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Preparation and phenol adsorption property of tobacco stem based modified porous materials

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Abstract. Tobacco stem based modified porous materials were prepared by a combined methods of fermentation, microwave drying, anulation, semi-carbonization and modification, in which the residue of tobacco stem was used as raw material, and the KOH was used as modifier. The structural characteristics and properties of the porous materials were characterized by the scanning electron microscopy, specific surface areas, pore analyzer and infrared analyzer. The adsorption isotherm model, the adsorption kinetics analysis, the adsorption thermodynamics of phenol solution were analyzed. The results showed that: the excellent produced conditions for the porous materials were as follows: The surface of the porous materials modified by the KOH was typical porous structure ,which mainly based on a large number of cavities and pores. The material had higher specific surface areas and pore volumes. The porous materials possesses more abundant functional groups, such as -OH, -CH and other functional groups, so that the material had a certain pro-organics. The adsorption isotherm model of phenol solution was simulated, which accorded with Freundlich isotherm adsorption equation model. The quasi-second-order kinetic model is suitable for the adsorption of the modified porous materials. The study of the adsorption thermodynamics showed that the adsorption was physical adsorption, and the adsorption behavior was exothermic.

1. Introduction

Porous materials have very important applications in many fields [1]. Activated carbon, zeolite molecular sieve and active alumina are common porous materials. In addition, some materials are developed for the selective adsorption of certain components [2-4]. There are many reports on the preparation of activated carbon materials from biomass. With coconut shell as raw material, the activated carbon with a certain proportion of microporous and mesoporous materials was prepared by using sodium hydroxide aqueous solution [5]. With gelatin and starch as raw materials, activated carbon with good CO_2 adsorption capacity was prepared by dry chemical modification [6]. Using rice husk, peanut shell, soybean straw and so on, biomass carbon was prepared with strong adsorption performance of methylene blue [7].

With the rapid development of industry in China, the number and types of wastewater discharge have increased rapidly, which have caused serious pollution to the water, so that the health and safety of human beings can not be ignored [8]. As one of the highly polluted wastewater, phenol - containing wastewater is the main pollutant. The phenol is a protoplasmic poison that can react with proteins in cells, formation of insoluble protein material, which causes the cells to lose its vitality, so become the highlight of the pollution is the most phenol containing wastewater. The residue extracted from

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tobacco stem is the waste after processing. Because of the loose structure of residue extracted from tobacco stem, the raw material is easy to get and non-toxic, so which can be recovered to prepare porous materials. The porous materials were prepared by a combined method of fermented pretreatment, microwave drying, semi-carbonized and modification, in which the residue of tobacco stem was used as carbon resource, and KOH was used as modifier, respectively. Using phenol as the object, the effect of the ratio of modifier and carbonizing materials on the structural properties of the porous carbon materials and the effect of the adsorption of phenol were studied. Because of weak acid and weak polar phenol, KOH modification was used to increase non polar and basic features of the surface hole carbon, to improve its effect on phenol wastewater containing phenol in selective adsorption ability, to provide help for the effective utilization of pore structure of the materials.

2. Experiment

2.1. Materials and Instruments

Porous materials, self-made; extraction equipment, self-made; TQ-2000Y pulverizer; 40, 60 mesh standard sieve; Mini Glatt experimental fluidized bed; GSL-1600X tube furnace; QUANTA-TA200 desktop scanning electron microscope; NOVA2200e surface area and porosity analyzer; Bruker TENSOR27 infrared spectrometer.

2.2. Experimental Methods

The residue extracted from the tobacco stem was crushed and put into the extraction equipment for heating extraction, cooling and filtering after extraction. The residue was pretreated by fermentation and then dried by microwave to obtain the residue powder. The semi-carbonized porous material was prepared by spray granulation in a fluidized bed. The porous semi-carbonized material was granular material with irregular shape. The granular material of 850 μ m was obtained by screening. Put the granular materials into GSL-1600X tube furnace, treat at 250 °C for 30 min. Remove the material after cooling to room temperature. Then the material was modified by KOH, and the KOH/carbon ratio was 3:1.Then the modified materials was washed with distilled water to the neutral pH, and finally baked to constant weight at 70 °C, the modified porous material was obtained.

