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# Adsorption of Phenanthrene in Soil to Biochar Modified by β-Cyclodextrin

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## Abstract

In this study, the adsorption effect of β-cyclodextrin modified biochar (BC) on phenanthrene (PHE) in contaminated soil was investigated, aiming to provide an efficient and environmentally friendly remediation strategy for Polycyclic Aromatic Hydrocarbons (PAHs) contaminated soil. Through kinetic and isotherm analysis, β-CDBC-CA showed excellent phenanthrene adsorption performance, and the adsorption effect increased with the increase of time and was affected by temperature. The results show that β-CDBC-CA can not only effectively adsorb phenanthrene in soil, but also serve as a surfactant to help desorption phenanthrene adsorbed by soil organic matter and improve the efficiency of microbial degradation. The experimental data showed that the Elovich model could describe the adsorption behavior of β-CDBC-CA on phenanthrene well, while Langmuir and Freundlich models performed better in fitting parameters, revealing the adsorption mechanism of phenanthrene in contaminated soil by β-cyclodextrin-modified biochar. In addition, temperature has a significant effect on the adsorption capacity of β-CDBC-CA, and its application in soil remediation can be optimized by adjusting temperature. This study not only provides new materials and technical means for soil remediation but also provides important data support for an in-depth understanding of the environmental behavior of PAHs. By citing relevant research results, this study further improves the control and understanding of environmental risks of PAHs, which is of great significance for the protection of ecological environment and human health.

## Keywords

PAHs, Biochar, β-Cyclodextrin, Modification, Adsorption, Soil Remediation

## 1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs), a class of aromatic hydrocarbons with two to seven benzene rings, are a type of Persistent Organic Pollutants (POPs) widely present in the environment. PAHs are mainly derived from the incomplete combustion process of natural organic energy and mineral release during mining [1]. PAHs have strong lipophilic and hydrophobic properties [2], and with the increase of ring number, their lipophilic and hydrophobic properties also increase, so PAHs are easy to adsorb soil organic matter [3]. The PAHs in the air and water are usually adsorbed on the small particles in the atmosphere and water, and pollute the soil through the precipitation of rain and the exchange of soil and air on the surface [4]-[6]. Surface soil plays an important role in the storage and transformation of PAHs [7]. The molecular structure of PAHs is relatively stable, and PAHs in soil are difficult to be degraded by microorganisms or transformed in other ways due to adsorption in soil organic matter [8]. PAHs have carcinogenic, mutagenic, teratogenic and other toxic effects, and even in small amounts, they are highly carcinogenic, posing a serious threat to human health, food security and natural ecological environment [9]. In the investigation and evaluation of soil pollution in China, the evaluation reference value of PAHs in soil is 100 μg/kg, while according to the study of Han *et al.* [10], the average value of 16 PAHs in the surface soil of China is 0.730 mg/g, and the pollution level of PAHs in the soil of China is higher than that of other Asian countries [11]. Therefore, it is very important to find a low-cost and efficient PAHS remediation method. Traditional physical remediation technologies, such as pyrolysis and incineration, have problems such as high cost and easy secondary pollution [12], while bioremediation technology, although environmentally friendly, is limited by microbial activity, pollutant availability and other factors [13]. Chemical remediation technology, especially the use of biochar, graphene and other remediation materials for immobilization of pollutants, has attracted wide attention due to its high efficiency, persistence and low cost [14].

Biochar is a carbon-rich porous material generated by high-temperature pyrolysis of animal and plant biomass. The surface of biochar is rich in hydroxyl, carboxyl, carbonyl and other functional groups [12]. Therefore, biochar has a large specific surface area and adsorption capacity, which can effectively adsorb and fix pollutants in soil. Therefore, biochar is a kind of PAHs remediation material with research value [15]. The adsorption capacity of biochar for organic pollutants is affected by biomass sources, surface functional groups, pyrolysis temperature and specific surface area [16]-[18]. The number of functional groups loaded on the surface of biochar is limited, and the pore structure is easily blocked by impurities. Therefore, it is necessary to activate the pore cleaning with acid or alkali solution to increase the specific surface area, increase the number of functional groups, and improve the adsorption capacity of pollutants [19]. Zhang *et al.* [20] studied to improve the reduction performance of zero-valent iron sulfide loaded biochar. Before nano-zero-valent iron loading,

biochar was modified by three pretreatment methods: oxidizer ($H_2O_2$), base (NaOH) and acid (HCl). The results show that the specific surface area, surface electric load and surface functional groups of the three kinds of biochar are all increased with the successful loading of nano zero-valent iron. Weissmann *et al.* [21] pointed out that grafting fluorine-containing functional groups on the surface of carbon materials can improve the hydrophobicity of carbon material adsorbents. Yavari *et al.* [22] formed a highly efficient biomass adsorbent on biochar by using chitosan grafted in a low concentration acetic acid solution to fix herbicides in soil. Through characterization, it was found that the specific surface area of biochar was reduced after chitosan modification, but the adsorption capacity and cation exchange capacity were significantly increased by the increase of functional groups on the surface of biochar.

