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Effect of Orthophosphoric Acid on Morphology of Nanoporous Carbon Materials

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The structural-adsorption characteristics of nanoporous carbon materials (NCMs), obtained by thermochemical activation of vegetable raw materials by orthophosphoric acid with different mass ratio, are investigated in the article using the method of low temperature nitrogen sorption and scanning electron microscopy. Calculations of the specific surface area and pore size distribution allowed to determine the optimal parameters of the mass ratio of the activator and the raw materials, in which the obtained material has the highest parameters of the porous structure. The optimum conditions for NCMs obtaining are established, which can be used as electrodes of electric energy storage devices.

Key words: Nanoporous carbon materials, Surface area, Thermochemical activation.

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1. INTRODUCTION

Nanoporous carbon materials (NCMs) have a wide range of applications in science and production, thanks to the combination of unique physical and chemical properties [1, 2]. A special role is played by their sorption ability, which determines the high efficiency of NCMs in clinical detoxification, poisoning, purification of drinking and sewage waters from technological contamination, soil remedy, as well as electrodes of electrochemical capacitors [3, 4]. Given the wide range of applications and despite the long history of their study, carbon materials are an extremely interesting subject of research, because the variety of raw materials, methods of activation and chemical treatment of the surface is quite large.

Providing the carbon material of the necessary sorption properties, depending on the scope of its application, is carried out both in the process of its receipt, and by the chemical and thermal treatment of the finished material [5, 6]. It should be noted that the sorption properties of carbon material will depend to a large extent on the structure and composition of the raw material. Therefore, its choice in many cases may be decisive, depending on the areas of NCM application [7].

The most common methods of porous carbon material obtaining is physical or chemical activation of carbonaceous raw materials. Chemical activation usually occurs at temperatures 400-800 °C and is accompanied by the use of dehydrating agents (phosphoric acid, zinc chloride, potassium hydroxide).

Thus, finding out the effect of the obtaining conditions (carbonization temperature and chemical activation regimes) on the surface area value and the pore size distribution and, consequently, its morphology is an important scientific problem.

2. EXPERIMENT

The products of vegetable origin (hemp shive) were subjected to chemical activation were used as a raw

material (RM). The weight of the final product and its structure depend on the concentration and ratio of the initial components, temperature and activation time. A prerequisite for chemical activation is the removal of residual activation reagents and inorganic residues contained in the original carbonaceous material. When treating vegetable raw materials by orthophosphoric acid, the latter acts as a dehydrating agent that inhibits the resin formation, which leads to an increase in the mass yield of porous carbon and a decrease in temperature and activation time compared with physical activation methods. When obtaining activated carbon by chemical activation of plant material by orthophosphoric acid, the ratio between the amount of acid and precursor is important for the development of the porous structure of the product obtained:

$Y = (m(\text{H}_3\text{PO}_4)) / (m(\text{RM}))$, that was equal 0.25:1; 0.5:1; 0.75:1; 1.25:1; 1.5:1; 1.75:1; 2.00:1.

The sample mass was measured before experiment with accuracy 10^{-3} g using analytical weights.

The next activation steps were performed according to the methodology of obtaining of acid-activated carbon materials. For this, the hemp shive was dried and ground to a fraction of 0.25-1 mm. The resulting material was divided into portions and mixed with orthophosphoric acid at concentrations of 4-32 % with a step of 4 %. The mixture was thoroughly stirred for 1-2 hours, then the samples were dried at 100°C for 24 hours to constant mass. The carbonized material was placed in a vertical cylindrical furnace and heated to 450, 500 and 550 °C at a heating rate 10 °C/min in an argon atmosphere at gas flow rate 30 ml/min. When the desired temperature was reached, the isothermal exposure was carried out for 60 min. After cooling the material to room temperature, it was washed by hot distilled water to a neutral pH and dried at 80 °C until constant mass was obtained.

The resulting carbon materials were denoted according to the ratio of the mass of orthophosphoric acid and

the raw material and the isothermal exposure time. For example, BK-025-450 is a material obtained by mixing the acid with RM at a ratio $Y=0.25:1$ and activated at 450°C .

