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Porous Structure of Carbon Materials Obtained from the Shell of Walnuts

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Samples of porous carbon material (PCM) were obtained by carbonization of the feedstock (walnut shells). Small-angle X-ray scattering (SAXS) was used to study the porous structure of the obtained carbon materials. The fractal dimension of the surface increases and significant changes are observed in the distribution of the pore volume of the PCM samples with an increase in the carbonization temperature of the initial feedstock, which is especially pronounced for the sample obtained at 700 °C. It is shown that PCM obtained at 400 - 700 °C are macroporous materials, the maximum porous volume corresponds to pores with radius $R \approx 30$ nm, and samples obtained at 700 - 1000 °C are mesoporous with $R \approx 5$ nm.

The characteristics of the porous structure of the obtained materials were calculated on the basis of isotherms of low-temperature adsorption-desorption of nitrogen and it was shown that the carbonization temperature significantly affects the specific surface area and pore volume of PCM. It was determined that to obtain of PCM with an optimal ratio of micro- and mesopores, the temperature is 800 °C, at which the specific surface area of the carbon material is 238 m²/g with an average pore diameter of 2.2 nm.

Keywords: porous carbon material, porous structure, small-angle X-ray scattering, low-temperature porometry.

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Introduction

The porous carbon material is of particular interest as a material, is widely used in various industries, and as the areas of application expand, the requirements for the parameters of its structure are growing [1-3]. The main method for obtaining of PCM is pyrolysis (carbonization) of the feedstock at different temperatures, followed by thermal or chemical activation [4, 5]. The theoretical foundations of pyrolysis of plant biomass suggest that any materials containing polymeric carbohydrates and lignin as the main component can be subjected to thermal treatment, during which carbon-containing carbonize

will be obtained [6, 7]. Thus, straw of various cereals, fruit seeds, nutshells, bamboo, sugarcane stalks, corn cobs, stalks and husks of rice, buckwheat and hemp, sunflower husk, etc., can be used for pyrolysis, that is, everything that is not is still used in industry and constitutes the bulk of the waste sent for disposal annually.

The aim of this work is to study the effect of the carbonization temperature of raw materials of plant origin (walnut shells) on the morphology and structural-adsorption characteristics of the obtained carbon materials.

I. Experimental

Carbon materials were obtained by thermal carbonization in the temperature range 400 °C to 1000 °C with a step of 100 °C. The walnut shells, peeled from the kernels, were used as a raw material. After that, the walnut shells were poured into an autoclave and placed in an oven, where they were heated to a predetermined temperature. The heating rate was 5 °C/min. Conceptually, the applied methodological approach is close to that described in [8].

Carbon nanoporous materials have become important materials that are widely used in energy storage and storage systems. The use of these materials requires a clear understanding of their nanoporous structure. In particular, the porosity of the materials together with the pore shape and the total specific surface area must be precisely known. Therefore, we used the methods of low-angle X-ray scattering and low-temperature porometry as effective and complementary methods for studying the porous structure of carbon materials.

The SAXS spectra were measured on an automated DRON-3 diffractometer equipped with three-layer collimators for primary and scattered radiation. To monochromatize the scattered Cu K α radiation, a flat pyrolytic graphite single crystal mounted on a diffracted beam was used. The scattering intensity curves are corrected for background scattering and collimation corrections for the height of the detector receiving slit. The distribution functions of the effective pore radius were determined by the method of the indirect integral Fourier transform equation connecting the scattering intensity with the pore distribution function in a polydisperse system of spherical particles:

$$I(s) = \int_0^{R_{max}} i_0(sR) \cdot m(r) \cdot D_v(R) dR,$$

where $I(s)$ is scattering intensity, $i_0(sR)$ is scattering form factor by a system of polydisperse spheres, $D_v(R) = \frac{4}{3}\pi R^3 \cdot N(R)$ is volumetric pore distribution function, $N(R)$ is the number of pores with an effective radius. For function calculations $D_v(R)$ is used the GNOM software package. The average pore radius was determined by formula:

