### **RESEARCH ARTICLE**

## Study of impregnated cellulose thermal treatment process and properties of obtained active carbon

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**Abstract:** Single-stage process of obtaining active carbon by thermal processing of plant raw materials (mixture of different types of wood sawdust), impregnated with the mixture of phosphoric acid, urea and nitric acid salts has been developed. Active influence of impregnates on the process of carbonization and formation of carbon residue has been formed. It is established that carbon residue obtained in the interval of heating  $20^{\circ}$ C-( $500^{\circ}$ C- $700^{\circ}$ C), possesses high sorption activity to the vapors of organic compounds and has ion-exchange capacity. It has been showed that the value of carton residue depending on the impregnate used in the wood increases compared to the yield of non-treated initial raw materials by 3.1 times at  $600^{\circ}$ C and by 4.2 times at  $700^{\circ}$ C.

**Keywords:** impregnate, thermal decomposition of wood, porous sorbent, specific surface, activity by benzene, iodine

### 1 Introduction

Scientific-technical progress set a number of complicated problems in front of a humankind that it never faced before. The relationship between humanity and environment occupy an important place among these problems. The load associated with fourfold growth of population and 18-fold increase of the volume of world production was put on the nature. Understanding the importance of water for people does not prevent a human from polluting the source of life by oil and oil products, heavy metals, radioactive substances, inorganic pollutants, sewage waters, chemical fertilizers. The solution for the problem of water purification from chemical pollutants is possible at creation and implementation of waste-free technologies of product manufacturing, incorporation of purification facilities and the use of effective filters for adsorption of gaseous compounds and sorbents with high capacity and selectivity to adsorbed compounds.

The problem of creation of nee adsorbents for purifi-

cation of sewage waters and gaseous toxic compounds from production activity of a humanity is very actual and important.

At present activated carbons are widely used in many processes of chemical technology, pharmaceutical and food industry, for purification of gases and sewage waters. Constant increase of the quality of active carbons and decrease of their cost promotes successful development of modern adsorption techniques, what is reasoned by the improvement of production technology<sup>[1]</sup>. The raw material for obtaining active carbons is anthracite.<sup>[1,2]</sup>

The production of raw carbon on the first stage at 500°C is thought in known methods of obtaining active carbons on the first stage followed by its subsequent activation in oxidative gas (carbon dioxide, water vapor) atmosphere at 900–1000°C at the second stage or carbonization – activation of the wood impregnated by zinc chloride at 700°C during 4–6 hours and multiple times rinsing of obtained product with acid, alkali and hot water. The production of active carbon is associated with substantial long energy consumption and with the complexity of its synthesis.<sup>[2–8]</sup> That is why the development of less energy consuming and safe methods of synthesis of active carbon is a very actual problem.

The purpose of the work is the development of singlestage process of synthesis of active carbon by thermal treatment of plant raw materials, impregnated with catalysts of cellulose carbonization process and poreforming substances, and studying of the influence of

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composition of impregnates on the yield and parameters of porous structure of the carbons.

### 2 Materials and methods

### 2.1 Initial raw materials

The sawdust of mixed different wood types (waste of wood-processing industry, consisting of softwood sawdust (80-85%) and hardwood sawdust (15-20%)) was used as initial raw material and phosphoric acid, urea, salts of nitric acid (potassium, lithium, ammonium) were used as impregnates of plant raw materials. Thermal treatment of impregnated plant raw materials was performed in gas oven at the heat treatment temperatures (HTTs) 20-700°C and the speed of temperature increase  $20^{\circ}$ C min<sup>-1</sup>. After thermal treatment obtained carbon was thoroughly rinsed with boiling distilled water in a bath at a module 1:15 during 30-40 minutes. The carbon was dried on air afterwards.

### 2.2 Research methods of heat treatment products

The change of specific surface of obtained carbons was performed in adsorption vacuum unit using torsion quartz balance at the temperature 20°C by the sorption of CCl<sub>4</sub> following the method of Brunauer, Emmett, Teller (BET). The volume of micropores was calculated according to the Dubinin-Radushkevich equation in accordance with the theory of volumetric filling of micropores (TVFM) on isotherm of sorption (herewith the value of maximum volume of condensed CCl<sub>4</sub>vapor is determined by at *P/P<sub>s</sub>*=0.15-0.98 using adsorption in micropores and on the surface of intermediate pores)<sup>[9]</sup>.

