

*Original Research*

# Effects of Tea Residue Biochar on Phosphorus Adsorption-Desorption in Soil

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## Abstract

Adsorption and desorption of phosphorus (P) by biochar affect the effect of soil phosphorus fixation. In order to investigate the effect of tea residue biochar on the adsorption and desorption of phosphorus in tea garden soil and reduce the leaching loss of phosphorus in soil, the adsorption and desorption characteristics of phosphorus in tea garden soil were studied by equilibrium adsorption method. In the simulated culture experiment, biochar was prepared at different pyrolysis temperatures (400°C, 500°C, 600°C) and added at different concentrations (0.25%, 0.50%, 1.0%, 2.0%). Results showed that the P adsorption capacity in tea garden soil treated by three types of biochar trends was BC400>BC500>BC600, the BC400 treatment with 1.0% showed the best results. The P adsorption process by soil, dominated by monolayer adsorption, reached a significant level by matching the Langmuir equation ( $0.95 < R^2 < 0.98$ ). On the contrary, the application of tea residue biochar to soil significantly reduced the soil P desorption. In addition, environmental factors (temperature and pH) significantly affected on P adsorption process ( $P < 0.05$ ). The current results suggested that tea residue biomass carbon can improve the soil's ability of fixation to phosphorus and reduce the leaching of phosphorus.

**Keywords:** adsorption-desorption, biochar, phosphorus, pyrolysis temperature, tea residue

## Introduction

As Phosphorus (P) is an important nutrient element in plants, it is a major limiting factor of water eutrophication. Most insoluble P compounds exist in soil [1] and the utilization rate of P fertilizer in soil is generally less than 20% [2]. P is a non-renewable resource [3]. Most of P exists in a fixed state after it

is applied to the soil, making it difficult for plants to use [4]. In addition, the excessive application and low utilization rate of P fertilizer leads to significant P accumulation in the soil, increasing the risk of P loss in the soil and becomes one of the primary causes of water eutrophication. The loss degree of soil phosphorus depends on climate and terrain [5], air quality [6], fertilization status, slope, crop coverage, soil conditions, human activities [7] and other factors. The addition of soil biochar not only solves the problems of unreasonable disposal of agricultural wastes and environmental pollution [8], but also increases

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the content of soil organic matter, reduces the toxicity of soil heavy metals [9], promotes the activity of enzymes and improves the level of soil fertility [10]. It is of great significance to improve the soil structure and reduce the pollution of soil and water loss to the ecological environment [11]. Therefore, improving the adsorption capacity of soil to phosphorus is of great significance to the study of soil phosphorus management.

Biochar is a highly aromatic material with a high carbon content, decomposed by straw, rice husk, sawdust, fallen leaves, and other plant fiber wastes and animal manure at high temperatures in the case of hypoxia or hypoxia [12]. Biochar has broad application prospects [13] in soil improvement, pollution control, carbon sequestration [14] and emission reduction [15] due to its unique porous structure, large specific surface area [16], negative charge [17] and surface functional groups [18]. Previous research has shown that biochar can directly release P, improve the available P concentration in acidic soil [19], or indirectly affect the release of P by changing soil pH and organic matter content [20]. However, due to the complexity and variability of soil P adsorption characteristics [21], the research results on the P adsorption mechanism of biochar on acid soil are still controversial. Rashmi et al. [22] pointed out that the biochar addition can increase the calcium content in soil, thus promoting the adsorption of P in acidic soil. In contrast, Mukherjee S. et al. [23] revealed that the soil adsorption sites were occupied by P released by biochar, therefore, the addition of biochar would reduce the adsorption of P. Although the application of biochar prepared from different raw materials to the soil affect the P adsorption process, the adsorption results differ [24]. In addition, studies have found that the pH, ash content and available P content of biochar prepared at high temperatures are significantly higher than those of low-temperature carbon [25]. Therefore, the type and temperature of biochar affect the adsorption-desorption of soil phosphorus.

Anhui province is a famous tea-producing province in China [26], and its tea production ranks third in China. In recent years, due to the increasing tea beverage markets and the continuous development of the tea industry, a significant number of tea dregs have been produced. In this context, the main objective of this study was to evaluate the adsorption-desorption of P in soil by biochar. The tea residue was used as a carbon source to synthesize biochar by pyrolysis. Combined with environmental factors, the biochar prepared at different pyrolysis temperatures was taken as the research object, Linear regression, root mean square error, mean absolute error and  $R^2$  were used to evaluate and analyze the data [27], and the influence of its input into tea garden soil on the adsorption-desorption performance of P on soil was discussed, which providing a theoretical basis for the resource utilization of tea residue and the improvement of soil P utilization efficiency.