The above studies indicate that the acid-base activation is an important modification method to enhance the ability of biochar to adsorb organic pollutants by connecting other macromolecules to the surface of biochar. $\beta$-cyclodextrin ($\beta$-CD) is a kind of cyclic oligosaccharide with hydrophobic cavity and hydrophilic outer surface structure, which is produced by amylolytic reaction and is non-toxic to the ecological environment and human health. In recent years, the production of cyclodextrin has become a hot spot in the field of environmental remediation. Cyclodextrin has strong water solubility, so it is necessary to graft cyclodextrin on the surface of biochar through crosslinking agents [23]. While increasing the adsorption capacity of biochar for PAHs, it is also necessary to graft cyclodextrin on the surface of biochar. Cyclodextrin can be used as a surfactant component to desorb the PAHs that are absorbed in soil organic matter [24] [25] and improve the degradation efficiency of soil microorganisms to various organic pollutants such as PAHs [26] [27].

The purpose of this study was to explore the application effect and molecular mechanism of $\beta$-cyclodextrin modified biochar in remediation of PAHs contaminated soil. The adsorption and desorption of PAHs by $\beta$-cyclodextrin modified biochar was studied in order to provide a new, low-cost, efficient and environmentally friendly technical means for the ecological remediation of typical PAHs polluted soil.

## 2. Experiment

### 2.1. Experimental Reagents and Instruments

The straw biochar was obtained by pyrolysis in a tube furnace at 300˚C after straw cleaning. Dichloromethane (AR), methanol (AR), anhydrous sodium sulfate (AR), hydrochloric acid (AR), epichlorohydrin (AR), sodium hydroxide (AR), citric acid (CA) (AR), and $\beta$-cyclodextrin (AR), phenanthrene (AR) and acetone (AR) produced by Aladdin Company are used. The water used in the experiment was deionized water produced by pure water equipment.

The concentration of phenanthrene was measured using a high performance liquid chromatograph (HPLC) produced by Shimadzu Corporation.

### 2.2. Synthesis of Biochar Modified by β-Cyclodextrin

Based on the previous experiments and characterization by Guo Qing *et al.* [28] in our research group, β-cyclodextrin modified biochar was prepared for the experiment. Four groups of 5g dried straw biochar were prepared, and each group was added to 500 ml of 1 mol/L NaCl solution, CA solution, HCl solution and deionized water for 24 h, then washed with deionized water to neutral, and then dried in a blast oven at 110˚C to constant weight. Add the biochar into the flask, then add 500 ml deionized water, adjust the pH value to 4 with hydrochloric acid, add 5 ml epichlorohydrin, stir at 25˚C for 12 h, then add 7.78 g β-cyclodextrin and 200 ml 6%NaOH solution, stir for 12 h, pour the biochar mixed solution out, wash to neutral, and carry out vacuum filtration. Place the remaining solids in the oven at 60˚C to constant weight. The four groups of products were named β-CDBC-Na, β-CDBC-CA, β-CDBC-H and β-CDBC.

### 2.3. Adsorption of Phenanthrene by Modified Materials

9 samples of 10.0g contaminated soil containing organic contaminant phenanthrene were accurately weighed into 100 ml plastic centrifuge tubes with plugs, and remediation materials BC, β-CDBC, β-CDBC-Na, β-CDBC-CA and β-CDBC-H were added, respectively. At the same time, 2 groups of mass gradients were set, the addition amount of remediation materials was 5% and 10%, respectively. The remaining one was the control group. The influence of different repair time on the repair effect was observed. The time gradient was set as 3 d, 7 d, 14 d, 21 d, 42 d and 84 d, and the data were recorded.