$R_g = \left(\frac{\sum_{k=1}^N D_k}{\sum_{k=1}^N (D_k/R_k^3)} \right)^{\frac{1}{3}}$, where N is number of experimental points on the curve $D_v(R)$. To determine the specific pore surface area, we calculated the value of the integral characteristics of the scattering intensity curves, such as the integral invariant of the Porod (Q_p) and the constant of the Porod, (K_p), which are proportional, respectively, to the volume and surface area of the pores [9]:

$$Q_p = \int_0^{s_{max}} s^2 I(s) ds + \frac{K_p}{s_{max}}, \quad K_p \approx \frac{\int_{s_{min}}^{s_{max}} s^4 I(s) ds}{(s_{max} - s_{min})},$$

where s_{min} , s_{max} is minimum and maximum value of the wave vector. The specific surface area was calculated by the formula: $S_p = \frac{\pi K_p}{Q_p}$.

The structural-adsorption characteristics of PCM were determined using the method of low-temperature (-196 °C) porosimetry on an Autosorb Nova 2200e automatic gas analyzer (Quantachrome, USA) [10]. The samples were pre-degassed in vacuum at 180 °C for 18 hours. The specific surface area was calculated using the equation BET (S_{BET}) in the region of the isotherm limited by the range $p/p_0 = 0,005 - 0,035$. The t-method proposed by de Boer and Lippens was used to estimate the volume (V_{mic}) and specific surface area (S_{mic}) of micropores. The pore size distribution was calculated using the BJH methods and the density functional theory – DFT (Density Functional Theory) method using the desorption isotherm. The total pore volume (V_{Σ}) was estimated from the volume of nitrogen adsorbed at a relative pressure $p/p_0 = 0.99$. The mesopore volume was calculated as the difference between the total pore volume and the micropore volume [11].

II. Results and discussion

Figure 1 shows the typical curves of SAXS intensity in double logarithmic coordinates for carbon samples. The monotonic decay of the curves over the entire angular interval indicates a chaotic distribution of scattering inhomogeneities. The dependence is inherent in all PCM samples, regardless of the preparation temperature. As can be seen from the figure, in the range of wave vector values from

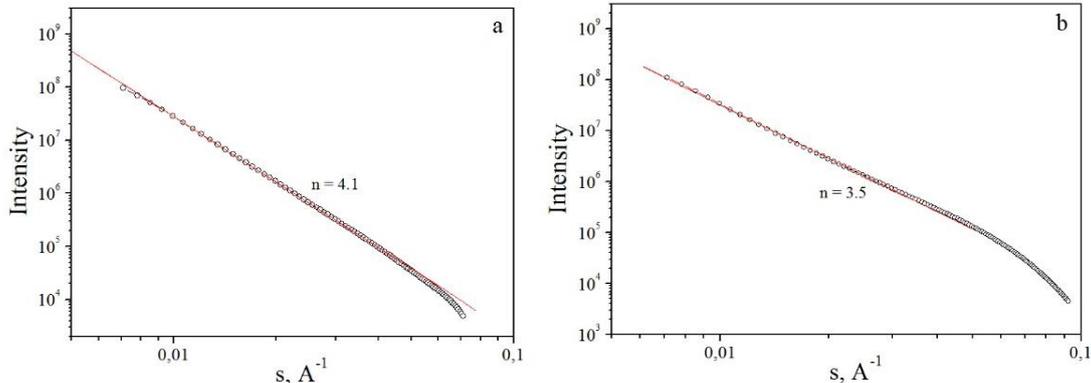


Fig. 1. Curves of the intensity of small-angle scattering of PCM samples obtained at 400 °C (a) and 800 °C (b).

$$s_0 = 0.007 \text{ \AA}^{-1} \text{ to } s_l = 0.04 \div 0.05 \text{ \AA}^{-1},$$

a linear decrease in the scattering intensity is observed, indicating a power-law dependence $I(s) \sim s^{-n}$. In the samples carbonized at temperatures of 400–600 °C, the slope index is close to $n \approx 4$, which indicates the fulfillment of the Porod law on scattering by a smooth interface between the pores and the carbon base [12].

