Modification of carbon sorbents by ozonation

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Abstract. The paper presents the results of a study of changes in the textural and physicochemical properties of the carbon sorbent surface after oxidative modification with an ozone-oxygen mixture. For the study, we used a carbon sorbent sample obtained on the basis of long-flame coal. It is shown that oxidative modification with the mixture leads to an increase in the surface area of the studied sorbent, mainly due to the growth of micro- and mesopores. In this case, according to IR spectroscopy data, an increase in the content of oxygen-containing groups on its surface is observed.

1. Introduction
The problem of environmental pollution has recently been relevant all over the world. The rapid development of industry, the increase in the number of cars, the use of water in agriculture lead to increased pollution of water bodies. Various carbon sorbents are widely used for the purification of aqueous media. When choosing sorbents, an important role is played by the specific surface area, pore volume, and the presence of oxygen-containing groups on the sorbent surface [1, 2].

To change the structural and physicochemical properties of carbon sorbents, as well as to improve their sorption properties, various oxidation methods are used [3, 4], such as oxidation with nitric and sulfuric acid [5], atmospheric oxygen, and hydrogen peroxide [6].

A promising, but insufficiently studied, is the method of ozone oxidation [7-13]. Oxidation with an ozone-oxygen mixture has a number of advantages: the process can be carried out at low ozone concentrations, room temperature and atmospheric pressure, while no toxic waste is generated.

The aim of this work is to study the effect of ozone oxidation on the structure and properties of carbon sorbents.

2. Results and discussion
The object of research was a carbon sorbent obtained in the process of medium-temperature (750 °C) carbonization of long-flame coal. Ozonation of the sorbent sample (weighed portion of 5 g) was carried out in a thermostatically controlled rotating reactor at a temperature of 25 °C with a continuous supply of an ozone-oxygen mixture (flow rate 15 L/h, ozone concentration 30 mg/L).

The ozone-oxygen mixture was obtained by the traditional method in a gas discharge of a barrier type in an OGVK-02K ozonizer manufactured by MELP (St. Petersburg) with an ozone productivity of up to 2 g/h. Ozone was synthesized from bottled oxygen. The ozone concentration at the inlet and outlet of the reactor was determined in a continuous automatic mode using an IKO-02 device.

Upon completion of the ozonation of sorbents, intermediate products of the reaction of ozone with surface functional groups (ozonides) were destroyed by heat treatment at 120 ° C for 2 hours [14].
The specific surface area and porous structure of the sorbent samples before and after ozonation were investigated by low-temperature nitrogen adsorption on an ASAP-2400 instrument (Micromeritics Instrument Corporation, Norcross, GA, USA) after thermal vacuum training of the samples at a temperature of 200 °C and a residual pressure below 0.001 mm Hg. The nitrogen adsorption isotherm was measured at a liquid nitrogen temperature of 77 K in the relative pressure range from 0.005 to 0.99. The data were processed by the Brunauer - Emmett - Teller (BET) method with the calculation of the specific surface area ($A_{\text{BET}}$, m$^2$/g) and the average pore diameter ($D_{\text{av}}$, nm). The total pore volume ($V_\Sigma$, cm$^3$/g) was calculated from the maximum pore filling. For this series of samples, the pore filling in the range up to 150 nm was calculated at the point $P/P_0 = 0.99$. To obtain a differential pore size distribution and to determine the effective pore diameter ($D_{\text{eff}}$, nm), the data of the Barrett - Joyner - Halenda method (BJH method) were used. [15]

IR spectra of coal samples in the form of pellets with KBr were recorded on an Infralum-FT-801 FT-spectrometer in the range of 550-4000 cm$^{-1}$. When determining the optical density of the bands, a straight line drawn between the maximum transmission in the region of 650 and 1800 cm$^{-1}$ was taken as the baseline. Then, the optical density of the bands was normalized to the 1465 cm$^{-1}$ band [16].

The treatment of a sorbent sample with an ozone-oxygen mixture leads to an increase in its mass due to the formation of oxygen-containing compounds on its surface. The absorption of ozone (at its concentration of 30 mg/L) did not exceed 20%.

A typical isotherm of nitrogen adsorption-desorption by the samples of the studied sorbents is shown in Figure 1.

Figure 1. Nitrogen adsorption-desorption isotherms by sorbent samples: 1 - initial; 2 - ozonized 1 hour; 3 - ozonized 2 hours; 4 - ozonized for 3 hours

It was determined that the highest adsorption capacity for nitrogen in the region of low relative pressures is possessed by the sorbent obtained after 3 hours of oxidative exposure, which may indicate higher values of its specific surface area compared to the rest of the samples.

The parameters of the porous structure, calculated from the nitrogen adsorption-desorption isotherms, for the initial and ozonized samples are given in Table 1.
Table 1. Characteristics of sorbent samples

| Sample No. | Sample | Specific surface area $S_{BET}$, m$^2$/g | Total pore volume $V_Σ$, cm$^3$/g | Pore volumes, cm$^3$/g | Relative content, % | $D_{av}$, nm |
|------------|--------|------------------------------------------|---------------------------------|------------------------|---------------------|-----------------|
|            |        |                                          |                                 | $V_{micro}$ | $V_{meso}$ | $V_{macro}$ | $V_{micro}$ / $V_Σ$ | $V_{meso}$ / $V_Σ$ | $V_{macro}$ / $V_Σ$ |
| 1          | Initial sorbent | 303 | 0.159 | 0.107 | 0.025 | 0.027 | 67.3 | 15.7 | 17.0 | 0.21 |
| 2          | ozonized 1 hour | 351 | 0.164 | 0.109 | 0.028 | 0.027 | 66.5 | 17.1 | 16.4 | 0.19 |
| 3          | ozonized 2 hours | 360 | 0.168 | 0.110 | 0.029 | 0.029 | 65.5 | 17.3 | 17.2 | 0.19 |
| 4          | ozonized 3 hours | 371 | 0.175 | 0.114 | 0.029 | 0.032 | 65.1 | 16.6 | 18.3 | 0.19 |

The specific surface area of the initial sample is 303 m$^2$/g and the total pore volume is 0.159 cm$^3$/g. When the surface is modified by oxidation with ozone, the specific surface area increases, the maximum increase in which is noted after 1 hour of exposure, and the development of mesoporosity and a slight decrease in the volume of micropores are noted.

