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Laboratory of new technologies for processing hydrocarbon raw materials

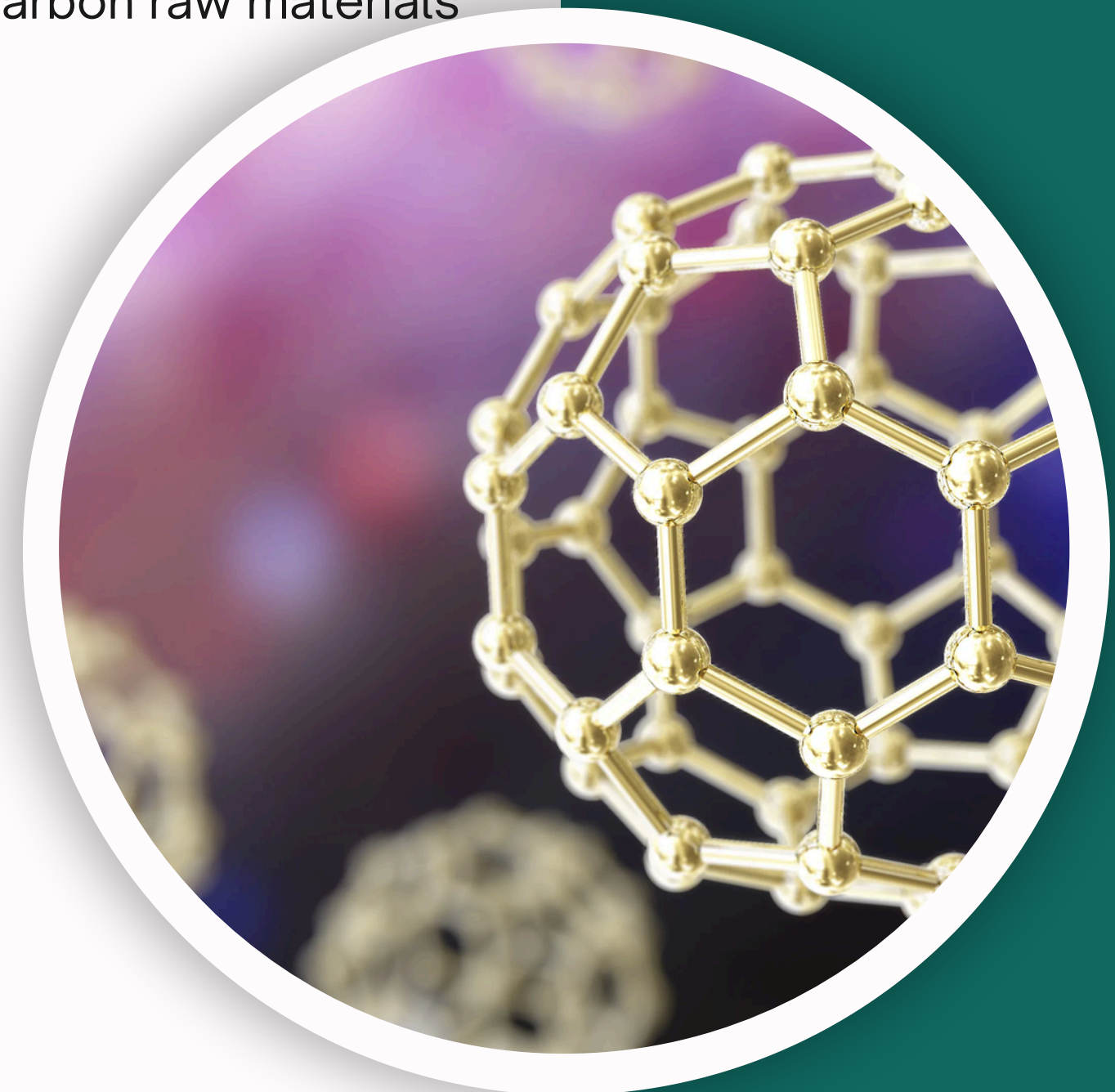
**Қазақстан көмірі негізінде алынған көміртекті
сорбенттер мен наноматериалдар, олардың
қолданылуы**

**Carbon sorbents and nanomaterials
from Kazakhstan coals, their scope of
application**

**Углеродные сорбенты и наноматериалы из
Казахстанских углей, сфера их применения**

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KazNANS, leading researcher at the Institute of Coal
Chemistry and Technology LLP





01



This presentation will be devoted to materials for the production of carbon sorbents and nanomaterials based on Kazakhstani coals and their scope of application.

Coal from Kazakhstan is unique in its chemical composition.



02

03



In the laboratories of our Institute, the physico-chemical compositions of coals from the Shubarkol, Ekibastuz, Karaganda, Maikuben, Oy-Karagai, Kushmurn, Korzhunkul basins and other open pits were studied

on the basis of which the applicability of these coals to a specific technology was determined and various products were obtained in a bench installation, including carbon sorbents, nanomaterials such as nanofibers, nanotubes, graphene-like materials, nanocomposite materials, etc.



04

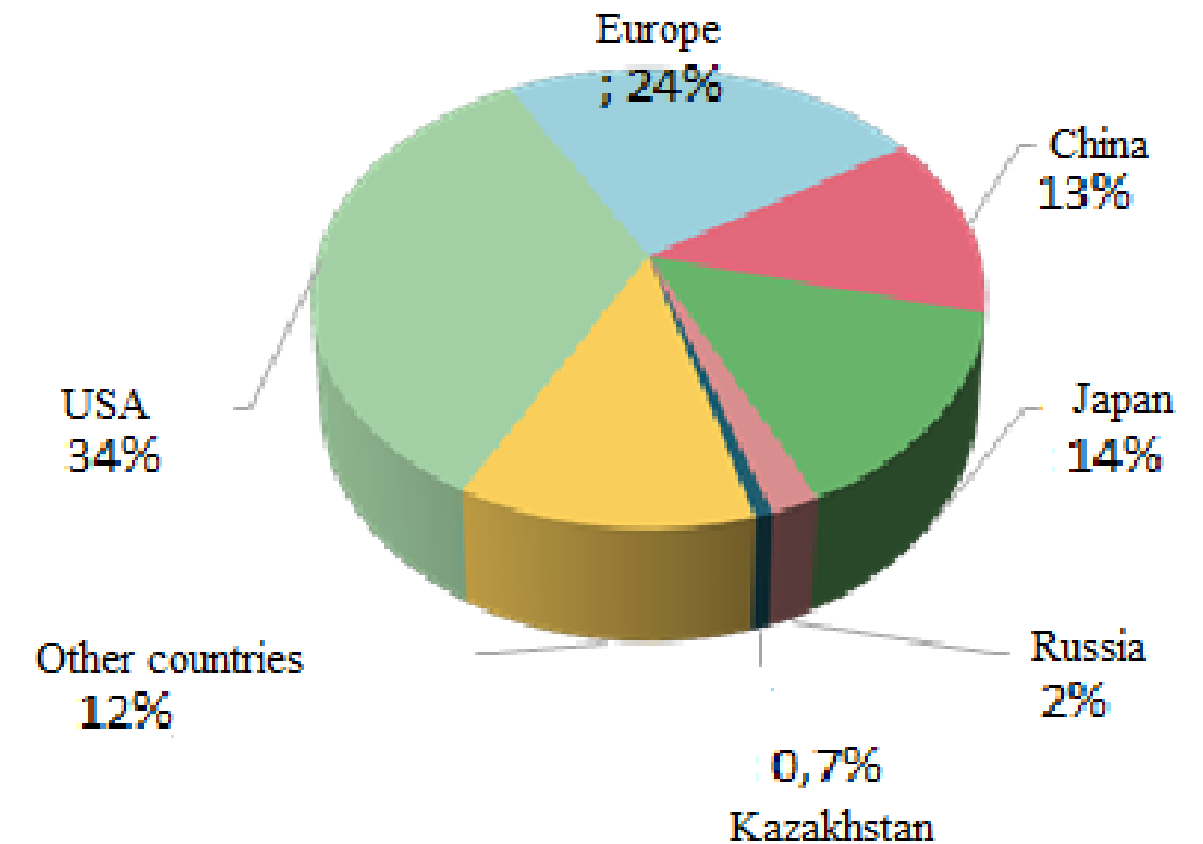
SOCIAL AND ECONOMIC EFFECT

As a result of the study in Kazakhstan, for the first time, domestic technologies for obtaining highly efficient porous adsorbents will be developed and introduced. When implementing the proposed technology, the possibility of import substitution of similar types of products significantly increases, which is especially important for our country.

The cost of 1 ton of adsorbent on the world market ranges from **3 to 200 thousand US dollars** and exceeds the cost of raw materials several hundred times

Currently, Kazakhstan is forced to purchase all types of sorbents abroad. Sorbents are currently purchased in Russia, Japan, USA, Germany and China at inflated prices

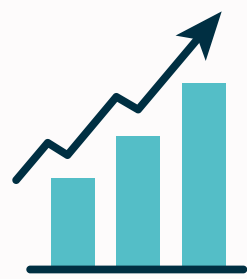
The well-established production of carbon sorbents will provide the water economy of the Republic of Kazakhstan with effective and inexpensive sorbents of domestic production, which will contribute to the improvement of the environment and water resources, which will ultimately have a beneficial effect on the health of the population.



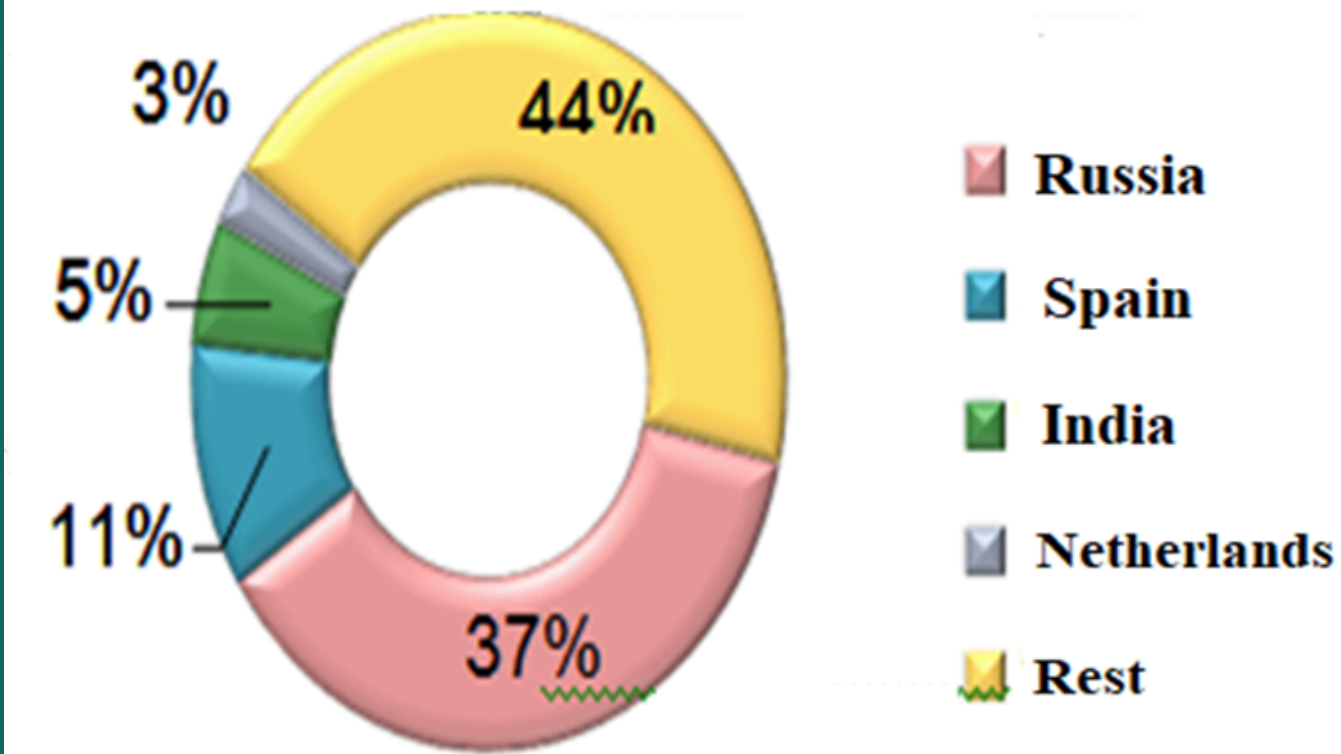
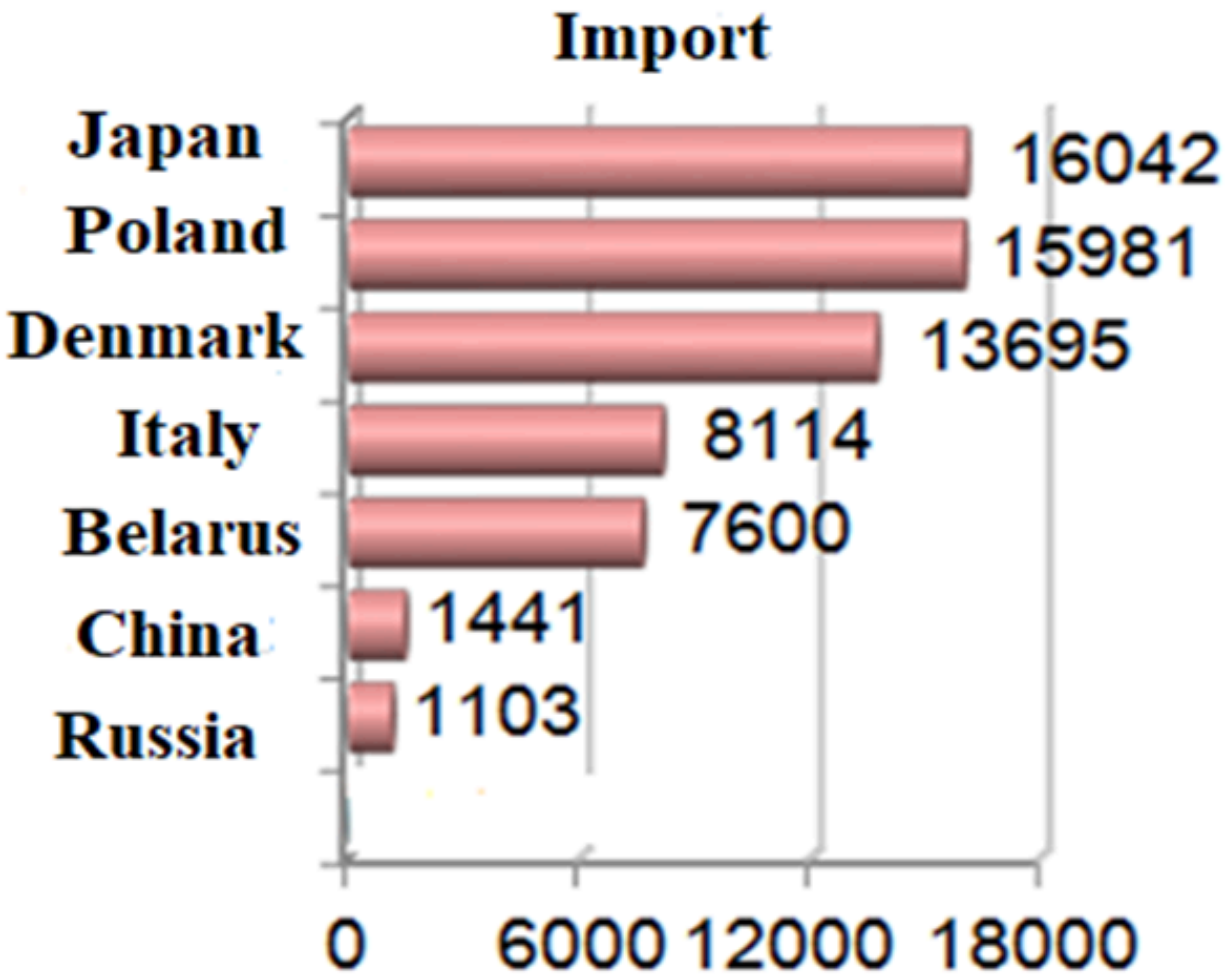
In the world market, the main producer of activated carbon is the United States, which accounts for 34% of the annual production of this product category. Europe, with a share of 24%, ranks second in terms of production of activated carbon.