At the same time, in the samples obtained at temperatures of 700–1000 °C, there is a significant decrease in the slope index in this angular interval. Since the value of n is in the range $3 \leq n \leq 4$, this result indicates scattering by a nonsmooth (fractal) surface with a fractal dimension $D = 6 - n$. Figure 2 shows that the fractal dimension of the surface shows a pronounced tendency to increase with increasing of carbonization temperature, which is especially evident for the sample obtained at 700 °C. A further increase in the carbonization temperature does not lead to a significant change in the fractal dimension of the surface.

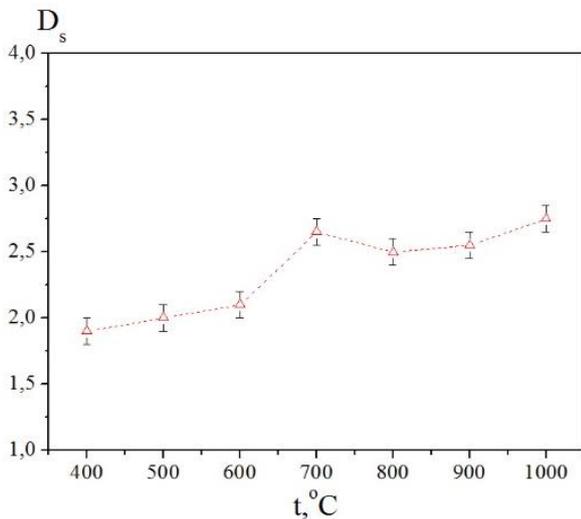


Fig. 2. Dependence of the fractal dimension of the "carbon base - pore" interface on the carbonization temperature.

Deviation from the power change of the scattering intensity is observed in the range of values of the wave vectors from $s_l = 0.04 \div 0.05 \text{ \AA}^{-1}$ to $s_{\max} \approx 0.1 \text{ \AA}^{-1}$. At the same time, on the curves of scattering intensity, rebuilt in the Guinier coordinates $\ln I(s) = f(s_2)$, a linear dependence is observed in this range of s values (Fig. 3). This result can be explained by scattering by monodisperse pores of the smallest size, for which the dependence $I(s)$ is described by the Guinier formula [12]:

$$I(s) = I(0) \cdot \exp\left(-\frac{1}{3}s^2 R_g^2\right),$$

where $I(0)$ is the total scattering length, R_g is the radius of inertia of the pores.

The pore volume distribution functions are shown in Fig. 4 illustrate significant changes in the distribution of the porous space, which correlate with changes in the fractal characteristics of the samples. As can be seen, the most significant changes in the pore distribution are observed in the samples obtained at temperatures above

