# Effects of Different Biochar on Adsorption Performance of Nitrogen, Phosphorus, and Cadmium in Farmland Soil

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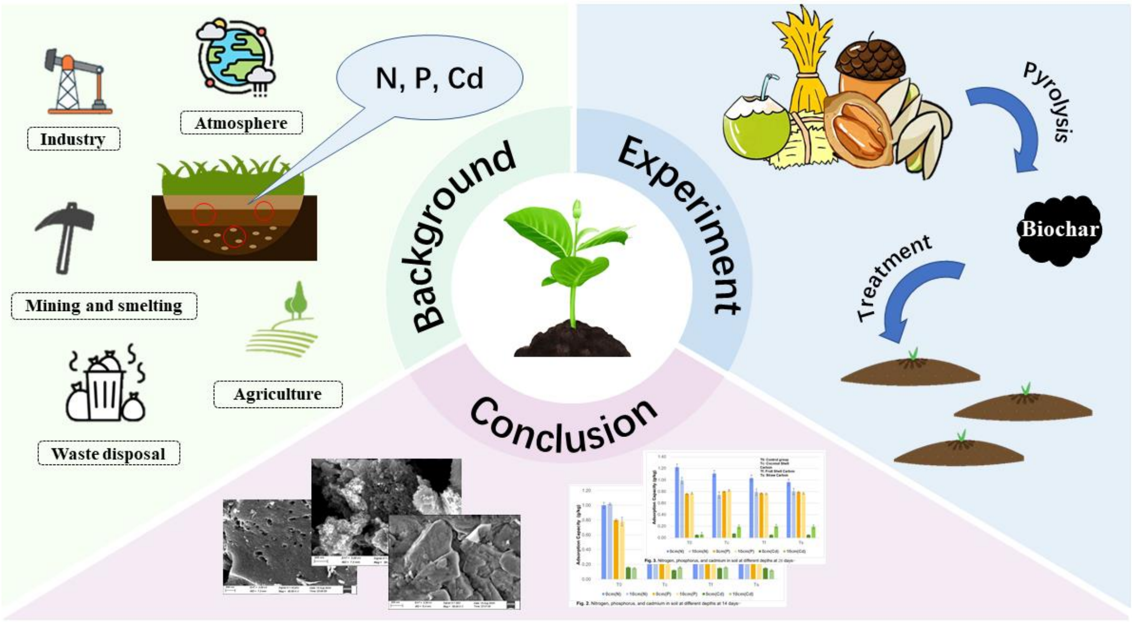
## GRAPHICAL ABSTRACT



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With the acceleration of urbanization, while the amount of fertilizers used in agricultural production is increasing rapidly in industrial development, heavy metal pollution is also becoming more severe. Excessive use of fertilizers can lead to soil acidification, compaction, and degradation, while the sharp increase in heavy metal pollution observed also has adverse effects on soil quality and crop quality. Therefore, to prevent the loss of phosphorus from soil, improve the utilization rate of nitrogen in soil, and control cadmium pollution, the effects of biochar on the adsorption of nitrogen, phosphorus, and cadmium in soil were explored in this study. The following four experimental treatments were conducted: no biochar application, straw charcoal application, fruit shell charcoal application, and coconut shell charcoal application. Samples were collected from different soil depths (0 cm and 10 cm) after both 14 days and 28 days. The contents of total nitrogen, phosphorus, and cadmium were compared. The research findings indicate that these three types of biochar exhibit significant adsorption effects on nitrogen and phosphorus elements. Nevertheless, the adsorption effect on cadmium is not pronounced, potentially due to the stability of the biochar, the activity of microorganisms in the soil, and the alteration of cadmium speciation, which consequently results in an increase in cadmium content.