The estimation of statistical exchange capacity is determined after the transfer of ion-exchange groups of the sorbent into  $H^+$  form by the exposure during 1 day in HCl solution, subsequent rinsing with distilled water until neutral reaction and then reverse titration of the carbon with NaOH using HCl solution according to GOST 20255.1-89 (in Russian)<sup>[10]</sup>.

Total volume of pores, activity of carbon by the iodine and statistic activity on benzene was determined according to GOST 6217-74 (in Russian)<sup>[11]</sup>.

### **3** Results and discussion

Our multi-year experimental research dedicated to the protection and cellulose tissue from fire showed, that the process of impregnation of cellulose-containing raw materials includes the stage of filling the capillary space of sapwood and also the pores of cellular walls at heating, when the solution gets to the amorphous part and then to crystal part of polysaccharides, and the interaction of impregnating solution with polysaccharides and lignin.<sup>[12–16]</sup> The incorporation of impregnating solution into the structure of the wood substantially changes the process of degradation of the polymer, properties and the yield of obtained carbon residue. Derivatograms of the wood impregnated with different compositions were recorded in order to study the process of carbonization and pore-forming of carbon, the correlations between the compositions of inhibitors, change of the weight at heating, preservation of different elements and the yield of carbon residue were established. Thermal treatment of impregnated wood was accompanied by the loss of adsorbed chemically bonded and included water. Depending on the composition of impregnates chemical destruction of the polymer leads to the release of different volatiles and the formation of carbon residue. Thermal destruction of the wood is accompanied by complicated chemical processes when the destruction of polysaccharide chains takes place, so as the condensation of lowmolecular compounds that are already present and being formed in impregnating solution and the formation of inorganic polymer compounds on their basis.

### 3.1 Study of the features of thermolysis of impregnated sawdust

In order to choose optimal composition of wood impregnate that is catalyzing carbonization process, the study of the features of thermal decomposition of wood impregnated with compositions L-1, L-2, L-3 and L-4 was performed in the air at temperature interval 20-700°C using the derivatograph (MOM, Hungary). The following compositions were used as impregnates: (1) composition L-1, the ratio (mass parts) of nitrogen (amide) to phosphorus, to nitrogen (nitro-groups) and nitrogen (ammonium) respectively is 1:9:1.1:1.42. (2) composition L-2, the ratio of nitrogen (amide) to phosphorus, to nitrogen (nitro-groups) and metal is respectively 1:9:0.6:0.32. (3) composition L-3, the ratio of nitrogen (amide) to phosphorus, nitrogen (nitro-groups) and metal (potassium) respectively is 1:9:0.9:2.84. (4) composition L-4, the ratio of nitrogen (amide) to phosphorus is respectively 1:9 (Table 1). The derivatograms of decomposition of initial and impregnated wood sawdust are presented on Figure 1.

The analysis of obtained data shows that the process of thermal decomposition of initial samples of wood sawdust (Figure 1(a)) is characterized by the maximum at 350°C on differential curve of mass loss. As it is known, the dehydration of cellulose depolymerization of lignine, therpenes, aliphatic acids and break of bonds of pyranose

The composition of the impregnate	Heating temperature (°C)	The safety of the phosphorus content in the final unwashed product $(\%)^*$	Ion exchange capacity (mg-eqv/g)
Initial sawdust	600	_	_
Initial sawdust	700	_	_
L-1	600	$88.00{\pm}0.05$	$1.30{\pm}0.07$
L-1	700	73.46±0.04	$0.90{\pm}0.05$
L-2	600	89.31±0.01	$1.00{\pm}0.05$
L-2	700	79.47±0.01	$0.70{\pm}0.03$
L-3	600	$88.03{\pm}0.05$	$1.00{\pm}0.08$
L-4	600	$72.05 \pm 0.06$	$0.81{\pm}0.03$
L-4	700	68.40±0.02	$0.45\pm0.12$

Table 1. Phosphorus content and ion-exchange capacity at obtaining of carbon with a final temperature of 600°C, 700°C

Note: <sup>\*</sup> The preservation of the phosphorus (%) in final unwashed product – is the ratio of the phosphorus content in the product obtained at corresponding pyrolysis temperature to the value of injected phosphorus content, recalculated taking into account the changed mass of the sample at the pyrolysis temperature under consideration, provided that there is no loss of phosphorus.

ring of natural polymer. The mass loss occurs with the speed of more than 20 mg.deg<sup>-1</sup> and is 57% from the initial weight at 500°C, 19%.