The determination of adsorption characteristics of NCMs was carried out using nitrogen adsorption at temperature (-196°C) by surface area analyzer Quantachrome Autosorb (Nova 2200e). The samples were previously degassed in a vacuum at 180°C for 20 hours. The specific surface area (S_{BET} , m^2/g) was determined by multipoint BET method in limited range of relative pressure $P/P_0=0.050-0.035$. The total pore volume (V_{total} , cm^3/g) was calculated by the number of adsorbed nitrogen at $P/P_0 \sim 1.0$.

The morphology studies were realized using JSM-6700F scanning electron microscope with JED-2300 energy-dispersive system for microanalysis.

3. RESULTS AND DISCUSSION

Parameters of the porous structure (surface area, pore size distribution and total pore volume) were determined on the basis of nitrogen adsorption / desorption isotherms analysis. The amount of absorbed gas is proportional to the mass of the sample at adsorption of nitrogen by carbon material. This dependence, called the sorption isotherm equation, is described as:

$V = f(P/P_0)$, where P and P_0 denote the equilibrium and saturation pressure of nitrogen at -196°C , respectively. Quantitative analysis of adsorption isotherms makes it possible to conclude about the value of the specific surface, the porosity of the adsorbent, and the nature of the interaction between the adsorbent and the adsorbate.

Nitrogen adsorption / desorption isotherms for investigated carbon materials obtained at different Y values and different temperatures of activation heat treatment are presented in Figs. 1-6. Curves shown in Figs. 1, 2 belong to the isotherms that are characteristic of multilayer adsorption of micro- and mesoporous materials of organic origin. There is a hysteresis loop at all isotherms (H4 type classified by IUPAC), which is associated with sorption processes in the narrow pores. The adsorption isotherms for a series of samples BK-025-450 – BK-075-550 (Fig. 1, a) are classified as type I. This type of isotherm is characteristic of microporous solids.

The same is observed for nitrogen adsorption isotherms of BK-100-450 – VK-100-550 (Fig. 2). However, it can be stated in this case about the growth of the relative amount of mesopores as follows from the increase of the hysteresis loop width.

This tendency develops when Y grows, in particular for samples BK-125-450 – BK-125-550 (Fig. 3). There is a type H4 hysteresis loop at the adsorption isotherms for these samples, which is associated with the presence of mesopores in a microporous carbon material. The amount of sorbed nitrogen by carbon material is increased when the relative pressure $P/P_0 \approx 1$, as evidenced by the deviation of the adsorption curve from the horizontal position. This phenomenon can be explained by the morphology of activated carbon particles, in which the meso- and macropores inside the carbon particle are connected by micropores with its surface.

The micropore is filled and further adsorption is

practically stopped at relatively low pressures (Fig. 3). Further uplift of the adsorption branch of the isotherm at high pressures is probably due to capillary condensation in the meso- and macropores when steam is available on the mechanism of multiple condensation-evaporation processes. Adsorbate after filling all pores remains in them blocked by micropores. Nitrogen, sorbed in large pores, cannot desorb at low pressure,

