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Production and characterization of modified biochar by corn cob and its ability to absorb phenol

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Abstract. The adsorption performance of KOH modified biochar as adsorbent for phenol in aqueous solution was investigated. The effects of initial pH of the solution, initial concentration of phenol, contact time and temperature on the adsorption capacity of phenol were investigated. Adsorption isotherms, adsorption kinetics and thermodynamic analysis were examined. The results showed that the specific surface area of modified biochar was $487.64 m^2 \cdot g^{-1}$, the content of C is 72.06 wt.% and the value of H/C is 0.05, the aromatization degree of modified biochar is very high. The results showed that the maximum adsorption capacity of the modified biochar is 217.06 mg$\cdot$g^{-1} at 298 K, which is higher than that of biochar. The adsorption process accords with the Freundlich adsorption isotherm model and pseudo-second-order kinetic equation. Thermodynamic analysis shows that adsorption is spontaneous and exothermic.

1. Introduction

Biochar is a kind of solid carbon material obtained by pyrolysis and carbonization of plant biomass animal manure and municipal sludge under the condition of hypoxia or oxygen restriction[1]. It is a kind of refractory solid material with high carbon content and high aromatization, which has superior thermal stability, porosity and high specific surface area. Biomass materials come from a wide range of sources, agricultural and forestry waste, livestock and poultry waste, municipal waste and so can serve as raw materials for the preparation of biochar[2]. As a further resource, agricultural and forestry waste has been widely studied by scholars all over the world. It is full of resources and low in utilization. The preparation of biochar can provide a useful channel for the recycling and utilization of agricultural wastes. In recent years, the majority of scholars have used organic waste such as animal manure, animal bones, plant roots, sawdust and wheat straw to absorb harmful heavy metal ions and organic pollutants in the soil. Other researchers use biochar to prepare electrode materials for lithium ion batteries[3-4].

Phenolic organic wastewater is highly toxic and difficult to degrade, which directly endangers aquatic organisms in the process of oxidation and degradation, which results in the decrease of oxygen content and deterioration of water quality, which leads to the death of aquatic organisms. Phenolic untreated wastewater is harmful to human health[5-7]. Toxic substances in the wastewater are enriched in water, vegetables, fruit, grain and other crops, and finally enter into the human body, which is a serious threat to human health[8-9]. It is pointed out that 90% of human cancer is induced by chemical carcinogens in the surrounding environment, and organic compounds account for more than 80% of these carcinogens. The clean treatment and recycling of phenolic organic wastewater have profound and

positive effects on the sustainable development of water resources. In this paper, the preparation process, microstructure and adsorption properties for phenol of corncob biochar were studied. The kinetics, adsorption isotherm and thermodynamic characteristics of the adsorption process are studied. It serves as a theoretical basis for the application of corncob biochar in the field of organic pollution wastewater treatment[10].

2. Materials and methods

2.1. Preparation of biochar

The raw material of biomass was obtained by drying corn cob in natural air, washing it with oxygen displacement water and anhydrous ethanol alternately for three times, and drying in a vacuum drying box at 105°C for 12 hours. The dried corncob was crushed and ground through a 100 mesh sieve. The biomass powder was gathered and set aside. Under the protection of N_2, the biomass powder was heated up to 600°C at 5°C·min^{-1}, keepping heating for 2 h. And then cooled to 150°C, the product was taken out. After cooling to room temperature, the product was washed to neutral with deionized water, and the product was dried at 105°C for 8 hours to obtain the initial biochar, named BC, and put it in a sealed bag and put it in a dehumidifying storage tank[11].

2.2. Preparation of modified biochar

Using ethanol as solvent, the biochar was soaked in KOH solution, and the impregnation ratio was 1: 3(wt.%). The mixture of biochar and KOH was obtained by vacuum drying at 75°C for 12 h. The mixture was heated up to 600°C at 5°C·min^{-1} and activated for 120 min under N_2 protection. After natural cooling to 150°C, the product was cooled to room temperature, washed with 1mol·L^{-1} hydrochloric acid for 1 h, then washed to neutral with distilled water. The modified biochar was obtained by drying the washed product in 105°C vacuum drying box for 8 hours. The modified biochar was named MBC and was dried and preserved.