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## INTRODUCTION

Nitrogen and phosphorus are important elements in the soil ecosystem and play an important role for both agricultural production and environmental protection. However, problems such as excessive application of nitrogen and phosphorus fertilizers and the resulting heavy metal pollution are becoming increasingly serious (Dou and Guo 2022). For example, Hong *et al.* (2023) monitored the risk of eutrophication in the water quality of Lung Ngoc Hoang Nature Reserve using multivariate statistical methods. They found severe pollution such as $Fe^{2+}$ in the area. How to manage these elements and reduce their negative impacts on the environment has become a focus of scholarly attention. Biochar is a carbonaceous material obtained from organic wastes through carbonization and combustion processes (Ma *et al*. 2022) . Because of its special structure and chemical properties, biochar is widely used for agricultural production, environmental protection, among others (Zheng 2007). For example, Wijitkosum (2023) used biochar prepared from disposable bamboo chopsticks through pyrolysis for research, and the results showed that it has high potential for reducing greenhouse gas emissions and carbon sequestration. Pan *et al.* (2024) used magnesium ion modified wheat straw to prepare biochar for removing phosphates from water pollution. Zhai *et al.* (2021) used cotton biochar to investigate its adsorption effect on cadmium ions in water. In addition, Aneke and Joy (2023) used other methods to remove pollutants. They built a test platform and conducted leachate experiments, achieving removal rates of 98%, 99%, and 99.9% for arsenic, cadmium, and lead, respectively. Under the same soil and nano slag dosage and equilibrium conditions, the contents of Zn, Cu, Fe, Ni, and Hg reached 98%, 95.45%, 93.3%, 97%, and 89%, respectively.

Elements such as nitrogen, phosphorus, and cadmium (Li *et al.* 1998) in the soil matrix have strong adsorptive capacity in biochar (National Bureau of Statistics of the People's Republic of China 1988), therefore, biochar application can effectively reduce the migration and transformation of these elements, thus substantially impacting the soil environment (Dai *et al.* 2016). Research on its effect on the nitrogen cycle in soil has become a hot topic. Biochar has a strong adsorptive capacity because of its macropore structure, high specific area, and richness of functional groups (Huang *et al.* 2016). Research has shown that biochar can effectively adsorb nitrogen, phosphorus, and cadmium ions from the soil, thus improving soil nutrient utilization and environmental quality. In conclusion, research on the adsorption of nitrogen, phosphorus, and cadmium from soil by biochar is of great importance. The knowledge obtained not only can help to solve the problem of phosphorus deficiency in soil, but it also can help to control the loss of nitrogen from soil, reduce cadmium pollution, promote plant growth, increase crop yield, reduce the use of chemical fertilizers, mitigate environmental pollution, and reduce resource waste. At the same time, biochar utilization also has important economic and environmental importance and can be used to achieve both energy development and sustainable agricultural development.

Biochar is a carbon-rich product that is produced by pyrolysis of biomass in a reactor under limited oxygen supply and reasonably elevated temperature conditions (Gautam *et al.* 2021). The International Biochar Initiative defines biochar as solid material obtained from the carbonization of biomass. Common raw materials used to produce biochar are generally obtained from agricultural by-products, feces, and industrial waste (Ren 2022), examples of which are rice husks, straw, wood, peel, sludge, garbage, livestock manure, and paper residues. Research also identified considerable differences in structural characteristics and functions of biochar from different sources (McKendry 2002). Biochar is mainly composed of nutrients such as carbon, hydrogen, oxygen, sulfur, potassium, calcium, sodium, and magnesium, with a carbon content exceeding 60% (Lü *et al.* 2015).

Biochar has a relatively high specific area, high porosity, and multiple functional groups. It has a good adsorptive effect for a variety of pollutants and therefore plays an important role in research on pollutant adsorption (Ahmad *et al.* 2014).Biochar has stable aromaticity as well as loose and porous structural characteristics. Its application in soil can effectively reduce soil bulk density, increase soil porosity, and improve and enhance soil respiration (Fang *et al.* 2014). The rich carbon, organic matter, and mineral contents in its structure can improve the soil acid-base system, enhance the soil buffering capacity, delay nitrogen and phosphorus losses, and maintain the stability of the soil structure; consequently, the soil can better retain water and fertilizer (Wu *et al.* 2014).

