

Adsorption properties of carbon adsorbents based on wood waste

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Abstract. This article investigates the adsorption properties of carbon adsorbents obtained from wood waste. The work aimed to study the effect of heat treatment and steam activation on the structure of coal and its ability to adsorb benzene. Electron microscopic, X-ray phase, and IR spectral analyses were carried out to achieve this goal. The results of electron microscopic analysis showed that the grain size of sample FK-600 was smaller than that of other samples. Still, the surface morphology of all solids was characterized by roughness and unevenness. Particularly heterogeneous surface morphology was observed in steam-treated activated carbons, indicating strong oxidation. X-ray phase analysis showed the presence of carbonate and silicon salts of metals in adsorbents obtained at 400 and 600°C. IR spectral analysis made it possible to reveal functional groups on the surface of carbon adsorbents. Thermal treatment and steam activation changed the number and type of functional groups. This work studied the influence of heat treatment and steam activation on the structure of coal and its ability to adsorb benzene. The analysis of adsorption isotherms showed that the adsorbents have a microporous structure and exhibit type I Brunauer isotherms. Experimental data indicate a significant increase in the specific surface area and adsorption volume with increased activation temperature. Heat treatment at higher temperatures and steam activation also contribute to opening additional pores in carbon adsorbents. The results obtained allow a deeper understanding of the interaction of carbon adsorbents with benzene and optimize the processes for obtaining such adsorbents based on wood waste. This is of great practical importance for water and air purification from organic pollutants and may lead to the development of more efficient and environmentally friendly purification methods.

1 Introduction

The modern development of many industries requires more stringent environmental protection measures, which leads to an increased demand for affordable and effective adsorbents. With their developed porous structure, activated carbons are widely used due to their availability, environmental safety, and various applications. They are used to adsorb

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pollutants from the liquid or gas phase and as catalysts, catalyst supports, and gas storage or media purification.

Currently, the most common activated carbons are produced from fossil coals and wood due to the ease of forming a porous structure during carbonization and activation processes using oxidizing gases.

However, commercially produced activated carbons are relatively expensive, so new raw materials and biomass are being explored more and more. A wide range of waste products can be used to produce effectively activated carbons. [1-5]. All these works aim to create activated carbons, which have been tested for the removal of heavy metal ions, dyes, derivatives of organic acids, and phenol.

The contaminant ions can be adsorbed due to the highly porous structure of ACs and the ability to absorb dissolved organic and inorganic substances, some pesticides, pharmaceuticals, etc. The widely used material for producing ACs is based on carbon-rich organic material. Nowadays, from the ecological aspect, waste biomass is among the most used raw material. For example, coconut shells, almond shells, bamboo, banana peels, com cobs, rice bran, grape processing industry waste, wood industry waste, agricultural by-products, etc. [6,7]. The woody biomass contains cellulose, lignin, and hemicellulose in its structure. This is also a relatively low-cost source for AC obtaining with good characteristics and a well-developed surface can be achieved [8].

The structure and properties of activated carbon depend on the nature of the starting material, which is determined by the biochemical composition and affects the pyrolysis process, product yield, wear rate, and ash amount. [9,10]. Raw materials with a high carbon content and a low content of inorganic substances are preferred in producing activated carbon. Using agricultural waste and biomass contributes to the sustainable production of activated carbon. It also reduces greenhouse gas emissions due to its lower sulfur and nitrogen content than fossil coals [11].

In our country, scientific and research work is being carried out on obtaining adsorbents based on plant waste and studying their properties, as well as on the adsorption of organic and inorganic substances on natural and synthetic adsorbents [12,13]. In addition, they studied the production of adsorbents based on grape seed waste [14], peanut pods [15], and their physico-chemical and adsorption properties. It is important to study the change of the adsorption volume according to the temperature difference of thermal treatment of coal adsorbents obtained based on tree stem waste. A literature review shows that relatively few comparative studies have been conducted to increase knowledge about the effect of activated carbon properties on the efficiency of adsorption of organic pollutants from aqueous solutions in single- and multi-component systems. These studies are of both theoretical and practical importance as they help optimize adsorption methods for water and wastewater treatment technologies. Therefore, this paper presents the results of a study of physical activation (thermal activation without and with water vapor) of maple stem waste on its composition, porous structure, and adsorption activity concerning benzene vapor.