### 2.4. Experimental Study on Adsorption Mechanism of Phenanthrene by Modified Materials

#### 2.4.1. Adsorption Kinetics Experiment

11 samples of 0.50 g soil, 0.05 g β-CDBC -CA and 50 mL of phenanthrene with a mass concentration of 50 $mg \cdot L^{-1}$ were placed in a 100 mL plug centrifuge tube at 25˚C and an oscillation velocity of 140 $r \cdot min^{-1}$ for 5.30 min and 1, 1.5, 3, 5, 8, 12 h respectively. At 16, 20, 24 h, the corresponding samples were taken out for centrifugation, and the supernatant was taken to test the concentration of phenanthrene by liquid chromatography. In addition, kinetic adsorption experiments of BC and without biochar were continued. Finally, the graph drawing analysis is carried out.

#### 2.4.2. Adsorption Isotherm Experiment

11 samples of 0.50 g soil and 0.05 g β-CDBC-CA were added into 100 mL stopcock centrifuge tube, and 50 mL methanol solution of phenanthrene was added. The methanol solution concentrations of phenanthrene were 5.0, 11.0, 18.0, 25.0, 31.0, 37.0, 44.0, 50.0, 55.0, 60.0 and 66.0 $mg \cdot L^{-1}$, respectively. The samples were uniformly mixed and oscillated at 25˚C for 24 h before being taken out. Centrifuge for 10 min (4000 $r \cdot min^{-1}$), take the supernatant to determine the concentration of phenanthrene, and do isothermal adsorption experiments with BC and without

biochar. The above experimental steps were repeated to perform parallel experiments at 15˚C and 35˚C.

## 3. Result and Discussion

In order to determine the removal effect of BC and *β*-cyclodextrin modified biochar materials on PAHs, the effects of different repair materials, the amount of materials added and the repair time were investigated. As shown in Figure 1, compared with the blank group (CK), it was easier to adsorb and remove phenanthrene by adding repair materials. For the same repair material, the longer the repair time and the addition amount of 1.0 g (10%), the best repair effect; Among BC, *β*-CDBC, *β*-CDBC-Na, *β*-CDBC-H and *β*-CDBC-CA repair materials, *β*-CDBC-CA has the best repair effect, and its final repair rate can reach 56.90%, and the repair rates of its and other repair materials are 36.79%, 42.03% and 48.13%, respectively. The difference of repair effect of different materials probably due to the specific surface area and pore size. The final removal results can also verify that the biochar composite material has achieved the purpose of modification to a certain extent.

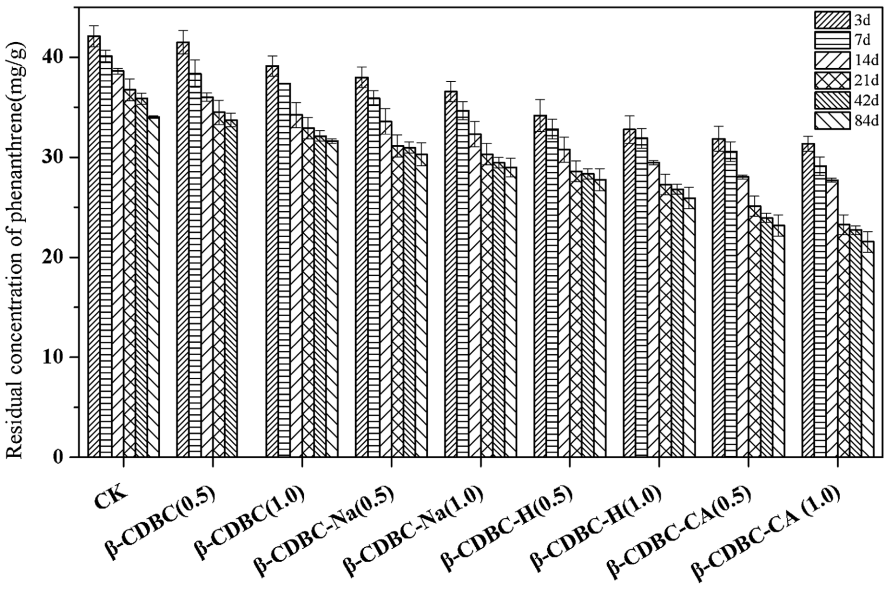


Figure 1. Residual concentration of phenanthrene after repair with multiple repair materials.

