Artículo de investigación

Investigation of physicochemical properties and structural characteristics of pyrolysis product of wood waste

Investigación de propiedades fisicoquímicas y características estructurales del producto de pirólisis de residuos de madera

Investigação das propriedades físico-químicas e características estruturais do produto da pirólise de resíduos de madeira

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Abstract

In this paper, the object of investigation is a solid product of pyrolysis of wood waste. The structural characteristics and physical-chemical properties of the solid pyrolysis product obtained in the production conditions, characterizing the sorption properties with respect to pollutants contained in aqueous media - the specific area, surface structure, pore size and size distribution are characterized.

The specific surface, volume and radius of the pores were determined by capillary condensation of nitrogen. The specific surface area of the pyrolysis product of wood waste is 310.5 m2/ g. The volume and radius of the pores determined by the t-method and the BJH method are 0.229 cc/g and 19.3 A, respectively. The elemental composition and surface structure of the pyrolysis product were studied by scanning electron and x-ray microscopy. The obtained data indicate the presence of sorption properties. According to the definition of the dispersed composition, the pyrolysis product of wood waste mainly contains particles of sizes from 0.1 to 3 mm (86.6%). The specific value of the bulk density of the pyrolysis product is not inferior to that of known adsorbents. And they are 295 g/dm3. The moisture content of wood waste after treatment with pyrolysis does not exceed the normative value and accounts for 2.7%.

It is established that utilization of wood waste by low-temperature pyrolysis makes it possible to obtain a sorption material.

Resumen

En este trabajo, el objeto de investigación es un producto sólido de pirólisis de residuos de madera. Se caracterizan las características estructurales y las propiedades físico-químicas del producto de pirólisis sólido obtenido en las condiciones de producción, que caracterizan las propiedades de sorción con respecto a los contaminantes contenidos en medios acuosos: el área específica, la estructura de la superficie, el tamaño de los poros y la distribución de tamaños. La superficie específica, el volumen y el radio de los poros se determinaron mediante la condensación capilar de nitrógeno. El área superficial específica del producto de pirólisis de los residuos de madera es de 310,5 m2 / g. El volumen y el radio de los poros determinados por el método t y el método BJH son 0.229 cc / gy 19.3 A, respectivamente. La composición elemental y la estructura de la superficie del producto de pirólisis se estudiaron mediante microscopía electrónica y de rayos X de barrido. Los datos obtenidos indican la presencia de propiedades de sorción.

Según la definición de la composición dispersa, el producto de pirólisis de los desechos de madera contiene principalmente partículas de tamaños de 0,1 a 3 mm (86,6%). El valor específico de la densidad aparente del producto de pirólisis no es inferior al de los adsorbentes conocidos. Y son 295 g / dm3. El contenido de humedad de los residuos de madera después del tratamiento con

Keywords: Pyrolysis, wood waste, sorbent, wastewater.

pirólisis no excede el valor normativo y representa el 2,7%.
Se ha establecido que la utilización de residuos de madera mediante pirólisis a baja temperatura permite obtener un material de sorción.

Palabras claves: Pirólisis, residuos de madera, sorbente, aguas residuales.

Resumo

Neste trabalho, o objeto de investigação é um produto sólido de pirólise de resíduos de madeira. As características estruturais e propriedades físico-químicas do produto de pirólise sólido obtido nas condições de produção, caracterizando as propriedades de sorção em relação aos poluentes contidos em meio aquoso - a área específica, estrutura superficial, tamanho de poro e distribuição de tamanho são caracterizadas.
A superfície específica, volume e raio dos poros foram determinados por condensação capilar de nitrogênio. A área superficial específica do produto da pirólise de resíduos de madeira é de 310,5 m2 / g. O volume e o raio dos poros determinados pelo método t e pelo método BJH são de 0,229 cc / ge 19,3 A, respectivamente. A composição elementar e a estrutura superficial do produto da pirólise foram estudadas por microscopia eletrônica de varredura e de raios-X. Os dados obtidos indicam a presença de propriedades de sorção.
De acordo com a definição da composição dispersa, o produto de pirólise de resíduos de madeira contém principalmente partículas de tamanhos de 0,1 a 3 mm (86,6%). O valor específico da densidade aparente do produto de pirólise não é inferior ao dos adsorventes conhecidos. E eles são 295 g / dm3. O teor de umidade dos resíduos de madeira após o tratamento com pirólise não excede o valor normativo e representa 2,7%.
Estabelece-se que a utilização de resíduos de madeira por pirólise a baixa temperatura possibilita a obtenção de um material de sorção.

