significant change (P>0.05) in translocation factor (TF) of Cd in cabbage was shown when treated with 1% biochar (Table 2). However, a dramatic fall was shown when treated with 3% and 5% biochar. This demonstrates that high-level biochar can inhibit the transportation of Cd from the underground part to the aboveground part, and accordingly reduce the accumulation of Cd in the aboveground part of cabbage. Similar results were also addressed by Zhang et al. [20] and Zheng et al. [23]. However, in some other studies, Cd bioaccumulation increased after applying biochar [11, 19]. In addition, Prapagdee et al. [22] documented that Cd uptake by *Vigna radiata* L. increased with increasing cassava stem biochar application rate, and the Cd accumulation in plant root was higher than that in shoot. Cassava stem biochar application can promote Cd accumulation in roots, whereas it reduced its translocation from root to shoot. Therefore, it is very important to deal with each case on its merits – especially from the point of view of food safety.

Conclusions

In the present study, HGN-derived biochar demonstrates clear potential for the remediation of Cd pollution in soil contaminated with butachlor and Cd. With the enhancement amounts of biochar applied, soil pH and EC increased, whereas the available Cd dropped significantly (P<0.05). Further application of this biochar caused a significant biomass increase and a Cd content decrease of cabbage (P<0.05). The application inhibited Cd migration from the soil to the underground part and successively the aboveground part of cabbage, leading to reduce the bioaccumulation of Cd. High productivity plant HGN is easy to grow in South China, HGN biochar as a by-product of pyrolysis is easily obtained. Therefore, it will be a cost-effective and environmentally friendly candidate for immobilizing Cd and reducing its bioaccumulation.

Acknowledgements

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