The sawdust impregnated with the composition L-4 (Figure 1(b)) are characterized by three peaks. At lowtemperature region at 150°C physically connected water is removed, the destruction of carbamide takes place with formation of bi-urethane, ammonia and carbon acid, also the phosphorylation of preserved OH-groups of polysaccharide<sup>[17]</sup> is performed. The process goes with the speed of 8.2 mg.deg<sup>-1</sup>, mass losses are 6%. The second stage of thermolysis corresponds to the region of heating 190-300°C, where main processes of wood decomposition (dehydration, depolymerization, carbonization) take place. The maximum of speed on the first stage is observed at the temperature of 260°C, the speed of this process is 11 mg.deg<sup>-1</sup> (two times smaller then the speed of decomposition of initial sawdust), mass loss is 42%.

The third stage of thermal decomposition is observed in the region of temperatures  $300-370^{\circ}$ C. Maximum speed of mass loss of the sample in this region is significantly smaller, only 3.2 mg.deg<sup>-1</sup> and it is observed at the temperature of  $320^{\circ}$ C, the mass losses in mentioned range are about 7%. In this region of heating of impregnated sawdust further deep chemical destruction of the material takes place and also polycondensation of phosphoric acid with the formation of polyphosphorus compounds occurs. The yield of carbon residue obtained at  $500^{\circ}$ C, is 36%.

Structural transformations of the samples obtained after the stages of main mass loss are confirmed by IR-Fourier spectroscopy data. The transfers of spectra that are characteristic for polysaccharides into the spectra of carbon residues are observed on IR adsorption spectra of initial samples and sawdust after carbonization (temperature of thermolysis 350, 500 and 700°C), as well as at the temperature of  $250^{\circ}$ C and higher for impregnated samples. The bands in the frequency region 900–1200 cm<sup>-1</sup>, that are characteristic for carbohydrates disappear and adsorption bands at 1600-1650 cm<sup>-1</sup> that can be related to the adsorption of C=C bonds of formed carbons are found.

The process of decomposition of wood impregnated with the composition L-1 (Figure 1(c)) that additionally contains ammonium nitrate apart from phosphoric acid and carbamide, is characterized by the curve with 6 extremes (110, 150, 190, 240, 260 and 310°C). The first peak with maximum at 110°C is related to the loss of mass at drying of water (maximum speed of mass loss -  $0.65 \text{ mg.deg}^{-1}$ , the loss of mass in temperature region 90-130°C is 16%. The second peak with maximum at 150°C is associated with decomposition of carbamide, the beginning of this process is observed at 115°C, and this stage of decomposition finishes at 180°C. The mass loss of the stage being described are  $\sim 7.5\%$ , the process occurs with the speed 0.5 mg.deg $^{-1}$ . The third peak, where the maximum of mass loss speed is observed at 190°C, is related to the main process of thermal destruction (carbonization and pore formation), occurs with the speed 0.75 mg.deg $^{-1}$  and mass loss 11.5%. It is necessary to note that the introduction of ammonium nitrate into the composition of impregnate (compositon L-1) shifts the main wood sawdust degradation process into a low-temperature region on 160°C, for the system L-4 the shift is 70°C compared to non-impregnated sawdust. The fourth, fifth and sixth peaks with maxima observed at 240, 260 and 310°C respectively, are related to the processes occurring with the same speeds  $0.3 \text{ mg.deg}^{-1}$ , are characterized by the mass loss of 2.0%. It is known that in the range of 240-310°C decomposition of ammonium nitrate occurs with the formation of N<sub>2</sub>O, ammonia, nitrogen and oxygen. The products being obtained



**Figure 1.** (1) Integral and (2) differential curves of thermal gravimetric analysis of wood sawdust samples: (a) initial sawdust without impregnation, (b) sawdust impregnated by phosphorus-nitrogen formulation (L-4), (c) sawdust impregnated by phosphorus-nitrogen formulation with the addition of NH<sub>4</sub>NO<sub>3</sub> (L-1), (d) sawdust impregnated by phosphorus-nitrogen formulation with the addition of LiNO<sub>3</sub> (L-2)

are reactively active and can participate in the reaction of oxidation of the obtaining carbon material. The yield of carbon obtained with the composition L-1 at 500°C is 49 wt%.

