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Application of the mercury porosimetry method in the analysis of sorption materials

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Objectives. *This study aims to establish the available porosity of a sorbent based on carbonized rice husk and investigate its sorption properties for oil and oil products.*
Methods. *A rice-husk-based sorbent carbonized at 400°C for 30 min was selected as the subject. The porosity of this sorbent is analyzed with the help of mercury porosimeters, the Pascal 140 EVO and Pascal 240 EVO. The sorption properties of the sorbent are also studied when cleaning water containing oil and oil products.*
Results. *The test sample is a bulk porous material with a pore volume of 0.015 cm/g; porosity higher than 15% was found, and the pore size distribution is shown. Studies were conducted on the sorption of oil and oil products as well as the possibility of using the aforementioned sorbent as a filtering material in the purification of water containing oil products. We investigated the sorption processes under dynamic and static conditions. The methodology for measuring the porous structure of solid materials on the mercury porosimeter, Pascal 140 EVO, was examined. The texture characteristics of the sorbent's porous structure were determined, which is primarily the total volume of pores, the values of the specific surface area, and the volume of the microspores and mesopores.*
Conclusions. *The materials studied can be used as sorbents with a developed porous structure for purification of water with dissolved and emulsified petroleum products.*

Keywords: *porosimetry, porosity, sorbent, sorption, pore volumes, oil, petroleum products, rice husks.*

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Применение метода ртутной порозиметрии в анализе сорбционных материалов

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Цель. *Целью данной работы явилось установление доступной пористости сорбента на основе карбонизированной рисовой шелухи и исследование его сорбционных свойств по отношению к нефти и нефтепродуктам.*

Методы. *В качества объекта исследования был выбран сорбент на основе рисовой шелухи, карбонизированной при 400 °С в течение 30 мин. Для него проанализирована пористость с помощью ртутных порозиметров Pascal 140 EVO и Pascal 240 EVO, а также изучены сорбционные свойства сорбента в процессе очистки воды от нефти и нефтепродуктов.*

Результаты. *Показано, что образец сорбента на основе рисовой шелухи является объемно-пористым материалом с удельным объемом пор 0.015 см^3/г. Представлено распределение пор по размерам. Установлено, что доступная пористость составляет более 15%. Проведены исследования по сорбции нефти и нефтепродуктов, а также показана возможность применения указанного сорбента в качестве фильтрующего материала при очистке воды от нефтепродуктов. Сорбционные процессы исследованы в динамических и статических условиях. Изучены методические аспекты измерения параметров пористой структуры твердых материалов на ртутном порозиметре Pascal 140 EVO. Определены текстурные характеристики пористой структуры анализируемого сорбента: общий объем пор, величина удельной поверхности пор, объем микро и мезопор.*

Выводы. *Исследуемые материалы могут быть применены в качестве сорбентов, обладающих развитой пористой структурой, для очистки воды от растворенных и эмульгированных нефтепродуктов.*

Ключевые слова: *порозиметрия, пористость, сорбент, сорбция, объемы пор, нефть, нефтепродукты, рисовая шелуха.*

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INTRODUCTION

Currently, the use of raw plant material byproducts as sorption materials is critical. Studies of parameters, such as porosity, sorption capacity, mechanical strength, and others, provide information that allows us to predict the future use of raw plant material byproducts as sorption materials.

This work aims to establish the available porosity of a sorbent using carbonized rice husk (CRH) and study the sorption properties of oil as well as oil products.

Mercury porosimetry is one of the tools for studying the porous structure of a solid. It is very versatile because it provides information about a porous structure in a wide range of pore sizes, and its calculation equations are simple [1]. This method can also be used to measure the specific surface of dispersed bodies under conditions when the highly concentrated particulate matter, e.g., a powder, has a relatively low surface energy. Mercury does not wet the surface of its particles when there are no one-side open pores, and the pressure in the porosimeter allows mercury to penetrate the smallest micropores of the sample [2].

The method for measuring porosity with mercury porosimetry consists of adding mercury to a previously evacuated vessel with a sample and increasing the pressure sequentially. The level of mercury in the vessel decreases as it penetrates the pores. If this level is measured accurately enough, we can plot the pressure of the volume of the pressed mercury as a function of pressure, calculate the diameters of the filled pores and, construct a program [3].

MATERIALS AND METHODS

Rice husk grown in the Krasnodar krai was crushed to a particle size of less than 1 mm and used as a raw material for the production of the sorbent; it was subjected to carbonization for 30 min at 400°C.

The porosity, as well as the bulk, apparent, and real (skeletal) density, of the material was measured on a Pascal 140 EVO mercury porosimeter and Pycnomatic ATC helium pycnometer from Thermo Scientific, according to the guidelines in the Pascal mercury porosimeter user manual[1].

The pore volume distribution was calculated by the amount of mercury that penetrated the pores of the samples and the equilibrium pressure at which the penetration phenomenon occurred. The calculations rely on assumptions such as the surface tension of the mercury and the wetting angle of the solid material must be constant during the analysis; the pressure during mercury penetration is the equilibrium pressure; the pores have a cylindrical shape; and solid materials are not subjected to deformation under the influence of high pressure.

The following parameters were recorded during the experiment: the experiment temperature, calculated mercury density, degassing time before filling the dilatometer, air pulse, degassing pressure, maximum pressure, maximum speed increase, maximum speed decrease, increase in pump speed, decrease in pump speed, distance between electrodes, dilatometer cone height, dilatometer rod radius, dilatometer number, empty dilatometer weight, sample weight, skeletal density of the sample, and contact angle of the mercury sample.

RESULTS AND DISCUSSION

The data were obtained from the porosimeter. The skeletal density of the material, 1.18 g/cm^3, was measured with a helium pycnometer. We qualitatively determined the degree of compression; this could be adjusted using the SOLID software.

Figure 1 shows the intrusion curve (the dependence of the volume of depressed mercury on the applied pressure).

Figure 2 shows the pore size distribution data. Three peaks are clearly distinguished in Fig. 2, pores with a diameter of 9.1072, 36.1200, and 8.0432 μm. Based on the mercury intrusion data, the following material characteristics were calculated via the SOLID software:

– The total specific pore volume is 0.01578 cm^3/g.

– The specific pore surface area is 0.001 m^2/g

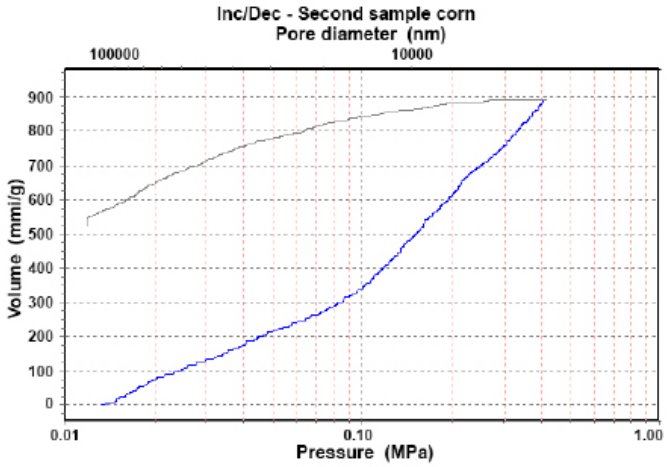

Fig. 1. Intrusion curve.

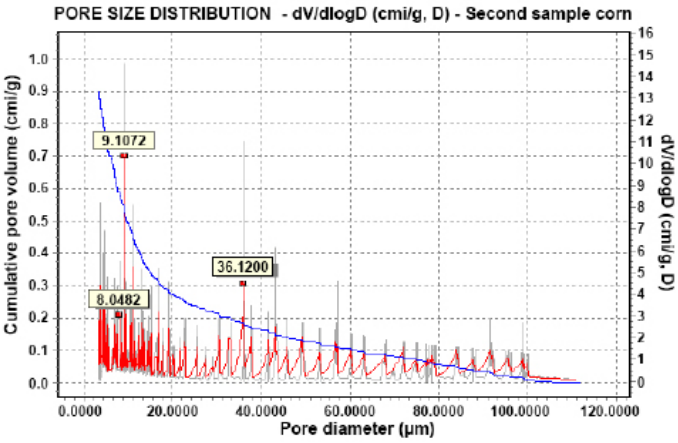

Fig. 2. Pore diameters of the carbonized rice husk.

(calculated according to the model of cylindrical and slit-like pores).

– The average pore diameter is 9.5113 μm (determined as four-fold pore volume divided by area. In this method, the pores are considered cylindrical).

– The median pore diameter is 10.9914 μm (defined as pore size calculated at 50% of the total pore volume).

– The most common pore diameter is 9.1072 μm (defined as the pore size at the maximum peak of the $dV/d\log D$ derivative).

We analyzed the pore size distribution of the test material. Figure 3 shows a histogram of the pore size distribution (information was obtained only on the Pascal 140 EVO device).

We constructed a histogram of the distribution of the specific surface area by pore size (Fig. 4) based on the model of cylindrical and slit-like pores.