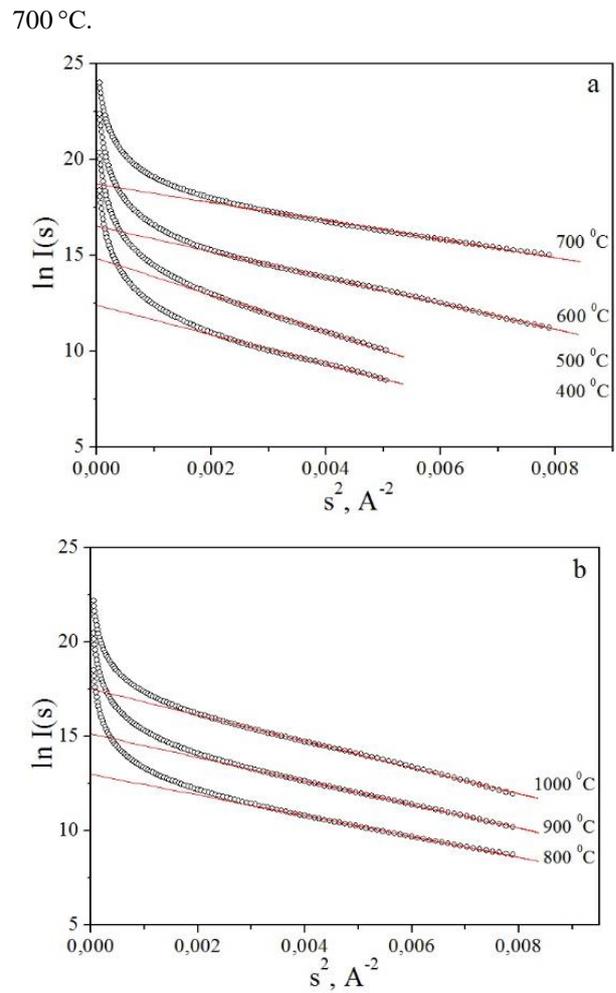


Fig. 3. Curves of scattering intensity, rebuilt in Guinier coordinates.

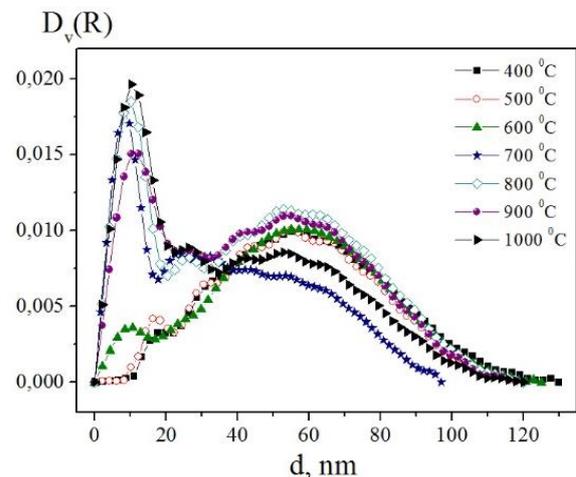


Fig. 4. Volumetric functions of pore distribution.

Figure 5 a shows the temperature change of the effective pore radius, which give the greatest contribution to the formation of the porous volume. With an increase in the carbonization temperature, an increase in the proportion of mesopores is clearly observed, which is especially pronounced for the sample obtained at 700 °C.

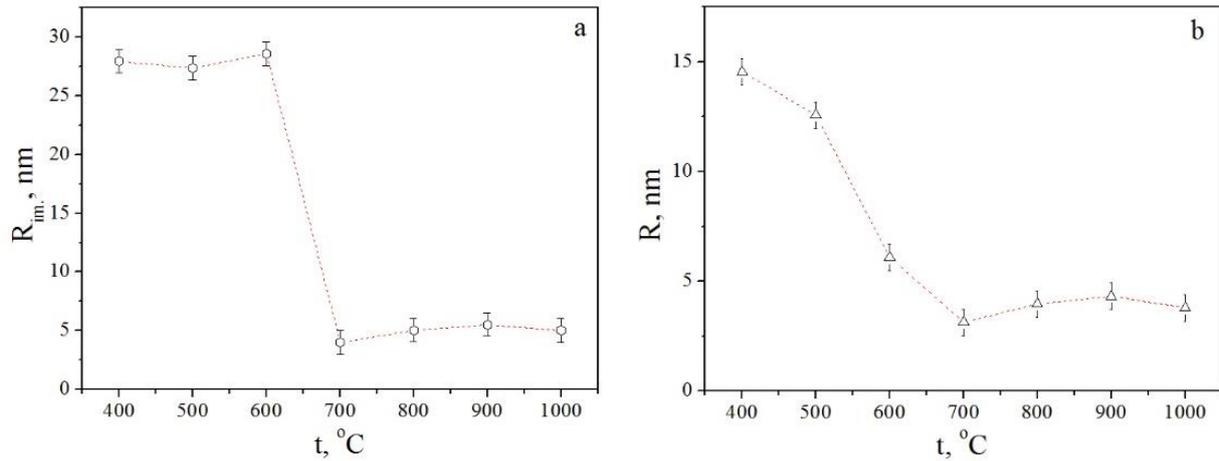


Fig. 5. Temperature change in the most probable (a) and average (b) pore radius.