Kazakhstan accounts for only 0.7% of the world production of activated carbon, Russia - 2%.

PRICE OVERVIEW



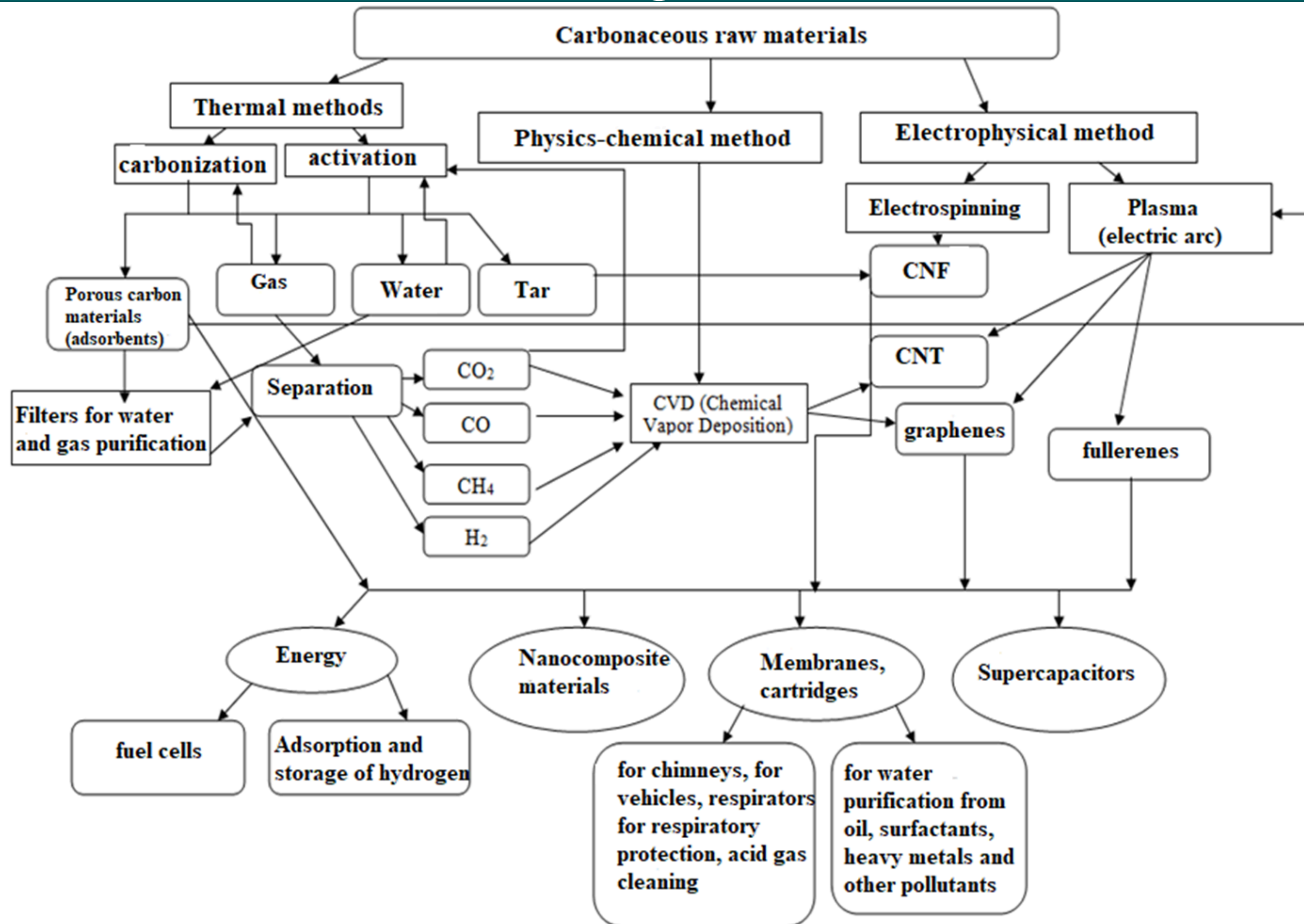
Kazakhstan imports the most expensive activated carbon from Japan - \$16,000 per ton. From Russia, as the main importer, activated carbon is imported at an average cost of \$1,103 per 1 ton of products.



In the medium term, the Kazakh activated carbon market will grow by at least 10-12% per year, primarily due to stricter environmental standards. In 2021, the market volume reached 10.7 thousand tons. In addition to the high demand for activated carbon for Kazakhstan as a whole, experts note the fact that the demand for high-quality activated carbon is growing.

The high quality of the activated adsorbent depends primarily on the raw materials used, as well as the technologies for its production. In Kazakhstan, against the background of significant import dependence of the activated adsorbent market, including high-quality ones, there is an urgent need for the development of domestic production, as well as the introduction of the latest processing technologies.

Scheme for obtaining carbon nanomaterials

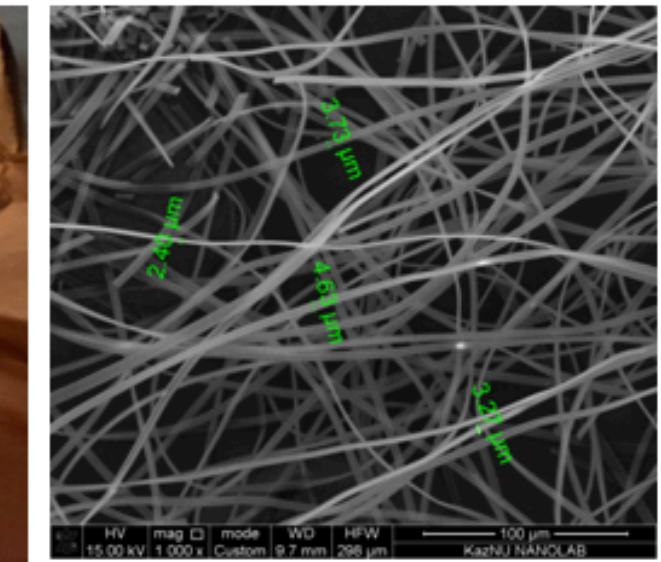


Today, the materials research community continues to discover and exploit new low-dimensional allotropes of graphite at a rate perhaps unprecedented in history. In this context, carbon nanotubes (CNTs), and more recently graphene, have become versatile platforms for the exploration of new materials and device architectures and are finding their applications in almost all areas of the research world, including conductive polymers, transparent electrodes, chemical sensors, and high-throughput technologies. frequency devices, optoelectronic sensors, alternative energy and biotechnology systems, to name a few.

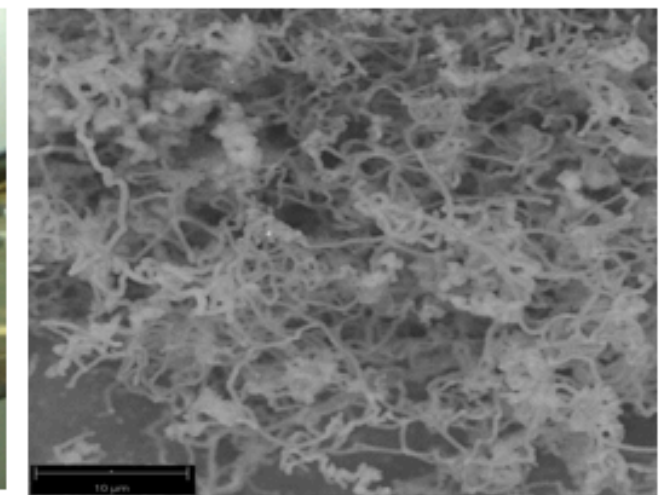
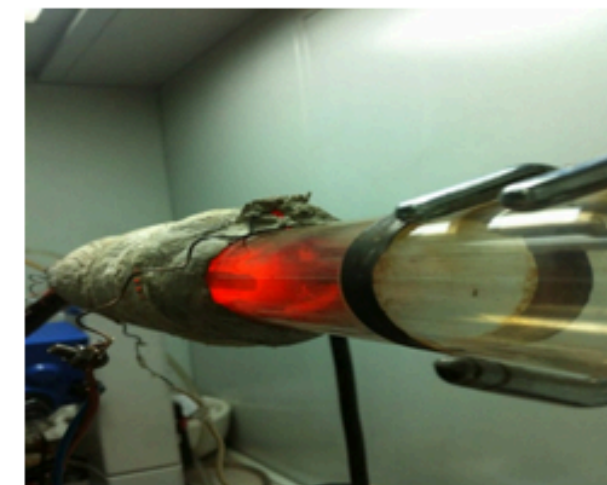
- Scientists from the Institute of Coal Chemistry and Technology LLP (Astana) have developed and manufactured laboratory and semi-industrial carbonization and activation installations, developed methods for producing carbon and composite PCM, and developed experimental samples of carbon nanomaterials. The resulting samples were tested for gas and wastewater and drinking water purification, for soil purification from pesticides, as electrode materials, for hydrogen storage, etc. The scientific novelty of our work lies in the creation of a domestic technology for processing carbon-containing mineral raw materials with high added value by carbonization and vapor-gas activation, impregnation with alkali, salt, electron beam irradiation, modification with nanoparticles, microspheres, silicon oxide, humic acid, which is an innovative approach for the synthesis of PCM.



Adsorbents based on coals of Kazakhstan



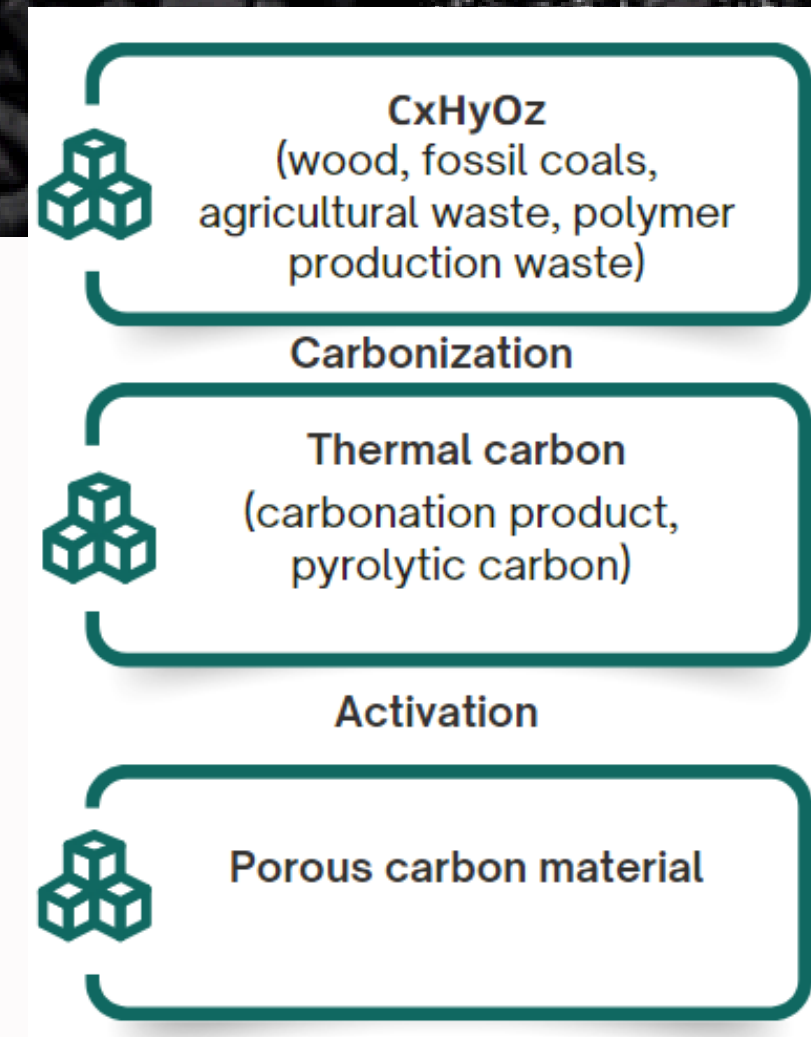
Carbon nanofiber based on coal tar



Carbon nanotubes produced by CVD

Activated carbon

Activated carbon (activated carbon, "carbolene") is a porous substance that is obtained from various carbon-containing materials of organic origin. Activated carbon contains a huge number of pores and therefore has a very large specific surface area per unit mass, as a result of which it has high adsorption.



high-temperature pyrolysis (carbonization) of solid carbon-containing raw materials (wood, natural coals, polymer materials) followed by treatment of the carbonization product with water vapor, carbon dioxide and other substances (activation stage)

APPLICATION OF ACTIVATED ADSORBENTS

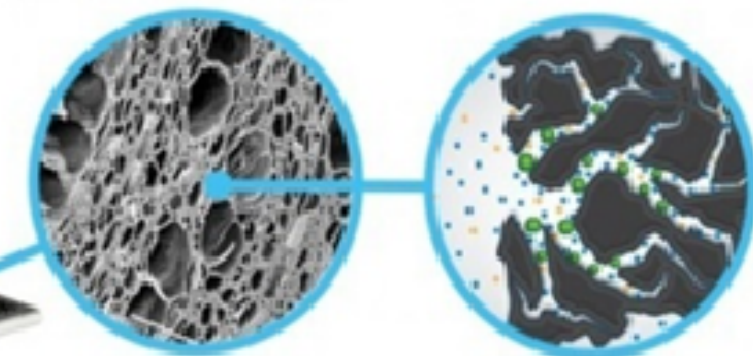
FILTERS FOR WATER PURIFICATION:



Scope of application: metallurgical enterprises, medicine, food industry, oil and gas complex, energy enterprises, as carriers of catalysts, electrode materials for the manufacture of supercapacitors and lithium-ion batteries, purification, separation and extraction of various substances, both liquid and gaseous.



FILTERS FOR GAS CLEANING:



The main part of the gases is retained in mesopores and micropores. Macropores retain the largest molecules and serve as transport channels and adsorption space.