## Material and Methods

### Experiment Materials

The tested soil was a typical tea garden soil (yellow brown soil), which was collected from the tea garden in Tongcheng County, China (N 31°522', E 116°533'). The region has a subtropical monsoon humid climate with an average annual temperature about 17°C. The average annual precipitation of 1300 mm-1500 mm. It has a mild climate, moderate rainfall, less frost and less snow and four distinct seasons. Soil samples were collected from the 0-20 cm topsoil layer, which were removed stones and roots, air-dried, ground and passed through a 2-mm sieve. The basic physical and chemical properties of each soil sample was determined according to the standard soil test method [28]. The concentration of total P was 72±3 mg/L. The basic physical and chemical properties of the soil in this area are as follows: the pH of the soil is 5.16, the concentration of CEC is 37.72 cmol·L<sup>-1</sup>, the content of organic matter is 19.14 g/kg, the content of total N is 6.39 g/kg, the content of Total P is 806.7 mg/kg, the content of available P is 2.9 mg/kg, and the content of available potassium is 256 mg/kg.

The waste tea dregs were collected from Huangshan tea factory in Anhui province. After removing the large particles impurities, the tea residue was ground to 2 mm sieve after air drying and put into use. The biomass carbon was prepared by oxygen limiting pyrolysis in muffle furnace. The N<sub>2</sub> was introduced as the protective gas, and the temperature was heated up to different temperatures (400°C, 500°C, 600°C) separately (10°C/min) and hold constant for 2 h of carbonation. After carbonization, cool to normal temperature, take out and grind 100 mesh sieve. The biomass carbon prepared at the pyrolysis temperature of 400°C, 500°C and 600°C was denoted by BC400, BC500 and BC600. The pH of biomass carbon was determined by the pH analysis of the composite pH electrode phs-3c after stirring at 25°C for 30 min. The CEC of biomass carbon was exchanged by ammonium acetate. Total N and organic C were determined by elemental analyzer (LECO Corp ration, St. Joseph, MI, USA). Total P was determined by molybdenum blue spectrophotometer (BioTek, epoch2, winooski, Vermont, USA). The results of the above basic physicochemical properties were mean values±standard deviation of duplicate measurements (Table 1).

### Culture Experiment

The mixture of soil and biochar (biochar/soil mass ratio is 0.25%, 0.5%, 1.0%, 2.0%) passing 2 mm sieve was put into the culture bottle and the water content was adjusted to 70 % of the field water capacity. The surface of the sample was covered with porous plastic film and the culture experiment was carried out in a closed incubator with a constant temperature

Table 1. Basic physical and chemical properties of biochar.

Sample	pH	CEC (cmol·L <sup>-1</sup> )	Total N (g/kg <sup>-1</sup> )	Total P (g/kg <sup>-1</sup> )	Organic C (g/kg <sup>-1</sup> )	BET (m <sup>2</sup> /g)
BC400	7.87a	34.89a	38.15a	4.34c	643c	1.156c
BC500	7.91a	23.57b	36.60b	5.06b	658b	2.298b
BC600	7.97a	21.82c	32.61c	5.86a	709a	3.481a

Note: Different uppercase letters indicate statistical significance at the  $P < 0.05$  using Duncan's multiple range test.

of 25°C (from November 2020). Deionized water was added every 3 days to maintain the initial water content, after 40 days, and air dry it, pass through 0.25 mm sieve for standby. There were 13 treatments in total, and each treatment was set to repeat 3 times.

### Isothermal Adsorption-Resorption Tests

In phosphorus sorption/desorption experiments, the 2.00 g soil and biochar mixture samples were placed in 50 mL centrifuge tubes and added into 20 mL  $\text{KH}_2\text{PO}_4$  solution with concentration of 0, 20, 40, 60, 80, 100, 120, 160 and 200 mg/L, according to  $m$  (sample):  $v$  (solution) = 1:20. 0.01 mol/L KCl solution was used as background electrolyte and 3 drops of chloroform was added to inhibit microbial activity. The centrifuge tube was oscillated at 25°C for 24 hours, then centrifuged at 5000 rpm for 10 min. The supernatant was immediately filtered through syringe filter with aperture of 0.45  $\mu\text{m}$ .

After the completion of the adsorption experiment, take the samples with the above concentration of 20, 100 and 200 mg/L, added 25 mL 0.01 mol/L KCl solution into the centrifuge tube to remove the supernatant, stir evenly and oscillate for 1 h. After equilibration at 25°C for 24 hours, centrifuged at 5000 rpm for 10 min, the supernatant was immediately filtered through syringe filter with aperture of 0.45  $\mu\text{m}$ . Take the filtered solution for testing.

### Evaluation of Environmental Factors Affecting P Adsorption Behavior

In order to study the effect of temperature on the P adsorption in soil, isothermal adsorption experiments were carried out at 288 k, 298 K and 308 k, which were denoted by  $T_1$ ,  $T_2$  and  $T_3$ . Before the test, adjusted the initial pH of P containing solution to 4.0 with 0.01 mol/L HCl or NaOH solution  $4.0 \pm 0.2$ ,  $7.0 \pm 0.2$  and  $9 \pm 0.2$ . The effect of pH of initial solution on P adsorption by soil was tested, which were denoted by pH = 4, pH = 7 and pH = 9. Each group was repeated 3 times.

### Data Analysis

The absorption capacity of biochar ( $Q$ , mg/g) is calculated by Equation (1):

$$Q = \frac{(C_0 - C_e) \times V}{M} \quad (1)$$

Where  $Q$  is the adsorption of capacity (mg/g);  $C_0$  is the concentration of initial solution (mg/L);  $C_e$  is the concentration of adsorption equilibrium solution (mg/L);  $V$  is the volume of initial adsorption solution (L);  $M$  is the mass of the sample (g).