2.3. Characterization of biochar and modified biochar

The content of C, H, N, S in biochar was determined by organic element analyzer, the oxygen contents were calculated by difference. The adsorption amount of nitrogen on the samples at 77K was determined by using specific surface area and pore meter, and the specific surface area of each sample was calculated according to BET equation. The infrared spectra were measured in the range of 4000-400cm^{-1} by the infrared spectrometer model 6700. The absorbance of phenol was measured by 752N UV-vis spectrophotometer.

3. Results and discussion

3.1. Properties of modified Biochar

The composition of elements, atomic ratio, ash content, specific surface area and charring yield of biochar and modified biochar are shown in Table 1. The carbon content in the modified biochar increased obviously, and the hydrogen, nitrogen and oxygen contents also decreased. As H/C value decreases, the degree of carbonization increases gradually. Porosity has a strong effect on the adsorption performance of activated carbon. The results showed that the activation of biochar provided high specific surface area and micropore volume in the presence of potassium hydroxide. The specific surface area of modified biochar is 487.64 m^2·g^{-1}, most of which are composed of micropores.

Table 1. Characteristic of the biochar and modified biochar.

	Biochar	Modified biochar
Elemental analysis(wt.%)		
Carbon	62.45	72.06

Hydrogen	2.87	3.78
Nitrogen	0.22	0.15
Sulfur	-	-
Oxygen (by difference)	34.46	24.01
Surface properties		
BET surface area ($m^2 \cdot g^{-1}$)	15.32	487.64

Although it is not easy to identify all chemical species on the surface of modified carbon with chemical modification, information about the chemical properties of carbon surface can be obtained by using FTIR technique. Figure 1 shows the FTIR analysis of biochar and activated carbon. Stretching vibration of hydroxyl group(—OH、C—H) with wide peak near 3409、874 cm^{-1}. The absorption peak at 2929 cm^{-1} is adipose -CH_2-asymmetric stretching vibration. The peak at 1754 cm^{-1} refers to the stretching vibration peak of C=O in the aldehydes. The peak at 1704 cm^{-1} is generally considered to be the stretching vibration peak of C=O in carboxyl or ketones. The absorption peak at 1589 cm^{-1} is the expansion vibration of the aromatic ring C=O、C=C. Stretching vibration absorption peak of phenolic hydroxyl at 1278 cm^{-1}. At 1118 cm^{-1}, the stretching vibration absorption peak of C-O in carbohydrates is observed. FTIR analysis showed that the surfaces of BC and MBC contained abundant oxygen-containing functional groups such as —OH、—COH and —COOH.

In order to observe its surface morphology, scanning electron microscopy (SEM) was used to observe the biochar and modified carbon. The SEM images of biochar and modified biochar are shown in figure 2. The surface morphology of biochar and modified biochar is significantly different. The SEM images show that there are almost no micropores in biochar, which was verified from microporous BET results (15.32 $m^2 \cdot g^{-1}$). According to the diagram, a complete pore structure was observed in the modified biochar activated by KOH, which can clearly display the pore line of the pore. However, the modified biochar showed almost uniform pore structure in the process of activation, indicating the formation of the new matrix. In addition, the activated carbon also showed uniform, highly porous and obvious honey comb structure, indicating that phenol is likely to be captured and adsorbed.