Pilot semi-industrial installations for obtaining PCM



Rotary-drum furnace



Rotary pulsation apparatus and ultrasonic reactor



Retort furnace

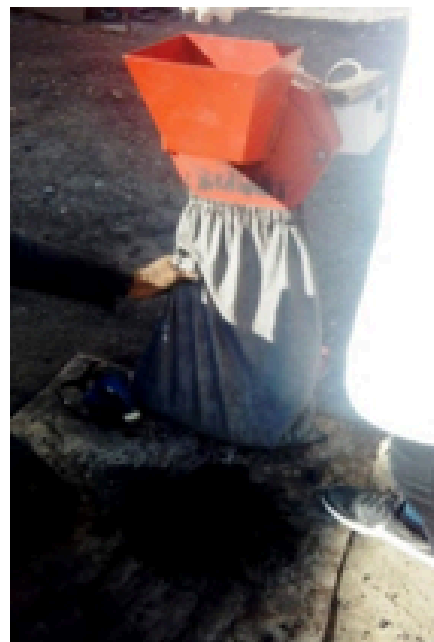


Experimental laboratory pulse-inertial installation

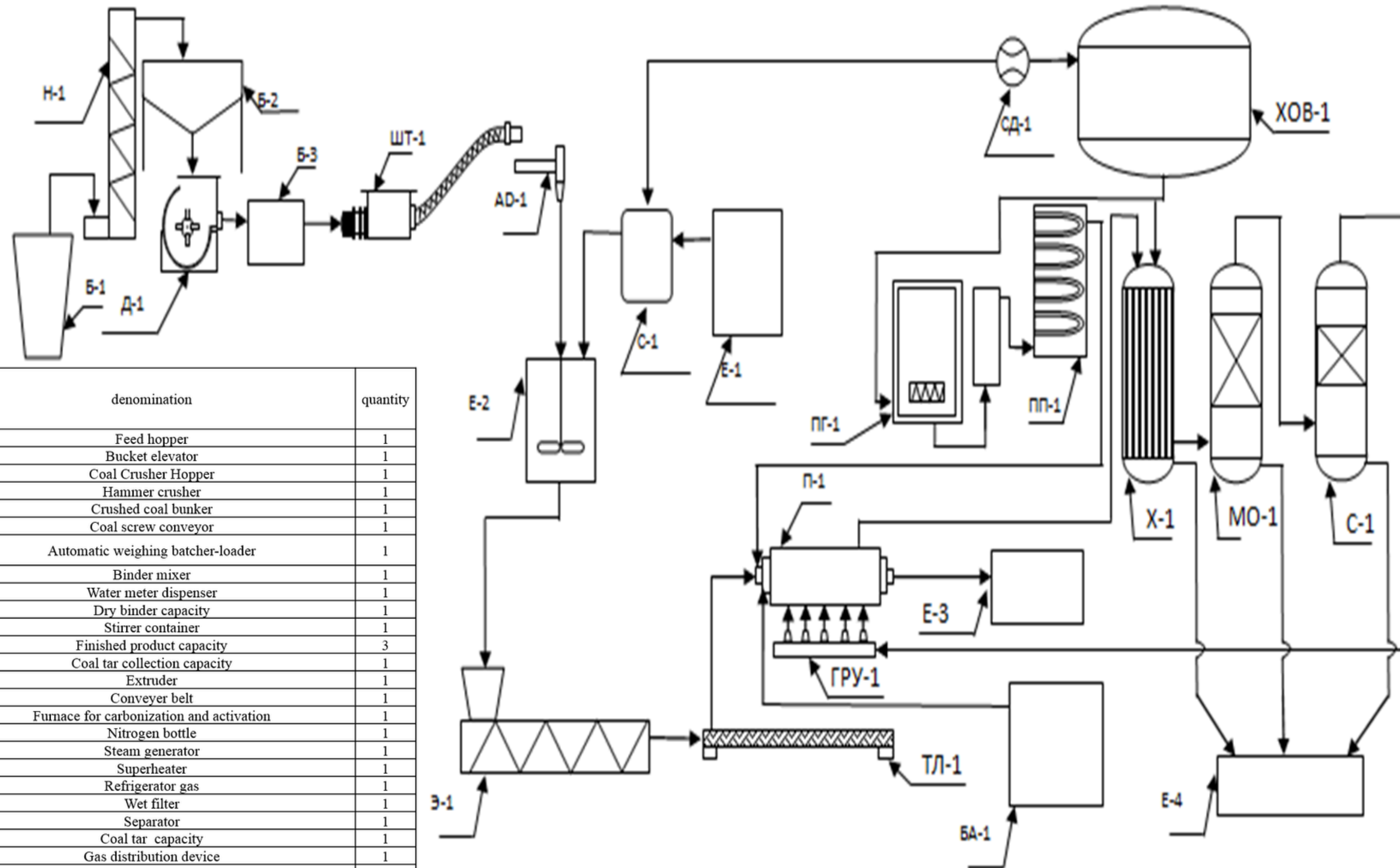
Obtaining PCM at pilot semi-industrial installations

Samples of activated carbon were obtained at the Institute of Coal Chemistry and Technology LLP (Astana) by carbonization (at 700 °C in nitrogen) and activation with water vapor for 1 hour. To obtain activated adsorbents, the initial product was previously ground to a fraction of 0.1 mm, then cylindrical samples (d = 0.2-0.3 cm) were obtained from it on an extruder. Then the product passed the stage of heat treatment (carbonization) and activation in an inert nitrogen atmosphere on a rotary drum furnace (with a volume of 50-100 kg).

The object of the study is carbon materials from the coals of the Shoptokol, Sarykol, Saryadyr deposits (five-meter, Sputnik, Nadezhny coal seams), Kushmuryn, Mamyt, Shubarkul (the Central mine) , "Oi-Karagai", "Zhalyn" and others.



Hardware design of a production facility for obtaining activated adsorbents



designation	denomination	quantity
B-1	Feed hopper	1
N-1	Bucket elevator	1
B-2	Coal Crusher Hopper	1
D-1	Hammer crusher	1
B-3	Crushed coal bunker	1
SHT-1	Coal screw conveyor	1
AD-1	Automatic weighing batcher-loader	1
S-1	Binder mixer	1
SD-1	Water meter dispenser	1
E-1	Dry binder capacity	1
E-2	Stirrer container	1
E-3	Finished product capacity	3
E-4	Coal tar collection capacity	1
EH-1	Extruder	1
TL-1	Conveyer belt	1
P-1	Furnace for carbonization and activation	1
BA-1	Nitrogen bottle	1
PG-1	Steam generator	1
PP-1	Superheater	1
H-1	Refrigerator gas	1
MO-1	Wet filter	1
S-1	Separator	1
E-10	Coal tar capacity	1
GRU-1	Gas distribution device	1
KHOV-1	Chemical water treatment unit	1

The results of the physicochemical characteristics of adsorbents (AC) based on coals from the Kazakhstan deposit

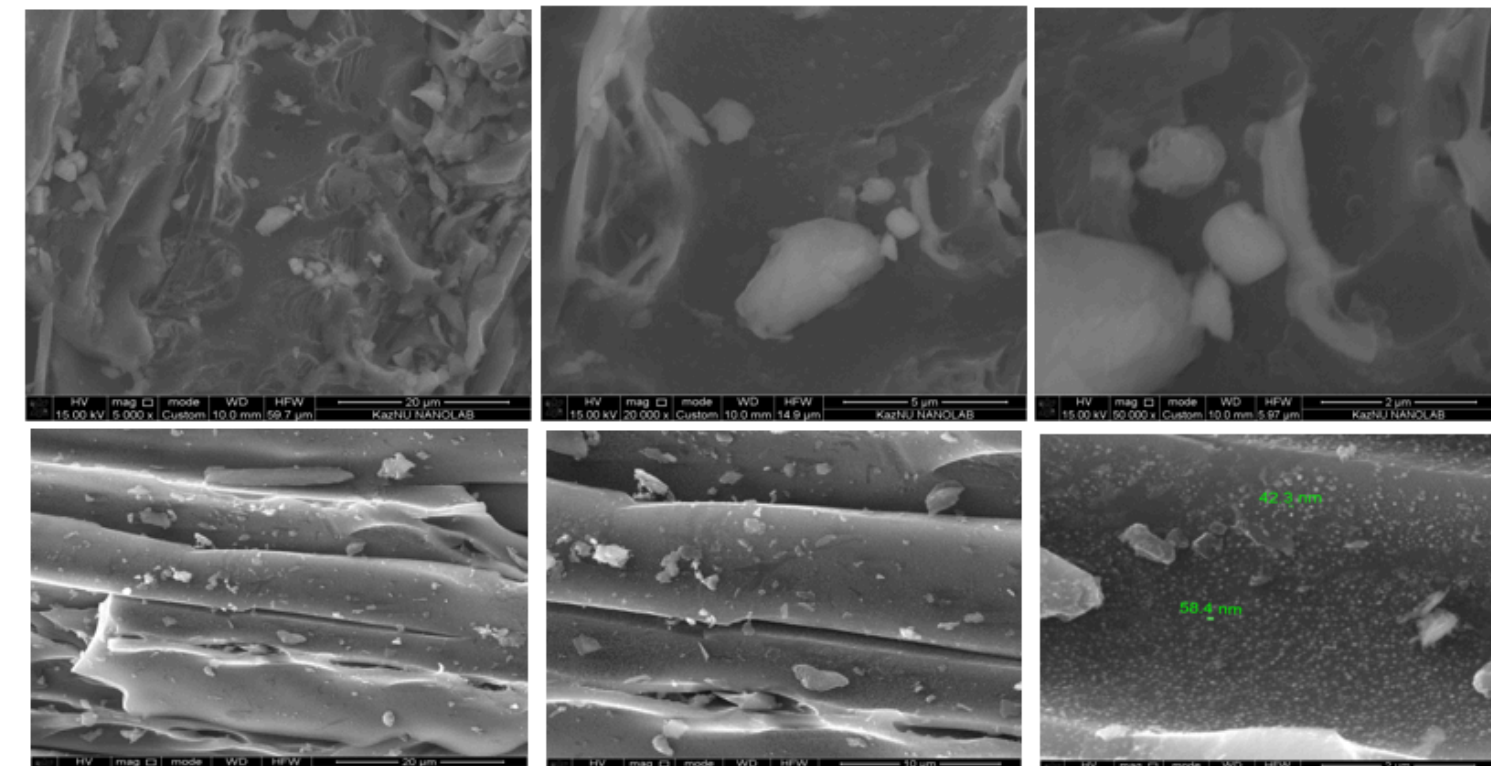
Name AC	W _т , %	A _т , %	V _д , %	Total pore volume in water, cm ³ /g	Bulk density, ρ g/cm ³	pH of water extract	Adsorption activity for methyl orange, mg/g	Specific surface, m ² /g	Specific pore volume, cm ³ /g
"Shoptokol"	0,56	25,08	27,96	0,448	0,536	9,51	57,5	348,99	-
"Sarykol"	0,75	70,52	5,39	1,099	0,640	9,20	26,00	179,39	-
«Pyatimetrovy»	0,62	27,14	4,05	0,420	0,561	7,30	26,15	148,53	0,064
«Sputnik»	0,26	53,34	5,11	0,570	0,603	8,26	20,05	148,85	0,064
«Nadezhny»	0,76	40,93	6,71	0,660	0,648	8,47	22,35	294,44	0,126
«Mamyt»	1,25	32,13	14,14	0,608	0,697	8,22	41,50	364,59	0,156
«Shubarkul»	3,30	11,25	5,50	0,864	0,637	8,53	35,00	442,81	-
«Kushmurun»	1,25	38,74	8,32	0,560	0,517	10,94	20,00	343,63	0,147
«Oi-Karagai»	2,83	26,571	19,12	0,5	0,603	10,34	52,50	266,86	-
«Bogatyr»	1,93	32,37	7,30	0,67	0,664	6,25	36,80	11,552	0,005

The results of the study of the elemental composition of adsorbents (AC) based on coals from the Kazakhstan deposit

Name	The content of elements, wt. %										
	C	O	Na	Mg	Al	Si	K	Ca	Fe	Ti	S
"Shoptokol"	60,69	19,44	-	0,58	5,29	10,09	1,05	0,75	1,60	-	-
"Sarykol"	52,42	19,81	0,44	0,47	4,87	10,32	1,85	1,39	7,14	0,55	0,04
«Pyatimetrovy»	88,60	8,22	-	-	0,22	1,43	-	-	-	1,32	0,21
«Sputnik»	59,98	22,62	-	-	3,73	13,67	-	-	-	-	-
«Nadezhny»	61,11	21,17	-	-	8,05	9,24	0,43	-	-	-	-
«Mamyt»	77,60	9,94	0,37	-	3,15	2,69	-	1,97	3,45	-	0,82
«Shubarkul»	87,58	9,92	0,14	0,17	0,55	0,54	-	0,64	0,31	-	0,17
«Kushmurun»	82,96	5,77	0,41	0,91	1,21	0,47	-	6,51	0,92	-	0,30
«Bogatyr»	78,81	12,30	-	-	-	2,58	4,85	-	-	1,30	-

Physicochemical characteristics of carbon nanosorbents from coals of the Shoptykol deposit

Denomination	Humidity (W _r), %	Ash content (A _r), %	Volatility (V ^d), %	Total pore volume by water, cm ³ / g	Bulk density ρ, g / cm ³	pH of the aqueous extract	Methyl orange adsorption activity, mg / g	Specific surface area, m ² / g (single point BET method)	Specific pore volume, cm ³ / g
The activated adsorbent "Shoptykol": KOH (50%) (1:1)	21.84	25.94	31.13	0,67	0,428	10,22	48,00	785,783	0,337
The activated adsorbent "Shoptykol": KOH (50%) (1:0,5)	14.35	32.89	23.74	0,71	0,508	10,56	41,00	437,692	0,187
The activated adsorbent "Shoptykol": (oxidized.): KOH (50%) (1:1)	24.88	6.24	31.26	0,56	0,402	9,13	34,00	1058,146	0,453
The activated adsorbent "Shoptykol": (oxidized.): KOH (50%) (1:0,5)	15.92	7.04	34.46	0, 61	0,427	9,06	35,10	1046,810	0,448
The activated adsorbent "Shoptykol": (oxidized.): KOH (50%) (1:0,5)	15.92	7.04	34.46	0, 61	0,427	9,06	35,10	1046,810	0,448
The activated adsorbent "Shoptykol" (700°C)	0,53	56,79	4,87	0,260	0,566	9,91	-	287,834	-
The activated adsorbent "Shoptykol": CNT (1 %)»	3,08	27,21	15.57	0,70	0,473	8,31	60,75	119,271	0,051