The adsorption process of P by tea garden soil and tea garden soil with biochar was fitted by Langmuir model (2) and Freundlich model (3).

$$Q = \frac{K_L C_e Q_{max}}{(1 + K_L C_e)} \quad (2)$$

Langmuir model:

and

$$Q = K_F C_e^{1/n} \quad (3)$$

Freundlich model:

Where  $K_L$  is the equilibrium constant of Langmuir adsorption model;  $Q_{max}$  is the maximum adsorption capacity (mg/g);  $K_F$  is the empirical coefficient of Freundlich adsorption model;  $1/n$  is a dimensionless coefficient related to the adsorption strength.

The desorption capacity of biochar ( $Q_n$ , mg/g) is calculated by Equation (4):

$$Q_n = \frac{(V_a C_a - V_e C_e)}{M} \quad (4)$$

Where  $Q_n$  is the desorption amount (mg/g);  $V_a$  is the volume of desorption equilibrium solution (L);  $C_a$  is the concentration of desorption equilibrium solution (mg/L);  $V_e$  is the volume of residual sample of adsorption equilibrium solution (L);  $C_e$  is the concentration of adsorption equilibrium solution (mg/L);  $M$  is the mass of the sample (g) (The value of  $V_e$  can be regarded as equal to the weight of the sample residual solution).

To gain a better understanding of the phosphate adsorption process, the adsorption thermodynamics analysis was further explored, as indicated below.

$$\Delta G = -RT \ln K_m \quad (5)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (6)$$

$$Q_m = nRT \quad (7)$$

Where  $\Delta G$  is Gibbs free energy (kJ/mol);  $\Delta S$  is the entropy change of adsorption (J/mol);  $\Delta H$  is the enthalpy change of isosteric adsorption (kJ/mol);  $Q_m$  is the adsorption heat (J/mol);  $T$  is the absolute temperature;  $R$  is the ideal gas constant (8.314);  $K_m$  is the thermodynamic equilibrium constant, which is transformed from the  $K$  value in Langmuir equation and  $n$  is the value in Freundlich equation.

### Analytical Methods

The morphology and size of biochar was observed by SEM (JSM-7600F). The crystal structure of biochar was analyzed by X-ray diffraction (XRD Smartlab 9 kw). The surface functional groups of biochar were determined by Fourier transform infrared spectroscopy (FTIR) (Nicolet is10). In the isothermal adsorption test, the supernatant was poured out and filtered, and then determined by ascorbic acid phosphomolybdate blue colorimetry and ultraviolet spectrophotometer.

### Statistical Analysis

Data processing and analysis was performed with Microsoft Office Excel 2010 (Microsoft, Raymond, Washington, USA). The  $P$  adsorption curve was plotted by originpro8.0 (Originlab company, Northampton, Massachusetts, USA). PASW statistics 18 (SPSS, Chicago, Illinois, USA) was used for statistical analysis. The average was calculated from three replicates of each experiment. The statistical significance of difference was conducted through the analysis of variance (ANOVA). The level of accepted statistical significance was  $P < 0.05$ . According to the Michelin

guideline scale,  $P < 0.05^*$  was statistically significant,  $P < 0.01^{**}$  was highly statistically significant.

## Results and Discussion

### Characterization of Biochar

Biochar is composed of irregular plates and particles of different sizes [29]. As shown in Fig. 1 under a scanning electron microscope magnification of 5000 $\times$  the structure of the tea residue biochar changes depending on the pyrolysis preparation temperatures. The pore distribution of biochar prepared at 400 $^{\circ}\text{C}$  (BC400) was relatively disordered, and the surface texture was rough and uneven. With an increase in temperature to 500 $^{\circ}\text{C}$  (BC500), the volatile components of biochar cracked and precipitated, and the biochar began to fracture; When the temperature rose to 600 $^{\circ}\text{C}$  (BC600), the fracture phenomenon became more obvious and the fracture delamination phenomenon appeared.

Fourier transform infrared spectroscopy (Fig. 2) showed that the aliphatic unsaturated C-H stretching vibration absorption peaks appeared at 3432  $\text{cm}^{-1}$  for biochar with different pyrolysis temperatures, Aliphatic saturated C-H stretching vibration absorption peaks appeared at 2920  $\text{cm}^{-1}$  and 2845  $\text{cm}^{-1}$ , and the C=C stretching vibration absorption peak of the aromatic skeleton appeared at the wave number of 1612  $\text{cm}^{-1}$ . This indicated that the three biochars had similar molecular structure characteristics. BC400 biochar exhibited aliphatic C-H deformation vibration at a wavelength of 1312  $\text{cm}^{-1}$ , C-O-C stretching vibration of alcohols and ethers, and C-O stretching vibration of aromatic esters were observed at a wavelength 1114-13120  $\text{cm}^{-1}$ . The C-H bending vibration peak was observed at wavelength of 781  $\text{cm}^{-1}$ . This indicated a high concentration of aromatic components.