Sawdust impregnated by the composition L-2 (Figure 1(d)) is characterized by processes which proceed with maximum at 140, 180, 210, 240, and 300°C. The first stage of degradation of sawdust refers to the loss of crystallization water of the salt LiNO3·3H2O (maximum speed 0.8 mg.deg $^{-1}$ ) and is observed at 140°C, the mass loss at this stage reaches 6%. The second stage with maximum of mass loss at 180°C is associated with the processes of dehydration, carbonization of wood and pore formation of carbon residue. The shift of L-2 system into low-temperature region is 80°C. The mass loss at this stage is 16%, the mass loss rate is 0.9 mg.deg $^{-1}$ . In addition, there are extremes in the temperature range of 210, 240 and 300°C, which are associated with processes proceeding with mass loss rates of 0.3, 0.32 and  $0.2 \text{ mg.deg}^{-1}$  respectively. These processes can be related to the proceed carbonization of wood, to carbon pore formation, transformation of its structure, as well as the decomposition of lithium nitrate to form lithium oxide, nitrogen dioxide and oxygen, and oxidation of the resulting carbon residue<sup>[18]</sup>. The output of carbon from sawdust impregnated by composition L-2 is 58% at the temperature 500°C.

The process of heating wood impregnated by composition L-3, containing potassium nitrate, is very similar to the one described above and is characterized by the stage of the main decay of wood flowing at temperature of 185°C with a mass loss rate of 0.9 mg.deg<sup>-1</sup> and a mass loss of 16%. The shift into low-temperature region is 75°C. There are also two stages of decomposition with maximum at temperatures 470 and 600°C (the rate of mass loss is 0.4 and 0.5 mg.deg $^{-1}$  respectively), which are associated with the process of decomposition of potassium nitrate and the oxidation of obtaining carbon. In connection with the identity of the decomposition curve of wood treated by the composition L-3 (addition of potassium nitrate), and the curve of decomposition of sawdust impregnated by lithium nitrate (composition L-2), we are not providing the derivatogram of sawdust impregnated by composition L-3 in Figure 1. The yield of carbon residue is 57% at 500°C.

#### **3.2** Coal synthesis process

Synthesis of the carbon for assessment of its sorption properties was performed in a gas oven. The raw material impregnated with impregnate was loaded into a container, which is a steel tank, heating section, filled by ceramic material (developed at State Scientific Institution, "A.V. Luikov Institute for Heat and Mass Transfer of National Academy of Science of Belarus") is attached to it. The temperature was recorded using a chromel-droplet thermocouple. Carbonization – activation of sawdust in the oven proceeded in the atmosphere of volatile products of pyrolysis of wood and volatile products of burning propane – butane gas mixture. The process of carbon production is a closed one and, accordingly, environmentally friendly. The time of obtaining of active carbon with HTT 600°C is 30 minutes, unlike to the traditional (two-stage) method of producing active coal with preliminary processing of wood into raw carbon in the temperature range of 20-500°C and then activating of raw carbon by water vapor at 700-800°C during 6-8 hours with yield of no more than 25%.

### **3.3** Preservation of incorporated phosphorus in the resulting coal residue

The preservation of the phosphorus content and the value of the ion-exchange capacity in the resulting materials is presented in Table 1.

The preservation of the phosphorus content in the washed carbon residue varies slightly and amounts to 2.1% (for the composition with ammonium nitrate); for compounds with lithium and potassium nitrate it increases slightly until 3.3 wt%; the maximum ionexchange capacity is 1.3 mg-eqv/g is observed when using an impregnating composition with ammonium nitrate; for compositions containing lithium and potassium capacity by Na<sup>+</sup>change from 0.4 to 1.0 mg-eqv/g depending on pyrolysis temperature.