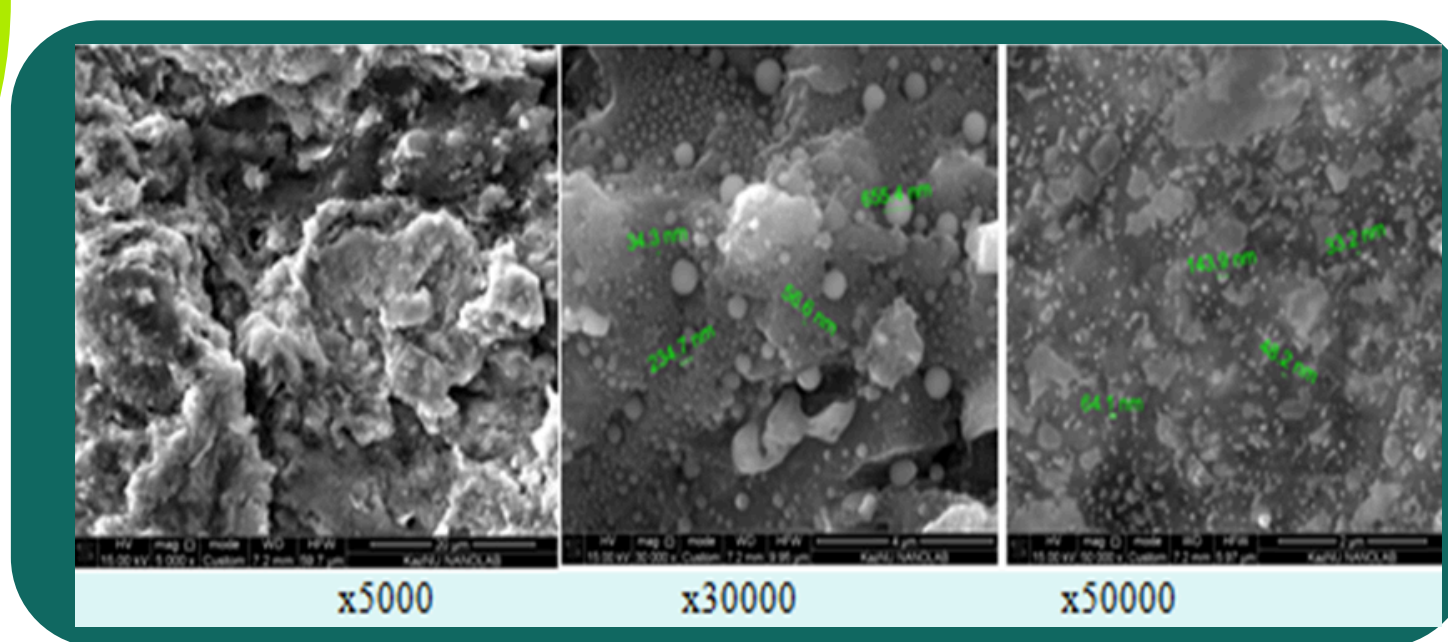


Electronic microscopic images of the initial (a) and activated adsorbent (b) based on coal from the Shoptykol deposit (Maikuben basin)

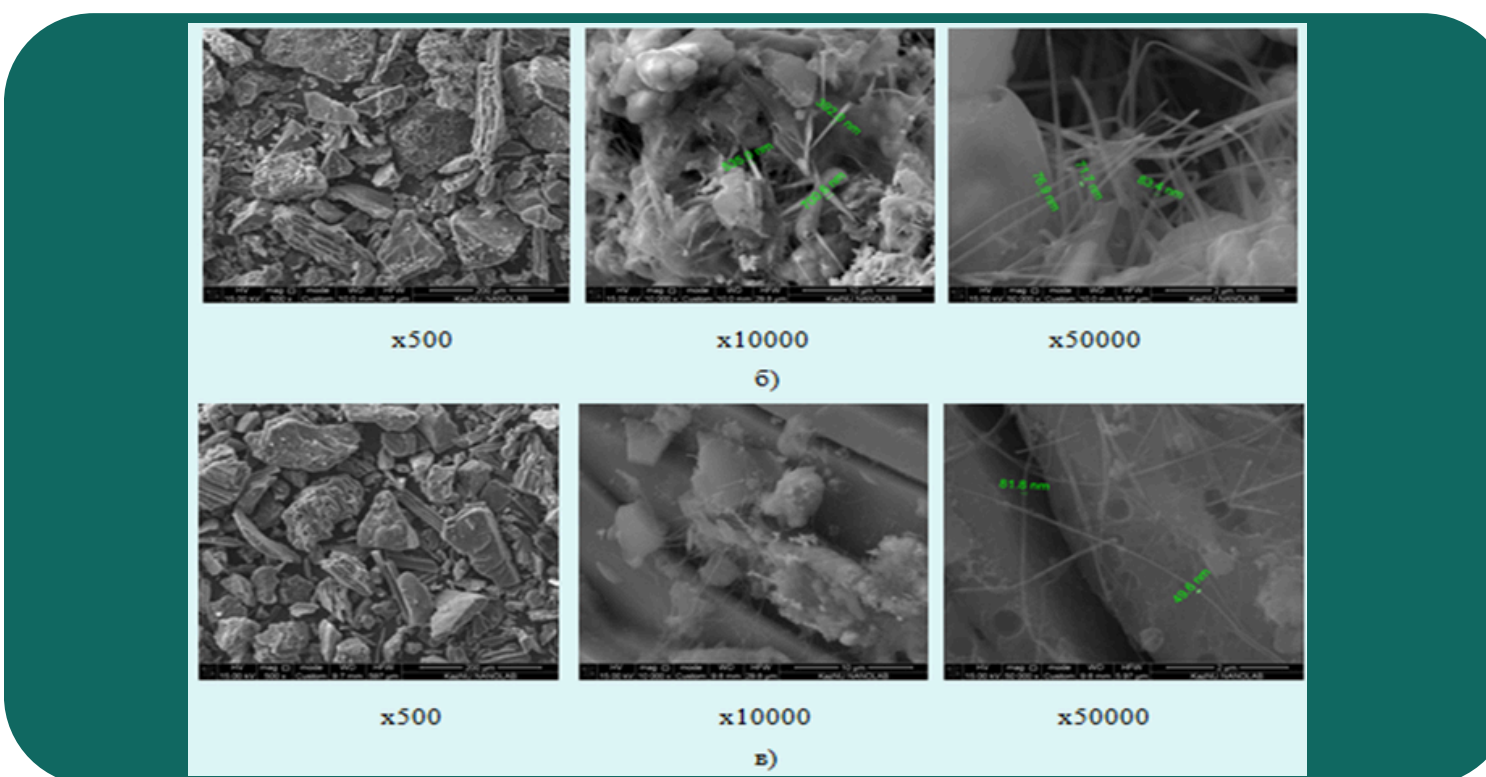
It can be seen in the adsorbent figures that finely dispersed carbon nanoparticles with a diameter of 40 to 100 nm were formed on the sample surface, this may be due to the fact that, as a result of carbonization, the forming reactive radicals interact with each other to form new substances.

The most likely reason for the appearance of nanoparticles on the surface layer is synthesis from the gas phase. The nucleation and growth of ordered carbon during carbonization of coal can occur through the self-organization of carbon nanoparticles without the participation of the mesophase.

In some places, a lamellar-stepped cleavage surface is observed



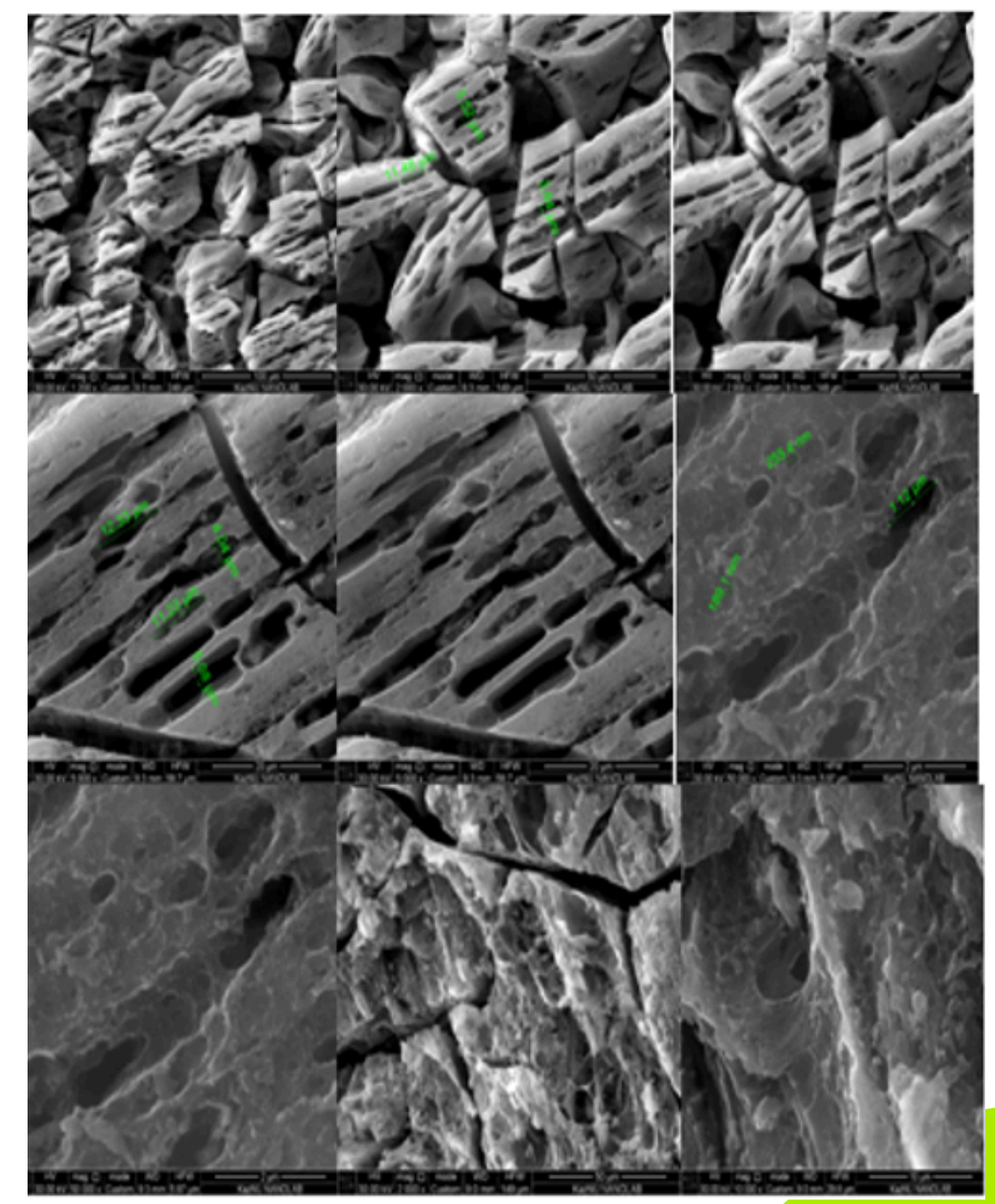
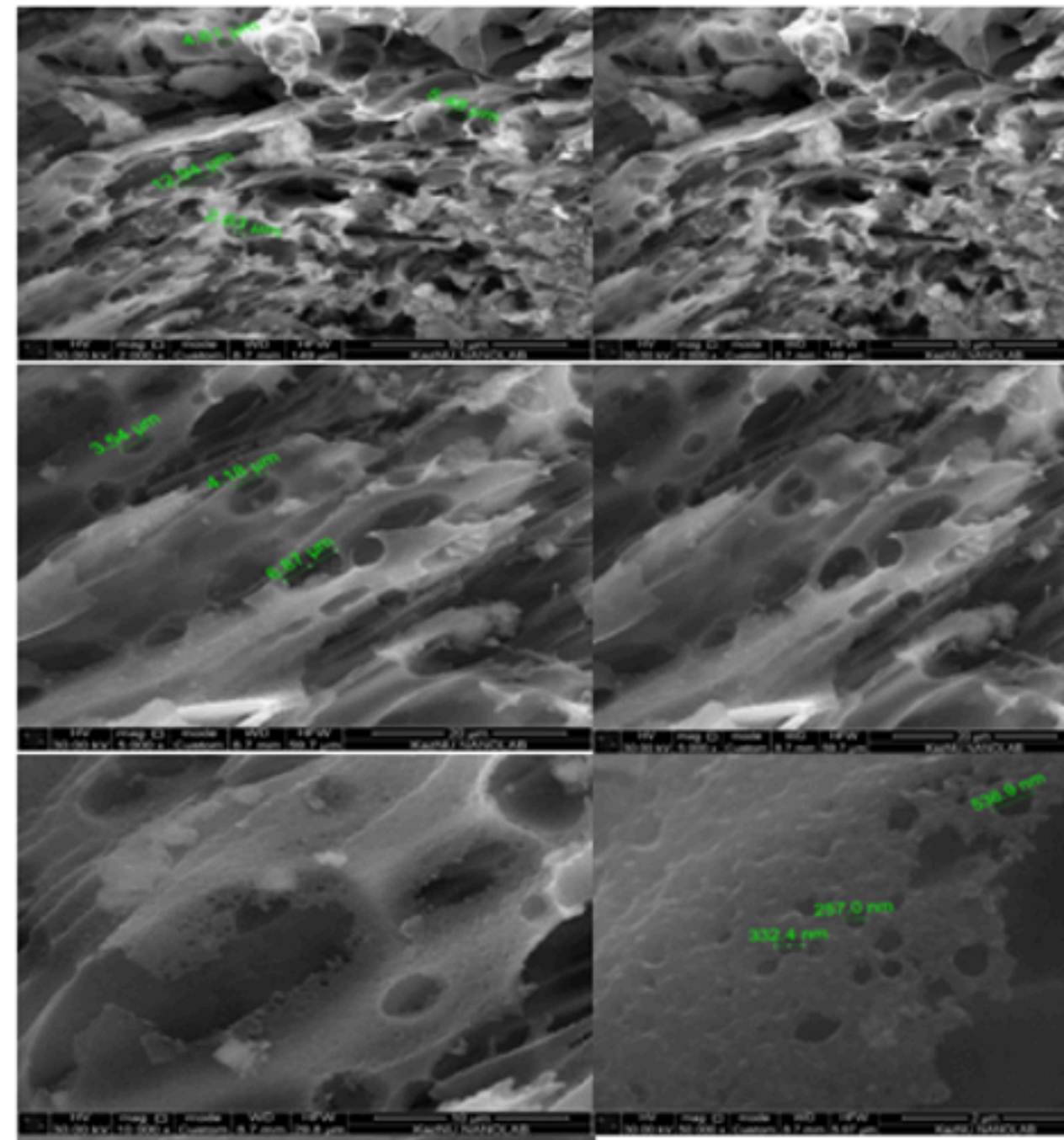
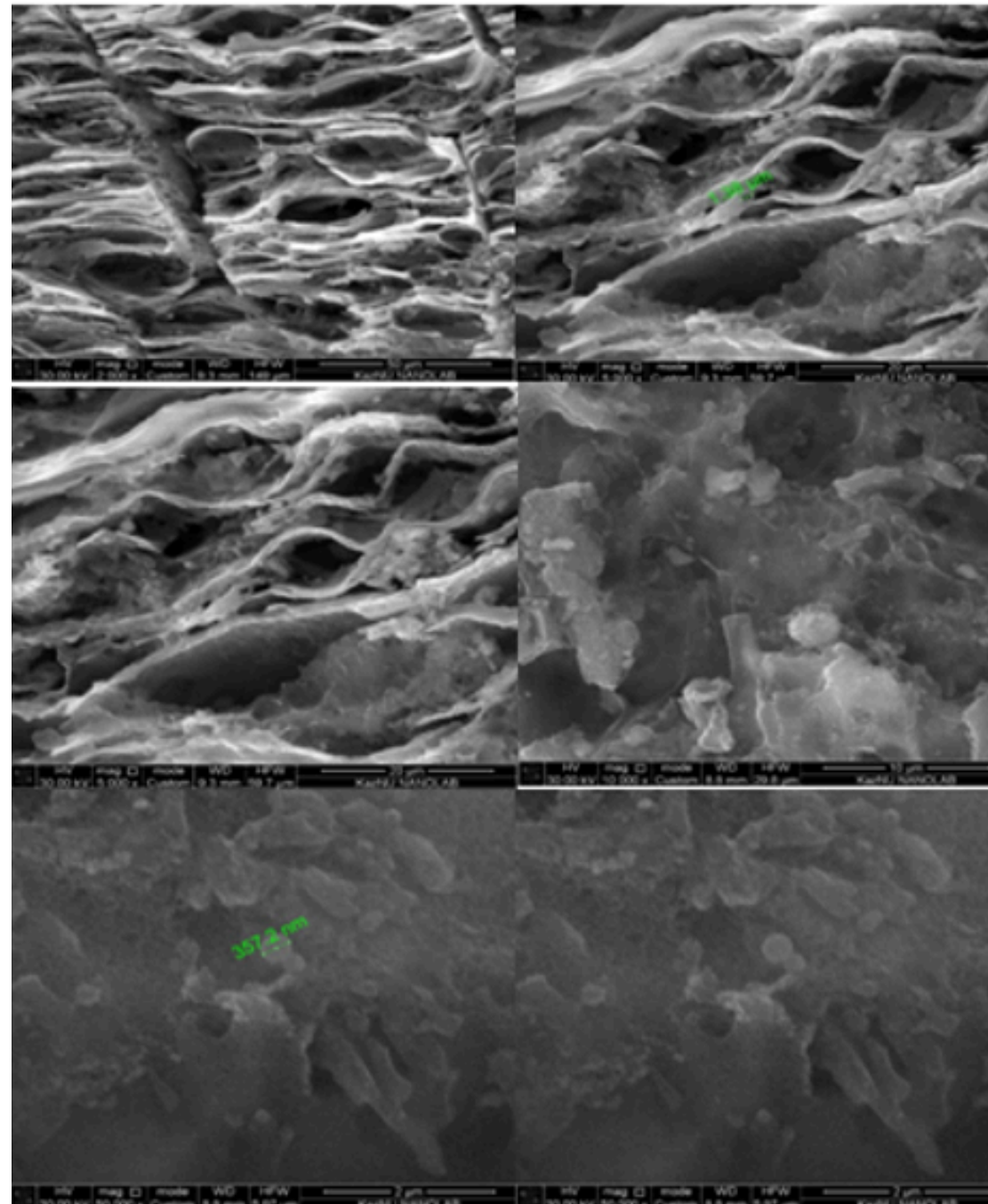
Electron microscopic images of activated adsorbent based on coal from the Shoptykol deposit, oxidized (Maikuben basin)