Figure 1. FTIR spectra of biochar and modified biochar.	Figure 2. SEM images of biochar and modified biochar.
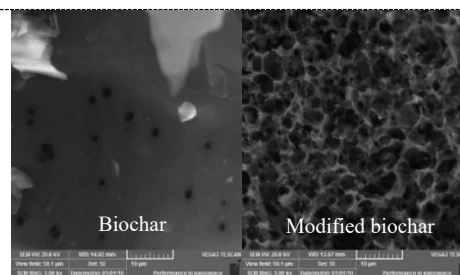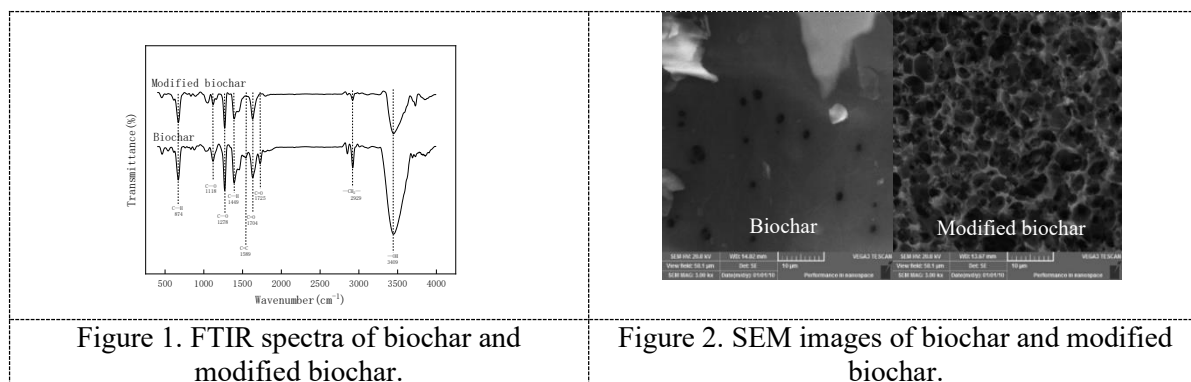
3.2. Effect of temperature on adsorption process

The adsorption isotherm of phenol by MBC is shown in figure 3. At the same equilibrium concentration, the maximum adsorption amount of phenol increased slightly with the increase of temperature, which indicated that the adsorption of phenol by MBC was an endothermic reaction, but temperature had little effect on it. The Gibbs free energy changes (ΔG^0), entropy change (ΔS^0) and enthalpy change (ΔH^0) are calculated by the following equation (1) and van't Hoff equation (2)[12]:

$$\Delta G^0 = -RTlnK_L$$

(1)

$$K_L = \frac{q_e}{C_e}$$

(2)

In the formula R [8.314 J·(mol·kg)$^{-1}$] is a gas constant, T(K) is the Kjeldahl temperature, K_L is the parameter of Langmuir isothermal model.
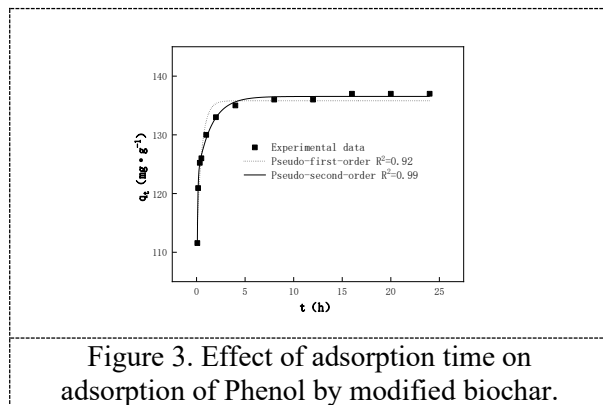