2.3. Methods of Analysis

The surface morphology of semi-carbonized porous materials was observed by scanning electron microscope. The specific surface area and pore structure of semi-carbonated porous materials were characterized by specific surface area and porosity analyzer. The working parameters were as follows: the degassing temperature was 90 °C, the degassing time was 2 h. The structure of functional groups of the samples was analyzed by infrared spectrometer, the spectral resolution was 4cm^{-1} , and the scanning range was $400,000\text{cm}^{-1}$.

2.4. Adsorption Test

0.1 g porous carbon materials were added to the concentration of 1, 2, 4 and 10 /L 100mL g of phenol solution respectively shocking 24h at 25°C. At a certain time interval, the 1 mL supernatant was removed, and the equilibrium concentration was calculated by the method of ultraviolet visible spectrophotometry. The value of q_e (/g mg) was calculated:

$$q_e = \frac{V(C_0 - C_e)}{m} \tag{1}$$

Where V was the solution volume (L), C_0 and C_e was the concentration of phenol (/L mg), m was the quality of activated carbon (g), respectively.

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3. Results and Discussion

3.1. Morphology and Structural Properties of Porous Materials

3.1.1. Morphology

The microstructure of the unmodified materials was shown in Figure 1. Figure 1(a) showed a large number of folds and cracks and small cavities on the surface. The reason for these results is that the porous samples comprised many different types of raw materials, and a large number of gaps and cavities formed under the binding and shear forces. Figure 1(b) showed the surface morphology of modified materials. It can be seen that the surface exhibits a large number of holes and pores after semi-carbonization and KOH modifying treatment. The pore distribution is disordered and irregular, and the holes connected to each other to form a network. The reason for the results is that chemical reactions occur between the materials .In the process of semi-carbonization, carbon dioxide reacts with carbon material, which causes partial oxidation of disordered carbon in carbon material to corrode into pores. At the same time, because the KOH molecule can be immersed in the porous material of semi-carbonization, through the chemical reaction between KOH and the carbon in the porous material, some of the carbon is etched, the etching position is the pore, and a large number of pore structures appear on the surface of the material.



Figure 1. SEM images of unmodified materials(a) and modified materials(b)

3.1.2. Specific Surface Area and Pore Structure

The Brunauer-Emmett–Teller test was carried out on the unmodified samples and modified samples. The specific surface area, pore volume and average pore size of unmodified samples were2.32 m^2/g ,0.013 cm³/g and 12.15nm, respectively. The specific surface area and pore volume of the modified porous materials were significantly increased to 113.15 m²/g and 0.079 cm³/g respectively, and the average pore size was reduced to 6.17 nm. That is caused by the initial pyrolysis of the material in the process of semi-carbonization nd the chemical reaction in the process of KOH modification (the reaction formula is as follows), which make the material possess higher porosity and specific surface area. The average pore size of the modified porous material is moderate, which can be used as the channel of adsorbed substance, and also can conduct capillary condensation at a certain pressure. The modified porous material has a better adsorption effect on aerosol particles.

$$6KOH + 2C \rightarrow 2K + 3H2 + 2K2CO3 \tag{2}$$

$$2C + K2CO3 \rightarrow 2K + 3CO \tag{3}$$

3.1.3. Surface Characteristics



Figure 2. IR spectra of before modification and modified materials

The FTIR spectrograms of the unmodified samples and modified samples were shown in Figure2. Special functional groups corresponding to the absorption position were analyzed according to the literatures[9-11]. In the FTIR analysis, the strong peak near3418.13 cm⁻¹ is attributed to the hybrid stretching vibration of O-H and N-H, and the peak near 2923.08 cm⁻¹ is probably the peak of CH₂ and CH₃. The strong peak near 1637.03 cm⁻¹ is the N-H stretching vibration of the primary amine, the strong peak near 1032.58 cm⁻¹ is the absorption band of the C-O-C symmetric and asymmetric stretching vibrations and the O-H unbalanced surface rocking vibration of the carboxyl group molecular aggregates. According to the above analysis, the material has many functional groups, such as hydroxyl, amine, and carboxyl groups and non-carbon elements. These kinds of functional groups could result in improving polar, hydrophilic, catalytic performance and changing the surface charge, which can enhance the interaction between the adsorbent and adsorbate. Therefore, the porous material will have a better adsorption capacity[12].

