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Structural and sorption properties of nanoporous carbon materials obtained from walnut shells

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Using the method of low-temperature nitrogen adsorption/desorption, the porous structure of nanoporous carbon materials obtained by alkaline activation of light industry waste (walnut shells) with subsequent thermal modification was investigated. The optimal relationship between temperature and modification time has been established. It is shown that an increase in the modification temperature reduces the transition time of micropores into mesopores and leads to a decrease in the specific surface area and total pore volume. Thus, the material obtained at a modification temperature of 400 °C and a holding time of 120 min is characterized by the maximum specific surface area of 940 m²/g. It has been investigated that an increase in the time of temperature modification leads to an increase in specific electrical conductivity.

Keywords: nanoporous carbon material, thermochemical activation, specific surface area, pore size distribution, specific electrical conductivity.

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Introduction

The study of sorption properties of materials with a highly developed surface is currently receiving the greatest attention of researchers due to the wide scope of their application [1-3]. The main advantage in this type of research is precisely those materials that, along with a highly developed surface, would have such characteristics as a wide range of applications, variability between the possibility of controlling their properties both during acquisition and adjusting certain parameters in subsequent modification. Activated carbon materials obtained from raw materials of vegetable origin (wood sawdust, nuts, fruit stones, rice husks, etc.) have an undeniable advantage when used in such research. Along with the properties mentioned above, these materials also have such an important property as environmental friendliness [4]. And this property is currently the main advantage of these

materials and makes them practically the main materials for research. Among the numerous advantages of this raw material, one should also include the wide-scale scope of their application: from the medical field (sorbents, blood purification, etc. [5]) to industrial applications (purification of drinking water, material for electrochemical power sources, etc. [6,7]).

The aim of the research is to obtain carbon materials based on food industry waste with controlled sorption properties and to adjust their properties using thermochemical activation for use as electrodes of electrochemical capacitors.

I. Materials and methods of research

Depending on the fields of application, researchers try to achieve specific properties of the developed surface, such as the ratio of the sizes of macro-, meso- and

micropores of carbon materials during the carbonization of raw materials. However, the correction of these ratios is usually acquired during their further modification through chemical and thermal activations. This is primarily related to the structure of the raw material, subsequent modification and composition of the precursor during chemical processing and thermal activation of the finished material [8]. Heat treatment and chemical activation usually take place at different temperature and time regimes depending on the raw material using dehydrating agents (phosphoric acid, zinc chloride, potassium hydroxide) [9].

Preparation of nanoporous carbon materials (NCM) was carried out by the method of thermochemical activation. At the first stage, mechanically crushed walnut shells were poured into an autoclave and heated to 300–350 °C at a heating rate of 10 °C/min and held at this temperature for 30 min. The obtained carbonate was mechanically crushed to a fraction of 250 µm and mixed with water and potassium hydroxide in a weight ratio of 1:1:0.5. The resulting mixture was stirred for 30 minutes and dried in vacuum oven at a temperature of 70–80 °C for 48 hours. After complete drying, the obtained material was poured into an autoclave, placed in a furnace and heated to 900 °C at a heating rate of 10 °C/min and held at this temperature for 30 min. Cooling was carried out with the furnace turned off. After complete cooling, the carbon material was washed with distilled water to neutral pH. In this way, we obtained thermochemically activated carbon material (L). Additional thermal activation was performed to open the internal porosity and increase the specific surface area of the carbon material. At the next stage, the obtained carbon material was subjected to thermal activation in an air atmosphere. Activation was carried out at a temperature of 400 °C for different time intervals from 30 to 240 min in steps of 30 min. The samples were numbered according to the time of thermal activation (LH30–LH240). For example, sample LH90 is a material thermally activated for 90 min at a temperature of 400 °C. According to the described method, series of carbon materials activated at a temperature of 450 °C (series – LD) and 500 °C (series – LH) were obtained.

Nitrogen adsorption/desorption isotherms for evaluating the porous structure of the carbon material were obtained using a Quantachrome Autosorb Nova 2200e sorbometer. Calculations were performed using the Brunauer-Emmet-Teller (BET) method for specific surface area, complementary Barrett-Joyner-Halenda (BJH) methods, Density Functional Theory (DFT), and the t-method for pore size distribution.

The content of chemical compounds in the studied materials was determined by burning the carbon material at a temperature of 1000 °C. The analysis of the composition of the obtained ash was carried out using the "EXPERT 3L" alloy elemental composition analyzer.