Electron microscopic images of the activated adsorbent "Shoptykol" (oxidized): KOH 1:1 (a) and "Shoptykol" (oxidized): KOH 1:0.5 (b)

An electron microscopic image of a carbon material, where particles of carbon nanotubes with a diameter from 50 to 85 nm are clearly visible. Thus, as a result of high-temperature carbonization processes of oxidized coal from the Shoptykol deposit, porous carbon nanomaterials were obtained with a specific surface of 1058.146 m²/ g, 1046.810 m² / g and a specific pore volume of 0.453 cm³ / g, 0.448 cm³ / g for the ratio 1: 1 and 1: 0.5, respectively. In this regard, the nanomaterial can be considered promising, in particular, as an adsorbent, superconducting materials, capacitors and fuel cells.

Porous carbon material based on ash and slag waste "Maikuben" (boiler house Akmol)



Study of the influence of an electron beam (at an industrial electron accelerator) on nanocomposite materials

Employees of the production and technological department of JSC "Park of Nuclear Technologies" carried out radiation treatment of carbon nanocomposite materials, in accordance with the terms of reference.

Experimental part: Before carrying out the radiation treatment to assess the dose and temperature distribution in the samples, the process was simulated using the ModeRTL.

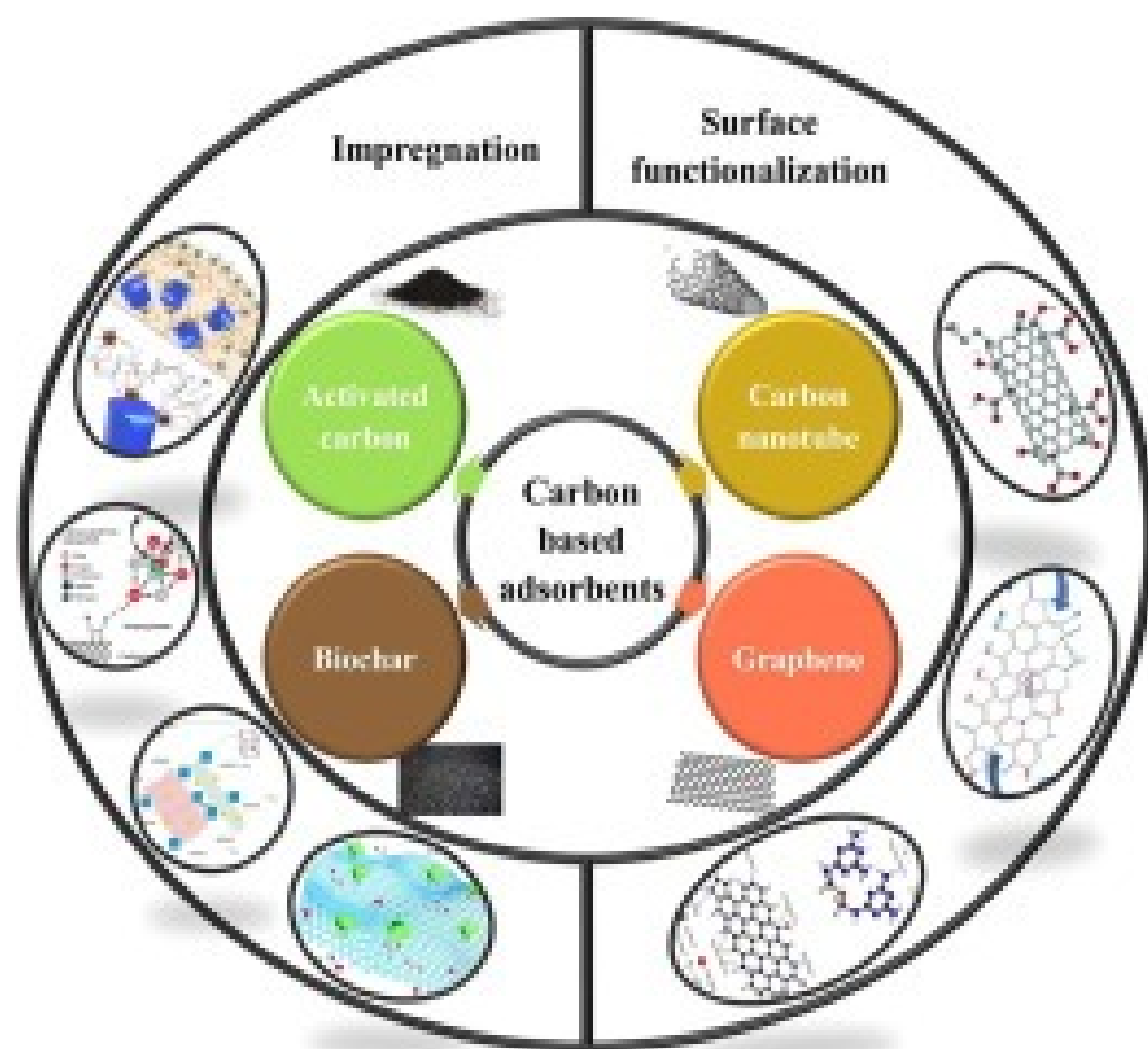


Рисунок N.1 - Гранулированный уголь «Шоптыколь»



Рисунок N.2 - Активированный адсорбент «Шоптыколь»



Рисунок N.3 - Гранулированный уголь «Шубарколь»



Рисунок N.4 - Активированный адсорбент «Шубарколь»



Рисунок N.5 - Гранулированный уголь «Шоптыколь:Шубарколь» (6:4)



Рисунок N.6 - Активированный адсорбент «Шоптыколь:Шубарколь» (6:4)



Рисунок N.7 - Гранулированный уголь «Шоптыколь:KON (50%) (1:0,5)»



Рисунок N.8 - Активированный адсорбент «Шоптыколь:KON» (1:0,5)



Рисунок N.9 - Гранулированный уголь «Шубарколь:KON (50%) (1:0,5)»



Рисунок N.10 - Активированный адсорбент Шубарколь:KON (50%) (1:0,5)»



From the analysis of the calculated data, the following technique was developed:

- The samples were repackaged in a polyethylene bag 40x40 cm in size, which ensured the required value of the electron path equal to 1.25 g / cm² and made it possible to perform one-sided processing of the samples



Repackaging of samples in a polyethylene bag 40x40 cm in size

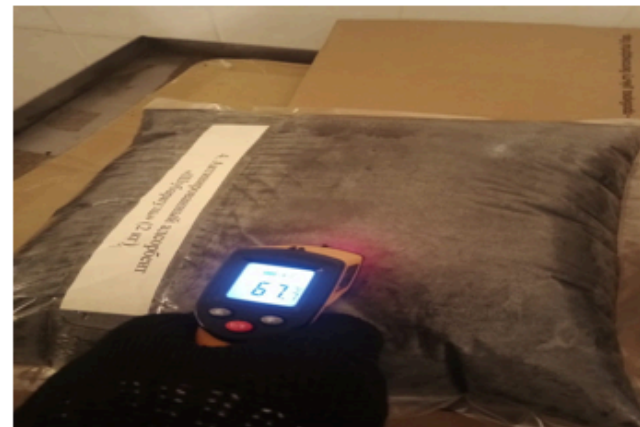
- the set of the required value of the absorbed dose was made stepwise with a step of 100 kGy (to prevent an excessive temperature gradient);
- in the process of gaining the required value of the absorbed dose, the temperature of the processed samples was controlled;
- the samples were processed to the values of the absorbed dose equal to 200 kGy in an inert medium (and argon gas was used as an inert medium);



Radiation treatment of samples at 100 kGy

- After the samples set the value of the absorbed dose equal to 200 kGy, the temperature of the samples was measured (the temperature of the samples was $\sim 70^{\circ}\text{C}$) and an intermediate examination of the samples with a description.

- the processing of samples from the values of the absorbed dose equal to 200 kGy to the values of the absorbed dose equal to 400 kGy was carried out in a gas mixture medium (a mixture of nitrogen and carbon dioxide in a ratio of 1/1 was used as the gas mixture);



Radiation treatment of samples at 200 kGy in an inert argon atmosphere

- After the samples set the absorbed dose value equal to 400 kGy, the temperature of the samples was changed (the temperature of the samples was 90°C) and the samples were examined with a description



Radiation treatment of samples at 400 kGy in an inert gas mixture (nitrogen and carbon dioxide in a ratio of 1/1)

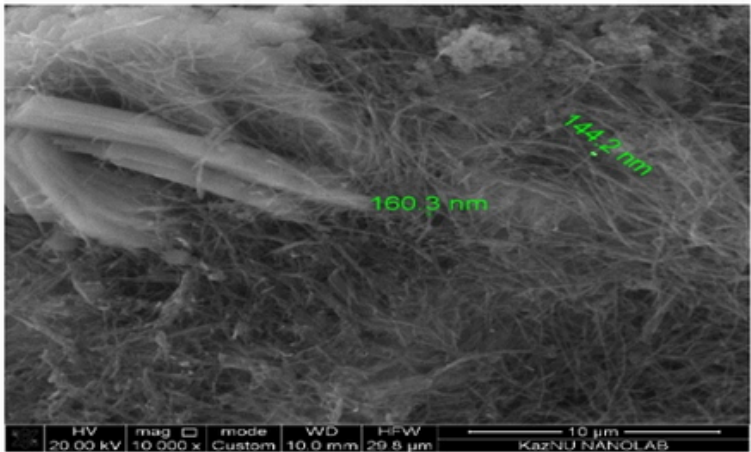
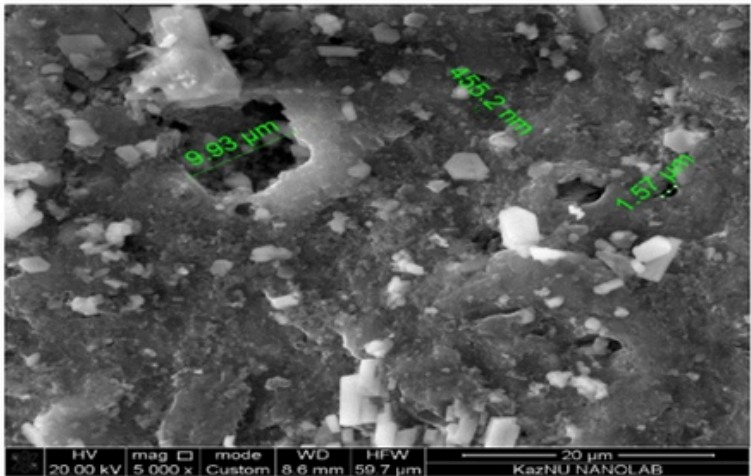
Physicochemical characteristics of initial and irradiated carbon materials

№	Name	(V ^a), %	(V ^d), %	(W ^{rt}), %	(A ^r), %	ρ _{bulk} , г/см ³	V _Σ on water, cm ³ /g	pH water extract	A _m , mg/g	A _{m.g} , mg/g	A _{iodine} , %	S _{BET} , m ² /g
1	2	3	4	5	6	7	8	9	10	11	12	13
1	Granular coal "Shoptokol" (non-irradiated)	34,90	45,89	12,02	10,25	-	-	-	-	-	-	-
2	Granular coal "Shoptokol" (irradiated)	36,73	46,75	11,30	11,42	0,75	0,49	6,00	17,00	115,0	31,75	1,51
3	Assets. adsorbent "Shoptokol" (non-irradiated)	7,55	19,34	1,40	20,69	0,70	0,43	9,35	19,00	50,0	45,72	146,35
4	Activated adsorbent "Shoptokol" (irradiation)	10,09	12,80	3,21	18,55	0,68	0,49	7,00	19,00	125,0	45,72	149,70
5	Granular coal "Shubarkul" (non-irradiated)	38,74	46,55	8,60	9,46	-	-	-	-	-	-	-
6	Granular coal "Shubarkul" (irradiation)	41,50	46,55	7,17	3,96	0,6	0,42	7,00	14,50	117,5	27,94	0,58
7	Activated adsorbent "Shubarkul" (non-irradiated)	12,05	14,77	2,66	16,24	0,63	0,36	10,20	16,00	162,5	16,51	80,51
8	Activated adsorbent "Shubarkul" (irradiation)	10,23	12,21	2,84	13,78	0,62	0,29	9,00	13,00	135,0	33,02	180,23
9	Granulated coal "Shoptokol:Shubarkol" (6:4) (non-irradiated)	39,43	48,75	10,80	9,33	-	-	-	-	-	-	-
10	Granulated coal "Shoptokol:Shubarkul"	38,45	46,62	10,47	7,89	0,6	0,52	6,00	12,50	192,5	31,75	1,65
11	Activated adsorbent "Shoptokol: Shubarkul" (6:4) (non-irradiated)	6,82	14,21	1,78	15,17	0,67	0,50	9,99	15,50	100,0	40,66	49,56

Physicochemical characteristics of initial and irradiated carbon materials

1	2	3	4	5	6	7	8	9	10	11	12	13
12	Activated adsorbent "Shoptykol: Shubarkul" (6:4) (irradiation)	7,58	9,46	3,01	17,37	0,62	0,687	7,00	15,00	162,5	33,02	35,26
13	Granulated coal "Shoptykol:KOH" 50% (1:0.5) (non-irradiated)	44,70	-	21,09	28,00	-	-	-	-	-	-	-
14	Granulated coal "Shoptykol:KOH" 50% (1:0.5) (irradiation)	20,52	39,62	34,33	21,14	0,68	1,826	8,00	11,50	175,0	3,81	-
15	Activated adsorbent "Shoptykol:KOH" 50% (1:0.5) (non-irradiated)	13,13	21,12	17,00	25,11	0,78	0,50	9,00	13,00	167,50	25,40	271,8 0
16	Activated adsorbent "Shoptykol:KOH" 50% (1:0.5) (irradiation)	13,13	21,12	17,00	25,11	0,71	0,268	8,00	11,50	135,0	27,94	376,7 5
17	Granular coal "Shubarkul:KOH" 50% (1:0.5) (non-irradiated)	39,06	-	20,80	36,90	-	-	-	-	-	-	-
18	Granular coal "Shubarkul:KOH" 50% (1:0.5) (irradiation)	29,40	-	26,00	38,46	0,75	0,56	7,00	-	370,0	-	0,64
19	Activated adsorbent "Shubarkul:KOH" 50% (1:0.5) (non-irradiated)	7,74	12,20	28,52	11,25	0,68	0,58	9,00	21,00	185,0	40,64	407,7 0
20	Assets. adsorbent "Shubarkul:KOH" 50% (1:0.5) (irradiation)	8,02	12,10	20,10	16.95	0,68	0,35	8,00	5,00	182,5	38,10	306,4 0

When analyzing the morphology of the surface of the samples, it was found that carbon nanotubes were formed in the sample after irradiation (Figure (b)) with a diameter of 144.2-160.3 nm, which are not observed in the original PCM (Figure (a)), which further contributes to the increase specific surface area of the sample. The formation of CNTs is possible by gas-phase deposition of carbon matrices on the surface of metal active particles (for example, titanium or iron) present in the composition of the product, which can act as a catalyst; this can also be associated with the formation of very high temperatures and pressures inside certain areas of the PCM, which leads to the formation of new carbon formations.