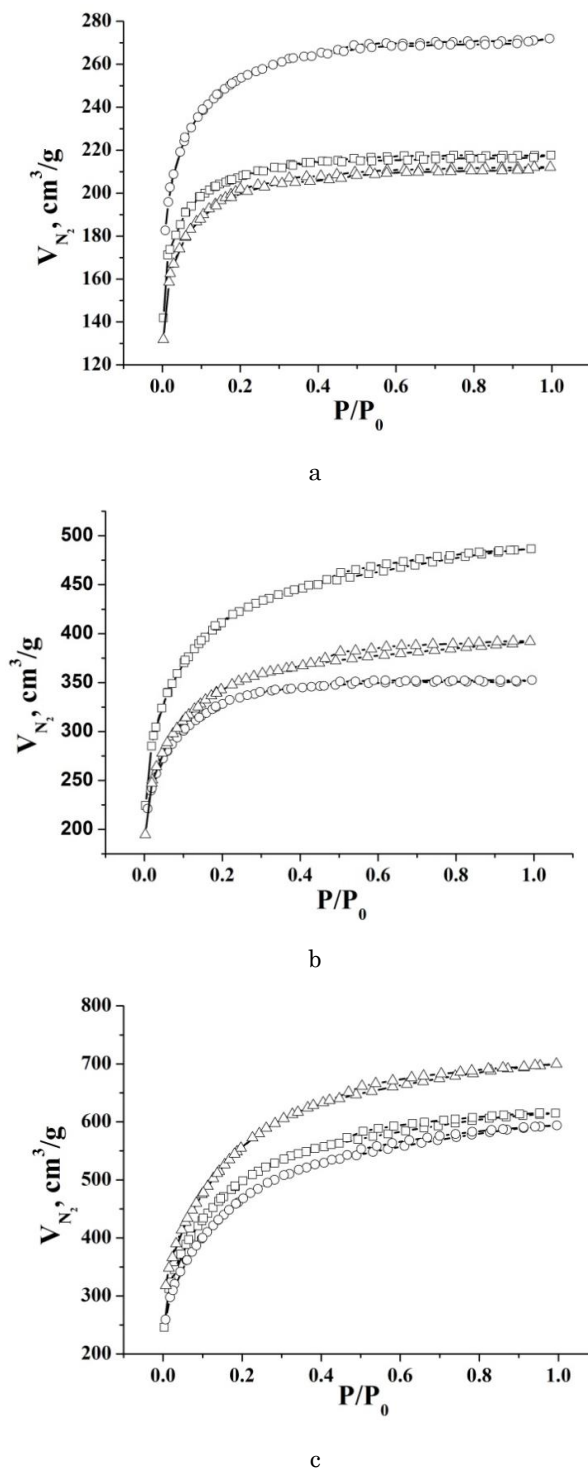


Fig. 1 – Nitrogen adsorption isotherms for samples BK-025-450 (□), BK-025-500 (○), BK-025-550 (Δ) (a), BK-050-450 – BK-050-550 (b), BK-075-450 – BK-075-550 (c)

except for a small part, which is in unblocked pores. It corresponds to a decrease in the desorption curve close to $P/P_0 \approx 1$. The hysteresis width, obviously, corresponds to amount of adsorbate in the blocked meso- and macro-pores. Given this, you can calculate the pore volume.

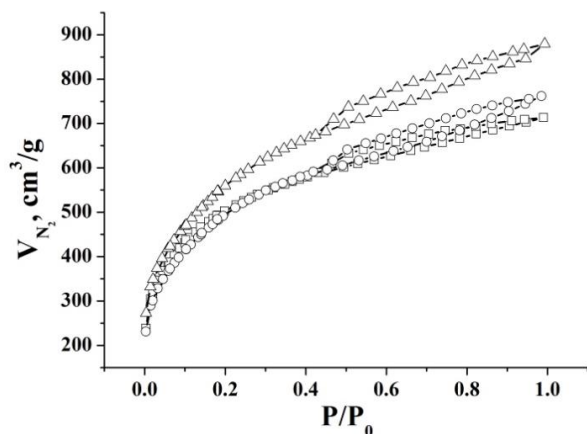


Fig. 2 – Nitrogen adsorption isotherms for samples BK-100-450 (□), BK-100-500 (○), BK-100-550 (Δ)

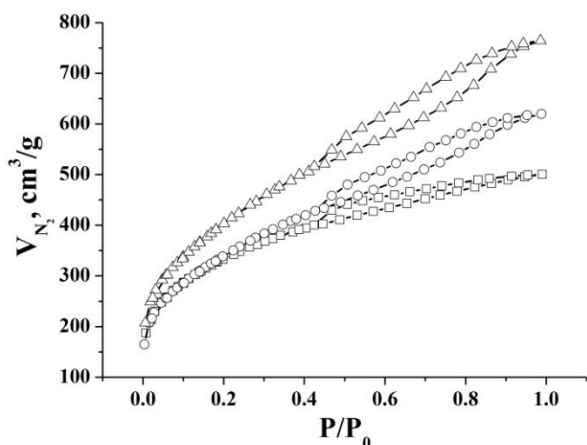


Fig. 3 – Nitrogen adsorption isotherms for samples BK-125-450 (□), BK-125-500 (○), BK-125-550 (Δ)