Palavras-chave: Pirólise, resíduos de madeira, absorvente, águas residuais.

Introduction

At present, the utilization of wood waste is an actual problem. With existing methods of processing, almost half of the biomass of a tree is lost, which naturally indicates a low level of technological processes of woodworking (Zhuravleva and Devyatlovskaya, 2007). This leads to the formation and accumulation of a large amount of wood waste.
If possible, wood waste may be used for production. For example, slats, slabs, etc. can be used to produce a large number of products: glued blanks, cellulose, alcohol, fodder yeast. Wood sawdust, shavings, bark are more limited in use. They have not yet found such wide and complete application as lump waste, although they have promising directions of use (Zhuravleva and Devyatlovskaya, 2007). They can be used for economic purposes, as a technological raw material for wood-chemical production. Less time consuming is the use of sawdust, shavings and bark as fuel and fertilizers (Zhuravleva and Devyatlovskaya, 2007).

At present, sawdust is used not more than 30% of the total volume (Zhuravleva and Devyatlovskaya, 2007). Unused part of sawdust is burnt, less often it is exported to landfills. The problem of utilization of sawdust is at the initial stage of the solution due to a number of reasons: low investment opportunities of national enterprises, worn-out equipment, outdated technologies (Zhuravleva and Devyatlovskaya, 2007).

An alternative way of utilizing wood waste, in particular sawdust, is pyrolysis processing. As a result of treatment with low-temperature pyrolysis, it is possible to obtain a number of useful products: gaseous pyrolysis fuel, liquid pyrolysis fuel and a solid residue (solid pyrolysis

product) containing a certain amount of carbon, which is therefore a potential sorbent. It is most expedient to use the obtained material as a sorbent for post-treatment of sewage from oil products and ions of heavy metals.
Utilization of wood waste with the help of low-temperature pyrolysis allows reducing the amount of accumulated wood waste and improving the quality of wastewater treatment.

Methods

The dispersion composition of the solid product of wood waste pyrolysis was determined by sieve analysis and using a laser particle size analyzer "Microsizer 201C" (Nasyrov et al, 2017).

To determine the bulk density, a solid product of pyrolysis of wood waste was placed in a 20 ml preliminarily weighed cylinder, shaken for 1 minute and the volume occupied before and after shaking was measured (Nasyrov et al, 2017). The moisture content of the solid pyrolysis product was determined using ML-50 moisture analyzer (Nasyrov et al, 2016).

The mass fraction of the ash of the pyrolysis product of wood wastes was determined as the ratio of the mass of mineral impurities after calcination of the sample and bringing it to a constant mass, to the mass of the dry sample taken for analysis. The mass of the dried sample was in the range (1-2.5 g) (Nasyrov et al, 2016).

To obtain characteristics such as specific surface area, pore size and volume, the studies were carried out by gas sorption on a Quantachrome 4200E instrument. Sorption-desorption isotherms were obtained. The determination of the specific surface area and the porous structure was carried out using the Brunauer-Emmett-Teller (BET) method.

To determine the volume of micropores in the presence of pores of larger diameter, the Halsey t-method was used. The distribution of meso- and macropores in size for the sample was determined by the Barrett-Joyner-Haland method (BJH). The Barrett-Joyner-Haland model (BJH) allows you to calculate the pore volume, as well as plot a pore size distribution chart in the coordinates, the pore radius is the pore volume corresponding to a given radius (Minori et al, 2011; Giraldo, 2013; Deliyanni et al, 2009; Zaini et al, 2009).

Results and Discussion

Figure 1. Solid pyrolysis product of wood waste

In appearance, the resulting sample is a black powder without foreign inclusions.

The adsorption properties of a potential sorption material are influenced by the structure and magnitude of the specific surface area, in particular the pore size and their size distribution (Nikolsky, 1968). The structure of the obtained pyrolysis product affects the speed of the adsorption process, determines the forms of the isotherm and the number of molecules absorbed in various sizes.

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In this work, the structure and properties of potential sorbents obtained as a result of pyrolysis of wood waste have been studied.