II. Results and discussion

The basis for calculating the values of the specific surface area (S_{BET}), the specific surface area of micropores (S_{micro}) and mesopores (S_{meso}), as well as the value of the total pore volume (V_{Σ}) and the volume of micropores

(V_{micro}), as well as the distribution of pores by the dimensions were the analysis of sorption isotherms [10–12]. Before the measurements, the samples were degassed at a temperature of 180 °C for 18 hours. Nitrogen adsorption/desorption isotherms for the studied carbon materials obtained by thermal treatment at a temperature of 400 °C with different exposure times of this treatment are shown in Fig. 1. All isotherms belong to the II type of isotherms according to the IUPAC classification and are characteristic of the formation of a polylayer on the surface with a high adsorption potential. A hysteresis loop is observed on almost all isotherms, which is associated with sorption processes in sub-nanopores (pore size between 0.1 and 1 nm according to the IUPAC classification [13]). The presence of a hysteresis loop for the investigated carbon materials and changes in its dimensions also indicate the presence of a relative number of mesopores. There is an open hysteresis loop, that is, a divergence of the adsorption/desorption curves in the region of low pressures for the carbonized material that was not subjected to heat treatment. It is characteristic of materials that retain the adsorbate over the entire range of relative pressures. Changes in the shape of adsorption/desorption curves indicate the development of a porous structure during heat treatment of carbon materials. Isotherms of other series with different temperatures and time of heat treatment have similar shapes, so they are not given in this paper.

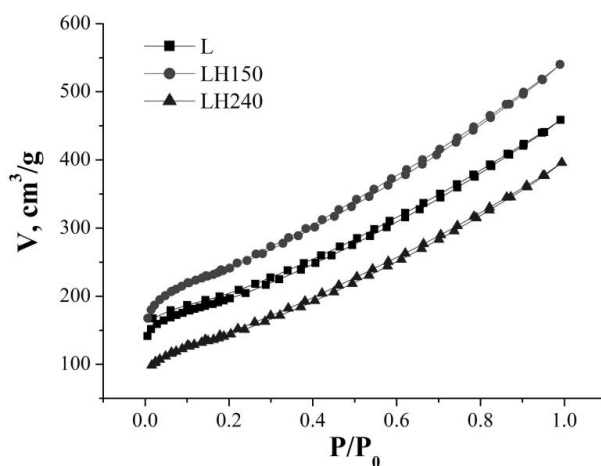


Fig. 1. Nitrogen adsorption isotherms of the obtained samples.

The parameters of the porous structure of the obtained materials are shown in the table 1. The specific surface area was determined by the BET method [14]. Several complementary methods were used to estimate the pore size distribution. The BJH method is usually used to determine the size distribution of mesopores (correctness interval is 3–60 nm), while using the desorption curve in the pressure range of (0.4–0.967) p/p_0 [15]. The mesoporous structure was developed for all the investigated materials of the LH series. The share of mesopores in the total volume of pores calculated by the t-method is 72–95 %. For samples of the LH series, the growth of micropores occurs up to 120 min, after the

Table 1.

Parameters of the porous structure of the obtained materials of the LH series

Sample	Specific surface area			V_{Σ} , cm ³ /g	V_{micro} , cm ³ /g	V_{meso} , cm ³ /g	$V_{\text{micro}}/V_{\Sigma}$, %	$V_{\text{meso}}/V_{\Sigma}$, %	d, nm
	S_{BET} , m ² /g	S_{meso} , m ² /g	S_{micro} , m ² /g						
L	707	528	179	0.709	0.081	0.628	0.114	88.6	4.016
LH 30	831	460	371	0.709	0.156	0.553	0.220	78.0	3.411
LH 60	868	445	423	0.695	0.173	0.522	0.249	75.1	3.203
LH 90	897	419	478	0.708	0.196	0.512	0.277	72.3	3.156
LH 120	940	443	497	0.727	0.201	0.526	0.276	72.4	3.092
LH 150	875	636	239	0.835	0.101	0.734	0.121	87.9	3.819
LH 180	782	576	206	0.761	0.086	0.675	0.113	88.7	3.896
LH 210	707	624	83	0.764	0.039	0.725	0.051	94.9	4.32
LH 240	511	511	–	0.613	–	0.613	0.000	100.0	4.795

specified time, the total volume of micropores decreases due to their burnout and transition to mesopores, the volume fraction of which increases by 40 %. At the same time, a decrease in the total specific surface area is observed both due to the transition of mesopores into macropores and due to the combustion of carbon material (Fig. 2). A further increase in exposure time leads to an uneven redistribution of macro- and mesopores. For the sample aged for 240 min, there are practically no micropores, and the percentage of material yield by mass is 33 %. The maximum volume of mesopores is observed for materials with a heat treatment time of 150–210 min. The decrease in the percentage mass of the material for the sample of the LH series is presented in Fig. 2.