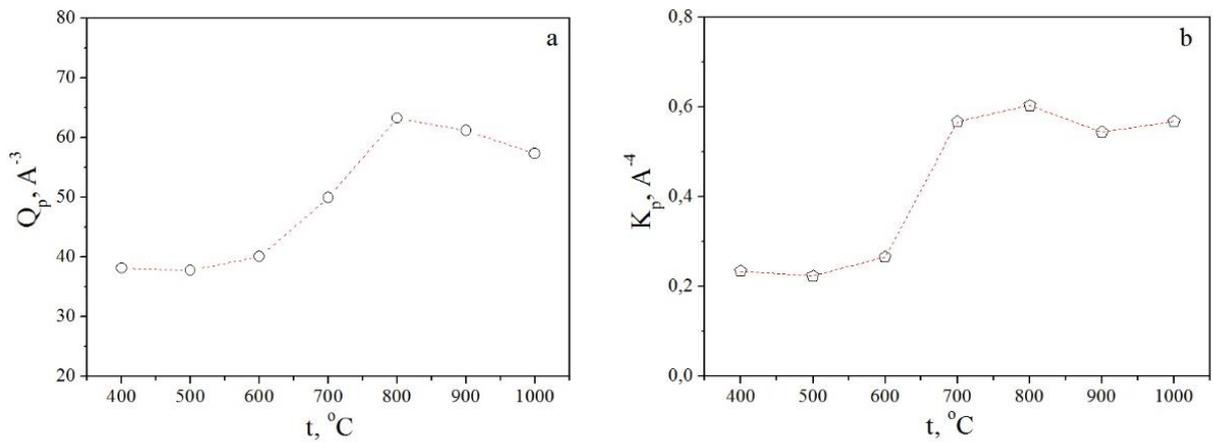


Fig. 6. Dependence of the integral invariant Q_p (a) and the Porod constant K_p (b) on the carbonization temperature of the initial feedstock.

It can be seen that the samples carbonized at temperatures of 400 - 600 °C are characterized by a macroporous structure, the maximum of the porous volume of which corresponds to times with $R \approx 30$ nm. At the same time, the samples obtained at 700 - 1000 °C are mesoporous with the most probable effective pore radius $R \approx 5$ nm.

The calculation of integral scattering invariants, such as the integral invariant of the Porod (Q_p) and the constant of the Porod (K_p), shows their increase with an increase in the carbonization temperature of the feedstock, which is also especially pronounced in the sample obtained at 700 °C (Fig. 6).

Carbonization at temperatures of 800 - 1000 °C does not lead to a significant change in the integral characteristics of scattering. As a result, the sample obtained at 700 °C with the smallest average pore radius is characterized by the highest value of the specific pore surface area (Fig. 7).

Specific surface area S_v and volume-averaged pore radius R were determined using integral scattering characteristics (integral invariant Q_p and the Porod constant K_p) and are given in Table. 1.

A further study of the effect of the carbonization temperature of the feedstock on the porous structure of the obtained PCM was carried out using the method of low-temperature porosimetry. For all investigated

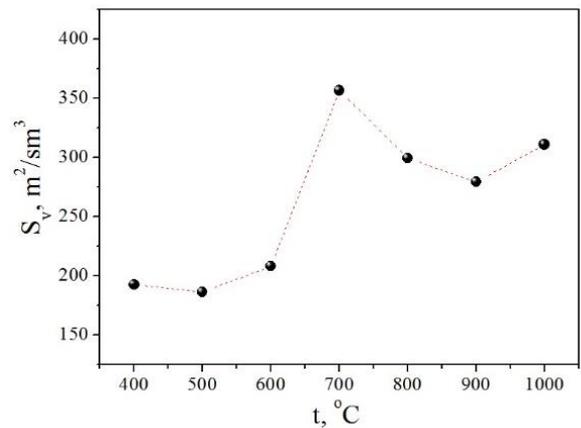


Fig. 7. Temperature dependence of specific surface area.