2 Materials and Methods

For this purpose, activated carbon samples were prepared by thermal (400,600,800°C) and steam (800°C) activation for 1.0 hours based on maple tree stem waste growing in the territory of our Republic as a research object. The obtained adsorbents were named as follows: FK-400, FK-600, FK-800, FK-800*.

Roentgenographic analysis of carbon adsorbents obtained based on waste of maple tree stems was studied. The crystalline properties of the obtained geological coal minerals were carried out on an XRD-6100 powder diffractometer (Shimadzu, Japan). CuK α was carried out under the influence of radiation (β filter, Ni, $\lambda = 1.54178 \text{ \AA}$, current and voltage 30 mA,

30 kV in an X-ray tube). At the same time, the constant rotation speed of the detector was 4 deg/min in increments of 0.02° (1/2 connection) with scan angles in the range from 4 to 80°. Samples were analyzed in a rotating cell at 30 ml/min rotation speed.

Quantitative and qualitative analysis of the compositions of the functional groups of the obtained carbon adsorbents was determined by IR spectroscopy (Shimadzu IRTracer100, Japan). The high spectra sensitivity (at a signal-to-noise ratio of 60,000: 1) leads to a sequential analysis of the number of impurities in different samples, despite the low intensity of the spectrum lines. The spectral resolution of IRTracer-100 0.25 cm⁻¹ with high resolution, especially in the case of gaseous compounds, provides for the determination of quantitative composition. The system for optimizing the interferometer operation, along with self-diagnostics, ensures stable operation of the device.

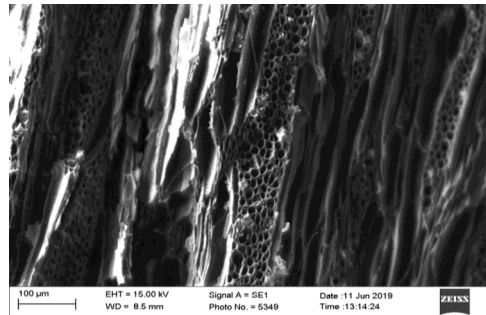
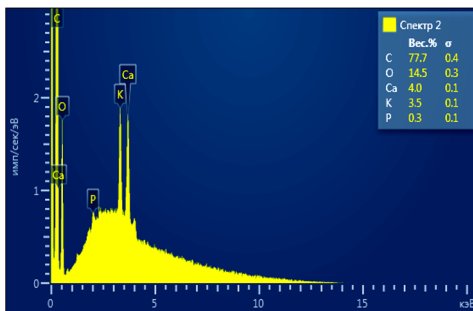
Benzene vapor adsorption isotherms were measured in an Mc-Ben-Bakra sensitive quartz spiral device. The pressure difference in the U-shaped mercury manometers and the change of the quartz spring were determined using the catometer V-630. The accuracy of the catheter is 0.05 mm. Before measuring benzene adsorption on the adsorbents, the system was vacuumed until the residual pressure was 1.33x10⁻³Pa, heated at 110°C for 8 hours, and then adsorption isotherms were obtained.

Based on isotherms of adsorption of benzene vapors on coal adsorbents and the equation of volume saturation theory of micropores, micropores of adsorbents (W_0), adsorption volumes for saturated states (V_s), and volume of mesopores were determined using the formula $W_{mc} = V_s - W_0$. The average radius of the pores was calculated according to the formula:

$$r_{av} = \frac{2 \cdot V_s \cdot 10^4}{S}$$

3 Results and Discussion

The composition and structure of carbon adsorbents obtained based on maple tree stem waste were studied using a scanning electron microscope at 1000x magnification. The results are presented in Figure 1.



a)

