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PRODUCTION OF COMPOSITE CARBON ADSORBENTS BASED ON TEXTILE CORD OBTAINED FROM CAR TIRE RESIDUES

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Carbon chemistry opens up very wide prospects in obtaining compositions based on carbon-containing raw materials, due to the achievements of recent years in this field. Due to their unique properties, extremely high chemical resistance, thermal resistance, heat resistance and specific strength, carbon materials have found application for the manufacture of carbon-containing refractory, high-temperature composite materials, modified electrodes as fillers for the tire and rubber industry, catalytic systems based on carbon-containing raw materials, etc. Frequently used carbon materials do not meet the requirements of the technological process, in some cases their use is economically unjustified, since they are expensive and have a small raw material base. Therefore, obtaining new efficient and cheap natural carbon materials from available types of industrial raw materials is one of the urgent tasks currently facing scientists and technologists. Textile wire, a product of processing rubber organic waste, can become a promising new raw material for the production of carbon-containing materials. Porous carbon materials were obtained in a laboratory installation, optimal parameters were determined, and the physico-chemical properties of the feedstock and the obtained adsorbents (ash content, humidity, volatility, density, sumar pore volume, elemental composition) were studied.

Key words: textile cord, tire waste, adsorbent, porous carbon nanomaterials.

АВТОМОБИЛЬ ШИНАЛАРЫНЫҢ ҚАЛДЫҚТАРЫНАН АЛЫНҒАН ТОҚЫМА СЫМЫНА НЕГІЗДЕЛГЕН КОМПОЗИТТІК КӨМІРТЕКТІ АДСОРБЕНТТЕРДІ АЛУ

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Көміртек химиясы осы саладағы соңғы жылдардағы жетістіктерге байланысты құрамында көміртегі бар шикізат негізінде композиция алудың кең перспективаларын ашады. Бірегей қасиеттеріне, өте жоғары химиялық төзімділігіне, ыстыққа төзімділігіне және меншікті беріктігіне байланысты көміртекті материалдар құрамында көміртегі бар отқа төзімді, жоғары температуралы композициялық материалдар, модификацияланған электродтар, шина және резеңке өнеркәсібі үшін толтырғыштар, құрамында көміртегі бар шикізат негізіндегі каталитикалық жүйелер және т. б. Жиі қолданылатын көміртекті материалдар технологиялық процестің талаптарына сәйкес келмейді, кейбір жағдайларда оларды пайдалану экономикалық тұрғыдан негізсіз, өйткені олар қымбат және шикізат базасы аз. Сондықтан, өнеркәсіптік шикізаттың қолжетімді түрлерінен жаңа тиімді және арзан табиғи көміртекті материалдарды алу қазіргі уақытта ғалымдар мен технологтардың алдында тұрған өзекті міндеттердің бірі болып табылады. Құрамында көміртегі бар материалдарды алу үшін жаңа перспективалы шикізат тоқыма сымы-резеңке органикалық қалдықтарды қайта өңдеу өнімі болуы мүмкін. Кеуекті-көміртекті материалдар зертханалық қондырғыда алынды, оңтайлы параметрлер анықталды, бастапқы шикізат пен алынған адсорбенттердің физика-химиялық қасиеттері (күл, ылғалдылық, құбылмалылық, тығыздық, кеуектердің қосынды көлемі, элементтік құрамы) зерттелді.

Түйін сөздер: тоқыма сымы, шина қалдықтары, адсорбент, кеуекті көміртекті наноматериалдар.