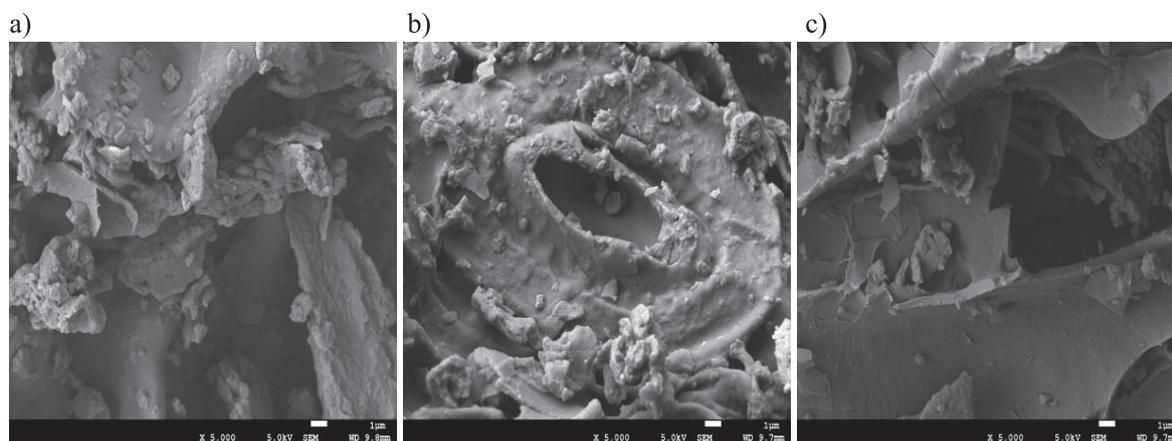


Fig. 1. SEM images of different biochars: a) BC400, b) BC500, c) BC600 (The treatment codes represent biochars made from tea residue. The figure 400, 500 or 600 represents the corresponding pyrolysis temperature).

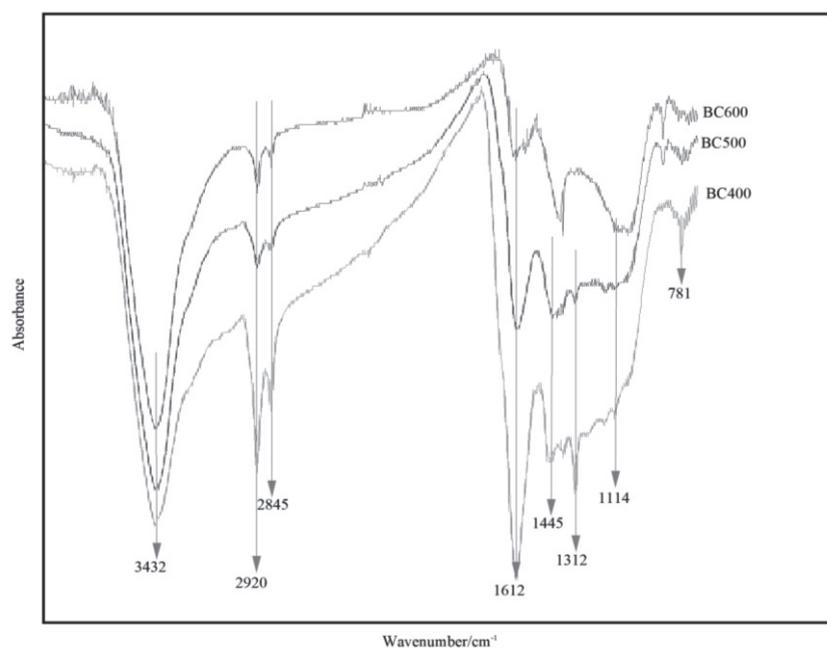


Fig. 2. The FTIR spectra of biochar at different pyrolysis temperatures.

#### *P Adsorption Capacity of Biochar*

Adsorption of phosphorus (P) in soil from biochar depends on the source of the biochar's raw materials [30], the pyrolysis temperature of the biochar, and the amount of biochar added to soil. The P adsorption isotherms of the tea garden soil with biochars produced at different pyrolysis temperatures are shown in Fig. 3. The variation trend of soil adsorption isotherms of different treatment temperatures were consistent based on the percentage of biochar added to soil: the maximum adsorption amount of P in soils decreased in the following order of biochar to soil percentages for biochar produced at all temperatures: 1.0% > 0.5% > 0.25% > CK > 2%. The adsorption capacity increased with increasing P concentration in the equilibrium solution. With increasing P concentration in the equilibrium solution, the adsorption capacity of phosphorus initially increased, and then tended to stabilize. Under high phosphorus concentration conditions, when the addition of biochar to soil was 1.0 %, the effect on adsorption of phosphorus in soil was the most significant, and the maximum adsorption capacity  $Q_{\max}$  was 1502.11 mg/g. Under different pyrolysis temperatures (BC400, BC500 or BC600), when the carbon was added to soil in a 1.0 % mix, the maximum adsorption of P  $Q_{\max}$  in soil increased by 314.36 mg/g for BC400, 260.32 mg/g for BC500 and 87.43 mg/g for BC600 compared with CK; When the addition of biochar increased to soil increased to 2.0 %, the maximum adsorption capacity  $Q_{\max}$  decreased by 4.08 mg/g for BC400, 44.96 mg/g for BC500 and 128.93 mg/g for BC600 compared with CK. The results showed that the addition ratio of biochar affected P adsorption, and the greatest