The adsorption performance of biochar for pollutants changes with the content of surface functional groups. Biochar contains an abundance of functional groups, such as carboxy, aromatic alcohol, and other oxygen-containing functional groups, which play important roles in adsorption (Zhang *et al*. 2021). Pyrolysis temperature and biochar raw material are two key factors for controlling the quantity and types of functional groups present on the biochar surface (Zhao *et al*. 2011). The biochar surface can be improved by increasing oxygen-containing functional groups, which increases its maximum adsorptive capacity for cadmium by 21.2% (Chen *et al*. 2021).

Among abundantly available renewable energy sources, biomass provides a type of energy with a wide array of sources, simple centralized processing, little environmental pollution, and broad prospects for development and utilization. According to statistical data, in 1999 the amount of crop straw alone reached approximately 640 million tons (Lehmann 2007), which now exceeds 700 million tons. However, 33 to 40% of straw is directly discarded on farmland or burned in the open, which not only wastes a large amount of straw resources, but also damages soil structure and reduces soil productivity. Using waste residues for the preparation of biochar can not only reduce waste landfill and environmental pollution caused by incineration, but also promote the utilization and development of agricultural resources.

In addition, as a relatively large renewable carbon resource in the world, biomass has unique advantages in environmental protection and resource recycling, and is considered to be the most promising renewable new energy source for future development .This resource is associated with large reserves, a wide distribution, easy access, renewability, and low price. The use of biomass conversion technology can effectively replace coal, oil, and gas, providing a new pathway for increasing revenue and reducing expenditure.

Inorganic soil pollution in China is mainly heavy metal pollution, and the pollution level is relatively serious in certain areas. According to the *National Soil Pollution Survey Bulletin*, the occurrence rate of the eight inorganic pollutants of Cd, Hg, As, Cu, Pb, Cr, Zn, and Ni in the soils of China are 7.0%, 1.6%, 2.7%, 2.1%, 1.5%, 1.1%, 0.9%, and 4.8%, respectively (Report on the National General Survey of Soil Contamination 2014) . In particular, farmland in the suburbs of most Chinese cities has been contaminated by heavy metals to varying degrees, which seriously affects the safety of food products and needs to be repaired or controlled urgently (Zhang *et al*. 2014) .

Biochar is mostly alkaline and its addition considerably increases the pH of acidic soils (Fan *et al*. 2013); however, its effect on increasing the pH of alkaline soils is not apparent (Li 2013) and biochar addition may even cause the pH to decrease. The effect of biochar on soil pH is related to the individual pH levels of both soil and biochar and the amount of biochar added (Yuan and Xu 2012). The greater the difference in pH values between biochar and recipient soil, the greater the amount of biochar added, and the more apparent the resulting change in soil pH (Luo *et al*. 2014). Under alkaline conditions, phosphorus can co-precipitate with Mg and Ca on the surface of biochar. Other heavy metals, such as Cd, Zn, Pb, and Hg, also co-precipitate easily (Wang *et al*. 2015) . They transfer to the biochar (where they are fixed) from the water body, and react specifically with iodide and iodate ions on the aromatic ring structure of the biochar (Lin *et al*. 2001).

## EXPERIMENTAL DESIGN

### Overview of the Experimental Area

The experimental site is located at a farm in Mengjin District, Luoyang City, Henan Province (34°83′N, 112°45′E), China. This site lies in a transition zone between the subtropical and temperate zones. The monsoon circulation has a substantial influence, with frequent winds and droughts in spring, hot and rainy summers, cool and sunny autumns, and little rain and snow in winter. Rain and heat occur at the same time, with precipitation concentrated in summer and an average annual temperature of 13.7 ℃. January is the coldest month with an average temperature of -0.5 ℃, and July is the hottest month with an average temperature of 26.2 ℃. The average precipitation is 650.2 mm. The duration of the frost-free period is 209 days. The annual sunshine duration is about 1869.7 h.