ПОЛУЧЕНИЕ КОМПОЗИТНЫХ УГЛЕРОДНЫХ АДСОРБЕНТОВ НА ОСНОВЕ ТЕКСТИЛЬНОГО КОРДА ПОЛУЧЕННОГО ИЗ ОСТАТКОВ АВТОМОБИЛЬНЫХ ШИН

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Химия углерода открывает весьма широкие перспективы в получении композиции на основе углеродсодержащего сырья, в силу достижений последних лет в этой области. Благодаря уникальным свойствам, чрезвычайно высокой химической стойкости, термопрочности, термостойкости и удельной прочности углеродные материалы нашли применение для изготовления углеродсодержащих огнеупорных, высокотемпературных композиционных материалов, модифицированных электродов, как наполнителей для шинной и резинотехнической промышленности, каталитических систем на основе углеродсодержащего сырья и др. Часто используемые углеродные материалы не соответствуют требованиям технологического процесса, в некоторых случаях их использование экономически неоправданно, так как они дороги и имеют небольшую сырьевую базу. Поэтому, получение новых эффективных и дешевых природных углеродных материалов из доступных видов промышленного сырья является одной из актуальных задач, стоящих в настоящее время перед учеными и технологами. Новым перспективным сырьем для получения углеродсодержащих материалов может стать текстильная проволока-продукт переработки резиновых органических отходов. Пористо-углеродные материалы получены в лабораторной установке, определены оптимальные параметры, изучены физико-химические свойства исходного сырья и полученных адсорбентов (зольность, влажность, летучесть, плотность, сумарный объем пор, элементный состав).

Ключевые слова: текстильный корд, отходы шин, адсорбент, пористые углеродные наноматериалы.

Introduction. The environmentally acceptable management of excess tires, which belong to the category of solid waste, and which are discarded every year worldwide by more than three million, is a problem worldwide [1]. The properties that make them desirable as tires, namely durability, make their disposal and recycling difficult, since they are almost immune to biological degradation [2]. A feature of the application of this technology is the method of processing, without the use of cryogenic technologies, which avoids harmful emissions into the environment and preserves the developed and active surface of the crushed rubber powder. With this method of tire recycling, it is possible to ensure minimal harmful emissions, and sometimes practically their absence [3]. The source of carbon-containing materials can be textile cord, which are stored in landfills in sufficient quantities for their industrial use. Taking into account the complex chemical compositions of carbon-containing raw materials, obtaining products of specified properties and composition becomes an urgent task of both theoretical and practical importance [4]. Many years of tire operation experience shows that the quality of the cord has a decisive influence on the technical resource, maintainability and other quality indicators. The cord in the tire works in harsh conditions, being subjected to a variety of static and dynamic stresses, multiple strains of stretching, compression, bending, torsion, etc.The following brands of cords are produced by the industry: viscose, nylon, anide, acid, polyester, glass cord, metal cord [5].

Viscose cord is used in the production of tires for trucks and passenger cars, motorcycles, tractors and agricultural machinery [6]. Transitional pores are those in which capillary condensation takes place, and macropores have such large radii that the phenomenon of capillary condensation becomes impossible [7]. The cord threads are positioned at a certain angle of the plane drawn through the wheel axis [8]. Carbon burns out over the entire grain volume, which leads to the development of a porous structure of coal with a significant increase in the volume of micro- and transitional pores [9]. Due to their unique properties, extremely high chemical resistance, heat resistance, heat resistance and specific strength, carbon composites have found wide application [10].

Porous carbon materials are obtained by heat treatment (carbonation) and/ or activation (using various oxidants) of carbon-containing raw materials and have the ability to efficiently separate gas and liquid mixtures due to the dimensional and sorption effect. Such materials are widely used as various sorbents, catalyst carriers, nanocomposite materials, substrates in new generation current sources (lithium-ion batteries, supercapacitors, ionistors and fuel cells), etc.

For the first time, we have obtained nanosorbents from carbonaceous waste – textile cord, by the method of carbonation and steam-gas activation. The scheme for the production of carbon materials based on textile cord for the purification of the gas phase and wastewater is shown in Figure 1.