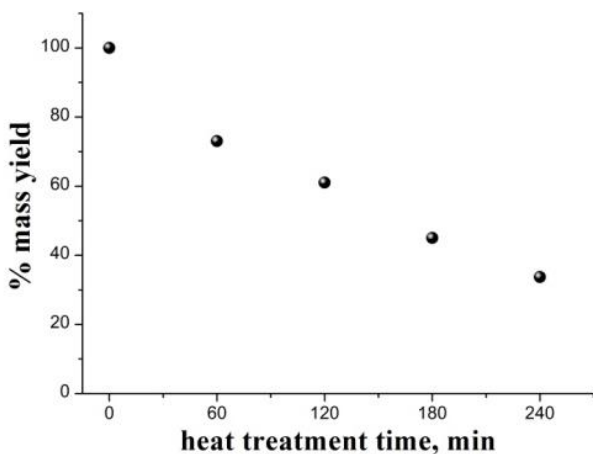


Fig. 2. Dependence of the mass of the obtained NCM on the time of temperature exposure (LH series).

For series of materials with a higher temperature of thermal modification, a decrease in the time of temperature influence on the maximum value of the specific surface area and the maximum volume of mesopores is observed. Thus, the peak value of the specific surface area with increasing activation temperature shifts toward decreasing activation time. For the LD series, the maximum value of the specific surface

area is 910 m²/g (heat treatment time 90 min), and for the LF series it is 870 m²/g (heat treatment time 60 min). However, the maximum value of the specific surface area for higher activation temperatures is not reached.

The characteristics of the mesoporous structure were described using the BJH method. For samples of the LH series, the maximum mesopore volume in the range of $V_{\text{meso}} = 0.11 - 0.12$ cm³/g is reached at 150–210 min. For practically all samples of the LH series, the maximum of the differential pore volume falls on the pores in the interval $d = 3.3-3.7$ nm. With the growth of the pore diameter a sharp decrease in the differential pore volume is observed, and for $d = 30-60$ nm in all the studied samples it changes monotonically in the interval $(1-2) \cdot 10^{-3}$ cm³/g. For samples of the LD, LF series, the peak of the differential pore volume falls on a similar pore diameter interval. The maximum mesopore volume for samples of the LD and LF series is in the range of $V_{\text{meso}} = 0.11-0.12$ cm³/g at 30–60 min, respectively. The dependence of the differential pore volume on their diameter for materials with the maximum value of the total pore volume in each of the series is shown in Fig. 3.

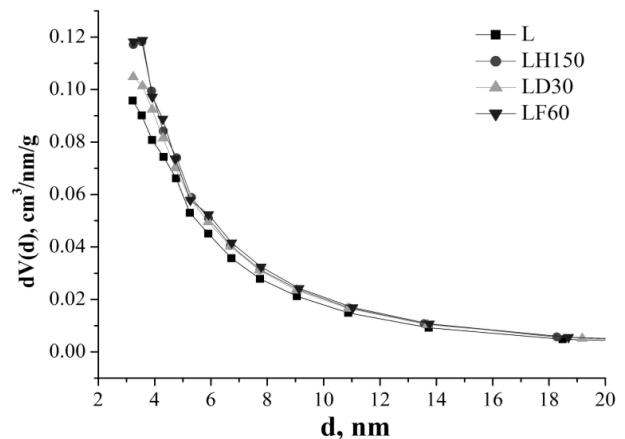


Fig. 3. Dependencies of the maximum values of the differential pore volume on the diameter for different series of the obtained materials.