materials, nitrogen adsorption-desorption isotherms were obtained (Fig. 8). All isotherms belong to type II isotherms, which are observed during polymolecular nitrogen adsorption on porous materials [10]. For all PCM samples, hysteresis is observed, which is associated with capillary condensation in the mesopores, and the divergence of the branches of adsorption and desorption in the region of low relative pressures p/p_0 , which is called

Table 1.

Parameters of the porous structure of the PCM.

$t, ^\circ\text{C}$	$Q_p \cdot 10^3, \text{nm}^{-3}$	$K_p \cdot 10^4, \text{nm}^{-4}$	D_v	R_{im}, nm	R, nm	$S_v, \text{m}^2/\text{cm}^3$
400	38.1	0.230	1.9	27.9	14.6	190
500	37.7	0.220	2.0	27.4	12.6	185
600	40.1	0.270	2.1	28.5	6.10	208
700	50.0	0.570	2.65	4.0	3.15	357
800	63.3	0.600	2.50	5.05	3.95	300
900	61.2	0.550	2.55	5.50	4.30	279
1000	57.4	0.570	2.75	5.0	3.80	311

low pressure hysteresis. In the literature, there are several explanations for the possible reasons for its appearance: irreversible chemical interaction of adsorbate-adsorbent; swelling of the spatial high molecular weight framework of the adsorbent;

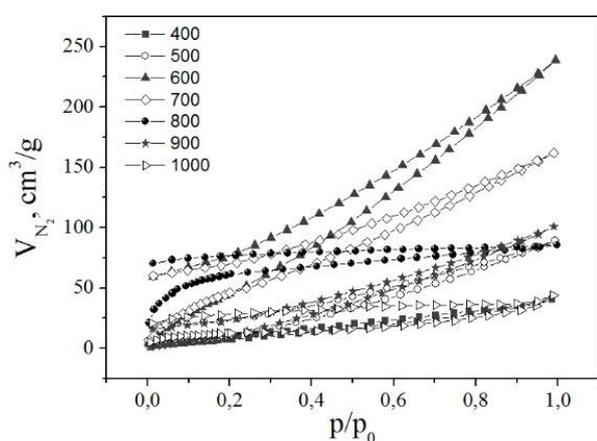


Fig. 8. Isotherms of nitrogen sorption for PCM.

irreversible content of adsorbate molecules in pores with a size close to the size of adsorbate molecules [13]. The nature of the isotherms indicates that the carbonization temperature affects the development of the porous structure of the carbon material.

The mesopore size of the studied PCM samples can be estimated by analyzing the pore size distribution curves obtained using the BJH method (Fig. 9).

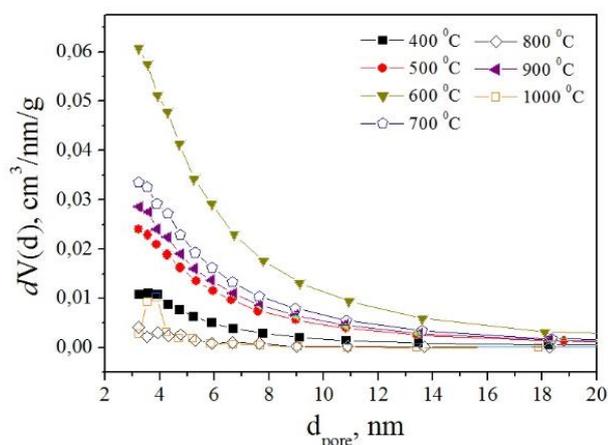


Fig. 9. Curves of pore size distribution for PCM according to the BJH method.