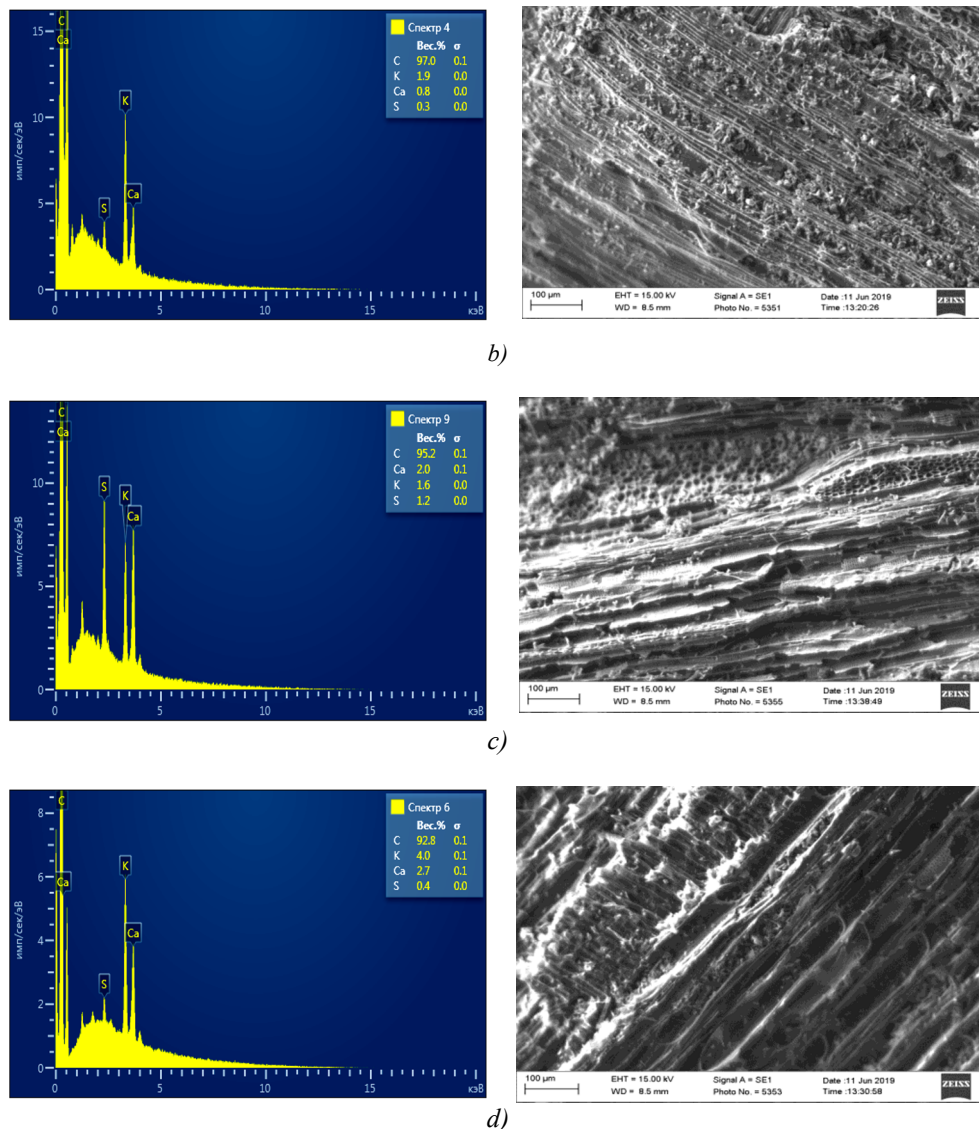


Fig. 1. Scanning electron microscope images of thermally and steam-gas activated carbon adsorbents based on sycamore stem waste: a) FK-400; b) FK-600; c) FK-800; d) FK-800*'

The grain size of sample FK-600 is smaller than that of other samples; however, the morphology of all complex bodies appears with pronounced roughness and unevenness. The most heterogeneous surface morphology appears to be observed in activated carbons activated with water vapor, resulting from the strong oxidation applied. Photomicrographs indicate random and curved individual layers of carbon consisting of randomly crossed graphite-like planes [16].