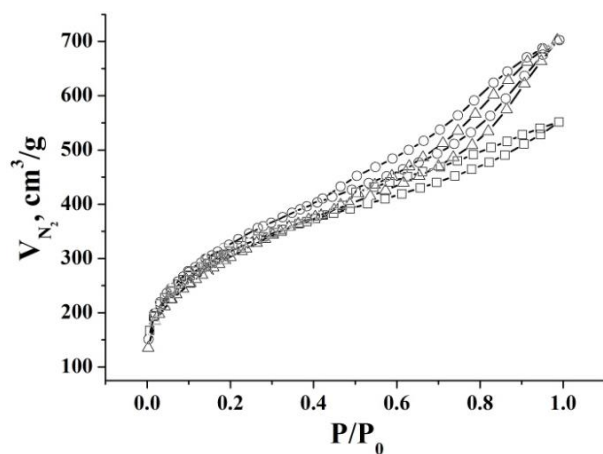


Fig. 4 – Nitrogen adsorption isotherms for samples BK-150-450 (□), BK-150-500 (○), BK-150-550 (Δ)

The sorption isotherms (Figs. 4-6) obtained for

samples with a ratio of $1.5 < Y < 2.00$, are typical for mesoporous materials. For materials obtained at high concentrations of orthophosphoric acid (samples BK-150-450 – BK-200-550), sorption isotherms are characteristic for type II, in which there is a H3 type hysteresis loop according to the IUPAC classification.

A characteristic feature of this type isotherms is the lack of a horizontal section of the sorption curves and the fact that the adsorption curve of hysteresis has a type for type II (according to the Brunauer classification) the isothermal form, that is, it indicates the presence of only polymolecular adsorption. Isotherms in this case have a slope, that is, the amount of adsorption increases with increasing pressure. This type of isotherm is associated with sorption processes in micropores and capillary condensation in meso- and macropores of materials of organic origin and adsorption on outer surface of particles.

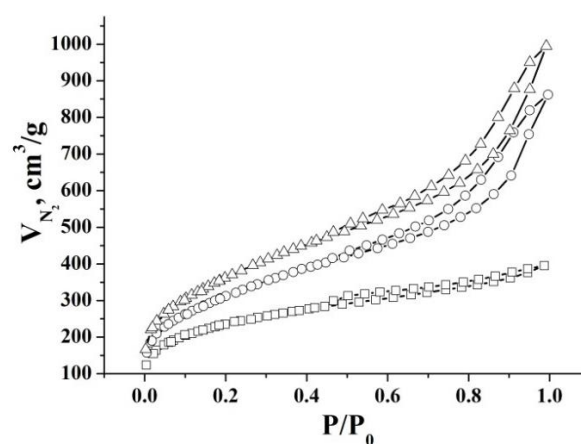


Fig. 5 – Nitrogen adsorption isotherms for samples BK-175-450 (□), BK-175-500 (○), BK-175-550 (Δ)

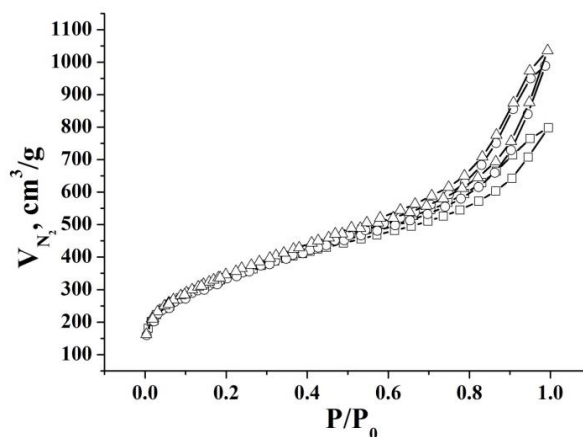
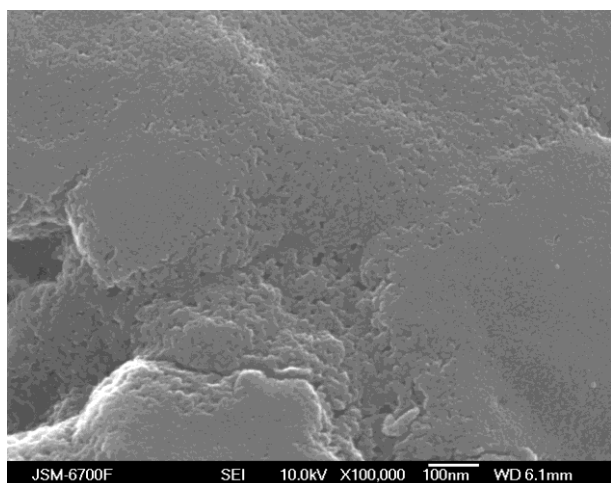