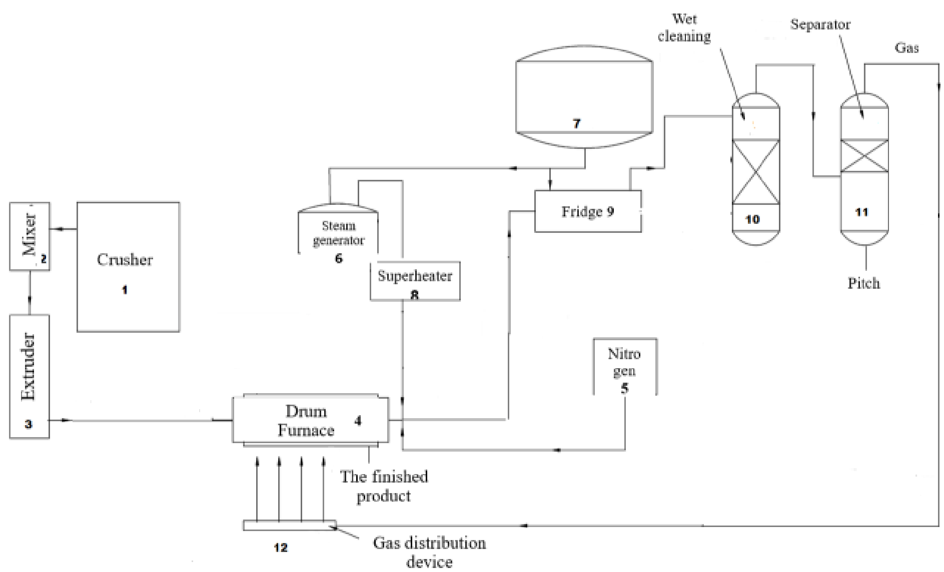


Figure 1 – Technological scheme of the installation for the production of adsorbent

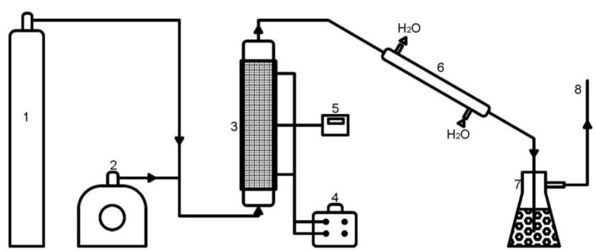


Figure 2 – Schematic diagram of a laboratory installation of steam and gas activation:

1 – gas cylinder (argon); 2 – steam generator; 3 – reactor; 4 – LATR; 5 – thermal sensor; 6 – direct refrigerator; 7 – flask for gas purification from resins; 8 – gas outlet

The work is aimed at developing a highly efficient technology and creating a pilot production of carbon nanoporous materials from waste materials. Carbon materials can be used to isolate and purify hydrogen from synthesis gas, release nitrogen from air; purify air from methane, monoxide and carbon dioxide; clean wastewater from toxic impurities, manufacture supercapacitors for lithium-ion batteries and catalyst carriers.

Materials and methods: The study used methods for obtaining carbon adsorbents (carbonation and activation) in laboratory conditions, methods for determining their physico-chemical and adsorption properties: determination of humidity, ash content, volatility, pH-aqueous extract, bulk density, adsorption activity by methyl orange, method for determining the total pore volume by water, elemental analysis, method BET for determining the specific surface area of the obtained materials, methods of water purification from oil and iron in laboratory conditions, methods of wastewater and gas purification from acidic components, etc.

Instruments were used: laboratory quartz reactor, rotary tubular furnace BR-12NRT, thermogravimetric analyzer (Thermostep Eltra), Crystallux gas chromatograph, Shaker Incubator ES-20/60, spectrophotometer (PD-303), pH meter, centrifuge, ultrasonic bath, muffle furnace, ultrasonic bath, scanning electron microscopy, X-ray-fluorescent analyzer, energy dispersion elemental analysis, etc.