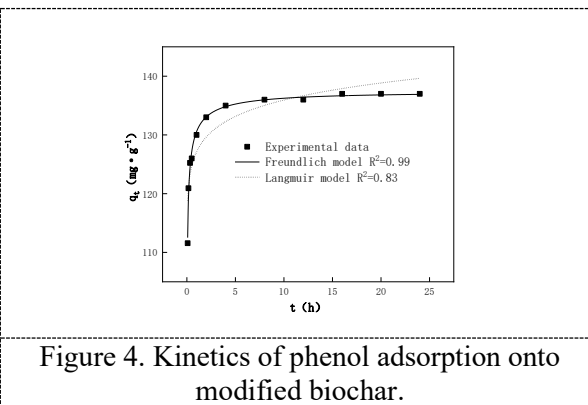| Figure 3. Effect of adsorption time on adsorption of Phenol by modified biochar. | Figure 4. Kinetics of phenol adsorption onto modified biochar. |

Table 2 shows that $\Delta G^0 < 0$ indicates that the adsorption process is spontaneous in the range of experimental temperature, and the value of ΔG^0 decreases with the decrease of temperature, which indicates that the decrease of temperature can improve the spontaneous characteristics of phenol adsorption and removal by MBC. It is helpful to promote the adsorption process. In addition, all ΔG^0 values are between -20~0 kJ mol^{-1}, indicating that the adsorption of phenol by MBC is mainly a physical adsorption process. $\Delta H^0 < 0$ indicates that the adsorption of phenol by MBC is an exothermic process, which is consistent with the experimental results. The negative value of ΔS^0 indicates that the adsorption process is accompanied by the change of structure between MBC and phenol, which indicates that phenol increases from the free state of dissolution in aqueous solution to the state of adsorption.

Table 2. Thermodynamic parameters for the adsorption of phenol onto modified biochar.

T(K)	KL	ΔG^0(kJ·mol^{-1})	ΔH^0(kJ·mol^{-1})	ΔS^0(kJ·mol^{-1})
298	3.08	-2.94	-7.99	-16.94
308	2.63	-2.48		
318	2.33	-2.24		

3.3. Adsorption kinetics

Biochar adsorption is a dynamic process, and the study of adsorption kinetics is to better understand the adsorption process and efficiency. A large number of adsorption processes can be described by two commonly used models, which are the pseudo-first order reaction kinetics equation of Lagergren and pseudo-second stage reaction kinetics equation. When the initial concentration of phenol solution is at 200mg·L-1, adsorption ability and Kinetics of modified Biochar for Phenol, as shown in figure 4.

A simple pseudo-first order equation (3) is given by Lagergren equation[13]:

$$log(q_e - q_t) = log q_e - \frac{k_1 t}{2.303}$$

(3)

The pseudo-second order equation based on the adsorption equilibrium capacity is studied. The equation is expressed in the following equation (4):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

(4)

Table 3. Kinetic parameters for adsorption rate expression.

q_e(exp) (mg·g⁻¹)	pseudo-first order kinetic model			pseudo-second order kinetic model		
	k_1(min⁻¹)	q_e(cal)(mg·g⁻¹)	R^2	k_2 (g·mg⁻¹·min⁻¹)	q_e(cal)(mg·g⁻¹)	R^2
140.31	0.29	17.89	0.89	0.10	140.85	1

All the constants and regression coefficients of the model are given in the table 3. On the basis of regression coefficient, pseudo-second order model is more suitable to describe adsorption kinetic data. The calculated value of q_e (140.85 mg·g⁻¹) is close to the experimental value of 140.31 mg·g⁻¹. It is shown that the pseudo-second-order kinetic model can prove that the adsorption mechanism is correct.

4. Conclusion

Pyrolytic studies have shown that corncobs can produce more valuable functional products (biochar), which are currently used only as agricultural and forestry waste. In this study, biochar prepared by pyrolysis of corncob was activated into modified biochar by chemical activation, which was used to remove phenol in aqueous solution. The parameters of ΔG^0 and ΔH^0 showed that the adsorption of phenol on MBC was spontaneous and exothermic. Kinetic studies show that the quasi-second-order model is suitable to describe the adsorption process of phenol. The isotherm study shows that the Freundlich isotherm model is in good agreement with the experimental equilibrium data. The results show that MBC activated by biochar can effectively remove phenol from wastewater.

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