Fig. 6 – Nitrogen adsorption isotherms for samples BK-200-450 (□), BK-200-500 (○), BK-200-550 (Δ)

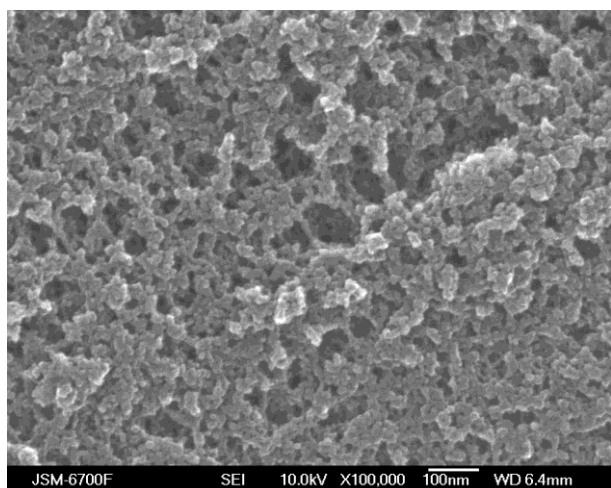
The growth of the Y ratio probably causes the degradation of the smooth surface of a carbon particle. The carbon material is characterized by microporous structure and developed surface area at low concentrations of orthophosphoric acid (Fig. 7, a, b).

The surface of carbon particles at high concentrations of acid undergoes significant corrosion (Fig. 7, c, d), resulting in increased micro- and mesoporosity of the NCM obtained.

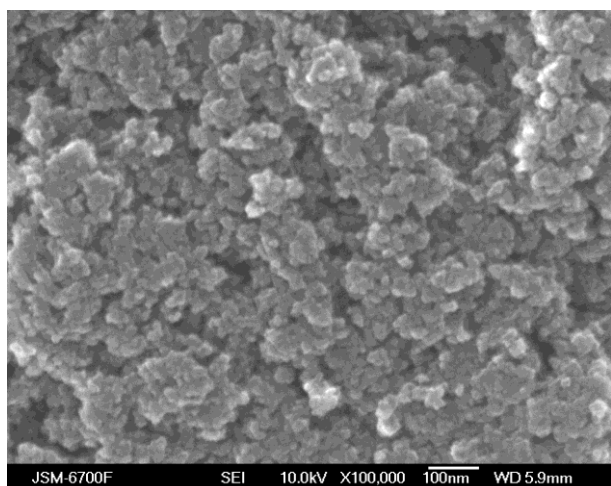
Thus, it is possible to obtain a material with a regulated pore system, controlling the carbonization temperature and the Y ratio. Carbon material is characterized by microporous structure and developed area of the surface at low concentrations of orthophosphoric acid.



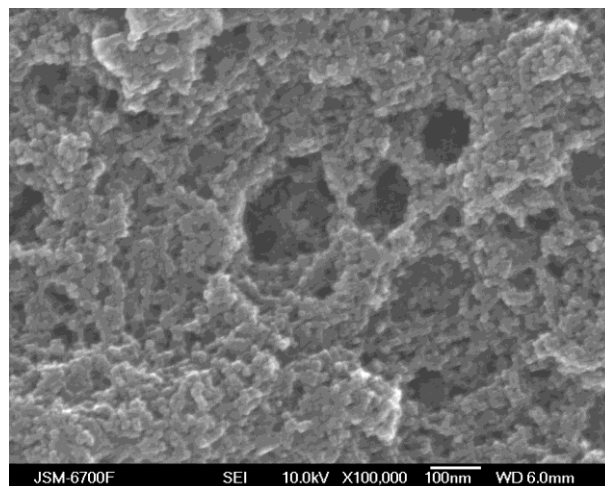
a



b



c



d

Fig. 7 – Microstructure of material surface BK-050-500 (a), BK-100-500 (b), BK-150-500 (c), BK-200-500 (d)

Increasing the Y ratio leads to the formation of mesoporous carbon material.