### 3.4 Formation of porous structure of coal and its characteristics

The characteristics of investigated active carbons obtained at 600, 700°C are shown in Table 2.

The results obtained on the study of the sorption activity of carbon obtained by heating wood-impregnated by phosphorus-nitrogen composition with nitric acid salts (ammonium, lithium and potassium) to 600-700°C, show, that their sorption activity on benzene varies from 0.15 to 0.61 g/g, and the ion-exchange capacity from 0.4 to 1.3 mg-eqv/g.

The study of the influence of duration of the clarification process of impregnated plant raw materials on the adsorption activity of the obtained carbons showed that the formation of the porous structure was almost completed within 20-30 minutes from the start of the heating process.

It can be seen from the obtained data that the increase in the temperature of thermolysis of cellulose-containing raw materials leads to the increase in the adsorption capacity for benzene vapor and somewhat decreases the value of the ion-exchange capacity for Na<sup>+</sup>. Increasing of the pyrolysis temperature more than 700°C is impractical, because the yield of carbon decreases, and the sorption activity varies slightly. Depending on the composition of the impregnate, the static capacity on benzene vapor with HTT 700°C is 0.16-0.61 g/g.

The experimental isotherms of adsorption of vapor of  $CCl_4$  by samples of active carbons obtained at 700°C are shown in Figure 2.

A sharp rise of isotherms on the initial section at low relative pressure values indicates about presence of micropores in the carbon. The character of the next filling of the inner surface of the adsorbents gives reason to assume the presence of mesopores.

According to the IUPAC classification, the form of the hysteresis loop of the isotherms of obtained adsorbents corresponds to microporous adsorbents (pore size < 2 nm).<sup>[19–21]</sup>

Table 3 shows characteristics of the porous structure of the obtained carbon:

 $V_s$  – volume of adsorption pores ( $V_s = V_m + V_{me}$ );

 $V_{mi}$  – volume of micropores;

 $V_{me}$  – volume of mesopores;

 $V_{sum}$  – total pore volume;

 $V_{ma}$  – volume of macropores ( $V_{ma}=V_{sum}-V_s$ );

 $S_{sp}$  – specific surface

Thus, carbon sorbents (L-1, L-2, L-3) are microporous sorbents with an effective radius of 1.2-1.5 nm, with a share of micropores from the total volume of sorption pores 0.56-0.85, the share of mesopores varies from 0.14 to 0.44.

The patent BY 17196 "Method of obtaining active carbon" was prepared and submitted as a result of this work<sup>[22]</sup>.

It is known that the formation of carbon during heat treatment of wood begins from less thermally stable components of wood, and then more stable polymer areas are include in the restructuring process. Within the limits of wood, decomposition begins in amorphous regions and then goes on ordered regions within the limits<sup>[23]</sup>. This leads to the fact that the resulting charcoal inherits the macrostructure of the original wood to a certain extent, this is a memory effect. Introduced impregnates undergo chemical and structural reorganization, form inorganic compounds, such as salts of Madrell and Correll, which perform the role of supports in the process of shrinkage of raw wood, preventing closure of pores in the forming carbons in the process of thermolysis of samples as a result of heating during wood degradation. Due to the proximity of the pore walls, the

		· ·		
The composition of the impregnate	Heating temperature (°C)	Yield of carbon (wt%)	Activity on benzene (g/g)	Activity on iodine (wt%)
Initial sawdust	600	17.01	0.03±0.01	_
Initial sawdust	700	12.03	_	-
L-1	600	46.07	$0.39{\pm}0.01$	_
L-1	700	42.51	$0.47{\pm}0.02$	37.82±0.01
L-2	600	54.73	$0.51 \pm 0.01$	_
L-2	700	51.25	$0.61 \pm 0.01$	30.15±0.03
L-3	600	53.36	$0.48{\pm}0.02$	_
L-3	700	48.41	$0.53 \pm 0.01$	$28.72 \pm 0.07$
L-4	600	32.52	0.15±0.02	-
I -4	700	30.08	0 16+0 02	25 11+0 04

 Table 2.
 Characteristics of carbon adsorbents (raw materials - sawdust of softwood)