increase in adsorption was observed when the addition ratio of biochar was 1.0 %. As shown in Fig. 3, the maximum adsorption amount of P in soils decreased in the following order: BC400 > BC500 > BC600, indicating that the pyrolysis temperature can significantly affect the adsorption of P. To further explore the effect of tea residue biochar prepared at different pyrolysis temperatures on the adsorption mechanism of P, the Langmuir equation and Freundlich equations were used to fit the isothermal adsorption process. The Langmuir equation refers to a single-layer surface adsorption process [31]. The Freundlich adsorption model is used to describe the chemisorption behavior between both monolayers [32] and multilayers [33], the empirical constant  $n$  can indicate the strength of adsorption performance. When  $1/n$  is less than 1, the adsorption process is easier [34]. Fitting the results of the Freundlich equation showed that the correlation coefficients were  $0.92 < R^2 < 0.98$ , which was an extremely significant correlation (Table 2). This further indicated that the Langmuir equation and Freundlich equation were suitable for the isothermal adsorption performance fitting of biochar for P in this study.  $K_L$  is the intensity factor of soil P adsorption [35], which generally indicates the affinity of P for soil colloids. The higher the  $K_L$  value is, the higher the P adsorption intensity is [36]. Among the treatments with different pyrolysis temperatures, the  $K_L$  value of the mixed tea garden soil treated with BC400 was the largest, which indicated that the adsorption capacity of the biochar at this pyrolysis temperature was the strongest, and the adsorbed P was stable and not easy to be desorbed.

In this study, the difference of phosphorus adsorption capacity of soil under the action of biomass

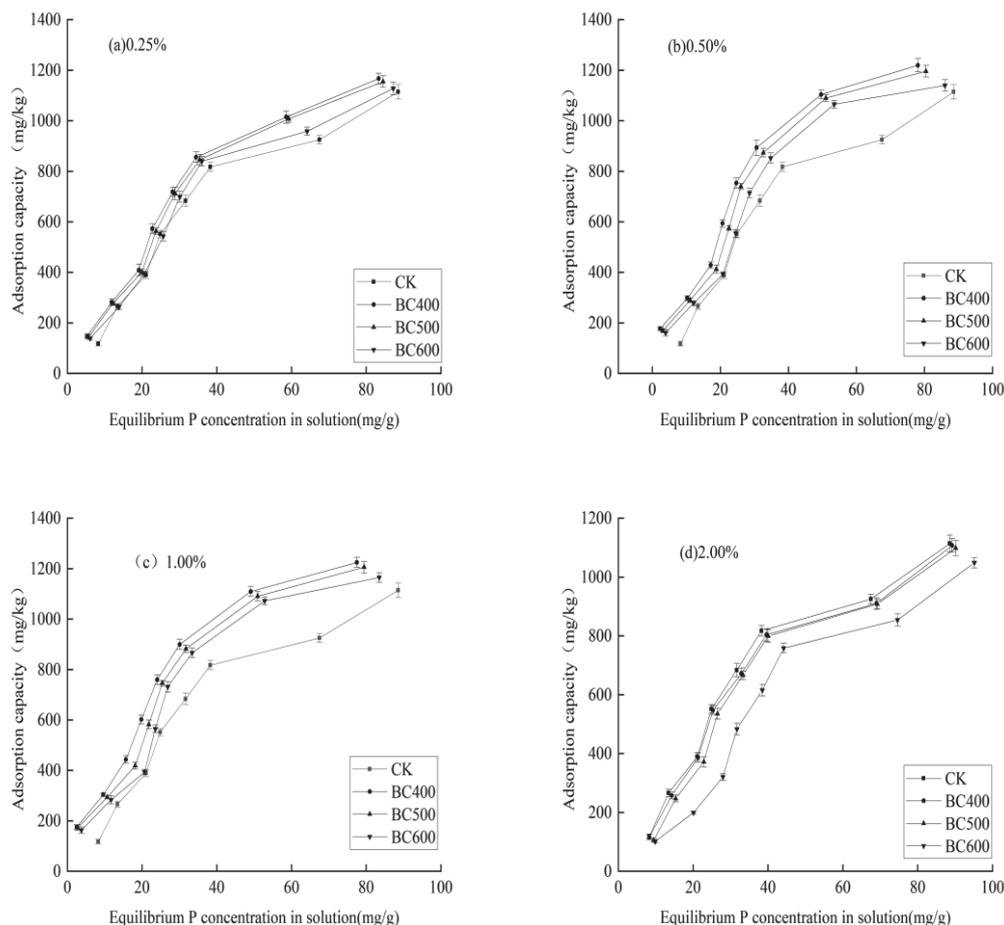


Fig. 3. Adsorption isotherms of different pyrolytic biochar in soil. Error bars represent standard error of triplicate samples (The figure 0.25%, 0.50%, 1.00% or 2.00% represents the addition ratio of biochar).