### 3.1. Adsorption Mechanism of Phenanthrene in Soil by *β*-Cyclodextrin Modified Biochar Materials

#### 3.1.1. Dynamic Adsorption Model

The results of kinetic adsorption of phenanthrene on soil are shown in Figure 2 and Table 1 The adsorption of *β*-CDBC-CA on the soil takes longer to reach equilibrium. In the rapid adsorption stage, phenanthrene rapidly adsorbs to the outer surface of *β*-CDBC-CA, where the adsorption capacity is strongest [29]. In the internal diffusion stage, intra-particle diffusion becomes the main reason to limit

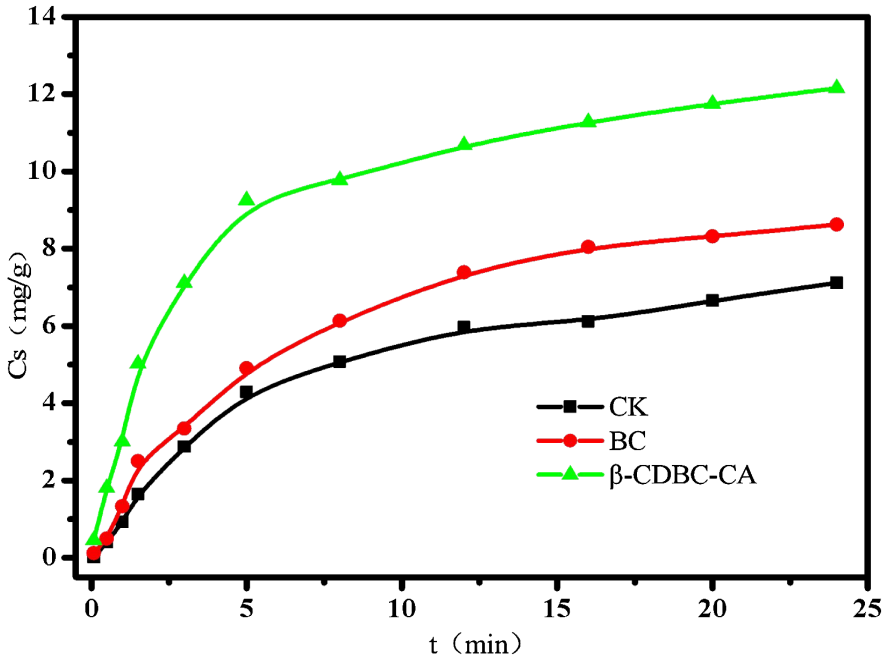


**Figure 2.** Adsorption kinetics of CK, BC and *β*-CDBC-CA.

**Table 1.** Adsorption kinetic parameter.

| Sample | First-order kinetic model $\lg(1-Cs/Qm)=a-bt$ | | | Elovich model $Cs=a+blnt$ | | | Double constant model $Cs=a+blgt$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | a | b | $R^2$ | a | b | $R^2$ | a | b | $R^2$ |
| PHE | −0.032 | 0.060 | 0.957 | 1.434 | 1.984 | 0.915 | 1.025 | 0.028 | 0.887 |
| +BC | −0.013 | 0.045 | 0.905 | 1.751 | 2.518 | 0.913 | 0.754 | 0.050 | 0.956 |
| +*β*-CDBC-CA | −0.015 | 0.098 | 0.824 | 2.342 | 4.624 | 0.956 | 0.559 | 0.444 | 0.936 |

the adsorption rate, and the Philippine adsorbed on the outer surface of *β*-CDBC-CA slowly enters the inner pore until it finally reaches equilibrium. Phenanthrene molecules can be mainly adsorbed in micropores and mesoporous pores of biochar structure [30]. However, the pore-filling mechanism [31] is not the only mechanism of phenanthrene adsorption, and the biochar aromatic groups can promote its hydrophobicity and interaction with phenanthrene. The kinetic experimental results of the adsorption of phenanthrene on soil are shown in **Table 1**. As a whole, the optimal adsorption model of BC and *β*-CDBC-CA is the Elovich model ($R^2$ 0.913 - 0.947), or the Elovich model and the double constant model may occur simultaneously.