To describe the size distribution of micropores, the QSDFT (Quenched Solid DFT) method of Density Functional Theory (DFT) [16] was used, which takes into account the structural heterogeneity of the surface of slit-like pores. The carbonized material is characterized by the presence of a peak in the region $d=1.0-1.2$ nm with a maximum $d=1.1$ nm (Fig. 4). A peak in the region of sub-nanopores (up to 1 nm) is clearly distinguished in the samples of the LH series, for all times of temperature exposure. With increasing temperature exposure time (up to 120 min), a peak shift from $d = 0.7$ nm (for sample LH-30) to $d = 0.8-0.9$ nm (for samples LH-90 – LH-120) is observed, which is also accompanied by an increase in the differential volume of pores (Fig. 4). That is, probably, at the given times of temperature exposure, the formation and burnout of pores of the specified diameter takes place. An increase in the time of temperature exposure leads to a monotonous decrease in the differential pore volume, and the LH-240 sample shows a wide and homogeneous micropores size distribution and a relatively low value of $dV(d) \leq 0,15$ cm³/nm/g. Samples of the LD series (Fig. 5) are characterized by the presence of peaks in a similar range. The difference is an insignificant increase in the differential volume of pores and the formation of peaks at shorter times of temperature exposure. For samples of the LF series (Fig. 6), the peak at $d = 0.9$ nm is present for the sample with a temperature exposure time of 30 min. A further increase in the time of temperature exposure leads to a decrease in the differential pore volume and a shift of the peak to the region $d = 0.6-0.7$ nm. That is, an increase in temperature probably leads to the combustion of carbon particles, which is manifested in a decrease in the volume of sub-nanopores. Thus, the time of temperature exposure is one of the determining factors for the formation of a mesoporous structure.

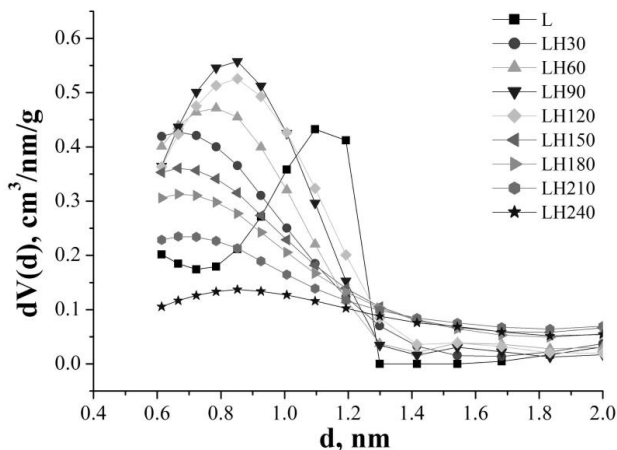


Fig. 4. Size distribution of micropores for LH series carbon materials (QSDFT method).

The dependence of the specific electrical conductivity on the time of temperature exposure is shown in Fig. 7. The carbon material was pressed at a pressure of 1.5 MPa. A further increase in pressing pressure leads to insignificant deviations in the changes in specific electrical conductivity values. An increase in the time of temperature exposure leads to an increase in specific electrical conductivity, which is probably due to a change in the structure of carbon particles, a significant burnout

of the carbon material, which in turn leads to densification and arrangement of its structure.

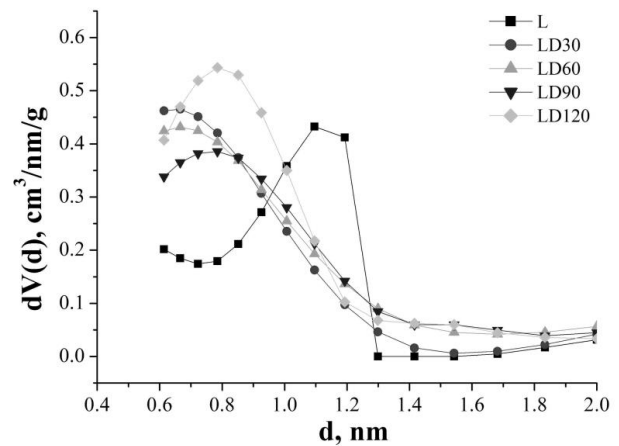


Fig 5. Micropores size distribution for LD series carbon materials (QSDFT method).

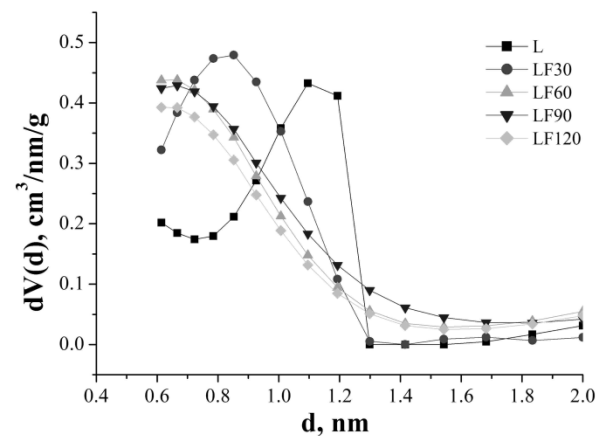


Fig. 6. Micropores size distribution for LF series carbon materials (QSDFT method).

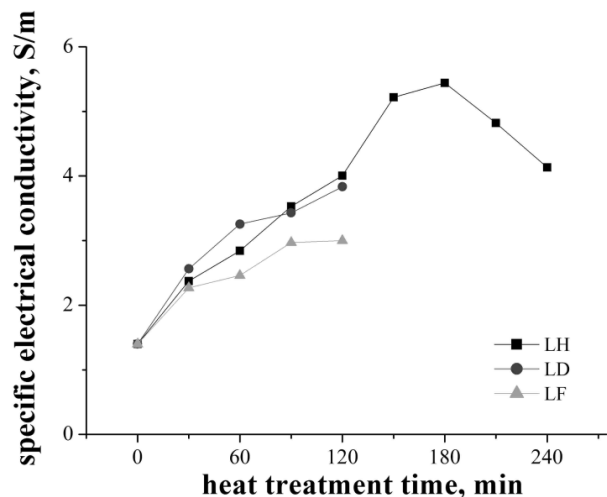


Fig. 7. Dependence of specific electrical conductivity on time of temperature exposure.

The content of chemical compounds in the obtained carbon materials was evaluated by burning it at a temperature of 1000 °C. Table 2 shows a number of existing compounds found in ash. An insignificant amount

(about 1.5%) of potassium oxide in the ash is due to the specificity of the method of obtaining porous carbon material.

Table 2.

The content of chemical compounds in carbon material

Chemical compound	The concentration of the compound in the ash, %	Mass of compound in ash, mg	The concentration of the compound in the carbon material, %
Al ₂ O ₃	3.032	5.49	0.164
SiO ₂	1.544	2.79	0.083
K ₂ O	27.288	49.39	1.474
CaO	15.363	27.81	0.830
Cr ₂ O ₃	0.637	1.15	0.034
Ni ₂ O ₃	0.224	0.41	0.012
MnO ₂	0.297	0.54	0.016
Fe ₂ O ₃	50.33	91.10	2.719
CuO	0.885	1.60	0.048
SO ₃	0.248	0.45	0.013
SrO	0.095	0.17	0.005

Conclusions

The technique of obtaining nanoporous carbon material from light industry waste (walnut shells) by thermochemical alkaline activation with subsequent temperature exposure to form an optimal pore size ratio was studied. A clear correlation was found between the volume and surface of micropores and the temperature and time of NCM modification. It was established that changing the modes of modification of carbon materials is an effective tool for regulating their porous structure,

which makes it possible to obtain samples with a predetermined morphology.

It was established that an increase in the treatment temperature leads to a decrease in the maximum specific surface area from 940 m²/g for the LH 120 sample to 870 m²/g for the LF 60 sample and a decrease in the temperature exposure time to reach the specified peak values.

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Структурно-сорбційні властивості нанопористих вуглецевих матеріалів, отриманих зі шкаралупи горіха

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Методом низькотемпературної адсорбції/десорбції азоту досліджена пориста структура нанопористих вуглецевих матеріалів, отриманих лужною активацією відходів легкої промисловості (шкаралупи горіха) з подальшою термічною модифікацією. Встановлено оптимальну залежність між температурою та часом модифікації. Показано, що зростання температури модифікації зменшує час переходу мікропор в мезопори та призводить до зменшення площі питомої поверхні і загального об'єму пор. Так, максимальною питомою площею поверхні 940 м²/г володіє матеріал, отриманий при температурі модифікації 400 °С та часі витримки 20 хв. Досліджено, що зростання часу температурної модифікації призводить до збільшення питомої електропровідності.

Ключові слова: нанопористий вуглецевий матеріал, термохімічна активація, питома площа поверхні, розподіл пор за розмірами, питома електропровідність.