Adsorption energetics of benzene vapors on activated adsorbent based on glycyrrhiza glabra root extract residues

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Abstract. Glycyrrhiza glabra root plant is mainly used in the pharmaceutical industry to obtain drugs. However, one of the important tasks is to obtain coal adsorbents with effective use of the remaining residues. We will have the opportunity to determine the full thermodynamic properties of the activated carbon adsorbent enriched with additional substances from the residues of the licorice root and to fully determine the adsorption properties of the obtained porous coal adsorbents using capillary and volumetric methods in a high-vacuum adsorption device and a high-sensitivity DAK 1-1 calorimetric apparatus. By determining the benzene adsorption isotherm, differential heat, entropy and equilibrium time of the obtained coal, the adsorption capacity of the new adsorbent, the location of the active centers, and the pore sizes can be described in detail.

1 Introduction

Carbon microporous adsorbents (activated carbons, active fibers, and fabrics) are a class of high molecular weight solid porous carbon materials that absorb substances of various chemical natures (in gaseous, vapor, and liquid media) onto certain surfaces [1, 2].

Dubinin M.M. according to the classification [3], based on the sorption mechanisms that occur in the adsorption pores and capillary phenomena, the pores of various adsorbents are divided into the following types: micro-pores, macro-pores (equivalent radius r greater than 100-200 nm), mesopores (1.5 -1, 6 <r <r <1.5-1.6 nm).

Carbon microporous adsorbents are significantly different from materials such as coke, pumice, graphite [4] because they contain micropores and supermicropores. In the same way, they differ from coal [5], which have a relatively high surface area due to small particle size (up to 100 m^2/g and above) and belong to non-porous carbon adsorbents. Adsorbed into micropores and supermicropores [6] because they are crucial for the adsorption of gases and vapors and in many cases for liquid phase adsorption [7]. It depends on the structure and geometric surface of adsorbates. Its value according to [8] is

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~400-1400 m^2/g, i.e. 15-55% of the theoretically possible value of 2630 m^2/g obtained for a hypothetical model of pure aromatic carbon of hexagonal shape with a condensed flat band structure [9]. The volume of micropores and supermicropores is usually in the range of 0.2 - 0.6 cm^3/g [10]. For the best samples of carbon adsorbents, it can reach 1.3 - 1.5 cm^3/g [11, 12].

A formula for calculating the geometric volume of micropores from the value of adsorption energy of standard benzene vapor was proposed [13]. The possibility of redescription of adsorption isotherms for several substances (benzene, ethyl chloride, carbon tetrachloride, etc.) using the equations of the theory of volume saturation of micropores (MHTN) was shown [14].

Thus, according to the MHTN equations and the parameters of the porous structure of activated carbon calculated from the adsorption isotherms of standard benzene vapor, it is possible to evaluate their adsorption properties with respect to vapors of a wide class of substances. However, it should be noted that in some cases there is a discrepancy between the parameters determined by the adsorption of benzene and other substances [14-28].

2 Object and methods

The adsorption isotherm of benzene on the resulting adsorbent was determined in the pressure determination section of the high-vacuum adsorption device. The differential heat of adsorption is measured by theoretical calculation of the pressure values and the energy output from the DAK 1-1 calorimeter in the Tian-Calve model. Volumetric and capillary (liquid) methods were used to determine the adsorption isotherm. The adsorption isotherm has an accuracy of 0.1% and a heat of 1% [29].

Adsorption of benzene vapor was carried out at 303 K on a sample of activated carbon adsorbent obtained from the root extract residue of the native Glycyrrhíza glabra plant. Absolute benzene was used in the adsorption process.

3 Results and discussion

Figure 1 shows the adsorption isotherm of benzene on activated carbon obtained from the residue of root extract of native plant Glycyrrhíza glabra at 303 K. The adsorption isotherm initially shows ln(P/P0)=-10.8. This means that coal is being adsorbed in the micropores. Considering that the size of the benzene molecule is 0.6 nm, it indicates the presence of micropores in our obtained adsorbent. At values of adsorption amount up to about 1.1 mmol/L, benzene adsorption is ln(P/P0)=-7.2. This means that benzene molecules are adsorbed in the internal micropores of coal. When adsorption reaches 4.75 mmol/g, the pressure in the device is 119.38 mm.sim. above will be equal. This value is equal to the saturation vapor pressure of benzene at a temperature of 300C, and coal is saturated with benzene.

Figure 1 shows the benzene adsorption isotherm of activated carbon obtained from the root extract residue of the indigenous Glycyrrhíza glabra plant at 303 K. The adsorption isotherm initially indicates that ln(P/P0)=-11.2 is adsorbed in the internal micropores of the adsorbent.