As can be seen from the study, mercury porosimetry allows one to obtain information about the porous

[1] Mercury porosimeters of a PASCAL EVO series and SOL.I.D software. User guide, P/N 31713070, Edition A, Italy, 2017.

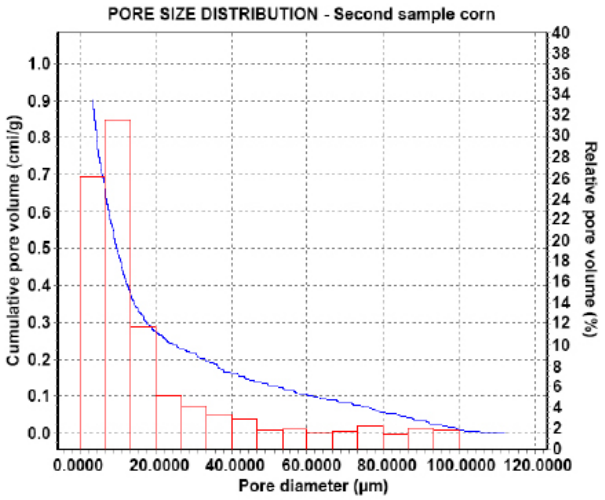

Fig. 3. Specific pore volume of the rice husk.

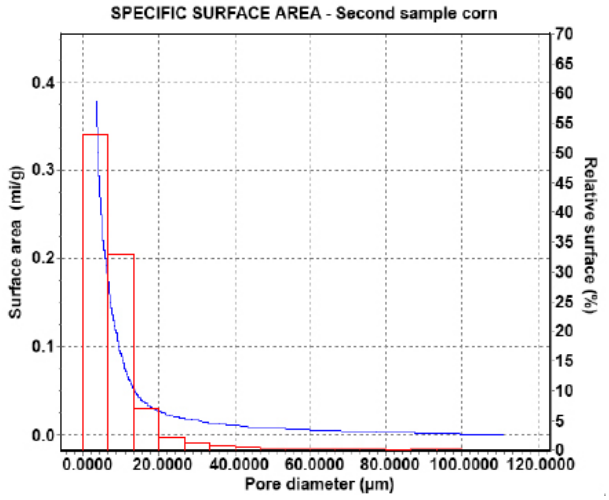

Fig. 4. Specific pore surface area of the carbonized rice husk.

structure of the studied sorbent, as well as its density and total surface.

Table 1 presents the results of the analysis of a sample of rice husk carbonized at 400°C.

After solving the main problem of determining the pore volume of the CRHs, we studied the sorption properties of this sorbent with oil and oil products in dynamic and static conditions. We used oil from the Malgobekskoe field of the Republic of Ingushetia, AI-93 gasoline, and summer diesel fuel to determine the sorption capacity of the CRH. The characteristics of the oil are given in Table 2 [4].

It was previously established that the sorption of oil and oil products under static conditions by various sorbents depends not only on the pore volume of the sorbents but also on the viscosity of the absorbed substance and the duration of contact [5]. The sorption capacity of the CRH was determined gravimetrically, calculated as the ratio of the mass of the absorbed oil and oil products to the mass of the sorbent in the range from 5 to 120 min. The effectiveness assessment of the studied sorbents was determined according to TU 214-10942238-03-95 [6]. The results of the sorption capacity of the sorbent based on CRH for oil and petroleum products are summarized in Table 3 (average of three definitions).

From the data shown in Table 3, it is apparent that the full sorption capacity of the studied sorbent is low. However, carbonized carbon-containing substances can be effectively used for wastewater treatment.

The sorption characteristics of the CRH were studied under dynamic conditions by filtering the solution to be purified through a fixed adsorbent layer to determine the possibility of wastewater treatment of water with oil and oil products using the CRH. The equilibrium conditions were achieved at a constant temperature of 25°C and an oil concentration of 23.5 mg/l. The initial concentration of oil in the water was determined by the gravimetric method [7], based on the separation of oil products from water by extraction with hexane. This was followed by chromatographic separation of oil products from compounds of other classes in a column filled with aluminum oxide. The effectiveness of the sorbent was evaluated for distilled water contaminated with oil with a concentration of 23.5 mg/l.

A column with a height of 50 cm and a diameter of 3 cm was filled with a sorbent to a height of 20 cm; the total mass of the sorbent was 5 g. The solution was fed from above, and it passed by gravity through the sorbent layer. In this case, the water transmission rate (space velocity) was 6 ml/min.