By comparing the two lines, it can be seen that the infrared spectra of porous materials before and after semi-carbonization and modification are roughly similar. But the peak intensity of spectral line significantly changed after modification, which indicated that modification can increase the functional groups of–OH and–CH. It shows that the material has a certain pro organic.

3.2. Freundlich Adsorption Isotherms for Phenol Adsorption

Figure 3 shows the adsorption isotherm of phenol by modified materials. Freundlich adsorption isotherm model is used to analyze the characteristics of phenol adsorption. It can be seen from figure 3 that the correlation coefficient of adsorption isotherm of modified porous materials is 0.95. According to R^2 , Freundlich isotherm adsorption equation model accords with experimental data.

$$\lg q_e = \frac{1}{n} \lg C_e + \lg k \tag{4}$$

Where N is Freundlich adsorption model index; K is Freundlich adsorption model constant; N and K are lgqe's slope and intercept for lgCe.



Figure 3. Freundlich adsorption isotherms of phenol adsorption

3.3. Adsorption Kinetics Analysis

0.1 g modified porous material was added to 100 mL phenol solution with concentration of 2 g / L and oscillated at 25 °C in a water tank. The amount of adsorption was measured at 5, 10, 30, 60, 90, and 120 min, respectively. Fig. 4 is the curve of the adsorption removal rate with time of the modified porous material on phenol. In order to study the adsorption mechanism and possible speed control steps, we tested the experimental data using a kinetic model .

The quasi-second-order reaction equation [13] is as follows:

$$\frac{\mathsf{t}}{\mathsf{q}_{\mathsf{t}}} = \frac{1}{\mathsf{k}\mathsf{q}^2\mathsf{m}} + \frac{1}{\mathsf{q}\mathsf{m}}\mathsf{t} \tag{5}$$

Where qm is the maximum adsorption amount in equilibrium, the unit: mgg^{-1} ; T he qt is the adsorption amount at the time of t, the unit: mgg^{-1} ;The k is the quasi second-order reaction, the unit: $gmg^{-1}min^{-1}$;The h can be regarded as the initial adsorption rate, the adsorption rate at t/q_rto 0. So h= kq_e², the equation is as follows:

$$\frac{t}{q_t} = \frac{1}{h}t + \frac{1}{q_m}t \tag{6}$$

It can be seen from figure 4 and Table 1, the fitting lines show a very good correlation. The correlation coefficient R^2 of the quasi-second-order kinetic model is suitable for the adsorption of the modified porous materials.



Figure 4. Fitting curve of the second order reaction (different concentration)

Table 1. Adsorption kinetics of phenol on porous materials: the second order reaction constant

K(g/mg min)	h	\mathbf{R}^2	gradient	intercept
0.97	2.98	0.9999	0.57	0.34

3.4. Thermodynamic Analysis of Adsorption

Temperature plays a very important role in the adsorption process. Therefore, the effect of temperature on the adsorption of phenol by modified porous materials was studied. The temperature of the adsorption process is changed and the other conditions remain unchanged. The initial concentration of the solution is 2 g/L, adding 0.1 g modified porous materials were oscillated for 24 hours in a constant temperature oscillation tank at 5°C, 15°C, 25°C, 35°C, 45°C, 55°C, 55 °C, respectively. The supernatant of 1 mL was taken after a certain timel and the equilibrium concentration was determined by the standard curve drawn by UV-Vis spectrophotometry. The formula of thermodynamic equilibrium constant is as follows:

$$K_{d} = \frac{(C_{0} - C_{t})V}{C_{t}W}$$
(7)

Where W is the mass of adsorbent; KD is the thermodynamic equilibrium constant. The value of lnKd at different temperatures is obtained, and a 1 / T plot is drawn. Δ H, Δ S can be obtained from the diagram, and Δ G can be obtained by calculation.