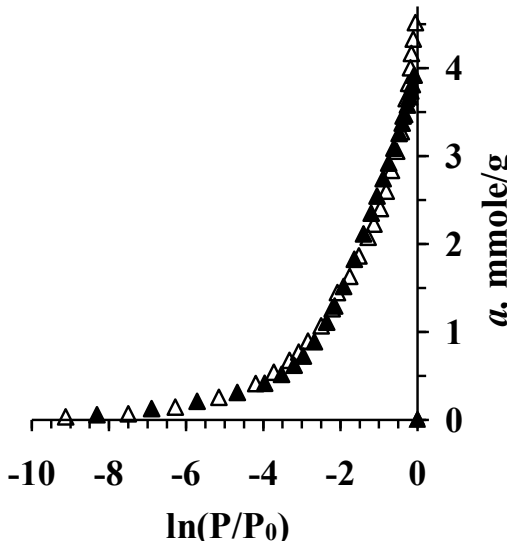

Fig. 1. Isotherm of benzene vapor adsorption on activated carbon adsorbent obtained from local licorice root at 303 K

Adsorption isotherm of benzene molecules onto activated carbon sample obtained from native licorice root residue was characterized using three-state micropore saturation theory equation (MHTN).

$$a=0{,}54\exp[(A/15{,}14)^3]+2{,}75\exp[(A/5{,}23)^5]+1{,}21\exp[(A/0{,}87)^3],$$

The amount of adsorption in α-micropores C_6H_6, A=RTln(P°/P)- free energy work (kJ/mol).

The differential heat of adsorption of benzene vapors on the coal adsorbent obtained for research work at a temperature of 303 K is presented in Fig. 2. Initially, the heat of adsorption of benzene is equal to 105.05 kJ/mol when α=0.055 mmol/g at the initial saturation, and it is observed that the heat value of adsorption of benzene molecules decreases slightly. Qd=85.16 kJ/mol at α=0.52 mmol/g. One of the main reasons for the high heat of adsorption of benzene molecules at low saturations is explained by their adsorption into micropores. Metal cations located in the micropores of the coal sample form p-complexes of (Men+S6N6)n type. It was further observed that the adsorption exhibits a single maximum heat at differential heat value of α=1.0 mmol/g and increases to Q=87.66 kJ/mol. In the subsequent stages of adsorption, the differential heat decreases. After a=4.2 mmol/g, the heat of adsorption equals the heat of condensation.

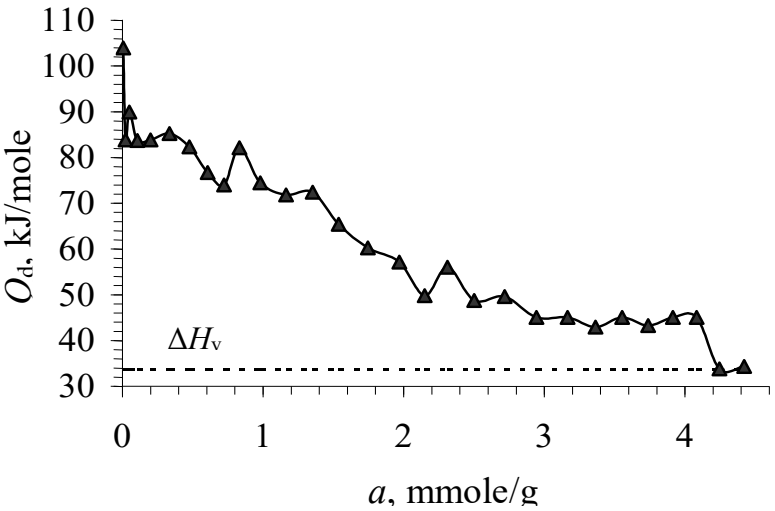

Fig. 2. Differential heat of adsorption of benzene vapors on activated carbon adsorbent from native licorice plant root residues at 303 K.

The horizontal dashed line is the heat of condensation of benzene vapor at 303 K

This decrease in the adsorption differential heat values is absorbed into the micro-, and mesopores of the coal, and the heats of adsorption decrease with increasing benzene saturation. Adsorption of benzene vapors on activated carbon for research work, the value of condensation heat equals to 33.8 kJ/mol, and a total of 4.6 mmol/g of benzene is adsorbed.

Adsorption entropy describes the state of motion of absorbed adsorbate molecules in the adsorbent. The entropy curve of the adsorbent-benzene system obtained from the local coal residues had a wavy appearance in accordance with the adsorbent saturation values (Figure 3).