Figure 2. Micropore size distribution curves calculated by the NL DFT method for sorbent samples: 1 - initial; 2 - ozonized 1 hour; 3 - ozonized 2 hours; 4 - ozonized for 3 hours

The obtained micropore size distribution curves within the framework of the non-local density functional theory (NL DFT) method have a polymodal character and demonstrate three pronounced micropore regions: 0.5–0.7 nm (ultramicropore region), 0.7–0.9 nm, and 1.0–1.7 nm (supermicropore region). At the same time, there is no ultramicropore region in the original sorbent (Figure 2).
For all ozonized samples, micropores are inhomogeneous and have a wide size distribution: from ultramicropores to supermicropores in the generally accepted micropore range of 0.4-1.7 nm (Figure 2). The largest amount of ultramicropores is possessed by a sorbent sample ozonized for 1 hour. An increase in the ozonation time leads to an increase in the relative number of mesopores. The resulting mesopore size distribution curves calculated by the BJH method have a predominantly bimodal distribution. Basically, the pore space is formed by small mesopores with a diameter of 2.5-5 nm with a maximum on the pore size distribution curves at 3 nm, and pores with a size of 10-35 nm (Figure 3). At the same time, the largest pore volume is characterized by a sorbent sample obtained by ozonation for 1 hour. An increase in the ozonation time, most likely, leads to the development of destructive oxidative processes on the surface of micropores, contributing to their further increase to the size of mesopores of small diameter.

Figure 3. Mesopore size distribution curves (a, b), calculated by the BJH method, for sorbent samples: 1 - initial; 2 - ozonized 1 hour; 3 - ozonized 2 hours; 4 - ozonized 3 hours

To identify the oxidative effect of ozone on the composition and content of functional groups on the surface of the sorbent, their IR spectral study was carried out, the results of which are shown in Table 2.

Analysis of the data obtained showed that during the entire time of ozonation, the intensity of the absorption bands of methyl and methylene groups at 2925 and 2858 cm\(^{-1}\) (Table 2) decreases, which indicates the oxidation of aliphatic fragments of the organic mass of the sorbent. With an increase in the ozonation time, the intensity of the bands at 1740 and 1700 cm\(^{-1}\) corresponding to the carbonyl groups of carboxylic acids and ketones (Table 2) increases. After 3 hours of ozonation, there is a significant increase in the intensity of the absorption band in the region with a maximum of 1230 cm\(^{-1}\), which characterizes various - C-O-bonds in phenyl groups (1300 - 1150 cm\(^{-1}\)), in aromatic ethers (1100-1030 cm\(^{-1}\)), peroxides (1000-820 cm\(^{-1}\)) and epoxides.

Table 2. Relative intensity of absorption bands (\(\nu\)), normalized to the 1465 cm\(^{-1}\) band

| No. | Absorption band \(\nu\), cm\(^{-1}\) | D\(_{3030}/\)D\(_{2925}\) |
|-----|-----------------------------------|------------------|
|     | 3450  | 3030  | 2925  | 1740  | 1700  | 1630  | 1230  | 1060  | 1030  | 800   |     |
| 1   | 20.00 | 0.60  | 3.72  | 0.74  | 0.65  | 6.98  | 0.56  | 0.74  | 0     | 0.19  | 0.16 |
| 2   | 6.74  | 0.13  | 1.28  | 0.70  | 0.46  | 2.04  | 0.30  | 0.32  | 0.33  | 0.30  | 0.03 |
| 3   | 4.29  | 0.14  | 1.67  | 0.89  | 0.46  | 1.04  | 0.36  | 1.07  | 1.07  | 0.46  | 0.23 |
| 4   | 15.11 | 0.72  | 0.65  | 9.42  | 1.43  | 6.76  | 1.22  | 2.15  | 2.15  | 0.43  | 0.32 |

The formation of epoxy groups is the result of the direct addition of atomic oxygen, formed during the decomposition of ozone, through the carbon-carbon double bond. The absorption band at 800 cm\(^{-1}\) is enhanced, which is in the range (799-900 cm\(^{-1}\)) of out-of-plane deformation vibrations of C-H bonds in aromatic systems and multinuclear condensed aromatic systems. In general, the noted changes in the IR spectra of ozonized sorbent samples can be interpreted as an increase in the polyconjugation of
aromatic structures in the organic mass of the sorbent due to ozonation, which is indirectly indicated by an increase in the parameter $D_{3030}/D_{2925}$, which characterizes the aromaticity of the object under study.

3. Conclusion
The results obtained show that ozonation of carbon sorbents is a method that allows modifying its surface. Modification of the studied sample with an ozone-oxygen mixture leads to an increase in its specific surface area and pore space, mainly due to the growth of micro- and mesopores. The process of ozonation of sorbents leads to a change in the state of their surface. According to the results of IR spectroscopy, an increase in oxygen-containing functional groups is observed on the surface of the sorbents.

4. References
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