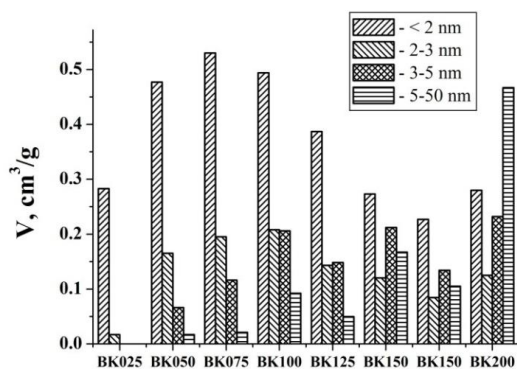
The pore size distribution of NCMs was obtained using the DFT (density functional theory) method. This method uses quantum-mechanical calculations to describe the adsorption isotherms and pore size distribution. The essence of the approach is to construct theoretical isotherms for various adsorbent-adsorbate pairs and their comparison with experimentally obtained ones. The calculations are carried out using the Density Functional Theory (DFT) theory. To obtain pore size distribution a slit-shaped pore model was used (Figs. 8-10).

Carbon materials are microporous with specific surface area ($S_{BET} \approx 750-1500 \text{ m}^2/\text{g}$) and pore volume ($V_{total} \approx 0.32-0.61 \text{ cm}^3/\text{g}$) at low ratios ($Y \leq 0.5$). The mesopore volume is in the range 15-30% of the total pore volume. When $Y = 0.75$ there is increasing in surface area of NCM to $2000 \text{ m}^2/\text{g}$; total pore volume to $1.1 \text{ cm}^3/\text{g}$ due to the appearance of 45 % mesopore and the presence of 5 % macropores irrespective of the activation temperature.

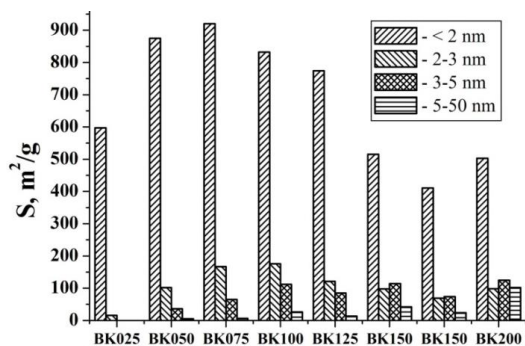
Further growth Y to 1.5 during activation leads to a decrease in surface area ($S_{BET} \approx 1200 \text{ m}^2/\text{g}$), but there is a sharp growth of mesopore volume to 85 % from the total pore volume. The contribution of micro- and mesopores to the total volume is approximately the same. It is set that samples obtained at $Y = 1.5$ and $550 \text{ }^\circ\text{C}$ have the maximum relative content of pores from 5 nm in size. However, it should be noted that the micropore area contributes most to the total surface area of the pores when $0.75 < Y < 1.5$.

NCMs obtained at activation temperature of $500-550 \text{ }^\circ\text{C}$ and $Y = 1.75$ are characterized by a maximum pore size distribution less 5 nm with a constant contribution of mesopores to total pore volume.

It was found that there is a tendency to decrease specific surface area of NCMs at $Y > 1.75$. As a result, the total number of micro-, meso- and macropores decreases too. However, it should be noted that the macropore contribution of more than 5 nm in size in this Y -range is maximal, reaching its maximum for the sample BK-175-500 and reaching up to 55 % of the total pore volume.