Electron microscopic images of the activated adsorbent "Shoptokol: KOH" 50% (1:0.5)
a – before irradiation; b – after irradiation

Results of the study of PUM sorption (by CO2)

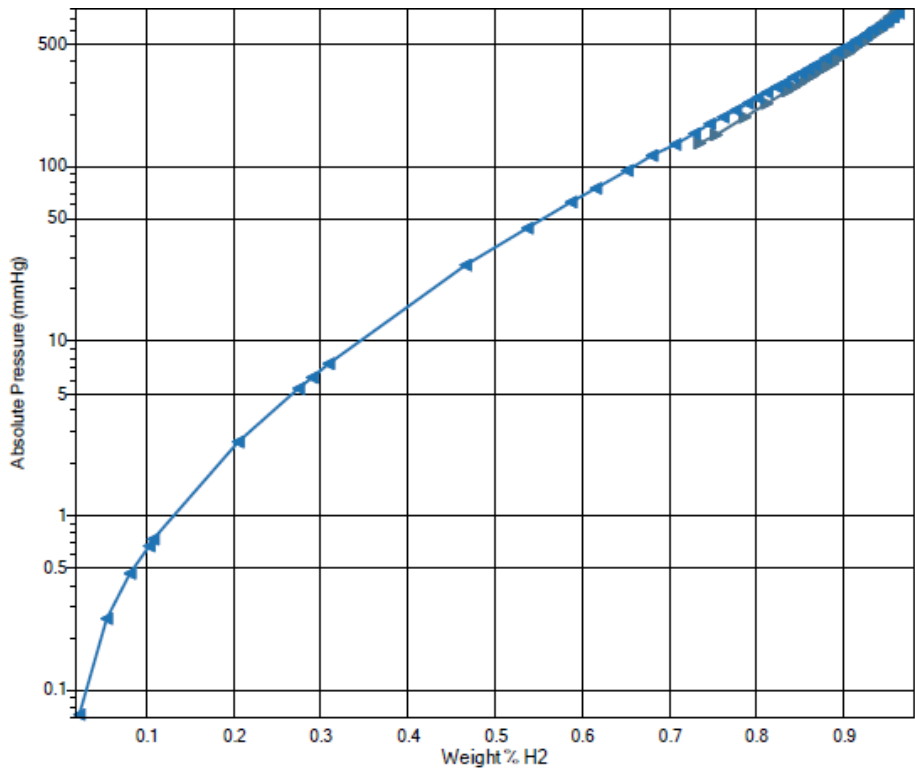
№	Name	Dubinin-Radushkevich			Dubinin-Astakhov			
		Maximum capacity of micropores, mmol/g	Limit micropore volume, cm³/g	Equivalent surface area, m²/g	Maximum capacity of micropores, mmol/g	Limitation of micropore volume, cm³/g	Equivalent surface area, m²/g	Average equivalent pore width, Å
1	Activated adsorbent Shoptokol:KOH (50%) (1:0.5)	4,3966	0,2096	450,1092	9,2206	0,4395	1 285.5476	13,6762
2	Activated adsorbent Shoptokol:KOH (50%) (1:0.5) (irradiated)	5,6939	0,27144	582,9209	22,3992	1,0677	2 598.6155	16,4356

According to the results of a thermogravimetric analysis study, the volatility and moisture values of the samples decreased after irradiation. Also, the specific surface area and adsorption activity for iodine increased several times, for PCM based on Shubarkol coal the initial specific surface area is 80.51 m2/g, after electron irradiation the indicator increased to 183.23 m2/g, almost 2 times. The same dependences are observed in samples of the activated adsorbent "Shoptokol: KOH" 50% (1:0.5) - 271.80 m2/g, after irradiation - 376.75 m2 / g, which may be due to additional activation by an electron beam in the presence of CO2, which contributes to the formation of a porous structure and an increase in the inner surface of the material.

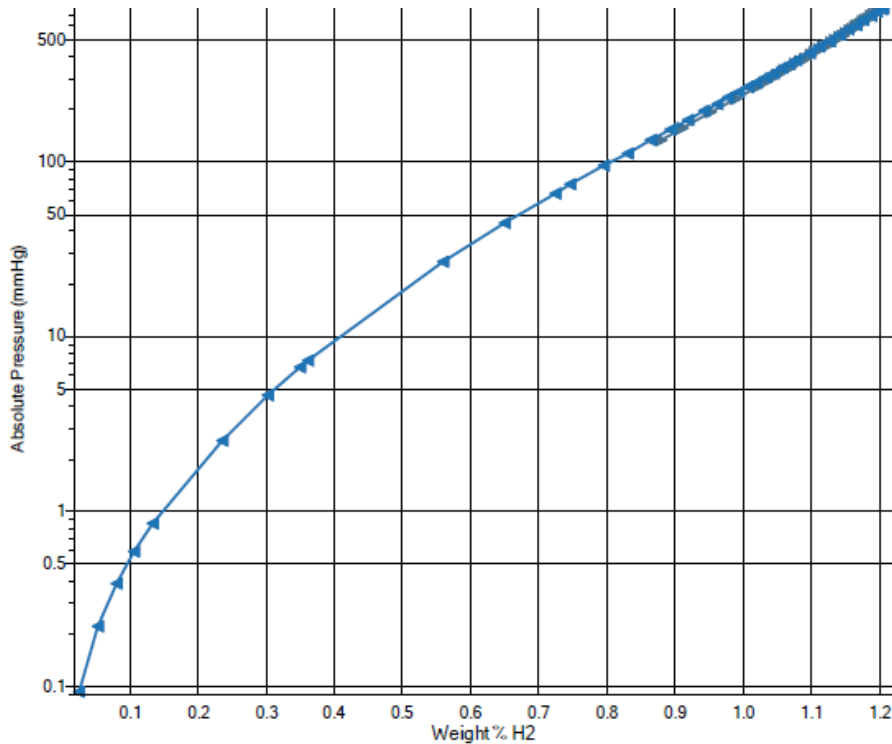


Analyzer 3Flex, Micromeritics

Name	S specific surface area, m2/g (by H2)	Amount of adsorbed H2 gas
	S _(BET)	%
Activated adsorbent “Shoptokol: KOH” (1:0.5)	386	0,96
Activated adsorbent “Shoptokol: KOH” (1:0.5) irradiated	475	1,19



Activated adsorbent “Shoptokol: KOH” (1:0.5)



Activated adsorbent “Shoptokol: KOH” (1:0.5) irradiated

PCMs were tested for gas purification at Sorbents of Kuzbass LLC (Kemerovo, Russia). According to the specific retained volume of gases and the selectivity coefficient of gas separation, PCMs showed the best performance in purifying carbon dioxide, sulfur dioxide, nitrogen dioxide, propane, methane, which allows them to be used for purifying flue gases. PUM “Shoptykol impregnated with KOH” (irradiated) in comparison with the untreated initial sample showed the highest retention volume for carbon dioxide (159.9 cm³/g), propane (14 cm³/g) and butane (46.5 cm³/g) . Thus, a carbon nanocomposite can be obtained using a one-stage technology as a result of the simultaneous formation of carbon nanoparticles and the carbon matrix connecting them with the formation of a nanocomposite of the carbon-carbon system in the same reactor by impergation with alkali, heating at high temperature (800-900 C) and by electronic irradiation.

КОЛИЧЕСТВЕННЫЙ АНАЛИЗ							
1. Проба (образец):							
№ п/п	Определяемые показатели	Результаты испытаний					Единицы измерения
	Удельные удерживаемые объёмы газов (по данным газовой хроматографии) при 30 ⁰ С	№ 1 Акт.адсорбент "Шоптыколь с КОН"	№ 2 Акт.адсорбент "Шоптыколь с КОН" (облученный)	№ 3 Акт.адсорбент "Шубарколь с КОН"	№ 4 Акт.адсорбент "Шубарколь"	№ 5 Акт.коксовая мелочь "Шубарколь"	
1.	Азот	4,7	2,8	5,4	1,21	2,27	см ³ /г
2.	Кислород	5,0	3,40	5,2	2,14	3,47	см ³ /г
3.	Метан	13,7	11,4	26,10	3,01	7,84	см ³ /г
4.	Водород	0,59	0,51	0,46	0,42	0,73	см ³ /г
5.	Моноксид углерода СО	7,90	4,70	9,3	2,43	3,90	см ³ /г
6.	Углекислый газ	105,0	159,9	223,9	114,2	121,4	см ³ /г
7.	Диоксид серы SO ₂	поглощение полное	поглощение полное	552,7	поглощение полное	поглощение полное	см ³ /г
8.	Диоксид азота NO ₂	поглощение полное	поглощение полное	поглощение полное	поглощение полное	поглощение полное	см ³ /г
9.	Пропан (С ₃ H ₈) при Т=140 ⁰ С	11,5	14	27,5	13,2	5,4	см ³ /г
10.	Бутан (С ₄ H ₁₀) при Т=140 ⁰ С	26	46,5	139,2	74,1	113,4	см ³ /г
	Коэффициент селективности разделения газов (отношение удерживаемых объёмов)						
1.	CH ₄ / N ₂	2,9	4,1	4,8	2,5	3,4	
2.	CH ₄ / СО	1,7	2,4	2,8	1,2	2,0	
3.	СО /Н ₂	13,4	9,2	20,2	5,7	5,3	
4.	СО ₂ / CH ₄	7,7	14,0	8,6	37,9	15,5	

Испытания проводили (должность, подпись,Ф.И.О.):

Инженер - аналитик лаборатории

Суняева Т.В.

Заключение: протокол проверен и оформлен правильно

Директор ООО «Сорбенты Кузбасса»

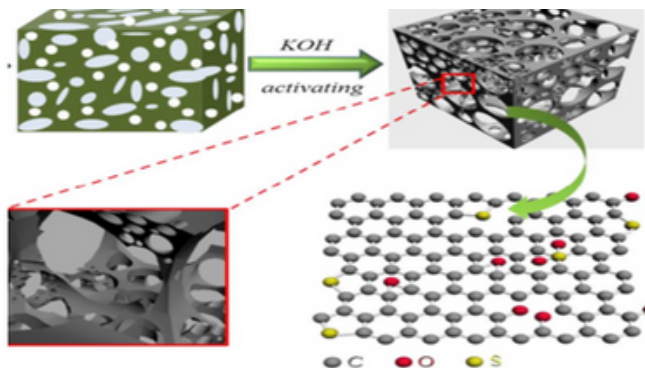
Бервено А.В.

Страница 2 из 3

Synthesis of carbon nanosorbents from coal



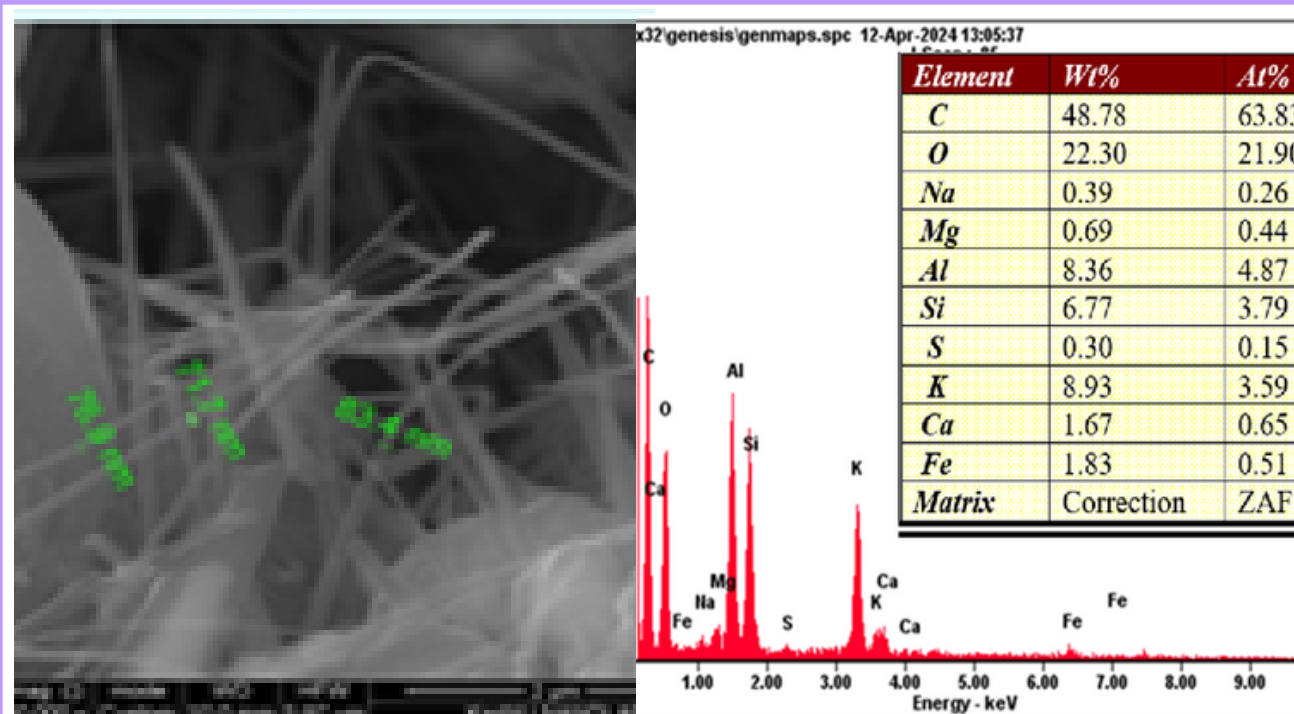
Various schemes for the production of carbon materials are known, including the preparation and modification of the original coal, carbonization and subsequent activation with a gas or a chemical reagent. One of the promising methods for producing porous carbon materials from carbon raw materials is the use of alkaline activators in heat treatment processes. Upon contact with alkali, the lattice of brown coal begins to rearrange itself already at room temperature, and when heated, alkali promotes the development of specific surface area, an increase in the total pore volume and the volume of micropores. Synthesis of carbon nanosorbents from the Shoptykol and Sarykol coal deposits (Maikuben basin), impregnated with potassium hydroxide. To obtain a nanosorbent, a sample of crushed (6.88-401 μm) oxidized brown coal (Wrt - 6.36%, Ar - 47.73%, Vd - 32.83%) was impregnated for 24 hours with a 50% alkali solution (KOH) at a certain temperature, the coal/alkali ratio is 1:0.5 and 1:1. Next, the mixture was dried and placed in a rotary tube kiln to carry out the carbonization process by heating to 800°C at a rate of 10°C/min and maintaining at 800°C for 60 minutes. Next, the samples were removed and placed in a dry atmosphere for cooling. The cooled adsorbent is washed from residual alkali and dried at a temperature of 105°C to constant weight.