### 3.1.2. Isothermal Adsorption Model

In this study, the adsorption isotherms of BC and *β*-CDBC-CA on phenanthrene on soil were investigated respectively at 15˚C, 25˚C and 35˚C are shown in **Figure 3**. The Linear model, Freundlich model and Langmuir model were respectively used for fitting analysis. The fitting parameters were shown in **Table 2**. Parameter

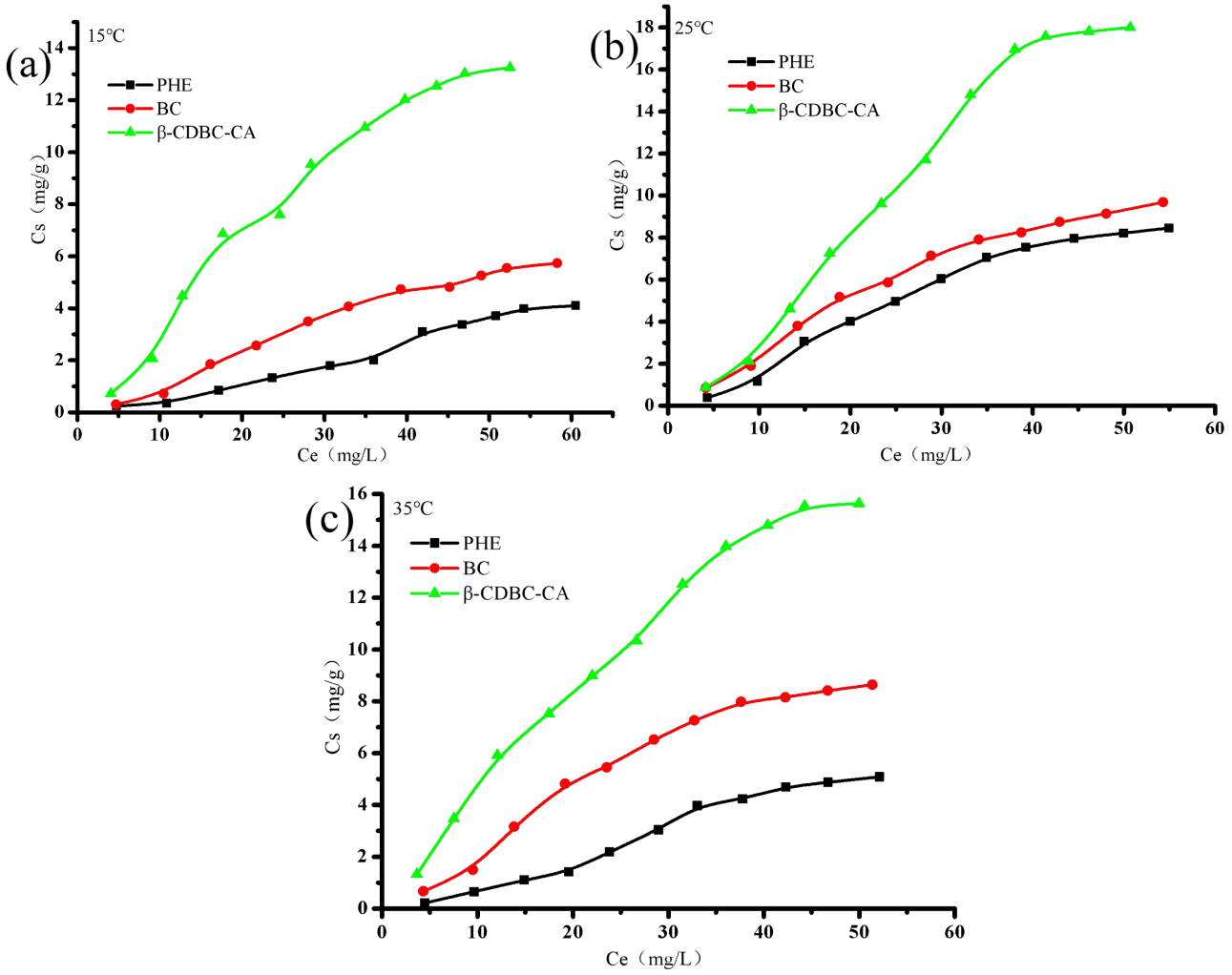


**Figure 3.** Adsorption isotherms of *β*-CDBC-CA in different temperature: (a) 15˚C; (b) 25˚C; (c) 35˚C.

**Table 2.** Isothermal adsorption parameters.

| Isothermal adsorption model | | Linear model $Cs = KCe + b$ | | | Freundlich model $lgCs = lgK + \left(\frac{1}{n}\right) * lgCe$ | | | Langmuir model $\frac{1}{Cs} = 1/(KQmCe) + 1/Qm$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| temperature | sample | K | b | R2 | K | 1/n | $R^2$ | Qm | K | $R^2$ |
| 15˚C | PHE | 0.078 | -0.416 | 0.976 | 0.024 | 1.177 | 0.979 | 4.011 | 0.004 | 0.982 |
| | +BC | 0.106 | 0.103 | 0.962 | 0.163 | 0.893 | 0.969 | 5.621 | 0.009 | 0.976 |
| | +*β*-CDBC-CA | 0.244 | 1.013 | 0.933 | 0.607 | 0.705 | 0.956 | 18.673 | 0.016 | 0.970 |
| 25˚C | PHE | 0.168 | 0.357 | 0.939 | 0.110 | 0.836 | 0.994 | 8.502 | 0.008 | 0.967 |
| | +BC | 0.177 | 1.109 | 0.935 | 0.554 | 0.732 | 0.996 | 11.949 | 0.015 | 0.983 |
| | +*β*-CDBC-CA | 0.412 | 0.427 | 0.961 | 0.696 | 0.898 | 0.960 | 22.077 | 0.005 | 0.963 |
| 35˚C | PHE | 0.115 | -0.424 | 0.966 | 0.065 | 1.021 | 0.959 | 5.728 | 0.012 | 0.986 |
| | +BC | 0.176 | 0.727 | 0.924 | 0.311 | 0.770 | 0.949 | 10.598 | 0.019 | 0.967 |
| | +*β*-CDBC-CA | 0.319 | 1.544 | 0.963 | 0.699 | 0.720 | 0.981 | 20.746 | 0.015 | 0.991 |

1/n in the Freundlich adsorption isotherm model was greater than 1, and $R^2$ (Langmuir 0.982) was greater than $R^2$ (Freundlich 0.979), so the adsorption of phenanthrene on the tested soil was more inclined to the Langmuir model. When the repair materials BC and *β*-CDBC-CA were added, $R^2$ (Langmuir) and $R^2$ (Freundlich) were both larger than $R^2$ (Linear). Meanwhile, when the parameter 1/n in the Freundlich adsorption isotherm model was less than 1, The adsorption of phenanthrene on the tested soil is more consistent with the adsorption isotherm of Freundlich model. Therefore, the Langmuir model and Freundlich isotherm model were the main adsorption isotherm models of the remediation materials BC and *β*-CDBC-CA for phenanthrene on the tested soil. The adsorption isothermal model of *β*-CDBC-CA for