Electron microscope images show that the elemental composition of coal samples obtained from the waste of maple tree trunks is almost unchanged. The presence of an oxygen element in the coal sample obtained only at 400°C indicates the presence of functional groups such as -OH, -CHO, -COOH on its surface. Also, during the activation of the obtained coal adsorbents in increasing order of thermal activation temperature (in the

range of 400-800°C), a certain amount of tars and other high-temperature decomposing organic compounds that blocked the entrance of the pores during activation, and during steam-gas (800°C) activation, amorphous carbon at a high temperature of water vapor it can be seen that additional pores and cracks were formed as a result of the effect.

The figure below shows the diffractogram of maple tree charcoal adsorbents.

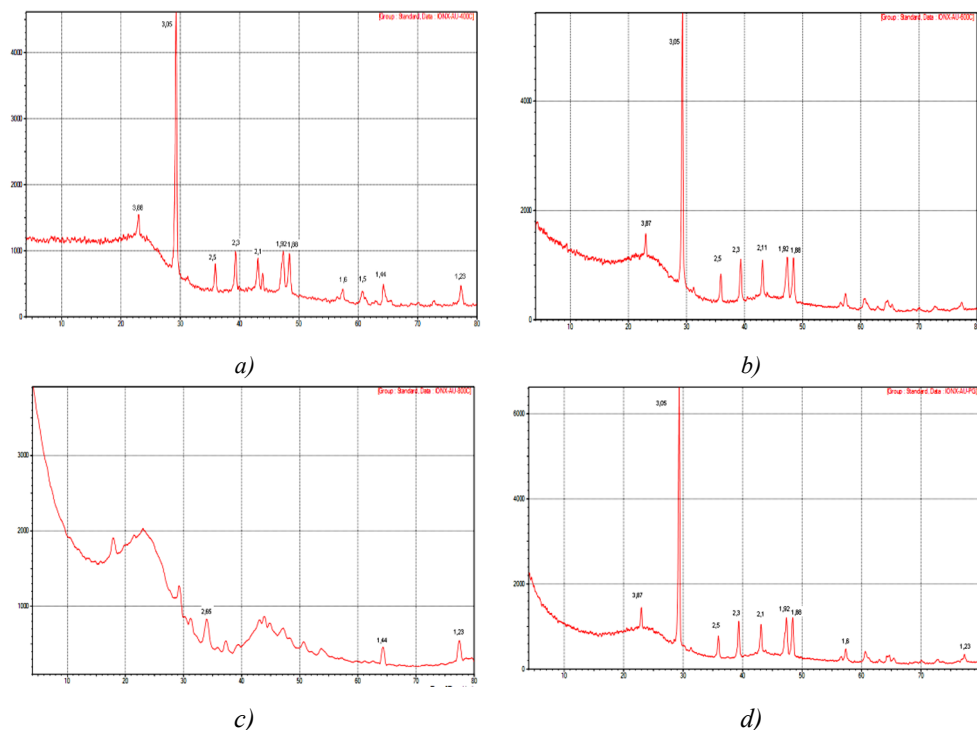


Fig 2. Diffractograms of carbon adsorbents obtained by thermal and steam-gas activation based on maple tree stem waste: *a) FK-400; b) FK-600; c) FK-800; d) FK-800**

It can be seen from the diffractogram of the adsorbents obtained based on maple tree stem waste that the adsorbents obtained at 400 and 600°C contain a certain amount of carbonate and silicate salts of metals. In these two coal adsorbents, the interfacial distance is 3.05043 ; 3.04926 cm^{-1} , and peak intensity at 826 ; 1051 nm indicates the presence of CaCO_3 . In the adsorbent sample obtained at 400°C , the interfacial distance is 1.92337 ; 1.88122 cm^{-1} and peak intensities of 126 , 129 nm , an interfacial distance of 1.92222 cm^{-1} and 1.88069 cm^{-1} and peak intensities of 161 nm , 173 nm in the coal adsorbent obtained at 600°C indicate that they contain K_2CO_3 . In addition, the interfacial distance of 1.60404 cm^{-1} and 1.52620 cm^{-1} , the intensity of peaks at 43 nm and 44 nm in the composition of adsorbents prove that potassium and calcium silicates are found in small amounts in their composition. Also, the interfacial distance of 1.23377 cm^{-1} and the peak intensity of 73 nm prove that carbon atoms form crystals in carbon adsorbents, as in graphite.