The thermodynamic functions of adsorption free energy, free enthalpy, free entropy are determined by the following formula [14]:

The formula of adsorption free energy (Δ G, unit: KJ mol⁻¹) is as follows:

$$\Delta G = -RT \ln K_c \tag{8}$$

Where R is a gas constant of 8.314×10^{-3} , the unit: 1: kJ mol⁻¹K⁻¹, K c is the equilibrium constant; T is a thermodynamic temperature, and the unit: K : K c was calculated by the following formula:

$$K_{c} = \frac{C_{0} - C_{e}}{C_{e}}$$
(9)

Where C_0 is the initial concentration of the adsorption solution, the unit: mg L⁻¹; Ce is the solution concentration after adsorption equilibrium, the unit: mg L⁻¹; Δ H is the adsorption enthalpy, the unit ;kJ mol⁻¹; Δ S is the adsorption entropy, and the unit :kJ mol⁻¹ K⁻¹;Kc can be obtained from Vanton Hoff equation. And the Van't Hoff formula is as follows:

$$\ln K_{\rm C} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$
(10)

The values of Δ H and Δ S can be calculated from the slope and intercept of linear equation by drawing 1 / T with lnKc.







porous materials

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Figure 5 shows the effect of temperature on the removal rate of phenol adsorbed by modified porous materials. It can be seen that the removal rate of phenol by modified porous materials decreases with the increase of temperature, which is an exothermic reaction process. According to the experimental results, the linear fitting results of adsorption of modified porous materials are obtained by combining the thermodynamic equilibrium constant with the fundamental relations of Gibbs free energy, enthalpy change and entropy change, as shown in figure 6.It can be seen from the diagram that the fitting equation is Y=882.142X-1.786, R² is 0.9427, The fitting degree of experimental results and Linear equations is high.

The thermodynamic parameters of phenol adsorbed by modified porous materials are listed in Table2. The adsorption free energy is negative value in the temperature range of 5~55°C, which indicate that the adsorption process is spontaneous. The ΔG value increases with the rise of temperature, which indicates that the increase of temperature is not conducive to the adsorption. It has been reported that when Δ H is less than 20 kJ mol⁻¹, the adsorption process is considered to be physical adsorption process. When Δ H value is in the range of 80 ~ 200 kJ / mol⁻¹, the adsorption process is considered as chemical adsorption [15, 16]. The Δ H is -7.334 kJ mol⁻¹< 20 kJ mol⁻¹, which indicates that the modified porous material is physically adsorbed at this concentration. Because Δ H < 0 and Δ S < 0 at this temperature range, the adsorption behavior of the modified porous materials for phenol at the concentration of 2 g /L is the entropy reduction process of heat release.

concentration(g/L)	temperature(K)	ΔG (Kj/mol)	ΔH (kJ/mol)	ΔS (kJ/mol)
2	278	-3.45		-0.015
	288	-3.04		
	298	-2.85	-7 334	
	308	-2.66	1.551	
	318	-2.62		
	328	-2.32		

Table 2. Thermodynamic parameters of phenol adsorbed by modified porous materials

4. Conclusion

Tobacco stem based modified porous materials with high porosity and specific surface areas were prepared by the method of fermentation, semi-carbonization and modification. The effects of modification on the morphology, structure and surface properties of the materials were analyzed. The adsorption isotherm, adsorption kinetics and adsorption thermodynamic properties were also studied. The KOH modification has obvious influence on the surface structure of the semi-carbonized surface, which produced a large number of cavities and holes on its surface with irregular distribution and interlaced into a mesh. The chemical reaction makes the specific surface areas and pore volume significantly increase, which made the materials possess better adsorption.

The adsorption isothermal model of the phenol solution was simulated, which was in accordance with the Freundlich isothermal adsorption. The adsorption kinetics of the phenol adsorption was studied, which showed that T The quasi-second-order kinetic model is suitable for the adsorption of the modified porous materials. The study of adsorption thermodynamics proved that the adsorption of the phenol solution by the porous materials was physical adsorption and the adsorption behavior was the entropy decreasing process of exothermic.

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