Results: The technological process was carried out in two stages: carbonation (700°C) (to remove volatile components and obtain a large-porous structure evenly distributed throughout the volume) and activation (800°C) (to obtain a microporous structure). The experiments were carried out on a laboratory installation of steam and gas activation

A drawing of the laboratory reactor is shown in Figure 2.

Carbonation was carried out in an inert argon medium in the temperature range of 400-800 C for 60 minutes. Argon was supplied from a cylinder (1) to a reactor with a predetermined flow rate of 20 ml/min, which was installed using a flow meter. After the reactor, the gas was sent to the refrigerator (6), from where part of the condensed gas was poured into the flask (7) for purification from resinous substances. The unreacted gases were discharged into the ventilation system (8).

At the next stage of preparation of the adsorbent, to improve its adsorption properties, activation with water vapor (consumption 10 ml/min) was carried out at a maximum temperature with an exposure time of 60 minutes.

Table 1 shows the temperature dependences of the components of the gas obtained as a result of carbonation and activation of the nylon cord. The formation of combustible gas components (CO, H_2, CH_4) occurs in accordance with the basic chemical reactions:

$$2H_2O \rightarrow 2H_2 + O_2 - 115700 \text{ kkal} \quad (1)$$

$$C + H_2O \rightarrow CO + H_2 - 28150 \text{ kkal} \quad (2)$$

$$C + CO_2 \rightarrow 2CO - 38400 \text{ kkal} \quad (3)$$

$$C + 2H_2 \rightarrow CH_4 + 18600 \text{ kkal} \quad (4)$$

Textile cord under heat treatment above 200°C begins to decompose to form a combustible gas, which contains hydrogen, carbon monoxide, alkanes and alkenes.

Table 1 – Gas composition of carbonation and activation of textile cord

Process	T1,°C	Composition of gases about, %								
		O2	H2	CO2	N2	CH4	CO	Ethane	Ethylene	Propane + Propylene
Carbonation	200	37.003	0.046	0.126	32.911	0.166	0.040	0.005	-	0.589
	300	37.874	0.259	1.139	68.089	0.083	-	0.009	0.335	0.020
	400	43.355	0.237	2.219	66.944	0.045	-	0.036	0.680	0.054
	500	34.788	3.380	1.874	58.749	1.082	-	1.095	0.705	1.012
	600	54.526	10.091	1.671	36.023	2.570	-	0.918	0.565	1.012
Activation	700	30.469	3.873	0.411	76.123	0.746	-	0.137	0.036	0.162
	800	28.204	5.608	0.302	75.943	0.813	0.436	0.066	0.080	0.082
	800 excerpt	27.532	3.304	0.157	81.477	-	-	0.038	0.058	0.006

Table 2 – Material balance of carbonation and activation of textile cord

№	Incoming products	Content, %	№	Outgoing products	Content, %
1	Textile cord	71,49	1	Solid residue (adsorbent)	22,8
2	Water (us.steam)	28,51	2	Generator gas	67,22
	Total	100	3	Liquid product (water+resin)	9,98
				Total	100

The study used methods for obtaining sorbents, methods for determining ash content, humidity, volatility of raw materials (thermogravimetric analysis), their physico-chemical and adsorption properties: elemental analysis; gas chromatography; SEM (scanning electron microscopy), which determines the total volume, density of sorbents.

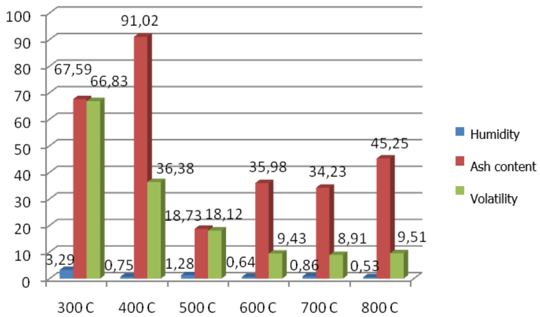


Figure 3 – Results on volatility, ash content and humidity of adsorbents from textile cord