### Materials

The experiment was conducted on farmland (Table 1) that had been cultivated evenly for the preceding 5 years. The experiment was carried out under natural environmental conditions. The experimental plot had a size of 1 $m^2$ and was separated by thin lines. The soil sampling depths were 0 cm (surface) and 10 cm. Soil samples were scraped from soil depths of 0 cm and 10 cm using a sampling tool. The soil samples were air-dried indoors, all plant roots were removed, and the samples were passed through a 2-mm soil sieve before being sealed and labelled. The mass of each bag of soil was approximately 200 g. The various types of biochar were produced by Henan Dakang Water Purification Materials Co., Ltd., China. The basic physical and chemical properties of soil are shown in Table 1. Biochar was made either from straw charcoal, fruit shell charcoal, or coconut shell charcoal. Its basic physicochemical properties are shown in Table 2. These biochars were uniformly obtained by pyrolysis at 600 °C for 2 h.

**Table 1.** Soil Basic Properties

| pH | Organic C (g/kg) | Total P (g/kg) | Total N (g/ kg) | Total Cd (g/kg) | Clay (g/kg) | Texture |
|---|---|---|---|---|---|---|
| 7.58 | 5.95 | 0.48 | 0.58 | 0.19 | 227 | Clay |

**Table 2.** Physical and Chemical Properties of the Different Biochar

| Sample | Preparation temperature (°C) | Surface Area ($m^2$/g) | Organic C (g/kg) | Total N (g/kg) | Total P (g/kg) | Total K (g/kg) | Total Na (g/kg) | pH | Mesh |
|---|---|---|---|---|---|---|---|---|---|
| Straw Carbon | 600 | 13.7 | 650 | 15.2 | 5.0 | 26.3 | 3.3 | 7-8 | 80 |
| Fruit Shell Carbon | 600 | 232.4 | 800 | 10.6 | 4.5 | 27.2 | 3.6 | 7-8 | 12 |
| Coconut Shell Carbon | 600 | 983.6 | 850 | 10.1 | 6.0 | 23.8 | 3.0 | 7-8 | 12 |

### Experimental Methods

Four treatments were set up in the experiment (Table 3) to study the effects of the application of different types of biochar on the total phosphorus content in soil at different depths (0 and 10 cm) over a period of 28 days. The soil under different conditions was named Dx-Ty (x: depth, y: days). The four treatments were: 1) control (T0): no biochar application; 2) application of 1 $kg \cdot m^{-2}$ straw charcoal (Ts); 3) application of 1 $kg \cdot m^{-2}$ fruit shell charcoal (Tf); and 4) application of 1 $kg \cdot m^{-2}$ coconut shell charcoal (Tc). The experimental fields were labelled as follows: the blank field was labelled as Field 1, the field with straw charcoal application was labelled as Field 2, the field with fruit shell charcoal application was labelled as Field 3, and the field with coconut shell charcoal application was labelled as Field 4. The purpose of this experiment was to explore the effects of three types of biochar on nitrogen, phosphorus, and cadmium content in soil through comparative experiments, laying the foundation for future research.

**Table 3.** Experimental Treatment

| Number | Treatment | Straw Charcoal ($kg/hm^2$) | Fruit Shell Charcoal ($kg/hm^2$) | Coconut Shell Charcoal ($kg/hm^2$) |
|---|---|---|---|---|
| 1 | T0 | 0 | 0 | 0 |
| 2 | Ts | 10000 | 0 | 0 |
| 3 | Tf | 0 | 10000 | 0 |
| 4 | Tc | 0 | 0 | 10000 |

The biochar was spread evenly onto the soil surface to prevent the biochar from mixing with the soil. Another layer of soil was spread evenly on top, and the soil surface is not treated in any way to ensure that the entire experiment is conducted under natural conditions.

## RESULTS AND DISCUSSION

### Analysis of Experimental Results

As shown in Fig. 1, the surface pore size of coconut shell charcoal was obvious, and the distribution of micropores was uniform. Combined with Table 2, it can be seen that coconut shell charcoal had a specific surface area of up to 984 $m^2/g$. A larger specific surface area means that there are more micropores in this material, which provide more adsorption sites and increase the adsorption capacity. The surface micropores of fruit shell charcoal were fuzzy and unevenly distributed, while the surface of straw charcoal was mostly in the form of flakes, which is consistent with their specific surface areas of 232 $m^2/g$ and 13.7 $m^2/g$, respectively, which are much smaller than the specific surface area of coconut shell charcoal.