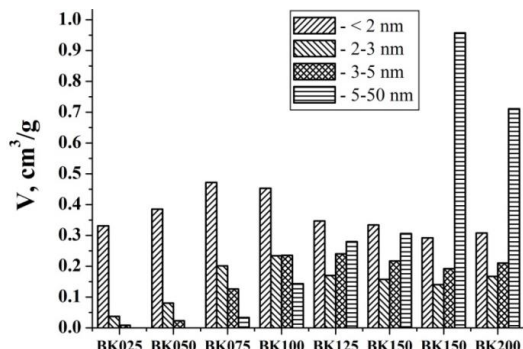


a

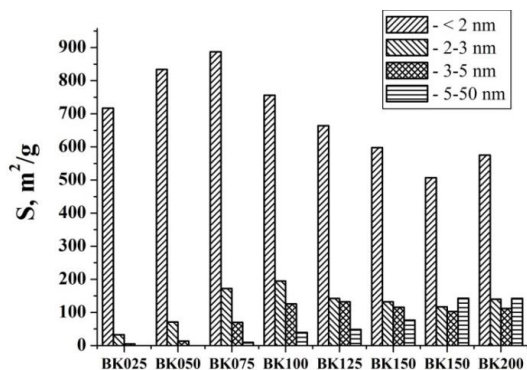


b

Fig. 8 – Pore volume (a) and specific surface area (b) for NCMs with different Y ratio (temperature of isothermal exposure 450 °C)

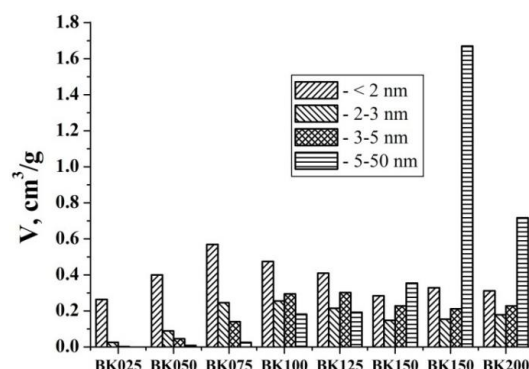


a

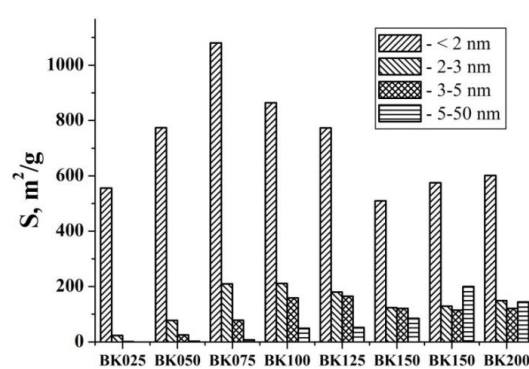


b

Fig. 9 – Pore volume (a) and specific surface area (b) for NCMs with different Y ratio (temperature of isothermal exposure 500 °C)



a



b

Fig. 10 – Pore volume (a) and specific surface area (b) for NCMs with different Y ratio (temperature of isothermal exposure 550 °C)

Thus, the maximum value of the specific surface area ($S_{BET} \approx 2000 \text{ m}^2/\text{g}$) is achieved for $Y = 0.75$ at 550°C due to the high contribution of micropore surface to the total area. The total pore volume reaches a maximum ($V_{total} \approx 1.6 \text{ cm}^3/\text{g}$) for samples BK-175-200.

4. CONCLUSIONS

1. Porous carbon material was obtained by chemical activation of the hemp shive by orthophosphoric acid with simultaneous heat treatment at various temperatures (450, 500 and 550 °C).

2. It is set that, the carbon material is characterized by a microporous structure and has a total pore volume of 0.9-1.1 cm^3/g at $Y \leq 0.5$. When Y grows, meso- and macropores are formed, which make up 75-90 % of the total pore volume at $Y \leq 1.75$.

3. It is found out that the change in the mass ratio of the activator (orthophosphoric acid) and the raw material (hemp shive) allows controlling of the material surface area (in the range 750-2000 m^2/g) and the pore size distribution in different percentages of their values.

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Вплив ортофосфорної кислоти на морфологію нанопористих вуглецевих матеріалів

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Структурно-адсорбційні характеристики нанопористих вуглецевих матеріалів (НВМ), отриманих термохімічною активацією рослинної сировини ортофосфорною кислотою з різним масовим співвідношенням, досліджено методами низькотемпературної сорбції азоту та скануючої електронної мікроскопії. Розрахунки питомої поверхні і розподіл розміру пор дозволили визначити оптимальні параметри масового співвідношення активатора і сировини, в яких отриманий матеріал має найвищі параметри пористої структури. Встановлені оптимальні умови для отримання НВМ, які можуть бути використані як електроди накопичувачів електричної енергії.

Ключові слова: Нанопористі вуглецеві матеріали, Площа поверхні, Термохімічна активація.