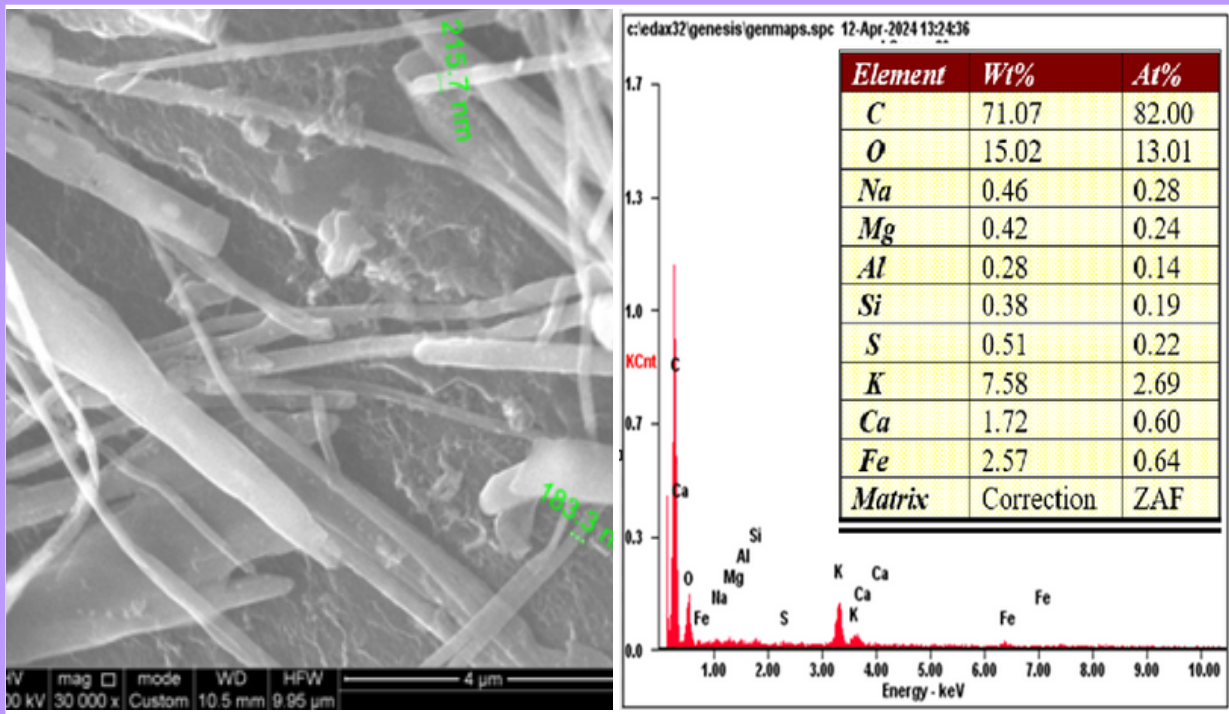
Formation of the porous structure of the adsorbent when activated with potassium hydroxide

Name	BET, m ² /g	Total pore volume, cm ³ /g	Micropores, cm ³ /g	Mesopores, cm ³ /g	Macropores, cm ³ /g	The total surface area of BJH adsorption for pores with a width from 17,000 Å to 3,000,000 Å, m ² /g	BJH Adsorption total pore volume from 17,000 Å to 3,000,000 Å wide, cm ³ /g	Average adsorption pore width BJH (4V/A), Å
Carbonized adsorbent " Shoptykol: KOH" 1:1, 900 °C	352,2855	0,293565	0,113839	0,129148	0,050578	98,7634	0,180251	73,003
Carbonized adsorbent "Shoptykol: K ₂ CO ₃ " 1:1, 900 °C	661,2451	0,406749	0,250443	0,121320	0,034986	67,3381	0,144887	86,065
Activated adsorbent "Shoptykol: NaOH" 1:1, 900 °C	653,0247	0,435334	0,204861	0,182514	0,047959	137,2048	0,21316	62,144

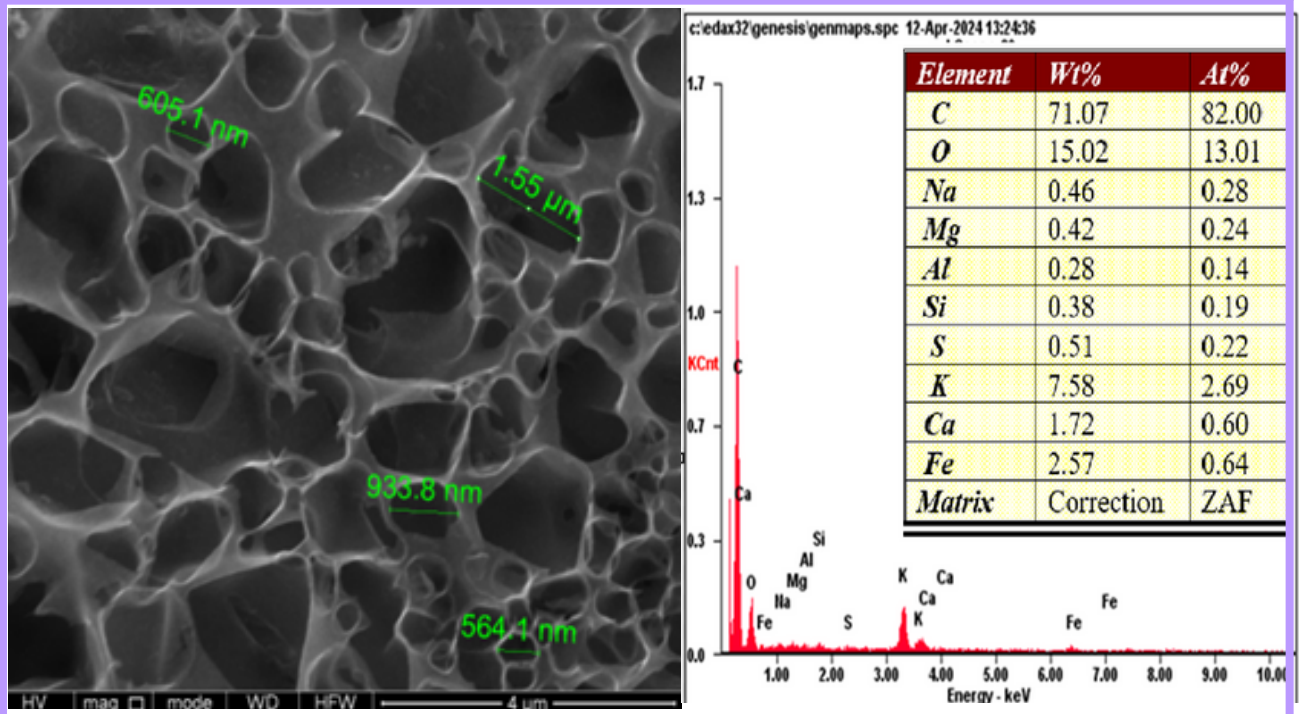
Name	Dubinin-Radostkevich			Dubinin-Astakhov			
	Maximum capacity of micropores, mmol/g	The maximum volume of micropores, cm ³ /g	Equivalent surface area, m ² /g	Maximum capacity of micropores, mmol/g	Limitation of the volume of micropores, cm ³ /g	Equivalent surface area, m ² /g	Average equivalent pore width, Å
Carbonized adsorbent "Shoptykol: KOH" 1:1, 900 °C	2,95472	0,140848	302,494846	9,41555	0,448829	1151,654633	15,589024
Carbonized adsorbent "Shoptykol: K ₂ CO ₃ " 1:1, 900 °C	6,68948	0,31888	684,847478	8,72539	0,41593	1307,453402	13,250144
Activated adsorbent "Shoptykol: NaOH" 1:1, 900 °C	4,322116	0,205985	442,386469	9,96985	0,475252	1308,895768	14,523758



During the analysis of the morphology of the obtained adsorbents, it is observed that the particle sizes of the surface of the adsorbent "Shoptykol KOH" 1:1 activated at 900°C range from 63.4 nm to 76.9 μm, and nanomaterials similar to carbon nanotubes were formed.



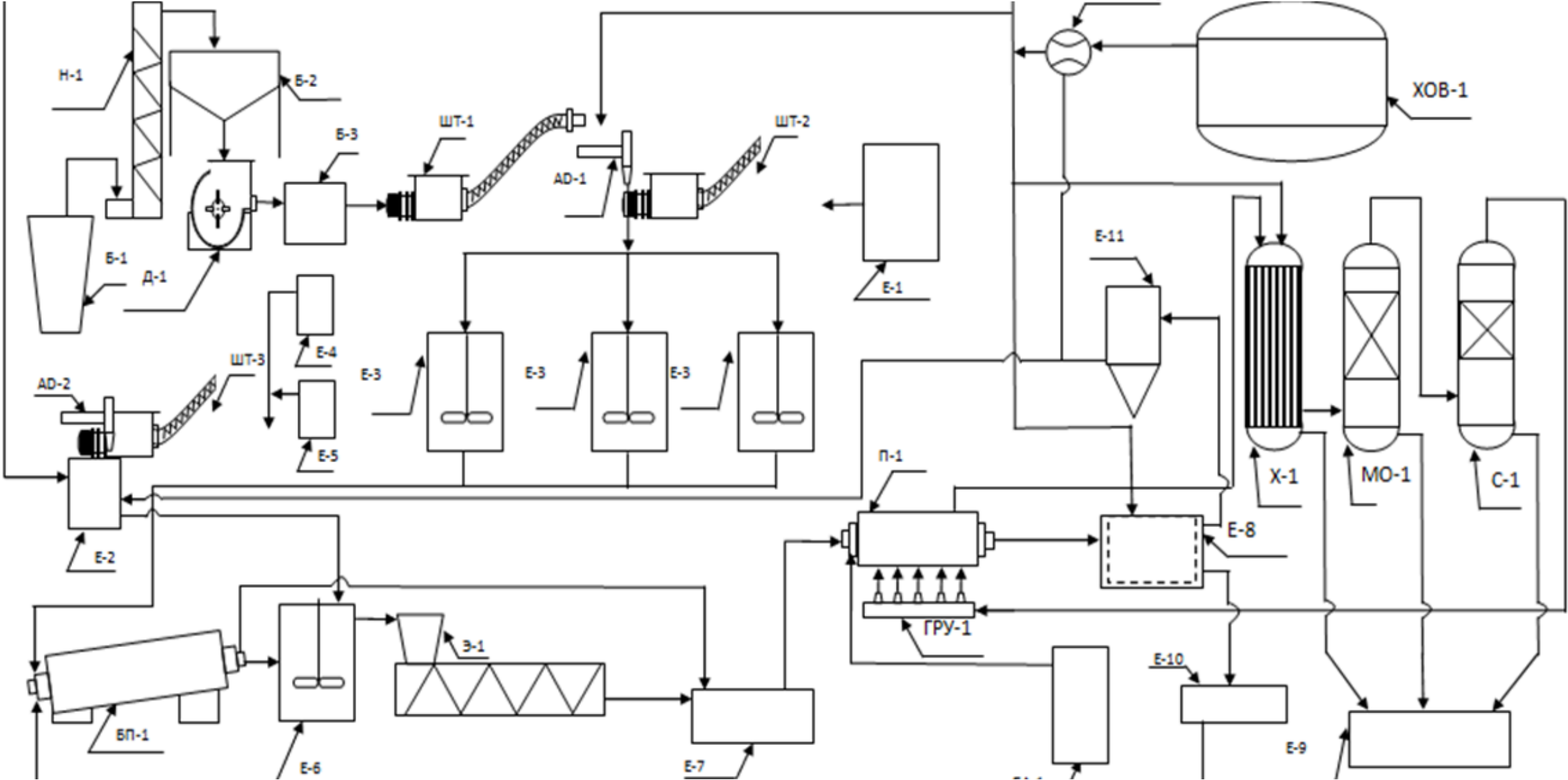
Alyngan adsorbentterdin morphologyson taldau kezind adsorbentterdin betinin bigshekterin olshemderi “Shoptykol-K2CO3” 1:1 900°C carbonizationlangan adsorbenttin 183.3 nm-den 215.7 nm-ge deyingi aralykta nanotikshe anktaldy.



During the analysis of the morphology of the obtained adsorbents, it was found that the particle sizes of the surface of the adsorbents "Shoptycol-NaOH" 1:1 900°C activated adsorbent was represented by a heterogeneous structure from 564.1 nm to 1.55 μm.