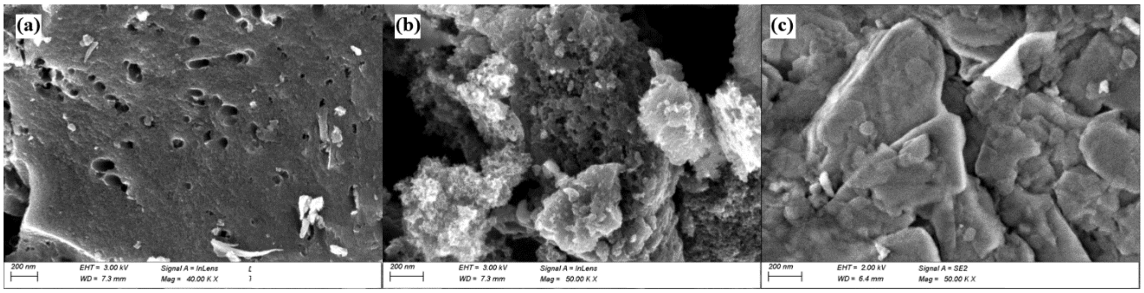

**Fig. 1.** SEM images of three types of biochar: (a) Coconut shell biochar, (b) Fruit shell biochar, (c) Straw biochar

**Table 4.** Contents of the Surface Soil of D0-T14

| Number | Element | Treatments | Mass (g) | MR (ppm) | Total (g/kg) |
|---|---|---|---|---|---|
| 1 | N | T0 | 0.4894 | 6.229 | 1.00 |
| 2 | | Ts | 0.4956 | 5.617 | 0.89 |
| 3 | | Tf | 0.4933 | 6.494 | 1.04 |
| 4 | | Tc | 0.4932 | 5.501 | 0.88 |
| 1 | P | T0 | 0.4938 | 0.483 | 0.80 |
| 2 | | Ts | 0.4940 | 0.449 | 0.74 |
| 3 | | Tf | 0.4936 | 0.471 | 0.78 |
| 4 | | Tc | 0.4924 | 0.454 | 0.75 |
| 1 | Cd | T0 | 1.0089 | 0.0087 | 0.16 |
| 2 | | Ts | 1.0048 | 0.0086 | 0.15 |
| 3 | | Tf | 1.0093 | 0.0086 | 0.15 |
| 4 | | Tc | 1.0011 | 0.0073 | 0.12 |

**Table 5.** Contents of the Surface Soil of D10-T14

| Number | Element | Treatments | Mass (g) | MR (ppm) | Total (g/kg) |
|---|---|---|---|---|---|
| 1 | N | T0 | 0.4843 | 6.286 | 1.02 |
| 2 | | Ts | 0.4886 | 6.653 | 1.07 |
| 3 | | Tf | 0.5058 | 6.561 | 1.02 |
| 4 | | Tc | 0.4821 | 6.403 | 1.05 |
| 1 | P | T0 | 0.4925 | 0.468 | 0.78 |
| 2 | | Ts | 0.4929 | 0.384 | 0.64 |
| 3 | | Tf | 0.4912 | 0.472 | 0.79 |
| 4 | | Tc | 0.5033 | 0.338 | 0.55 |
| 1 | Cd | T0 | 1.0044 | 0.0083 | 0.15 |
| 2 | | Ts | 1.0032 | 0.0073 | 0.12 |
| 3 | | Tf | 1.0012 | 0.0090 | 0.16 |
| 4 | | Tc | 1.0046 | 0.0087 | 0.16 |