IR spectra of carbon adsorbents obtained by thermal and steam-gas activation based on maple stem waste are presented in Fig. 3.

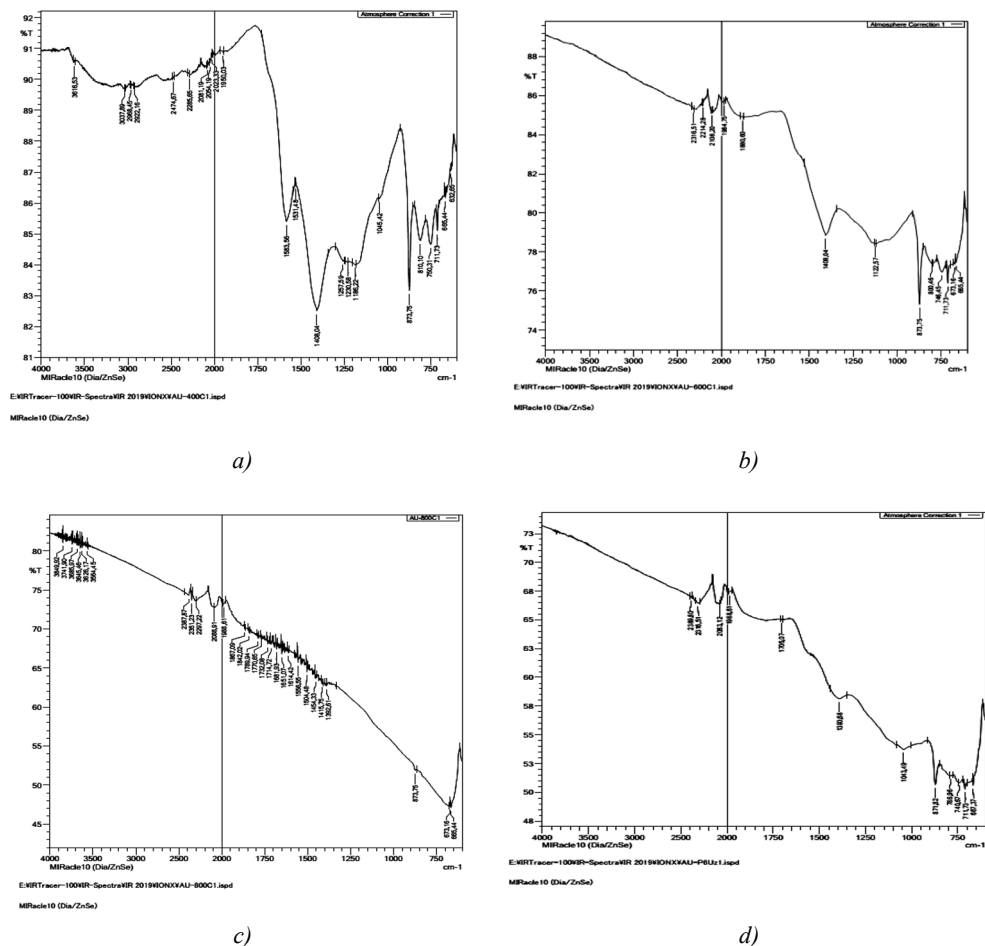


Fig. 3. IR spectra of carbon adsorbents obtained by thermal and steam-gas activation on basis of sycamore stem waste: a) FK-400; b) FK-600; c) FK-800; d) FK-800*

Based on the results of literature analysis and IR spectra of the obtained carbon adsorbents, the carbon adsorbent obtained at 400°C contains organometallic (400-900cm⁻¹), C-O-C (900-1200 cm⁻¹), C-Gal (500-1400 cm⁻¹), -C=O (1500-1800 cm⁻¹), -C≡C-, -C≡N, -N=C=O, -N=C=N- (2100-2300 cm⁻¹), -OH (3600±50cm⁻¹) functional groups can be seen. Coal adsorption at 600°C and 800°C shows the decomposition of some functional groups with increasing temperature. For example, you can observe interruptions in the connection of C-O and C=O in the functional groups, such as C-O-C (900-1200 cm⁻¹), C=O (1500-1800 cm⁻¹). Such processes lead to the formation of excess pores between carbon atoms