The results of the microstructure investigation by the scanning electron microscope of the brand "Jeol JSM-6390 LA" indicate that the pyrolysis product has a porous structure (Fig. 2). The porous structure allows to predict sorption properties.

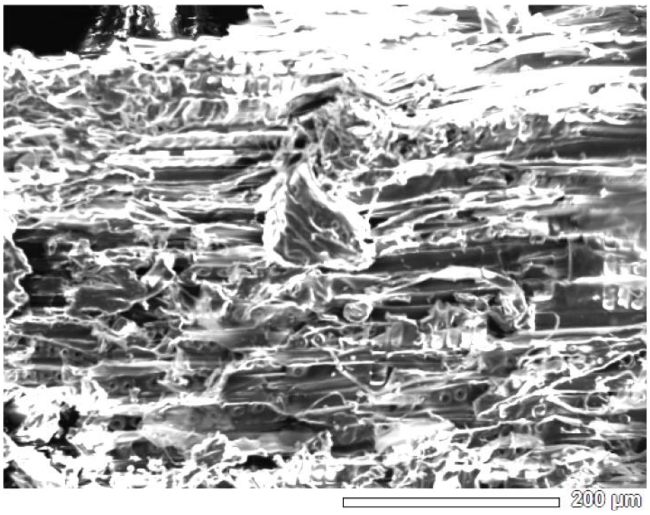

Figure 2. Structure of pyrolysis product of wood waste

According to X-ray phase analysis, the main components of the pyrolysis product of wood waste are carbon and oxygen (Fig. 3, 4, 5). The results are shown in Table 1.

Table 1 – Elemental composition of the pyrolysis product of wood waste

Element	Mass, %
C	70.90
O	28.36
Mg	0.08
Al	0.16
Si	0.11
K	0.14
Ca	0.25

The high content of organic compounds in the solid pyrolysis product of wood sawdust causes the total content of carbon and oxygen to be more than 99% of the elemental composition of the analyzed pyrolysis product. The mineral part accounts for less than 1% of the elemental composition.

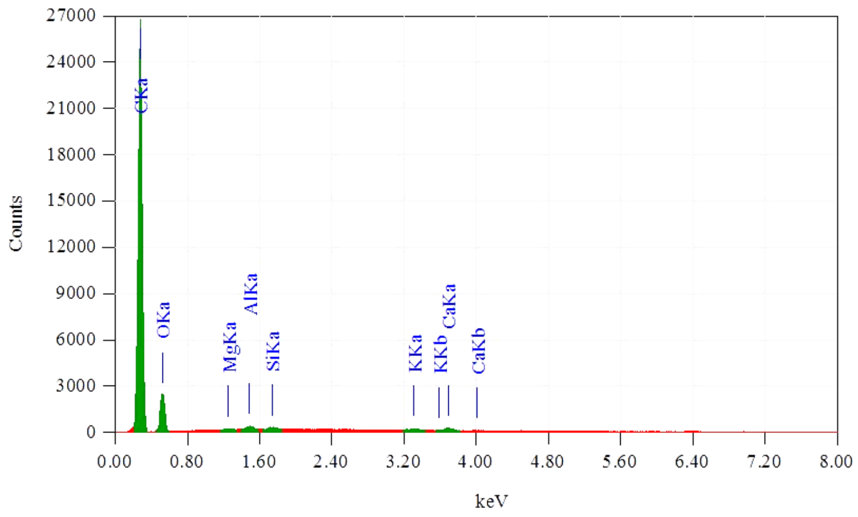

Figure 3. Spectrum obtained by XRF method

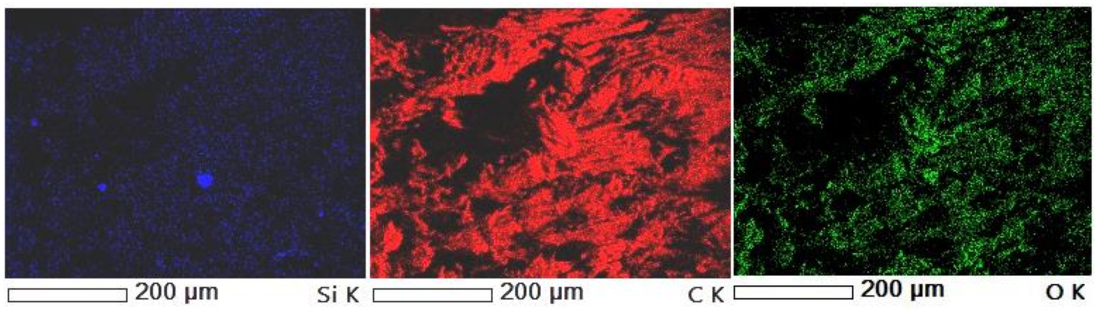

Figure 4. Distribution of elements on the surface of pyrolysis product of wood waste (silicon, carbon, oxygen)