carbon at different pyrolysis temperatures is BC400 > BC500, BC600. According to the SEM analysis, when the pyrolysis temperature of biochar was 500°C and 600°C, the structure of biochar was broken and the P adsorption capacity of soil was less than that of biochar at 400°C, indicating that the structure of the biomass was the main factor affecting P adsorption in soil. The results of this study are consistent with the results of Eduah J.O. et al. [37] on three types of soil improvement by biochar produced at different pyrolysis temperatures. The reason for this phenomenon may be that with the increase in pyrolysis temperature, it is difficult for the biochar to maintain its original internal structure, and it begins to fracture, thus reducing the sites of P adsorption on the soil surface and the total amount of P adsorption. As shown in Table 2, when the addition of biochar to soil was 1.0 %, the adsorption capacity of P was the largest. When the addition of biochar increased to 2.0 %, the adsorption capacity of soil was lower than that of CK. The results of Liu Z. et al. [38] and Mahmoud E. et al. [39] were consistent with the experiment, the content of available P in soil increased with an increase in biochar content, and the adsorption capacity of P in soil decreased accordingly.

The reason for this phenomenon may be that biochar is similar to lime. When a lower proportion of biochar is added to the soil, the modification of acidic soil by biochar leads to the precipitation of activated iron and activated aluminum with an increase in pH [40]. The newly precipitated polymers provide P adsorption sites in the soil, thus increasing the amount of P adsorption in the soil; organic anions and carbonates are the main forms of alkaline substances in biochar [41], and when the proportion of biochar increases to a certain extent, the organic anions provided by the biochar may compete with phosphate for the adsorption sites of the soil colloids. At the same time, biochar itself carries P, which is released after entering the soil, and so a higher proportion of biochar may hinder the adsorption of P.

#### P Desorption Capacity of Biochar

As an indicator of the adsorption strength, the desorption rate can reflect the firm degree of the combination of colloidal surface active adsorption sites and adsorbents [42]. As shown in Table 3, under different treatments (initial solution concentrations

Table 2. Isotherm parameters for the adsorption of phosphate on biochar.

Biochar sample	The addition ratio of biochar/%	Langmuir model			Freundlich model		
		$Q_{\max}$ (mg/g)	$K_L$ (L/mg)	$R^2$	1/n	$K_F$	$R^2$
CK	0	1187.75	0.00199	0.982	0.656	61.112	0.924
BC400	0.25	1359.58	0.00494	0.984	0.625	78.277	0.981
	0.50	1441.76	0.00576	0.965	0.580	105.129	0.971
	1.00	1502.11	0.01028	0.975	0.564	114.003	0.979
	2.00	1183.67	0.00193	0.983	0.669	56.749	0.983
BC500	0.25	1346.97	0.00408	0.983	0.639	72.294	0.980
	0.50	1428.15	0.00427	0.964	0.610	89.525	0.963
	1.00	1448.07	0.00547	0.965	0.596	95.931	0.966
	2.00	1142.79	0.00078	0.982	0.703	48.379	0.981
BC600	0.25	1215.02	0.00196	0.976	0.640	68.830	0.972
	0.50	1325.43	0.00222	0.962	0.617	80.456	0.952
	1.00	1354.47	0.00263	0.956	0.613	83.653	0.950
	2.00	1058.82	0.00070	0.971	0.803	27.977	0.965

of 20 mg/L, 100 mg/L and 200 mg/L), the desorption rate of P to soil increased with an increase in initial P solution concentration, and the maximum desorption of P to soil decreased in the following order: 200 mg/L > 100 mg/L > 20 mg/L. When the addition of BC400 was at 1.0 % and the initial P concentration

was 20 mg/L, the desorption rate was 15.23 %, when the initial P concentration was 100 mg/L or 200 mg/L, the desorption rates were 19.63 % and 27.19 %, respectively. On comparing biochar produced under different pyrolysis temperatures, the maximum desorption ability of P in soils was found to decrease

Table 3. Effect of biochar on P desorption rate at different temperatures.

Initial P concentration in solution (mg/L)	Biochar amendment rate (%)	BC400 (%)	BC500 (%)	BC600 (%)
20	0.00	38.45±0.22a	38.45±0.22a	38.45±0.22a
	0.25	22.02±0.05c	26.15±0.24b	32.86±0.35a
	0.50	17.35±0.04c	21.77±0.05b	27.00±0.04a
	1.00	15.23±0.28c	20.87±0.07b	25.41±0.08a
	2.00	40.77±0.4b	41.09±0.26b	42.24±0.07a
100	0.00	48.16±0.22a	48.16±0.22a	48.16±0.22a
	0.25	27.90±0.07c	28.03±0.04b	29.64±0.05a
	0.50	22.04±0.2c	24.19±0.05b	27.84±0.06a
	1.00	19.63±0.05c	22.71±0.04b	23.19±0.04a
	2.00	45.94±0.2b	46.24±0.13b	47.30±0.04a
200	0.00	52.39±0.24a	52.39±0.24a	52.39±0.24a
	0.25	41.82±0.08c	42.35±0.04b	43.68±0.06a
	0.50	37.25±0.17c	38.26±0.02b	39.31±0.03a
	1.00	27.19±0.09c	29.85±0.04b	32.30±0.04a
	2.00	53.16±0.04c	53.64±0.07b	55.36±0.04a

Note: The experimental results were indicated as mean±standard deviation. Different lowercase letters in the same column in the table indicate significant differences among treatments ( $P < 0.05$ ).