Carbon adsorbents obtained based on plant waste are hydrophobic adsorbents due to the very small number of active centers (polar ions) with the property of adsorbing polar molecules. Therefore, they are used in industry to adsorb organic compounds as additives. Adsorbates are divided into different groups according to their structure, properties, and nature. Organic π -bases, according to Bronsted classification of benzene and toluene molecules used as adsorbate, according to the Kiselev classification, can be considered as unsaturated aromatic hydrocarbons with π -bonds [17]. The adsorption of benzene vapors on the obtained coal adsorbents was studied. Adsorption isotherms are presented in Figure 4.

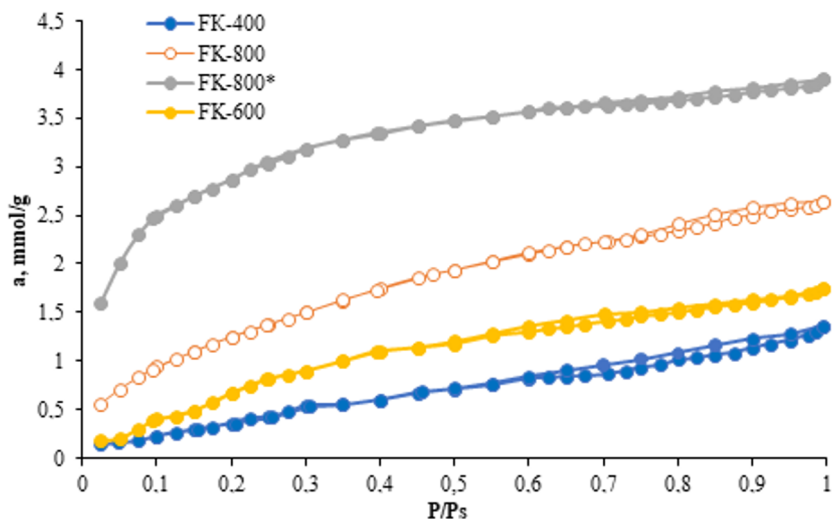


Fig. 4. Adsorption isotherms of coal adsorbents obtained by thermal and steam-gas activation based on maple tree stem waste with benzene vapor.

It can be seen from the adsorption isotherms in the mentioned systems that the amount of adsorption increases sharply from the zero value of relative specific pressure to $p/p_s \approx 0.3$, and then the adsorption slowly approaches the state of saturation. The sharp appearance of the adsorption isotherms at such a low relative pressure ($P/P_s \approx 0.3$) is the basis for saying that benzene vapors are adsorbed on surfaces with a high adsorption potential in the initial fillings.

Hysteresis in isotherms in the relative pressure range ($P/P_s \approx 0.7 - 0.8$) where the adsorption lines merged with the desorption lines to form adsorption rings. From this, it is reasonable to say that at high specific pressures, adsorption occurs by capillary condensation.

Adsorption isotherms of these samples with benzene vapor were found to belong to type I of the classification of adsorption isotherms proposed by Brunauer. The adsorbents that form the I-type isotherm are microporous adsorbents. This type of isotherm is characterized by forming an almost right angle to the $P/P_s = 1$ axis due to its sharp rise.

The shape of the adsorption isotherms depends on the properties of the adsorbent and absorbed substance and the forces of interaction between them. According to the temperature difference in the samples heat-treated at 400°C and 800°C, the saturation adsorption amount of the sample thermally activated at 800°C is 1.5 times higher than the sample heat-treated at 600°C, and the saturation adsorption amount is 1.94 times higher than the sample heat-treated at 400°C. According to the temperature difference, such a change in the amount of adsorption is the result of the increase in the number of cracks and pores in the coal as a result of the release of non-decomposed organic compounds at relatively low temperatures (400°C) and resinous substances at high temperatures (800°C) during thermal treatment of these adsorbents. For the obtained samples, heating from 400 to 800°C, i.e., thermal activation, increased their pore volume by almost 2 times, and activation with water vapor increased it by 3.2 times.