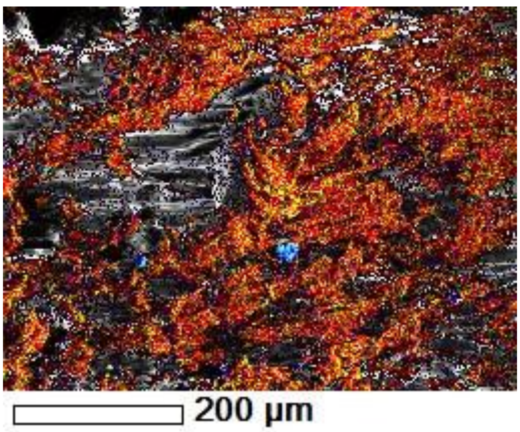

Figure 5. General distribution of elements

A dispersion analysis of the solid product of pyrolysis of wood waste was determined using a sieve analysis and using a laser particle size analyzer of the brand "Microsizer 201C". The results of the determination are presented in Table 2.

Table 2 – Particle size distribution (%)

Particle size, mm	Wood waste
<0.0006	0.3
0.001-0.0006	0.1
0.01-0.001	0.3
0.05-0.01	3.5
0.1-0.05	5.6
0.5-0.1	46.9
1-0.5	10.9
3-1	28.8
5-3	2.5
> 5	1.1

According to the granulometric analysis, the solid pyrolysis product of the wood waste contains mainly particles with sizes from 0.1 to 3 mm (86.6%).

The results of the moisture and ash studies are presented in Table 3.

Table 3 – Moisture and mass fraction of ash from solid pyrolysis product

Raw materials	Moisture, %	Mass fraction of ash, %
wood waste	2.7	40

The moisture content of the solid pyrolysis product does not exceed the normative value. The standard is 10% in accordance with GOST 4453-74 "Coal active clarifying wood powder".
Ash content, characterizing the presence of the mineral part, is significant and exceeds the ash content of the activated carbon sorbent (Nikolsky, 1968). This shows the need for demineralization of the pyrolysis product in order to improve its adsorption capacity, possibly by activating with acids or alkali solutions.

Table 4 presents the results of measuring the bulk density of the pyrolysis product.

Table 4 – Bulk density

Sample	Bulk density, g/dm3
solid pyrolysis product of wood waste	295

For comparison, in Table 5 shows the values of the bulk density of known adsorbents.

Table 5 – Bulk density of adsorbents

Parameters	Silica gel		Aluminosilicate	Activated carbon
	Fine-pored	Coarse-pored		
bulk density, g/dm3	800	500	700	200-600

Proceeding from the obtained results, the following conclusion can be drawn: the values of the bulk density of the pyrolysis product of wood waste obtained during the determination are not inferior to those of known adsorbents. And they are 295 g/dm3.

For the sorption material, it is necessary to investigate the following characteristics: specific surface area, volume and pore size. To obtain these parameters, studies on the sorption of gas on a Quantachrome 4200E instrument were carried out.

The sorption-desorption isotherm was obtained, which is shown in Fig. 6.

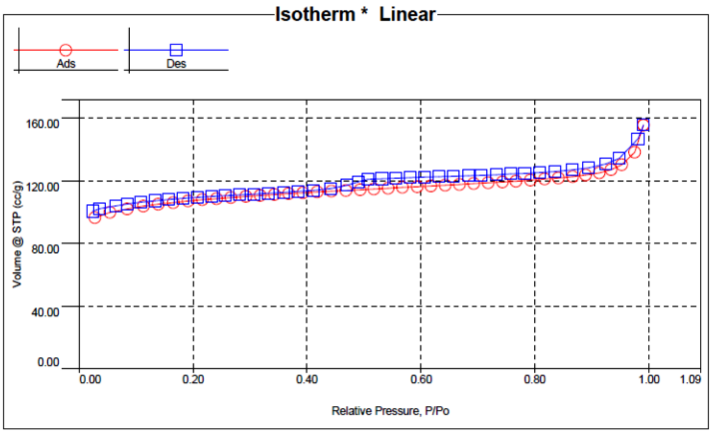

Figure 6. Sorption-desorption isotherm

The adsorption isotherm is used to determine the specific surface area and the porous structure. The most common method is the Brunauer-Emmett-Teller (BET) method. To determine the specific surface area, the BET method selects a section of relative pressures linear in the BET coordinates. The BET plot for nitrogen adsorption is shown in Figure 7.

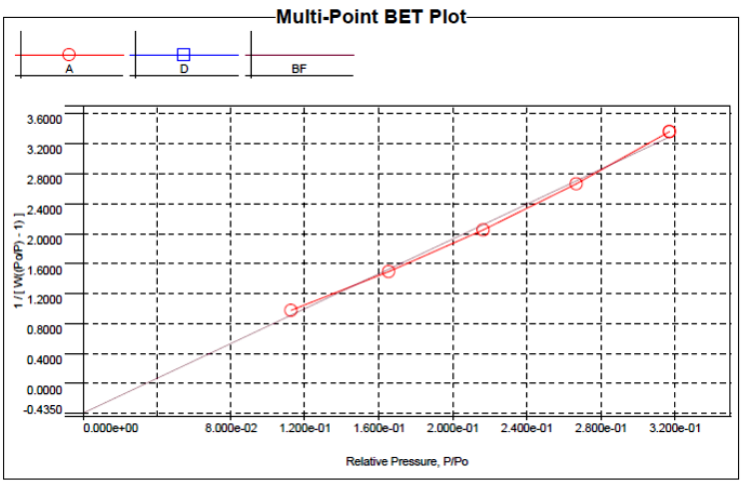

Figure 7. BET plot for nitrogen adsorption

The result of processing the experimental data by the BET method shows that the specific surface area of the sorption material is 310.5 m2/g.

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The specific surface area of the sample can be determined by the Langmuir method. As a result of processing the experimental data using the Langmuir method, the following results were obtained: 583.8 m2/g. The difference in the results is due to the fact that the BET method can be used to determine the specific surface area of materials that do not contain micropores. And Langmuir's method, on the contrary, is suitable for determining the surface area of only microporous substances.

For comparison, Table 6 shows the specific surface area of some sorbents.

Table 6 – Surface area of sorbents

Parameters	Silica gel		Aluminosilicate	Activated carbon
	Fine-pored	Coarse-pored		
surface area, m^2/g	450-500	270-350	300-350	600-1700

To determine the porosity of the sample, the Halsey t-method was used. The t-graph is shown in Figure 8.

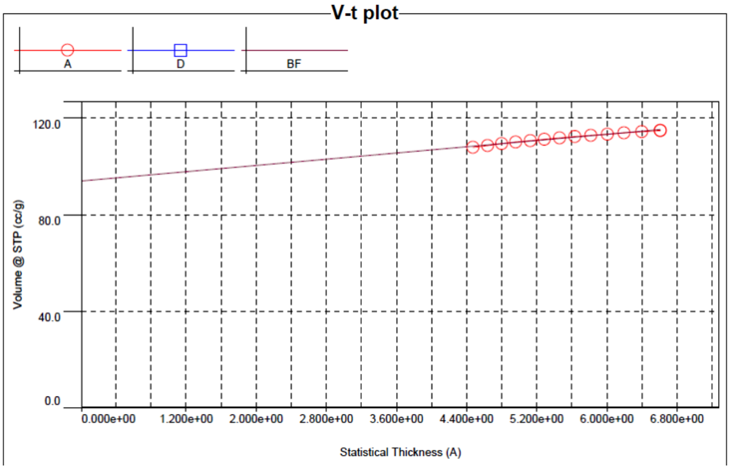

Figure 8. t-plot for nitrogen adsorption of sorbent

As a result of processing the experimental data on the t-method, the following values were obtained: the volume of micropores of pyrolysis products of mud sediments is 0.145 cm3/g.

The pore size distribution for a sample with mesopores is determined by the Barrett-Joyner-Haland method. The Barrett-Joyner-Haland model used to determine the porosity of the test sample allows us to calculate the pore volume and construct a graph of the pore size distribution in terms of the coordinates. The pore radius is the pore volume corresponding to a given radius (blue graph). The graph is shown in Figure 9.

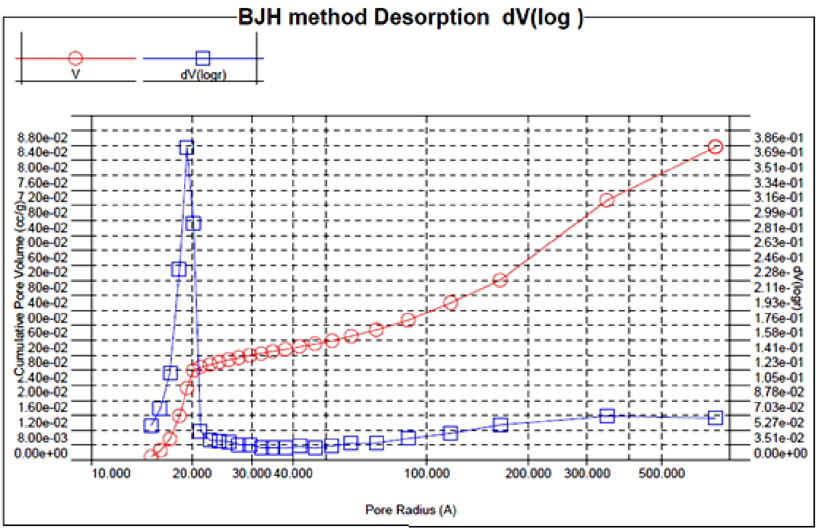

Figure 9. Pore size distribution according to BJH model

The results of processing the experimental data on the t-method and the BJH method are presented in Table 7.

Table 7 – Results of processing of experimental data on a t-method and BJH method

Parameters	Pyrolysis products of wood waste
micropore volume, cc/g	0.145
meso- and macropores volume, cc/g	0.084
pore size, A	19.3

For comparison, Table 8 shows the indices for some sorbents.

Table 8 – Volume and pore size parameters

Parameters	Silica gel		Aluminosilicate	Activated carbon
	Fine-pored	Coarse-pored		
pore volume, cc/g	0.280	0.900	0.570	-
pore size, A	5-30	70-100	20-25	less than 70

The characteristics of the obtained product of pyrolysis of mud sediments are presented in Table 9.

Table 9 – Characteristics of pyrolysis product

Sample	Colour	Foreign substance	Surface area*, m ^ 2/g	Pore volume, cc/g	Pore size, A
solid pyrolysis product of wood waste	black	no	310.5	0.229	19.3

* - Specific surface area of pyrolysis products by BET method

The data obtained (specific surface area, volume and pore radius) allow us to predict the sorption properties of pyrolysis products of wood sawdust relative to ITM and petroleum products.

Summary

1) Wood waste was treated with low-temperature pyrolysis in production conditions. Structural characteristics and physicochemical properties of the obtained samples that characterize sorption properties with respect to pollutants contained in surface and waste waters are studied.
2) Determination of the dispersed composition of the solid product of pyrolysis of wood wastes showed the predominant content of particles in the sample with sizes from 0.1 to more than 3 mm (86.6%).
3) The bulk density of the pyrolysis product of wood waste is 295 g/dm3 and is not inferior to that of known adsorbents.
4) The moisture content of wood waste after pyrolysis treatment does not exceed the normative value and accounts for 2.7%.
5) The ash content of the obtained pyrolysis product, characterizing the presence of inorganic substances in the sorbent, is significant, which indicates the need for demineralization in order to improve its adsorption capacity.
6) The elemental composition and surface structure were studied by scanning electron and X-ray microscopy. According to X-ray phase analysis, the main components of the pyrolysis product of wood waste are carbon and oxygen. The pyrolysis product has a porous structure.
7) The result of processing the experimental data using the BET method shows that the specific surface area of the wood waste pyrolysis product is 310.5 m2/g.
8) The volume and radius of pores determined by the t-method and the BJH method are 0.229 cc/g and 19.3 A.

The obtained data (specific surface area, volume and radius of pores) allow to predict the presence of sorption properties in the products of pyrolysis of wood waste.

Conclusions

Thus, it is shown that the utilization of wood waste, in particular sawdust, by low-temperature pyrolysis makes it possible to obtain a complex sorption material. Studies of structural characteristics and physical and chemical properties have shown the possibility of using the pyrolysis product of wood waste as a sorption material.

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