Method for producing coal-based adsorbents

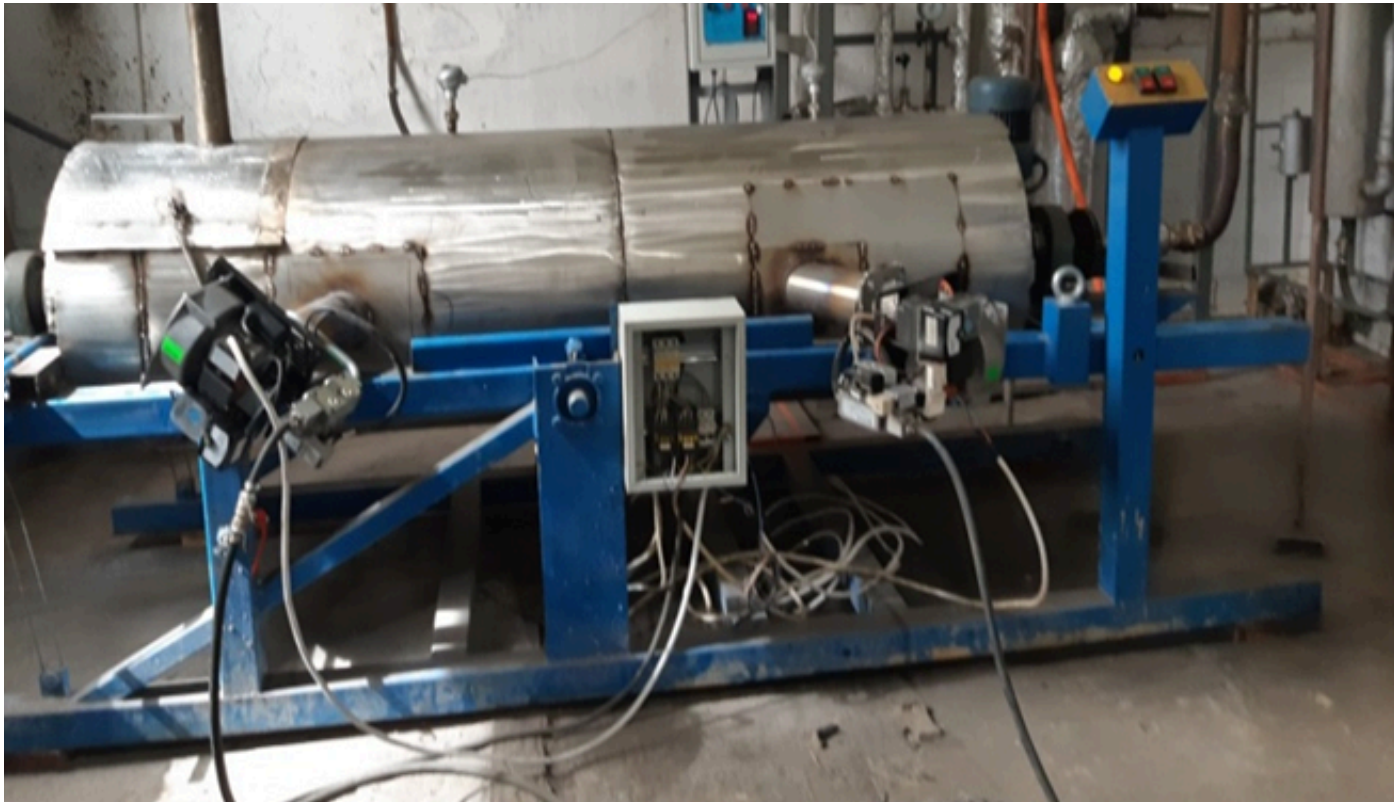
Explication of the equipment of the technological scheme for the production of adsorbents



Pyrolysis furnace

The material balance of carbonation and activation of Shoptkol coal.

Pos. identification	Naming
B-1	Loading bunker
H-1	Noria kovshovaya
B-2	Bunker coal crusher
D-1	Hammer crusher
B-3	Crushed coal bunker
SHT-1	Coal auger conveyor
SHT-2	Screw conveyor alkali for coal
SHT-3	Screw conveyor for preparation of binder
AD-1	Automatic weighing dispenser for preparation of coal
AD-2	Automatic weighing dispenser for binder preparation
SD-1	Water meter-doser
E-1	Capacity of dry alkali
E-2	Binder capacity
E-3	Capacity of exposure of coal in an alkaline solution
E-4	Capacity starch
E-5	Capacity of dry alkali for binder
E-6	Capacity of dried coal
E-7	Capacity of briquettes
E-8	Capacity for washing adsorbent
E-9	The capacity of removed resin
E-10	Capacity of washed adsorbent
E-11	Capacity of mechanical water purification
E-1	Extruder
P-1	Furnace carbonization and activation
BA-1	Cylinder with nitrogen
BP-1	Drum drying oven
X-1	Gas refrigerator
MO-1	Filter wet cleaning
C-1	Separator
GRU-1	Gas distribution device
HOV-1	Block of chemical water treatment



№	Name	content		№	Name	content	
		quantity	percent			quantity	percent
		kg	%			kg	%
1	A mixture of coal and alkali	7 932,203	81,63	1	adsorbent	3 000,000	30,87
	including	5 288,136	54,42	2	resin	11,660	0,12
	coal	345,844	3,56	3	evaporated moisture	1 984,226	20,42
	moisture of coal	2 644,068	27,21	4	losses	2 574,052	26,49
	alkali	1 784,866	18,37	5	washed lye	2 147,473	22,10
2	Binder	1 348,756	13,88				
	water	396,464	4,08				
	starch	39,646	0,408				
	alkali	9 717,069	100,00				
	TOTAL	9 717,069	100,00				
Specific rate of adsorbent yield (for finished products):							
0.57							
Specific rate of binder consumption (for finished products):							
0.59							
specific consumption rate of potassium alkali for coal, taking into account the return of potassium alkali (for finished products):							
0.18							



Plan of production of finished products and annual income

№ p/p	Name	Number of units	Cost of 1 unit	Amount, including VAT	VAT	Price without VAT
1	Feed hopper	1	7 300	7 300	782	6 518
2	Bucket elevator	1	2 450	2 450	263	2 188
3	Coal Crusher Hopper	1	2 440	2 440	261	2 179
4	Hammer crusher	1	10 000	10 000	1 071	8 929
5	Crushed coal bunker	1	2 440	2 440	261	2 179
6	Coal screw conveyor	1	6 610	6 610	708	5 902
7	Automatic weighing batcher-loader	1	151 150	151 150	16 195	134 955
8	Binder mixer	1	4 000	4 000	429	3 571
9	Water meter dispenser	1	775	775	83	692
10	Dry binder capacity	1	4 450	4 450	477	3 973
11	Stirrer container	1	5 000	5 000	536	4 464
12	Finished product capacity	5	4 450	13 350	1 430	11 920
13	Resin collection capacity	1	4 450	4 450	477	3 973
14	Extruder	1	20 000	20 000	2 143	17 857
15	Conveyor	1	6 610	6 610	708	5 902
16	Carbonization furnace	1	300 000	300 000	32 143	267 857
17	Nitrogen bottle	1	20	20	2	18
18	Steam generator	1	3 620	3 620	388	3 232
19	Superheater	1	1 355	1 355	145	1 210
20	Refrigerator gas	1	2 070	2 070	222	1 848
21	Wet filter	1	4 250	4 250	455	3 795
22	Separator	1	3 005	3 005	322	2 683
23	Resin capacity	1	4 450	4 450	477	3 973
24	Gas distribution device	1	8 780	8 780	941	7 839
25	Chemical water treatment unit	1	12 200	12 200	1 307	10 893
	Total			580 775	62 226	518 549

Name	Production of finished products per hour (tons)	Working hours per day	Production per day, (tons)	Production of products per month, (tons.)	Annual production (tons)	Selling price of 1 ton of finished products, (USD)	Total Annual income, (thousand USD)
Adsorbent	3,0	24	72	1 800	21 600	1 000	21 600

After payment of corporate income tax (CIT), the Project's net profit for 10 years will be within the range of USD 70,764.0 thousand, and EBITDA - USD 88,974.0 thousand, which indicates the high efficiency of the Project.

These calculations indicate that the invested funds in the purchase of fixed assets in the form of equipment will pay off in 10 years in 153 times ($88\,974: 580.8 = 153$), that is, the investment costs will pay off in the very first months of the Shop operation.

Detailed calculations are given in Appendix 11 "Forecast Report on Income and Expenses" in the financial and economic model (FEM) of the project.

For an investment project, not only the indicators of the project's profitability are important, but also the return on investment costs.

Therefore, calculations of "Cash flow" (cash flow) for the Project were carried out, on the basis of which such important indicators of the investment project as NPV and IRR were determined for 10 years.

The forecast cash flow report indicates that, starting from the first year of the Shop's operation, there are no cash gaps, all cash flows starting from the first year are positive.

The net present value of income (NPV) of the Workshop at a discount rate of 9.5% (The refinancing rate of the National Bank of the Republic of Kazakhstan as of 09.06.2020) will amount to USD 52,055.0 thousand and an internal rate of return (IRR) - 1,282.2% , which indicates the high efficiency and financial stability of the Project.

Calculations of determining the net profit for the Project (thousand USD)

Name	1 year	2 year	3 year	4 year	5 year	6 year	7 year	8 year	9 year	10 year	Total for 10 years
Income, total	19 286	19 961	20 659	21 382	22 131	22 905	23 707	24 537	25 396	26 284	226 248
Expenses, total	11 753	12 163	12 587	13 025	13 480	13 950	14 436	14 939	15 460	16 000	137 793
Operating profit	7 532	7 798	8 073	8 357	8 651	8 956	9 271	9 597	9 935	10 285	88 455
Profitability	64%	64%	64%	64%	64%	64%	64%	64%	64%	64%	64%
CIT, 20%	1 506	1 560	1 615	1 671	1 730	1 791	1 854	1 919	1 987	2 057	17 691
Net income	6 026	6 238	6 458	6 686	6 921	7 165	7 417	7 678	7 948	8 228	70 764
EBITDA	7 584	7 850	8 124	8 409	8 703	9 008	9 323	9 649	9 987	10 337	88 974

TANTALUM

Федеральное предприятие
Общества с ограниченной ответственностью «ТАНТАЛУМ»
Аттестованное аккредитованное РОССТ ИИ 31578/04/0001/01/13
Срок действия с 04.11.2019 г. по 04.11.2027 г.
Адрес: 140000, Московская обл., г. Пыльино, промzona Тростя, стр. 15

Удостоверен
Руководителем
Богданов В.В.

ПРОТОКОЛ ИСПЫТАНИЙ № 001-C/18-09/20
от 18.09.2020 года

1. Наименование и адрес заказчика 2. Характеристики объекта испытаний 3. Наименование и адрес исполнителя 4. Отбор образцов 5. Информационный штихер образцов 6. Цель испытания 8. Условия окружающей среды при проведении испытаний	Твердотельная с ограниченной ответственностью «Искусств. холмам утца технологический» Адрес: 010113, КАЗАХСТАН, город Нур-Султан, район Байконур, Простокат АЛ-Фараби, здание 26, 308, БИИИ 307-0001-00/01 Утилизаторы холмам утца мототехника «Штампальня» для очистки пылевой воды, сточных и оборотных промышленных вод, водных, дренажных и технологических газов, для дробления драгоценных металлов из промышленных растворов: «АУ Штампальня», марки АЛ-Мариновка ТОО «Искусств. холмам утца технологический» Испытание с ограниченной ответственностью «Искусств. холмам утца технологический» Адрес: 010113, КАЗАХСТАН, город Нур-Султан, район Байконур, Простокат АЛ-Фараби, здание 26, 308, БИИИ 307-0001-00/01 Отбор образцов проводится представителем заказчика в соответствии с ГОСТ 31184-2012, акт отбора образцов № 001-C/18-09/20 №001-C/18-09/20 СТ РК 2246-2012 "Утилизаторы. Общие технические условия" Целью испытаний является установление соответствия утилизаторов холмам утца мототехника «Штампальня» для очистки пылевой воды, сточных и оборотных промышленных вод, водных, дренажных и технологических газов, для дробления драгоценных металлов из промышленных растворов: «АУ Штампальня», марки АЛ-Мариновка ТОО «Искусств. холмам утца технологический», требованиям СТ РК 2246-2012 "Утилизаторы. Общие технические условия" Температура окружающего воздуха 20,22 °С Относительная влажность воздуха 66, 68% Атмосферное давление 746, 750 мм рт.ст
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9. Результат испытаний
Исполнитель: Испытания. Печенья К.Д.

Показатель (характеристика)	Методика испытаний	Нормированное значение	Результат испытаний
1	2	3	4
Размер частиц, мм		1-3	3
Гранулометрический состав, %, массовые доли оседа на сите с диаметром отверстий:			4
5,0 мм, не больше	СТ РК 2405-2013	7,0	6,3
10,0 мм, не больше		87,4	87,1
1,0 мм, не больше		0,6	0,2
0,1 мм, не больше	СТ РК 2407-2013	0,6	0,2
Максимальная доля пыли, %, не больше		0,6	1,4

Протокол испытаний № 001-C/18-09/20 от 18.09.2020 года

TANTALUM			
Испытательная лаборатория Общество с ограниченной ответственностью «ТАНТАЛУМ» Аттестат аккредитации РОСС RU.11578-10A03030.IEL13 Срок действия с 04.12.2019 г. по 03.12.2022 г. Адрес: 400000, Магистральная ул., д.Лопухин, поселок Тарасов, стр. 58			
Показатели (характеристики)	Методика испытаний	Нормированное значение	Результат испытаний
		3	4
Массовая доля железа, %, не более	СТ РК 1408-2013	2,5	20,7
Прочность на изгиб, %, не менее	ГОСТ 16188-70	75,0	87,5
Структурная прочность, %, не менее	СТ РК 2240-2012	85,0	92,5
Средний объем пор на квадрат, см ² , не менее	СТ РК 2404-2013	0,6	0,6
Адсорбиционная активность по йоду, %, не менее	ГОСТ 8217-74	60	64,8
Массовая доля хлора на сухое состояние топлива, Cl, %, не более	ГОСТ 9326-2002	0,1	0,09
Массовая доля мышьяка на сухое состояние топлива, As, %, не более	ГОСТ 10478-93	0,002	0,0004
Массовая доля общей серы на сухое состояние топлива, S, %, не более	ГОСТ 8606-93	1,2	0,55

ДОБРОВОЛЬНАЯ СЕРТИФИКАЦИЯ ПРОДУКЦИИ

СЕРТИФИКАТ СОПОТВЕСТВИЯ

№ РОСС КЗ.Н661.Н13387

Срок действия с 18.09.2020

по 17.09.2023

№ 000118

Орган по сертификации КА.РУ.Н13386

Орган по сертификации ООО "ШТИНГ" Адрес: 153000, РОССИЯ, Ивановская область, город Иваново, улица Богдана Хмельницкого, дом 148А Телефон: +7 4932711847 Адрес электронной почты info@sting.ru

ПРОДУКЦИЯ Утеплительные и/или фетровые утеплители на минеральной «ШТИНГ» для систем напытной изоляции, применяемые в объектах промышленного, гражданского, жилищного и транспортного сектора, для изготовления строительных материалов из промышленного сырья «АУ ШТИНГ», «АУ ШТИНГ», «Обура», «АУ ШТИНГ», «Обура», «АУ ШТИНГ», «КОБА», «АУ ШТИНГ», «КОБ» «Обура» и/или «А.М. Макромер ТОО ШТИНГ» (Утеплитель каменную и текстильный). Серийный выпуск.

код ОК
20.50.44.190

СОПОТВЕСТВИЕ ТРЕБОВАНИЮ НОРМАТИВНЫХ ДОКУМЕНТОВ
СТ РК 226-2012 "Утеплительные, теплоизоляционные материалы"

код ТН ВЭД
3882100000

ИЗГОТОВИТЕЛЬ Товарищество с ограниченной ответственностью «ШТИНГ» (Утеплитель каменную и текстильный). Адрес: 610011, КАЗАХСТАН, город Нур-Султан, район Байконур, Промысел АИ-Фабрика, здание 26, 308, 308/1 12746054990, телефон: 8177272 48-75-20, адрес электронной почты: info@sting.kz.

СЕРТИФИКАТ ВЫДААН Товарищество с ограниченной ответственностью «ШТИНГ» (Утеплитель каменную и текстильный). Адрес: 610011, КАЗАХСТАН, город Нур-Султан, район Байконур, Промысел АИ-Фабрика, здание 26, 308, 308/1 12746054990, телефон: 8177272 48-75-20, адрес электронной почты: info@sting.kz.

НА ОСНОВАНИИ Серийного выпуска № 0015-0-18-09-20 с 18.09.2020 года, выданной Исполнительной лабораторией Общества с ограниченной ответственностью «АБГАТ» (Испытатель аккредитация РОСС КЗ.Н13378.540330.01.813)

ДОПОЛНИТЕЛЬНАЯ ИНФОРМАЦИЯ

Серийная продукция: 3с

Руководитель органа

Эксперт

Подпись (Signature) of the official.

П.П. