

THE INVESTIGATION OF THE STRUCTURE OF BIOCARBON SYNTHESIZED FROM WHEAT STRAW

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Introduction

The unique physical and chemical properties of carbon materials allow to solve a large number of technical problems that ensure the environmental safety of man and the environment. If we consider the world production of activated carbon, it exceeds half a million tons per year. In industrialized countries, the produced mass of activated carbon per capita is about 0.5 kg, and in Ukraine this parameter is less than 0.02 kg. This is the reason for importing activated carbon from abroad, although Ukraine is rich in raw materials for the synthesis of activated carbon of its own production. If we discard fossil coal, which is a non-renewable resource, then great prospects open up for the use of lignocellulosic plant wastes. The investigations conducted in recent years have shown that the parameters of biocarbons are equivalent or even higher than those of commercial activated carbon.

Crop production in Ukraine annually generates huge amounts of various wastes, residues, scraps, for example, in the 2018/19 marketing year, only straw of cereals formed 250.85 thousand tons, and straw of other crops – 340.39 thousand tons. Such waste is a valuable raw material for the synthesis of activated carbon. The synthesis of activated biocarbon of a from wheat straw and investigation of its structural features is carried out in this work.

Methods

The synthesis was carried out using as activator a 5 % solution of H₃PO₄ at a temperature of 650 °C without a protective atmosphere. The pyrolysis process of organic materials was carried out in a Neoterm resistance furnace, model NT 1313, which placed in a glass fume hood in the laboratory room. The furnace is controlled by the KXP 4 microprocessor thermoregulator. A fume pump is connected to the fume hood to get rid of harmful and undesirable fumes or vapors emitted during heating.

Porous structure. Images of the synthesized samples were obtained using a scanning electron microscope Phenom Pro Desktop SEM. The obtained SEM images are shown on Fig. 1.

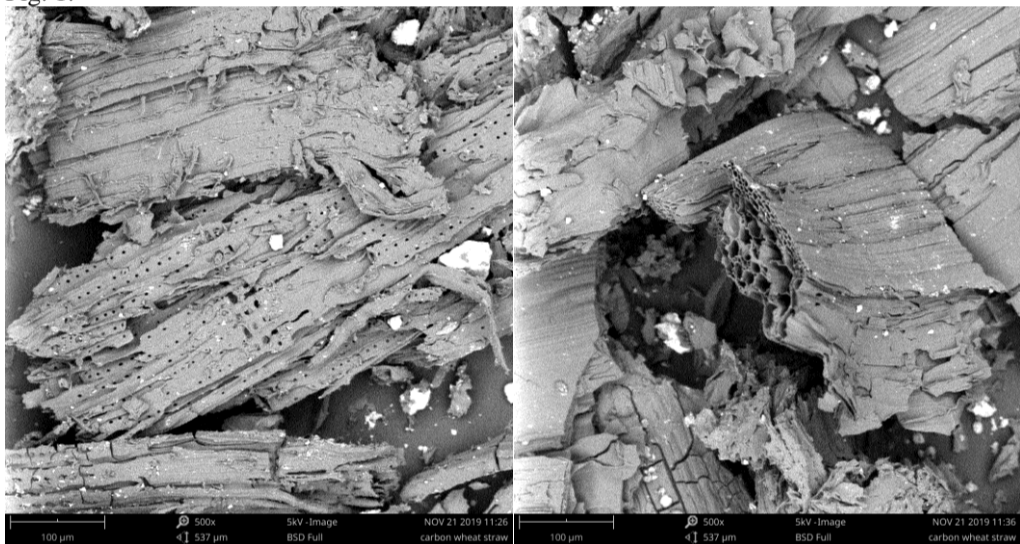


Fig. 1. SEM image of the synthesized activated carbon

The parameters of the porous structure of the activated carbon (specific surface area, total volume of the pores, volume of micropores, the average diameter of the pores) were assessed via isothermic adsorption/desorption processes of nitrogen at the boiling temperature ($T = 77$ K). They were evaluated by the means of automated analyzer Nova Touch LX2. The sample substances were degassed in the vacuum at the temperature of 473 K before the measurements throughout the duration of 16 hours.

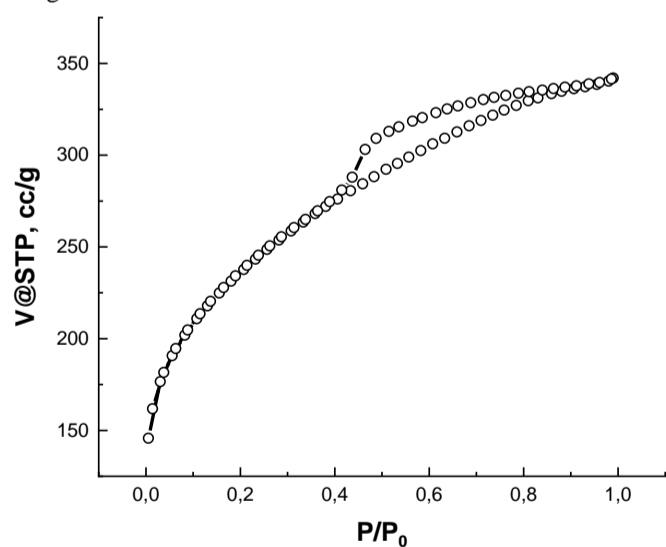


Fig. 2. Isotherm of N₂ adsorption and desorption on samples

The analysis of gas adsorption/desorption data (Fig. 2) by the BET method gives a specific surface area of 798.7 m²/g, pore volume 0.53 cm³/g, average pore diameter 1.32 nm.

X-ray diffraction. X-ray diffraction curves of the carbon materials were obtained using the diffractometer DRON-3 in Cu K α -emission ($\lambda = 0.1542$ nm), which had been monochromated through reflection from the plane (002) of the pyrographite monocrystal set on the path of the diffracted beam. Diffractograms were measured in the continuous detector scanning mode at the rate of 2 deg/min within the range of $2\theta = 5 - 120^\circ$ angles of diffraction. Diffraction spectrum processing (antialiasing, background subtraction, defining the locations and half-breadths of the maximums, compound maximum transformations into separate components) was conducted with the aid of the software suite called DHN_PDS.

Two wide diffuse maxima are observed on the X-ray diffractograms (Fig. 3), which correspond to the interplanar distances of 3.59 Å and 2.11 Å. In addition, the diffraction pattern has a sharp peak at 26.63° (3.35 Å), which indicates the presence in the sample of a certain proportion of polycrystalline graphite. It should be noted the increase in background scattering in the area of angles $2\theta = 5 - 10^\circ$, which is evidence of a developed porous structure, which is also confirmed by the data of small-angle scattering.

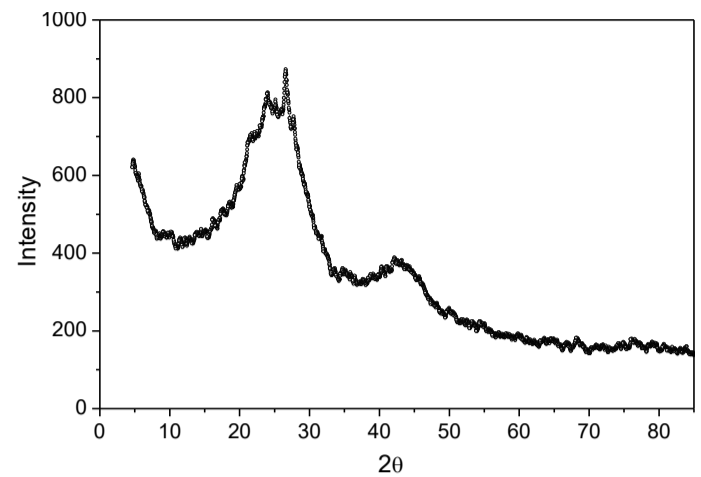


Fig. 3. X-ray diffraction patterns of the synthesized activated carbon

Small angle scattering. The measurements of small angle X-ray scattering (SAXS) spectrums were also obtained from the diffractometer DRON-3 in Cu K α -emission, which had been monochromated through reflection from the plane (200) of LiF monocrystal via the X-ray beam transmission through the sample. Collimating device for primary and scattered rays was used to limit the area of parasitic scattering of monocrystal-monochromator and primary gaps, as well as to decrease the intensity of background scattering in the air. The utilization of collimating device allows to conduct specter measurements of small-angle scattering beginning with $s = 0.1$ nm⁻¹, where $s = 4\pi \sin(\theta) / \lambda$ – wave vector, 2θ – the angle of scattering. The gap of 0.1 mm was situated in front of a detector which corresponds to spatial separation of the detector $\Delta 2\theta = 0.03^\circ$. The recording of the scattered emission was conducted in the scanning mode at 0.05° steps, and the exposure interval was $\tau = 125$ s. The primary beam abated by the sample absorption overlaps with the scattered emission in the area of the smallest angle scattering. In order to exclude the influence of the primary beam on the intensity of scattering, the following formula was applied: $I^*(2\theta) = I_{\text{exp}}(2\theta) - T \times I_0(2\theta)$, where $I^*(2\theta)$ – the true scattering intensity, $I_{\text{exp}}(2\theta)$ – the experimental scattering intensity, $I_0(2\theta)$ – the primary beam intensity distribution, $T = I_{\text{exp}}(0) / I_0(0)$ – the transmission coefficient (the quotient of the primary beam intensity which goes through the sample at the detector's zero position). To determine the transmission coefficient, the measurements of scattered intensity were conducted using the absorption filters approach with the detector's position $2\theta = 0^\circ$. A collimation correction was applied to the scattered intensity curves based on the height of the detector's receiving gap.

The obtained SAXS spectrum are shown on Fig. 4. The obtained spectrum has the form of a curve that decreases monotonically over the entire range of scattering angles. This behavior indicates a chaotic distribution of scattering inhomogeneities (pores) and, accordingly, the lack of correlation in their mutual arrangement.

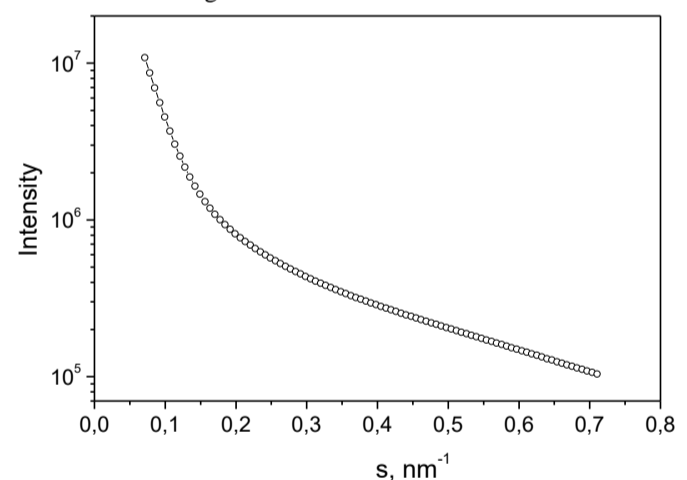


Fig. 4. SAXS spectrum of the synthesized activated carbon

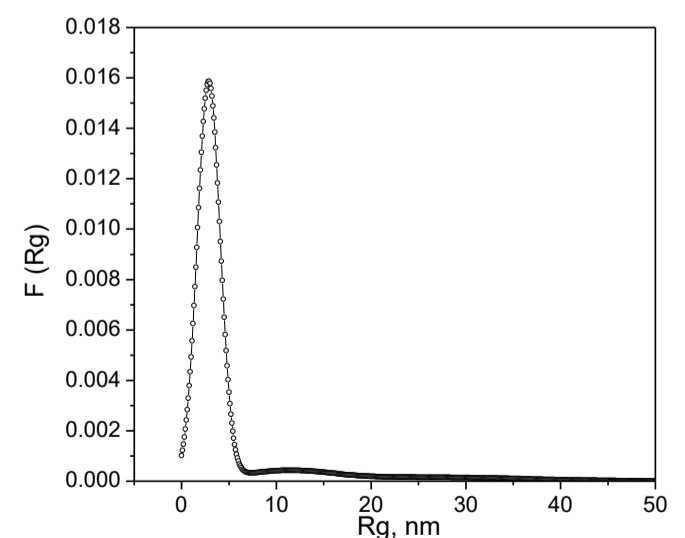


Fig. 5. The graph of the distribution function of the synthesized activated carbon

Pore size distribution. To determine the pore size distribution function, the indirect Fourier transform method was used. This method was implemented in the GNOM low-angle scattering data processing application package. In this work, the calculation of pore distribution functions in the investigated materials was performed within the model of polydisperse spherical particles (Fig. 5). The dominant contribution to the porous volume (about 85 %) is given by pores with a radius of up to 2.8 nm. As a result of the calculation we obtain a specific pore surface area of 781 m²/g.

Therefore, the proposed method of biocarbon synthesis makes it possible to obtain highly porous activated carbon with a large proportion of micropores.