Figure 9 shows that most of the pores are 3 - 5 nm in

size and fall within the range of correctness of determination (from ~2 to ~50 nm) the sizes of mesopores. From the maxima in these dependences, one can judge about the significant content of mesopores in the samples with an average diameter of 3 - 5 nm. In this interval, the Kelvin equation, which is used in the BJH model [14], can be applied, assuming that all pores are cylindrical. This assumption can introduce some error in the assessment of the pore size distribution for the samples under study. However, it is known that the BJH method is successfully applied to almost all types of porous materials. In addition, the desorption branch of the isotherm was used for the calculation, which in many cases is closer to thermodynamic equilibrium.

Based on the experimental nitrogen sorption-desorption isotherms, the characteristics of the porous structure of the PCM were determined (Table 2). The specific surface area was calculated using the multipoint BET method (Brunauer, Emmett, Teller) [15] with a linear dependence of $1/[W(p/p)-I]$ on p/p_0 in the adsorption isotherm range for the p/p_0 ratio ranging from 0.05 to 0.35. In this range, the BET plot is linear for all PCM samples (correlation coefficient $R^2 = 0.999$), which indicates good applicability of this model for calculating the specific surface area of carbon samples. In addition, the value of the constant C ($C = 50 \div 100$) indicates the possibility of using the BET method for obtaining and further applying experimental data, and is a criterion for the correctness of determining the specific surface area.

Table 2.

Parameters of porous structure of PCM.

Carbonation temperature, $^\circ\text{C}$	$S_{BET}, \text{m}^2/\text{g}$	$V_\Sigma, \text{cm}^3/\text{g}$	$V_{mic}, \text{cm}^3/\text{g}$	$V_{mic}/V_\Sigma, \%$	d, nm
400	39	0.063	-	-	6.5
500	80	0.138	-	-	6.9
600	207	0.370	-	-	7.2
700	223	0.251	-	-	4.5
800	238	0.133	0.064	48	2.2
900	80	0.156	-	-	7.8
1000	47	0.068	0.013	19	5.9

Table 2 shows that with increasing carbonization temperature from 400 $^\circ\text{C}$ to 800 $^\circ\text{C}$ increases the specific surface area of PCM, but a further increase in temperature

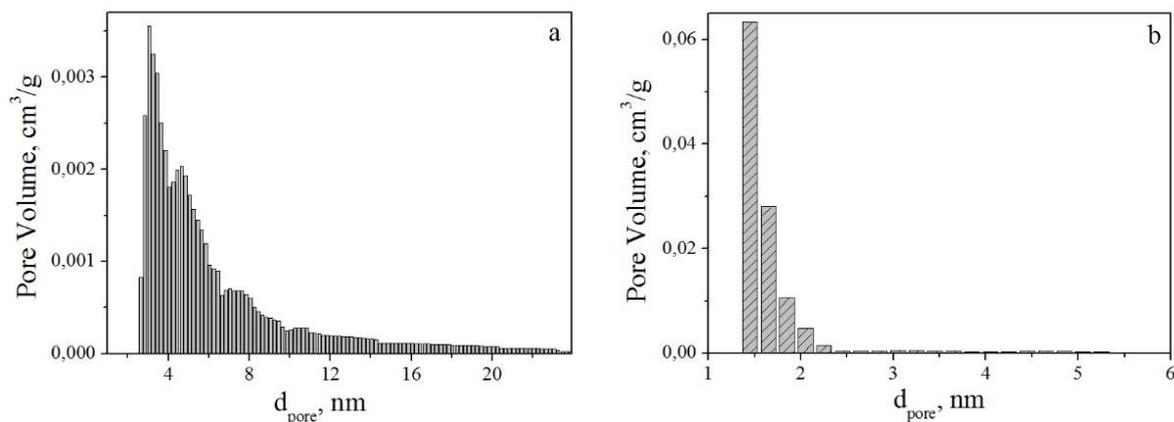


Fig. 10. Pore size distribution by the DFT method for samples carbonized at 400 °C (a) and 800 °C (b).