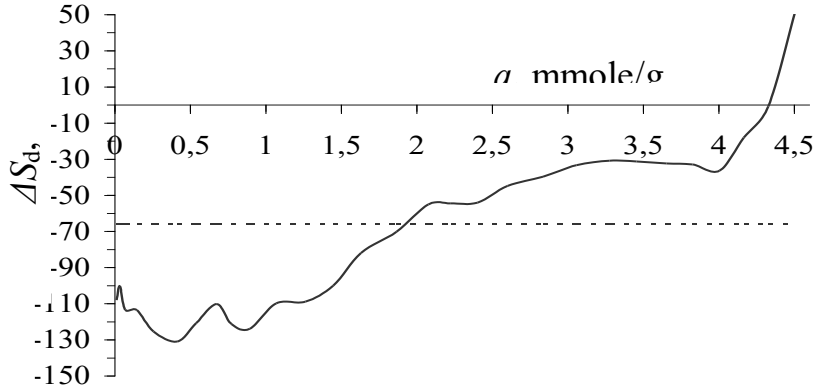

Fig. 3. Molar integral entropy of adsorption of benzene vapors on activated carbon adsorbent obtained from native licorice root residues at 303 K

It is known from the entropy graph that at values up to 2 mmol/g, benzene is strongly adsorbed, that is, it is located below the average integral entropy line. After 4.3 mmol/g, it

is higher than the standard state benzene entropy value. Adsorption entropy in the process up to 4.3 mmol/g indicates strong localization in the pores of the adsorbent.

In the initial stages of saturation, benzene molecules are strongly adsorbed in the micropores of coal, that is, benzene molecules are in an unexcited state, during the adsorption process up to -68.7 J/mole*K, benzene goes to the solid state entropy value. Then, benzene slowly changes to the entropy of the liquid state. The average integral entropy of benzene adsorption on coal obtained in the research work is -68.7 J/mole*K.

Figure 4 shows the thermal equilibrium time (thermokinetics) of benzene adsorption onto activated carbon adsorbent obtained from native licorice root residues. Research in free voltage provides additional energy and follows the Rakhmatkariev effect rule. In this activated carbon, the equilibrium time curves initially decrease steeply above 0.15 mmol/g and follow a wavy pattern after 0.15 mmol/g.

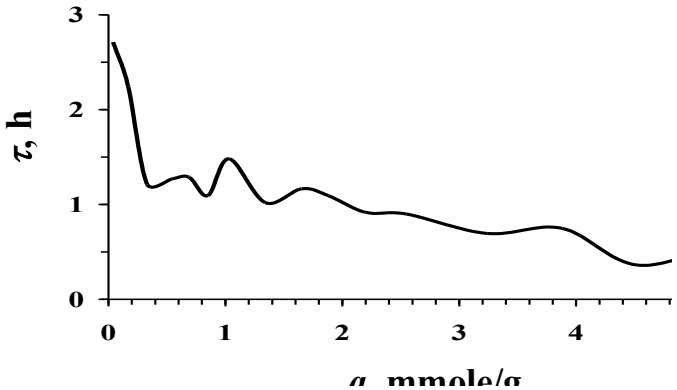

Fig. 4. Equilibrium time of adsorption of benzene vapors on activated carbon adsorbent from domestic licorice root residues at 303 K

The equilibrium time of benzene adsorption on activated carbon obtained from native licorice root residues is initially 2.8 hours. In this case, due to the small number of benzene molecules and the large number of pores, it takes more time for the equilibrium to be reached. At initial saturations, the activated carbon adsorbent obtained from native licorice plant root residues takes a little longer to reach equilibrium for benzene adsorption due to the large number of unadsorbed vacancies and cations not exposed to the adsorbate in the micropores. When the amount of adsorption reaches 0.12 mmol/ha, the adsorption thermal equilibrium time is 1.25 hours. Subsequent adsorption of benzene molecules produces small minima and maxima, and thermal equilibration takes 30 minutes.

4 Conclusion

In our research, the adsorption properties of activated carbon adsorbent obtained from the root residues of local licorice plant were investigated. The adsorption isotherm and differential heat are initially high, indicating that the adsorbent is adsorbed in the micropores. Due to the small size of the pores, absorbed benzene molecules release a large amount of energy. This ensures that the heat of adsorption is high. The adsorption isotherm of benzene vapor on the obtained activated carbon adsorbent was characterized using the equation of the volume saturation theory of micropores. Benzene is strongly localized in the micropores of the obtained activated carbon adsorbent, which indicates the formation of p-complexes. The main features of the obtained adsorbent are that the raw materials

necessary for the production industry are obtained by effectively using residual products of coal.

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