**Figure 2.** Isotherms of adsorption of vapor CCl<sub>4</sub> on active carbons obtained at HT 700°C: (a) sawdust impregnated by phosphorusnitrogen formulation (L-4); (b) sawdust impregnated by phosphorus-nitrogen formulation with the addition of NH<sub>4</sub>NO<sub>3</sub> (L-1); (c) sawdust impregnated by phosphorus-nitrogen formulation with the addition of LiNO<sub>3</sub> (L-2); (d) sawdust impregnated by phosphorus-nitrogen formulation with the addition of KNO<sub>3</sub> (L-3)

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The composition of	Volume of sorption pore (cm <sup>3</sup> g <sup>-1</sup> )		The share of	The share of volume		Volume of macropores $V_{\rm ma}$	Specific surface $S_{\rm sp}$	Effective radius	
the impregnate	adsorption pores	micropores	mesopores	micropores	mesopores	(cm <sup>3</sup> g <sup>-1</sup> )	$(cm^3 g^{-1})$	$(m^2 g^{-1})$	(nm)
	$V_{s}$	V mi	V <sub>me</sub>	$V_{\rm mi}/V_{\rm s}$	$V_{\rm me}/V_{\rm s}$				
L-1	0.64	0.5	0.14	0.78	0.22	1.51	0.87	1105	1.2
L-2	0.86	0.71	0.15	0.82	0.17	1.53	0.67	1440	1.5
L-3	0.69	0.59	0.1	0.85	0.14	1.54	0.85	895	1.4
L-4	0.43	0.24	0.19	0.56	0.44	1.45	1.02	690	1.2

Table 3. Characteristics of the porous structure and adsorption activity of carbon adsorbents with HTT 700°C

potential of interaction with adsorbed molecules is much larger, than in wider pores, and the value of adsorption at a given relative pressure, especially in the small regions of  $/_0$ , is also correspondingly larger. In mesopores (size 2-50 nm) capillary condensation occurs: a characteristic hysteresis loop is observed on isotherms. Macropores (size > 50 nm) are so wide that it is impossible for them to study the adsorption isotherm due to its proximity to the straight line  $P/P_0 = 1$ . The border between the various classes is not strictly defined, because depends from the form the pores and from the nature (especially polarizability) of the adsorptive molecules. Chemical and structural heterogeneity of impregnated wood contributes to the uneven shrinkage of its individual microregions in the process of thermal restructuring.

#### **3.5** The study of fine structure of coal

The study of thin structure of carbon in the process of its formation was carried out using x-ray analysis. Radiographs of carbon were taken on a diffractometer DRON-2 using copper radiation in the range of Bragg angles  $2\theta = 5.57^{\circ}$ . Obtained results showed that diffuse reflections with a maximum at  $2\theta$ -3°30', related to reflection from the planes 002 in packets of ordered carbon are on radiographs of carbons with HTTs 600-800°C<sup>[24]</sup>. The sizes of regions of coherent scattering (packets of ordered carbon) of active carbons were determined using the Selyakov-Scherrer formulas, the interplanar distance  $d_{002}$  was determined using the Wulf-Bragg formula<sup>[24]</sup>.

The results of the X-ray structural analysis of active carbons obtained at HTTs 600-800°C are shown in the Table 4.

It is known that carbon packets with an ordered structure are parallel planed planes (layers) of aromatic carbon, but azimuthally disordered into a crystal structure<sup>[24]</sup>. The distance between these planes ( $d_{002}$ ) for the initial carbon obtained at HTT 600°C is 0.410 nm (Table 4).

Introduction to wood raw materials of impregnates which catalyzing the process of carbonization of wood leads to decrease of interplanar distance from 0.410 to 0.379 nm (at HTT  $600^{\circ}$ C). D<sub>002</sub> decreases slightly at in-

 Table 4.
 Data of X-ray analysis of activated carbons obtained at various HTs

Impregnat	HTT (°C)	<i>d</i> <sub>002</sub> (nm)	<i>L</i> c (nm)	$d (\text{g cm}^{-3})$
Initial sawdust	600	0.41	0.8	1.52
L-1	600	0.39	0.8	1.7
L-1	700	0.38	0.83	1.74
L-2	600	0.4	0.8	1.61
L-2	700	0.39	0.81	1.66
L-3	600	0.38	0.8	1.7
L-3	700	0.375	0.85	1.75
L-4	600	0.379	0.85	1.72
L-4	700	0.375	0.97	1.8
L-4	800	0.375	0.9	1.81

creasing HTT to 800°C. The size of packet (Lc) change not significantly (from 0.81 nm to 0.90 nm).