Table 4. Thermodynamic parameters of P adsorption in soil.

Sample	T (K)	Langmuir model			Freundlich model			Q <sub>m</sub> (J/mol)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (KJ/mol·K)
		Q <sub>max</sub> (mg/g)	K <sub>L</sub> (L/mg)	R <sup>2</sup>	1/n	K <sub>F</sub>	R <sup>2</sup>				
1.0% BC400	288	1280.3	0.008	0.96	0.69	51.7	0.95	3467.9	-13.398	35.71	0.17
	298	1425.7	0.034	0.98	0.62	86.4	0.98	3994.2	-15.136		
	308	1613.0	0.184	0.98	0.56	136.2	0.98	4555.9	-16.809		

in the following order: BC600>BC500>BC400. The higher the temperature of biochar preparation, the stronger the P desorption capacity of the soil, which is consistent with the P adsorption capacity of biochar produced at different pyrolysis temperatures. The results showed that the maximum desorption ability of P in soils decreased in the following order: 2.0%>CK>0.25%>0.5%>1.0%, which indicated that adding a certain amount of biochar to soil could reduce the leaching of P and inhibit the desorption of P, but adding too much biochar could promote the desorption of P. In this study, the Langmuir and Freundlich equations fit the P adsorption behavior of soil under the condition of biochar addition, which shows that when the proportion of biochar added is within a certain range (0.25% - 0.5%), the P adsorption capacity of soil increases with increase in biochar addition.

Carbon adsorbed on biomass can not be completely desorbed, which is called desorption lag phenomenon, which generally exists in the process of soil pesticide/fertilizer interaction. In this study, the application of tea residue biochar significantly reduced the phosphorus desorption of tea garden soil, which is mainly due to the strong adsorption capacity of biochar, which can slow down the desorption or isolation of compounds and produce the lag phenomenon of absorption. A possible reason for this phenomenon is that when the concentration of P solution is low, the adsorption sites on the surface of biochar are relatively sufficient, and the adsorbed P is difficult to desorb. When the concentration of P solution is gradually increased, the P on the adsorption sites is gradually saturated, the adsorption capacity will be low, and the P adsorbed in other ways is easily desorbed. In the high concentration P solution, the higher the P saturation, the stronger the desorption capacity of P, and the greater the leaching risk of adsorbed P in the soil. In addition, the parameters calculated by the Langmuir model also verified this result. When the proportion of biochar added was low, Q<sub>max</sub> increased with an increase in biochar addition, indicating that adding an appropriate amount of biochar can promote the adsorption of P in soil. At the same time, adding appropriate amount of biochar can reduce the desorption rate of P and reduce the risk of P leaching. As tea residue is considered a waste by the beverage industry, it is easy to obtain, and so tea residue biochar has a broad application prospects in improving soil P fixation.

## Effects of Environmental Factors on the Adsorption Behavior of P

### *Effect of Temperature*

Temperature is an important factor affecting the characteristics of chemical reactions [43]. Soil ion adsorption is a reaction that is affected by temperature change [44]. In summary, when the addition of biochar was 1.0 % BC400, the adsorption-desorption effect of soil on P was the best, therefore, this sample was used to further study the adsorption behavior of phosphorus at different temperatures. The results of the thermodynamic parameters of P adsorption in soil are shown in Table 4. According to Table 4, the order of ΔH P adsorption in soil is 288 K>298 K>308 K, indicating that P is easy to be adsorbed when T = 308 K; The results showed that there were significant differences in the adsorption efficiency of phosphorus in soil under different environmental temperatures. The adsorption capacity of P in each soil at high temperatures was larger than that at low temperatures. Compared with the maximum adsorption capacity, the maximum adsorption capacity can be increased by 187.3 mg/kg based on a temperature increase of 10 K.

It can be seen from Table 4 that the increase of temperature promotes the adsorption of phosphorus, indicating that the adsorption of phosphorus by soil is an endothermic process. When the initial concentration of P solution continued to increase, the adsorption capacity of P in soil increased and finally stabilized. ΔG are all negative, which indicates that the adsorption reaction can take the initiative. The lower the free energy, the more favorable the adsorption reaction [45]. A positive value of indicates that the phosphorus adsorption process is endothermic [46]. ΔS is a measure of disorder or order before and after phosphorus adsorption by soil [47]. The multistage of adsorption energy sites is affected by ΔS value, which indicates that phosphorus is multi-level adsorption. It can be seen from Table 4 that the binding energy K value of phosphorus adsorption at high temperature is greater than that at low temperature, indicating that the adsorption strength of phosphorus can be improved by increasing temperature. This is consistent with the determination of adsorption heat Q<sub>m</sub>. The higher the temperature is, the larger the Q<sub>m</sub> value is. At high temperature, the more firmly the soil adsorbs