phenanthrene molecules on the tested soil was further verified. At 15˚C - 35˚C, the maximum theoretical adsorption capacities of *β*-CDBC-CA for phenanthrene molecules on the tested soil were 18.331 $mg \cdot g^{-1}$, 22.077 $mg \cdot g^{-1}$ and 20.746 $mg \cdot g^{-1}$, respectively. The actual adsorption capacities were 13.257 $mg \cdot g^{-1}$, 18.007 $mg \cdot g^{-1}$ and 15.629 $mg \cdot g^{-1}$, all of which were lower than the theoretical values. At 15˚C - 25˚C, the maximum adsorption capacity of *β*-CDBC-CA for phenanthrene molecules on the tested soil increases with the increase of temperature, which may be caused by thermal expansion, which expands the pores on the surface of biochar and exposes more phenanthrene binding sites [32]. At 25˚C - 35˚C, the maximum adsorption capacity of *β*-CDBC-CA for phenanthrene molecules on the soil tested decreases with the increase of temperature. Because the performance of biochar is affected by the pyrolysis temperature, the carbonized part has a large specific surface area and pore structure, which is easy to adsorb pollutants, and the uncarbonized part contains a large amount of organic matter. This part of organic matter may be more easily bound to the active site of biochar, thus reducing the possibility of phenanthrene binding, resulting in a decrease in the maximum adsorption capacity of phenanthrene molecules on the tested soil.

## 4. Conclusion

This paper mainly studied the preparation and application of *β*-cyclodextrin modified biochar materials, using different solutions to activate the preparation of *β*-CDBC, *β*-CDBC-Na, *β*-CDBC-CA and *β*-CDBC-H biochar modified materials, the adsorption test shows that *β*-CDBC-CA has achieved better modification effect. In addition, the adsorption of *β*-CDBC-CA on the soil for an even longer time basically reached equilibrium. The optimal kinetic adsorption model is Elovich model. Under the same temperature condition, the fitting related parameters $R^2$ (Langmuir) and $R^2$ (Freundlich) are both larger than $R^2$ (Linear), and the maximum fitting parameters $R^2$ of Langmuir model and Freundlich model can reach 0.991 and 0.996, respectively. Therefore, the adsorption mechanism of several repair materials prepared in this experiment is mainly based on Langmuir model and Freundlich model.

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## Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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