Obtained carbons should be attributed to nongraphitizing forms of carbon with weakly ordered structural organization,<sup>[25–27]</sup> because low-temperature dehydration of wood leads to the formation of intermolecular bonds (crosslinks), which further prevent the process of structural ordering (increasing the size of carbon packages and decreasing of the interplanar distance  $d_{002}$ ).

Based on the data obtained, the process of formation of active carbons can be schematically described by the following way:

(1) low-temperature carbonization of impregnated wood raw materials;

(2) uneven shrinkage of the material associated with the chemical and structural heterogeneity of impregnated wood, leading to the formation of the porous structure of carbon;

(3) thermal transformations of impregnates with the formation of heat-resistant inorganic compounds which prevent of closure of the pores of the carbon during its structural adjustment.

# 3.6 Investigation of practical use of obtained active coals for environmental safety purposes

Obtained carbons were tested on a sorption of methane at State Scientific Institution, "A.V. Luikov Institute for Heat and Mass Transfer of National Academy of Sciences of Belarus". Studied materials have fairly high sorption capacity on methane (8-12 wt%) at pressure 3.5 mPa and temperature 20°C. Improvement of bulk density of storage of methane can be achieved by increasing of the bulk density of the sorbents. Increase density of materials to 1.1 kg  $L^{-1}$  with safety of sorption activity can provide of methane storage density 180 L  $L^{-1}$ , which corresponds to the systems of storage and transportation of natural gas in a compressed form at a pressure 20–25 mPa<sup>[28]</sup>.

Coal adsorbents were tested for the purification of industrial water from organic pollutant (oils). The absorption of oil pollutant by obtained sorption material was carried out by passing water condensate through a layer of sorbent at  $4^{th}$  Heat Electrical Central Terminal (Minsk). As a result of the experiment it was found that the efficiency of sorption of pollutant by carbon material in 1.5 times higher than usual regularly used powdered carbons 207 produced by Speakman Carbon Limited (UK).

Obtaining of carbon adsorbent using considered impregnates allows to synthesize sorption cation-exchange material with highly developed porous structure.

### 4 Conclusions

The impregnates of pinewood sawdust (phosphoric acid and salts of nitric acid K, Li, NH4) were developed and single-stage environmentally friendly facilitated method of obtaining bifunctional microporous cheap active carbons with high adsorption activity and ion-exchange capacity by thermolysis of impregnated wood at heating in the interval 500-700°C (the yield of carbon at 600-700°C is 42.5-54.7%).

It was established that the impregnates being used are simultaneously the catalysts of low-temperature decomposition of wood (the shift of maximal rate of plant raw material decomposition is observed at 70-80°C lower, than the one for initial samples) and pore-forming compounds, and they actively participate in the process of carbonization of wood and activation of carbon residue.

The study of porometric characteristics of obtained adsorbents allowed to conclude that obtained active carbons have high specific parameters of porosity (total volume of pores is 1.51-1.54 cm<sup>3</sup>·g, micropores 0.50-0.71  $\text{cm}^3 \cdot \text{g}$  and mesopores 0.10-0.15  $\text{cm}^3 \cdot \text{g}$ ) and are related to microporous materials with effective radii 1.2-1.5 nm.

It is showed that obtained carbons are characterized by high sorption capacity in relation to benzene vapors (up to 0.61 g·g<sup>-1</sup>), activity by iodine (up to 37.82 wt.%), and also have cation-exchange capacity (up to 1.3 mg $eqv\cdot g^{-1}$ ).

### 5 Conflicts of Interest

The authors declare no conflicts of interest.

### 6 Authors contribution

Dr. Nina K. Luneva performed the synthesis of carbon sorbents, Mrs. Tatiana I. Ezovitova did the analysis of sorbents composition, sorption properties of active carbon were studied by Prof. Vyacheslav V. Shevchuk, the changes of crystal structure of active carbon were studied by Dr. Alexander A. Ratko using the method of X-ray analysis.

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