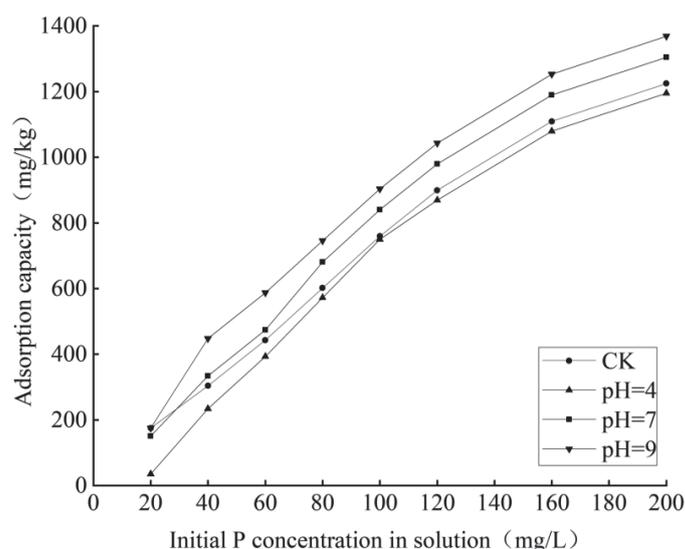


Fig. 4. Effect of pH of initial Phosphorus Solution on phosphorus adsorption.

Table 5. Correlation analysis of factors affecting soil P adsorption.

Variation	C(mg/L)	T(K)	pH	C×T	C×pH	T×pH	C×T×pH
Adsorption capacity (mg/g)	0.993**	0.987**	0.697*	0.984**	0.906**	0.901**	0.937**

Note: \* and \*\* respectively showed significant correlation between  $P < 0.05$  and  $P < 0.01$ .

phosphorus. This is consistent with the previous conclusion, that the adsorption of P in soil is an endothermic reaction, and the adsorption of P in soil is positively correlated with the temperature in the environment. In addition, the above characteristics of the endothermic reaction also show that the adsorption process of P is a chemical reaction rather than a physical adsorption [48].

#### Effect of pH

When the addition of biochar was 1.0% BC400, the results of P adsorption behavior of the initial solution change depending on the pH, as shown in Fig. 4. The of P adsorption increased in the following order of pH: 4<7<9. Compared to CK without biomass carbon, the maximum adsorption capacity of P increased by 341.45 mg/kg at pH of 4, 794.17 mg/kg at pH of 7, and 1069.35 mg/kg at pH of 9. the total maximum adsorption capacity of P was 2257.10 mg/kg at pH of 9. It indicates that the initial P solution significantly promoted the adsorption of P at different pH values.

In this study, the change in the pH value of the initial P solution concentration has an effect on soil P availability, in that reducing pH can increase the adsorption of P by organic coordination on soil particles. Ajmal Z. et al. [49] studied the adsorption, desorption and regeneration of phosphate, which showed that the adsorption capacity of phosphate increased with an increase in pH, this finding was

supported by the results of this experiment. The reason for this phenomenon may be that the increase of pH promotes formation of hydroxide precipitation from iron and aluminum oxides [50]. At the same time, the single P coordination complex rapidly transforms to the double P coordination complex, which reduces the concentration of free iron and aluminum oxides in acidic soil, thus reducing the adsorption of P. Therefore, increasing the pH of the initial P solution can increase the adsorption capacity of soil. To further explore the P adsorption effect of soil under different environmental conditions, a correlation analysis of the environmental factors affecting its adsorption capacity was carried out. As shown in Table 5 the initial concentration and temperature had extremely significant effects on the process of P adsorption ( $P < 0.01$ ). The pH of the solution had a significant effect on the process of P adsorption ( $P < 0.05$ ). The combined effect of these variables on P adsorption in soil is extremely significant. This confirmed that the initial concentration, temperature, and pH played an important role in the process of P adsorption.

#### Conclusions

In this study, after tea residue biomass carbon was input into soil, it could increase the adsorption of phosphorus and reduce the desorption of phosphorus rate. The adsorption desorption characteristics of tea

residue biochar on tea garden soil were significantly different at different pyrolysis temperatures, which showed that BC400>BC500>BC600, while the desorption rate was on the contrary, BC400<BC500<BC600.

Tea residue biochar promoted the adsorption process of P in soil when the proportion of biochar was within a certain range in the soil (0.25%-1.0%). In addition, the Langmuir equation can describe the process of phosphorus adsorption ( $0.95 < R^2 < 0.98$ ). When the proportion of biochar was within a certain range (0.25%-1.0%), the application of tea residue biochar to soil significantly reduced the soil P desorption, mainly due to the strong adsorption capacity of the biochar, which could slow down the desorption of compounds.

Environmental conditions strongly affected the adsorption of phosphorus in the soil. The adsorption of phosphorus in soil is spontaneous and is positively correlated with the temperature of the environment and the pH of the initial solution. Under the combined action of concentration, temperature, and pH, the correlation is 0.937. Therefore, adding an appropriate amount of tea residue biochar to the soil was found to be an effective approach to realize the utilization of resources, economy and environment.

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### Conflict of Interest

The authors declare no conflict of interest.

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