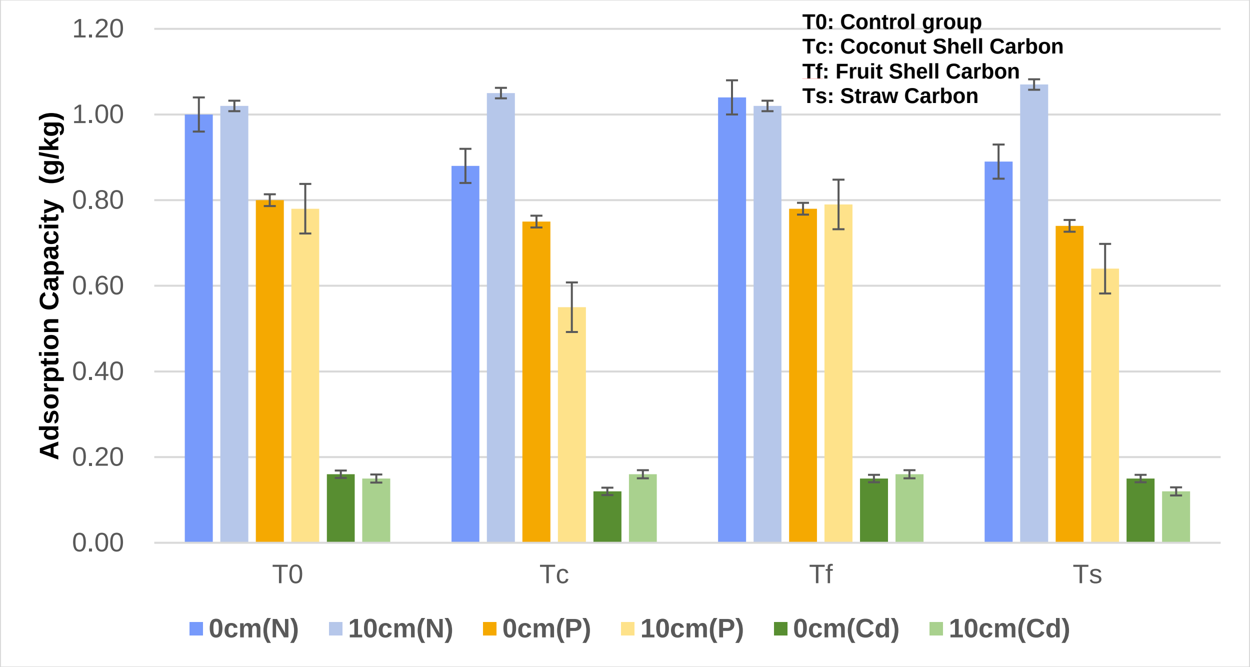

**Fig. 2.** Nitrogen, phosphorus, and cadmium in soil at different depths at 14 days

During the experiment, there was basically no significant change in the addition of nitrogen to biochar. However, according to Fig. 2, at 14 days, application of coconut shell charcoal caused the nitrogen content in the soil to increase from 0.88 g/kg to 1.05 g/kg, and the phosphorus content to decrease from 0.75 g/kg to 0.55 g/kg, both of which were significant changes. The increase in nitrogen may have emerged because coconut shell charcoal can improve aeration and water retention capacity of the soil. This promotes activities of microorganisms inhabiting the soil, thereby promoting nitrogen cycling and releasing and increasing the nitrogen in the soil.

**Table 6.** Contents of the Surface Soil of D0-T28

| Number | Element | Treatments | Mass (g) | MR (ppm) | Total (g/kg) |
|---|---|---|---|---|---|
| 1 | N | T0 | 0.4992 | 7.970 | 1.22 |
| 2 | | Ts | 0.5146 | 7.535 | 1.11 |
| 3 | | Tf | 0.4972 | 6.765 | 1.03 |
| 4 | | Tc | 0.5038 | 6.407 | 0.96 |
| 1 | P | T0 | 0.4795 | 0.454 | 0.76 |
| 3 | | Ts | 0.4883 | 0.488 | 0.80 |
| 3 | | Tf | 0.4796 | 0.462 | 0.77 |
| 4 | | Tc | 0.4769 | 0.469 | 0.79 |
| 1 | Cd | T0 | 1.0087 | 0.0130 | 0.05 |
| 2 | | Ts | 1.0095 | 0.0138 | 0.07 |
| 3 | | Tf | 1.0047 | 0.0127 | 0.05 |
| 4 | | Tc | 1.0041 | 0.0127 | 0.05 |