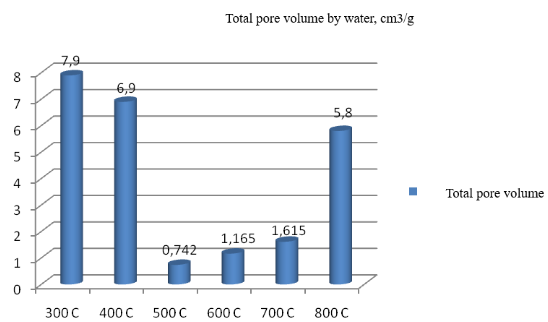


Figure 4 -Results of measuring the total pore volume of adsorbents in water at different temperatures

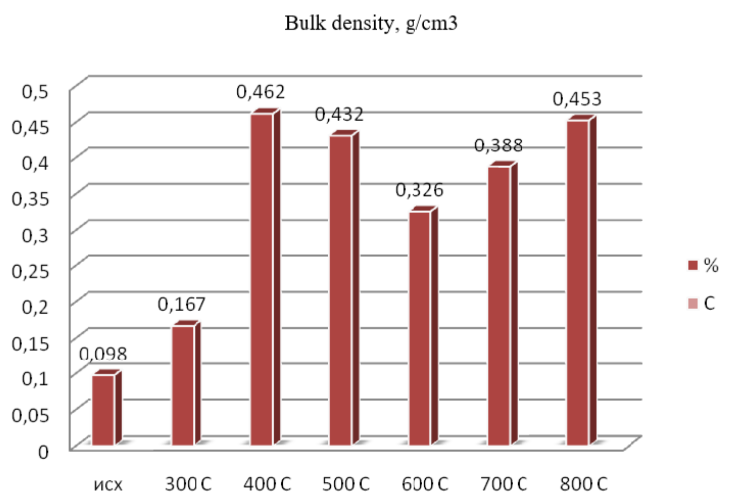


Figure 5 – Bulk density of adsorbents from textile cord

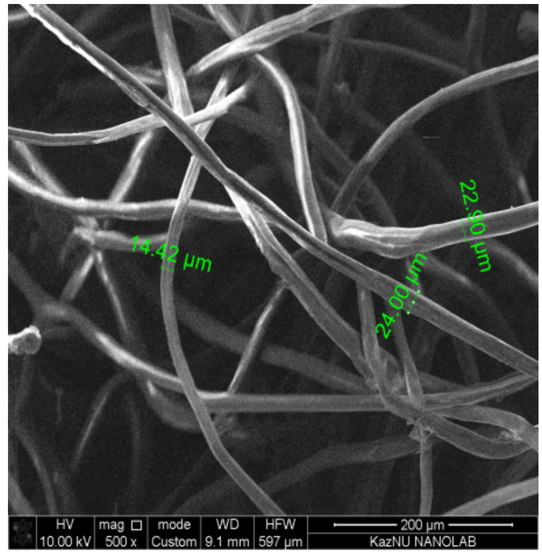
Based on the results of determining the total pore volume by water, porous materials obtained at 300°C, 400°C and 800°C showed the highest index from 5.8 to 7.9 ml/g. Therefore, this indicates a high degree of porosity of the adsorbent.

According to the results of determining the density of adsorbents, the lowest density of adsorbents was shown by the initial product (0.098 g /cm^3), also at 300°C, the value of which was 0.167 g /cm^3. The density of all adsorbents increased compared to the initial sample.

The study of the elemental composition, structure and dimension of the samples was carried out by energy dispersive X-ray spectroscopy on a SEM (Quanta 3D 200i) device with an energy dispersive analysis prefix from EDAX. The energy of the exciting electron beam in the analysis was 15 keV.