Table 1. Results of the porosity analysis of the material studied

Helium pycnometer real density, g/cm^3	Apparent density, based on mercury porosimetry, g/cm^3	Available porosity, %	Closed cell porosity, %	Specific pore volume, cm^3/g	Specific surface area of pores, m^2/g
1.18	0.3941	15.750	44.83	0.01575	0.001

Table 2. Physical and chemical parameters of the oil

№	Parameters	Experimental Method	Results of the Experiment
1	Density of the oil, kg/m^3 at 20°C	GOST 3900-85	833.7
2	Kinematic viscosity, cSt, at no higher than 20°C at no higher than 50°C	GOST 33-82	 12.35 5.28
3	Dynamic viscosity, mPa×s, at 20 °C at 50 °C	GOST 33-82	 10.3 4.40
4	Sulfur content, mass %, including: hydrogen sulfides mercaptans	GOST 1437-75 GOST 17323-71	0.31 Traces 0.0075
5	Chloride content, mass % (mg/dm^3)	GOST 21534-76	0.010 (82.03)
6	Silica gel resin content, mass %	GOST 11858-66	1.08
7	Paraffin content, mass %		2.1
8	Asphaltene content, mass %		0.03
9	Water content, mass %	GOST 2477-65	None
10	Mechanical impurity content, mass %	GOST 6370-83	0.001
11	Pour point, °C	GOST 20287-96	–20
12	Paraffin melting point, °C	GOST 4255-75	+54
13	Closed cup flash point, °C	GOST 4333-87	–17
14	Open cup flash point, °C		0
15	Flash point, °C		+11
16	Saturated steam pressure, kPa (mm Hg)	GOST 1756-52	24.4 (183)
17	Acidity, mg KOH/100 cm^3	GOST 5985-79	0.015
18	Ash content, %	GOST 1461-75	0.017
19	Molecular mass	GOST R 8.903-2015	213

Table 3. Sorption capacity of the carbonized rice husk (CRH) for oil and its products

Sorbent	Oil sorption capacity, g/g				
	5 min	10 min	30 min	60 min	120 min
CRH	4.3	4.7	4.9	5.1	5.2
	Sorption capacity for diesel fuel, g/g				
	4.4	4.6	4.8	5.0	5.0
	Sorption capacity for gasoline (AI-93), g/g				
	2.1	3.3	3.9	3.5	3.8

Table 4. Concentration of oil products in water before and after CRH filtration (sample volume is 250 ml)

Sorbent	Oil concentration, mg/l				
	Before filtration	After filtration			
		Sample 1	Sample 2	Sample 3	Sample 4
CRH	23.5	0.22	0.26	0.31	4.8

Purified water was collected in four 250 ml samples. At the exit from the column, the clear water obtained corresponds to RD 52.24.496-2005[2].

The maximum permissible concentration (MPC) of oil products in water, according to SanPiN 2.1.4.1074-01, "Drinking water. Hygienic requirements for water quality of centralized drinking water supply systems. Quality Control," is 0.1 mg/dm^3. The MPC of oil products in wastewater is 0.3 mg/l.

The analysis of water for residual oil content was carried out by infrared spectroscopy using an InfraLUM FT-08 IR Fourier spectrometer. It indicated that the oil concentration in the water is below the MPC for wastewater. The determination of the petroleum products present in the samples was carried out according to the procedure, M-01-39-2010[3].

Data on the concentration of petroleum products in purified water are given in Table 4.

As can be seen from Table 4, after the first three samples, that is, after 750 ml of contaminated water is filtered, oil products slip through the sorbent bed, pores begin to clog, and sorbent regeneration is required. The cleaning efficiency decreases from the first sample to the last, and the concentration of oil in the first two samples remains below 0.3 mg/l.

CONCLUSIONS

Using mercury porosimetry via a Pascal 140 EVO device, we determined the main characteristics of a sorbent made from CRH. The studied sorbent samples are volume-porous materials. The studied materials can be used as sorbents with a developed porous structure.

We established the sorption capacity of the CRH for oil and oil products, which amounted to 2−5 g/g. We investigated the sorption process of oil products with a sorbent of rice husk in dynamic conditions. We showed that the CRH sorbent purifies water with dissolved and emulsified oil products.

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The authors declare no conflicts of interest.

[2] Guidance document RD 52.24.496-2005: *Temperatura, prozrachnost' i zapakh poverkhnostnykh vod sushi. Metodika vypolneniya izmerenii* (Temperature, transparency and smell of surface water of land. Methodology for making measurements) (approved by Roshydromet, May 15, 2005) (in Russ.).

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