Based on the adsorption isotherms of benzene vapors on coal adsorbents, the monolayer capacity a_m , saturation volume v_s (or adsorption a_s), and their relative surfaces S were calculated from the important indicators of adsorbents. The obtained results are presented in Table 1.

Table 1. Structure and sorption indicators of benzene vapor adsorption of coal adsorbents obtained by thermal and steam-gas activation based on sycamore stem waste

Adsorbents	Activation temperature, °C	Monolayer capacity, a_m , mol/kg	Relative reference surface, $S \cdot 10^{-3}$, m ² /kg	Amount of adsorption a_s , mol/kg
FK-400	400° C	0.33	79	1.36
FK-600	600° C	0.57	138	1.74
FK-800	800° C	1.06	255	2.64
FK-800*	800° C+water vapor	2.0	482	3.86

It was found that the specific surface area (S) and saturation volume (a_s) of coal adsorbents increase with the increase of the activation temperature in all studied samples. Activation under these conditions leads to the opening of additional pores in the coal adsorbent layers due to the release of various gases and tars in the coal. Compared to the obtained adsorbents, it was found that the structure-sorption indicators for the sample activated with water vapor at 800°C are higher than other adsorbents. Compared to FK-800, it was found that the specific surface area (S) increased by 1.9 times and the saturation volume (a_s) by 1.5 times.

It was determined that the volume of micropores (W_0) and the adsorption volumes for their saturated states increased, and the average radius of the pores decreased as the temperature of thermal activation increased. It was found that as the activation temperature increases, the amount of micropores increases compared to the number of mesopores; therefore, the average radius of the pores of adsorbents decreases. The obtained results are presented in Table 2.

Table 2. Indicators of pore volumes for benzene vapor adsorption of coal adsorbents obtained by thermal and steam-gas activation based on sycamore stem waste

Adsorbents	Activation temperature, °C	$W_0 \cdot 10^3$	$V_s \cdot 10^3$	$W_{me} \cdot 10^3$	Average pore radius r_{av} , Å
FK-400	400° C	0.093	0.121	0.028	30.6
FK-600	600° C	0.138	0.155	0.017	22.5
FK-800	800° C	0.213	0.235	0.022	18.4
FK-800*	800° C+water vapor	0.295	0.343	0.048	14.2

It was found that heating the obtained carbon adsorbents from 400°C to 800°C, i.e., thermal activation, increases their pore volume by almost 2 times, and activation with water vapor increases it by 3.2 times. The volume of mesopores compared to the adsorption volume (V_s) was 23.1% for FK-400, 11% for FK-600, 9.4% for FK-800, and 14% for FK-800*.

4 Conclusions

The study of the effect of heat treatment and steam activation on the structure of coal showed that these processes significantly affect the grain size and surface morphology of coal samples. The sample heat treated at a higher temperature has coarser grains than the other samples. On the other hand, steam-activated samples have a more heterogeneous surface with random and curved carbon layers.

Heat treatment also leads to the decomposition of the functional groups on the coal's surface, which can affect its adsorption properties. Steam activation, on the other hand,

promotes the formation of additional pores and cracks in the carbon structure, which can lead to an increase in its surface area and an improvement in its adsorption properties.

The study of the adsorption of benzene vapors on the obtained carbon adsorbents showed that their adsorption properties depend on heat treatment and steam activation. Benzene adsorption occurs on surfaces with high adsorption potential at low relative pressures. There is a hysteresis in the region of high relative pressures, indicating adsorption by capillary condensation.

Adsorption isotherms of benzene on carbon adsorbents belong to type I according to the Brunauer classification, which indicates the microporous structure of adsorbents. Heat treatment at higher temperatures and steam activation increases the pore volume and surface area of the adsorbents. The specific surface area and saturated adsorption volume increase with increasing activation temperature

Thus, the processes of heat treatment and steam activation have a significant effect on the structure and adsorption properties of coal adsorbents. Optimization of these processes can lead to the creation of adsorbents with increased adsorption capacity and efficiency for various applications, including purification from water and air pollutants.

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