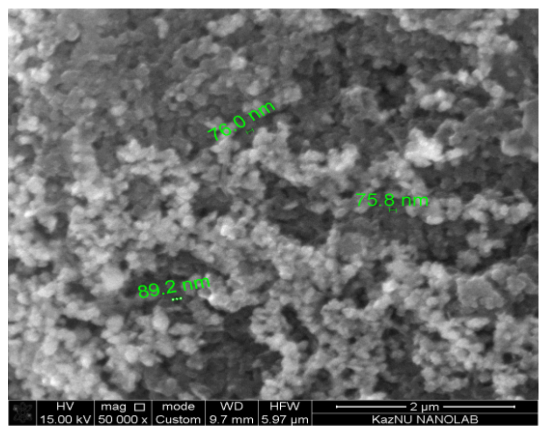
The elemental composition of the initial textile cord is shown in Figure 6.

Element	Wt%	At%
C	74.10	81.40
O	20.76	17.12
Na	0.32	0.18
Al	0.15	0.07
Si	0.29	0.14
S	0.60	0.25
Ca	0.34	0.11
Fe	0.90	0.21
Cu	0.62	0.13
Zn	1.91	0.38



(a)

Element	Wt%	At%
C	89.64	93.71
O	6.23	4.89
Na	0.86	0.47
Al	0.08	0.04
Si	0.20	0.09
S	0.29	0.13
Ca	0.49	0.19
Fe	0.05	0.02
Cu	0.30	0.09
Zn	0.32	0.07



(b)

Figure 6 - SEM images of the original (a) and activated (b) textile cord

In Figure 6 (a), fiber particles with a diameter of 10 to 25 microns are clearly visible, the structural elements take the form of fibrils – filamentous formations.

The results of the analysis of micrographs show (Fig.6 (b)) that after heat treatment, the surface structure changes with smaller particle sizes (up to ~145 nm), fine carbon nanoparticles with a diameter from 70 to 600 nm were formed, this may be due to the fact that as a result of carbonization and activation, the forming reactively-capable radicals interact with each other to form new substances. The nucleation and growth of ordered carbon during the heat treatment of textile cord can occur by self-organization of carbon nanoparticles without the participation of mesophase, however, additional research is required to clarify this issue.

In the laboratory of the Institute of Coal Chemistry and Technology LLP, the obtained carbon nanoporous materials were tested to purify gases (composition: H_2S, CO, CO_2, CH_4, N_2, H_2) from harmful substances H_2S, CO_2, N_2 to obtain mainly combustible components CO, CH_4, H_2. The results of the elemental analysis before and after gas purifications with determination of the degree of purification are presented in Table 3.

Table 3 – Approbation of adsorbents from textile cord for gas purification

Name	Gas concentration %					Degree of purification, %				
	H2	CO2	CH4	CO	H2S	H2	CO2	CH4	CO	H2S
Crude source gas	46,817	2,091	7,05	7,546	0,045	-	-	-	-	-
Activated Textile cord	0,165	0,075	0,151	0,047	0,007	99,6	96,4	97,8	99,3	84,4

Conclusion: Known methods of cleaning natural objects are not always effective, and are often environmentally unsafe. The use of organic waste for wastewater and atmospheric treatment is acceptable from an economic and environmental point of view, but as a rule, such materials do not have sufficiently capacious sorption properties and therefore they need to be carbonized and activated. As a result, sorbents with a surface different from the original mineral are obtained and combine the useful characteristics of the starting material and synthetic sorbents.

In the course of the work done, a laboratory installation for the production of adsorbents was assembled, work was carried out to improve the methodology and technology for the production of nanosorbents, with the determination of optimal technological parameters. The physicochemical properties of the feedstock and the obtained adsorbents (ash content, humidity, volatility, bulk density, total pore volume, elemental composition) were also studied. The resulting product has been tested for gas purification. The degree of gas purification (%) was H_2-99.6; CO_2-96.4; CH_4-97.8; CO-99.3; H_2S-84.4.

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