(900 °C and 1000 °C) causes a decrease in S_{BET} , probably due to graphitization and compaction of PCM. It should be noted that an increase in the carbonization temperature of the feedstock in the range from 400 °C to 800 °C leads to a decrease in the volume of mesopores and the growth of micropores. Under conditions of thermal carbonization of the raw material at a temperature of 800 °C, the value of S_{BET} reaches a maximum and is equal to 238 m²/g, the ratio of the volume of micropores to the total pore volume is 48 %, and the average pore diameter of this sample is 2.2 nm (Table 2).

Typically, the BJH method is used in the pressure range (0.4 - 0.967) p/p_0 , however this method is not correctly used for pore size distribution with a diameter < 2 nm. Therefore, the DFT method was used to analyze the microporous structure of PCM (Fig. 10). An NLDFT model (slit-like pores) was used to obtain the pore size distribution.

Analysis of the dependences obtained by the DFT method (Fig. 10) indicates that with increasing carbonization temperature from 400 °C to 800 °C leads to the formation of micropores with a diameter of 1.5 -2 nm, and the largest volume of micropores of appropriate size has a carbon material, obtained at 800 °C. Analysis of isotherms indicates that a significant contribution to the specific surface area and total pore volume is made by micropores with a diameter of ~ 1.5 -2 nm and mesopores of 3 - 4 nm (Fig. 9, Fig. 10).

Conclusions

The method of thermal carbonization of raw materials (walnut shells) of plant origin as one of the main methods of obtaining porous carbon materials has been tested. Moreover it is shown that this method allows obtaining PCM with a high specific surface area.

The change in the fractal and porous structure of the

obtained PCM is investigated depending on the carbonization temperature of the raw materials (walnut shells). The fractal dimension of the surface increases and significant changes are observed in the distribution of the porous space of the PCM samples with an increase in the carbonization temperature of the initial feedstock, which is especially evident for the sample obtained at 700 °C.

The obtained PCM, depending on the carbonization temperature of the raw materials (walnut shells), have different morphology and pore size distribution. Carbonization at a temperature of 800 °C makes it possible to obtain PCM with a specific surface area of up to 237 m²/g, a total volume of 0.133 cm³/g, and an average pore size within 2.2 nm.

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Пориста структура вуглецевих матеріалів отриманих із шкарлупи волоських горіхів

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Шляхом карбонізації вихідної сировини (шкарлупи волоських горіхів) отримано зразки пористого вуглецевого матеріалу (ПВМ). Малокутове X-променеве розсіювання (SAXS) було використано для вивчення пористої структури отриманих вуглецевих матеріалів. Фрактальна розмірність поверхні зростає та спостерігаються суттєві зміни в розподілі об'єму пор зразків ПВМ зі збільшенням температури карбонізації вихідної сировини, що особливо проявляється для зразка, отриманого при 700 °С. Показано, що ПВМ, отримані при 400-700 °С, є макропористими матеріалами, максимум пористого об'єму яких відповідає порам з радіусом $R \approx 30$ нм, а зразки отримані при 700-1000 °С є мезопористими з $R \approx 5$ нм.

На основі ізотерм низькотемпературної адсорбції-десорбції азоту були розраховані характеристики пористої структури отриманих матеріалів та показано, що температура карбонізації істотно впливає на питому площу поверхні та об'єм пор ПВМ. Встановлено, що для отримання ПВМ з оптимальним співвідношенням мікро- і мезопор є температура 800 °С, при якій досягається питома площа поверхні вуглецевого матеріалу 434 м²/г з середнім діаметром пор 2,7 нм.

Ключові слова: пористий вуглецевий матеріал, пориста структура, малокутове X-променеве розсіювання, низькотемпературна порометрія.