**Table 7.** Contents of the Surface Soil of D10-T28

| Number | Element | Treatments | Mass (g) | MR (ppm) | Total (g/kg) |
|---|---|---|---|---|---|
| 1 | N | T0 | 0.4747 | 6.277 | 0.99 |
| 2 | | Ts | 0.4918 | 4.900 | 0.74 |
| 3 | | Tf | 0.5020 | 5.329 | 0.79 |
| 4 | | Tc | 0.4930 | 5.313 | 0.80 |
| 1 | P | T0 | 0.5011 | 0.478 | 0.77 |
| 2 | | Ts | 0.4969 | 0.508 | 0.82 |
| 3 | | Tf | 0.4982 | 0.470 | 0.76 |
| 4 | | Tc | 0.4854 | 0.463 | 0.77 |
| 1 | Cd | T0 | 1.0030 | 0.0134 | 0.06 |
| 2 | | Ts | 1.0077 | 0.0186 | 0.19 |
| 3 | | Tf | 1.0051 | 0.0190 | 0.20 |
| 4 | | Tc | 1.0058 | 0.0186 | 0.19 |

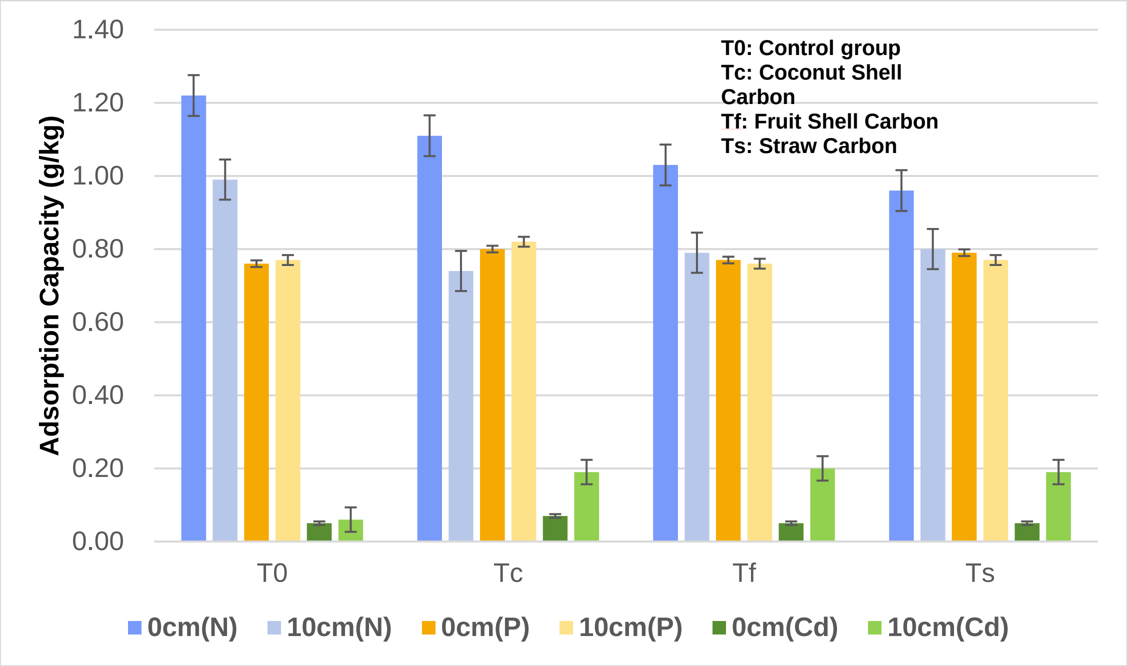

**Fig. 3.** Nitrogen, phosphorus, and cadmium in soil at different depths at 28 days

According to Fig. 3, at 28 days, for all types of biomass charcoal as well as the blank control, the nitrogen content had decreased significantly. The effects of the application of different biomass charcoals on cadmium were also different. When straw charcoal was used, the cadmium content increased significantly from 0.07 to 0.19 g/kg. When coconut shell charcoal was used, the cadmium content increased from 0.05 to 0.19 g/kg. The alkaline soil is conducive to the adsorption of cadmium ions, but the adsorption effect of biochar on cadmium ions was not significant, and even the increase may have been due to the small pore size of coconut shell charcoal, which hinders the transport of cadmium ions. The insignificant cadmium ion effect of soil treated with straw charcoal may be due to its small specific surface area and sheet-like structure, all of which reduce the contact area between cadmium ions and biochar, thereby reducing its adsorption performance. In addition, it may also be related to the type and quantity of biochar used. The increase in cadmium ion content may be due to the instability of biochar, which leads to the re release of adsorbed cadmium ions into the soil, or due to insufficient biochar addition, which provides fewer adsorption sites and cannot adsorb more cadmium ions, resulting in poor adsorption effect. Due to the selection of soil under outdoor natural conditions, the activity of soil microorganisms may affect the bioavailability and mobility of cadmium, leading to an increase in cadmium content in the soil, or the reaction between biochar and other components in the soil, changing the chemical form of cadmium and making it easier to detect, although the total amount does not increase.

Biochar reduces soil nitrogen loss by affecting the soil nitrogen biogeochemical cycling and the composition of functional microorganisms. The total amount of nitrogen in the soil was clearly increased. The porous structure of biochar provides strong adsorptive capacity. Within a certain range, the greater the porosity of biochar, the stronger its adsorptive capacity. This logic is also the main reason why coconut shell charcoal and fruit shell charcoal have stronger adsorptive capacities for nitrogen than straw charcoal. At 28 days, the reason for the observed decrease in nitrogen elements may be that microorganisms may decompose nitrogen in the soil into ammonia, nitrate, and other forms. These forms of nitrogen will evaporate in the atmosphere or be absorbed by plants, resulting in a decrease in the nitrogen content in the soil. Another possibility is that within 28 days, the nitrogen in the soil may gradually be lost to the groundwater or to other environmental factors through water erosion or soil seepage, resulting in a decrease in the nitrogen content in the soil. Based on practical experience, coconut shell charcoal had the most significant comprehensive impact, reducing soil nitrogen and phosphorus content at 28 days. It is suggested that if applied in practice, the pore structure of the biochar used should be well-developed and the specific surface area should not be too small; otherwise, its adsorption effect will be poor. Secondly, when using biochar for sudden treatment, the nature of the treatment object also needs to be considered. For example, alkaline biochar is more effective than acidic biochar for the treatment of cadmium ions. Therefore, when choosing biochar for adsorption treatment, it is necessary to fully understand and select the soil, treatment object, and properties of biochar, and then select the most suitable biochar.

## CONCLUSIONS

1. This study revealed several factors affecting the adsorption of soil nitrogen, phosphorus, and cadmium elements by biochar. The adsorption of cadmium in the environment by different types of biochar was not significant, possibly due to the small porosity of biochar. For both nitrogen and phosphorus elements, they decreased. The reason may have been that some microorganisms have decomposed them into volatile forms. As a result, the compounds may have evaporated into the atmosphere or become absorbed by plants, resulting in a decrease in nitrogen and phosphorus content in the soil. Alternatively, they may gradually be lost to groundwater or other environmental factors through water erosion or soil leakage.
2. Furthermore, due to limitations in sample size and research scope, the present results need to be further validated in future studies. Future work should consider a broader sample population and explore potential impacts. In addition, there are still difficulties in separating biochar for soil pollution control. In the future, magnetic materials can be loaded for modification, making it easier to remove them from the soil. The authors look forward to future research expanding the current findings and bringing more in-depth insights into the field.

## ACKNOWLEDGEMENTS

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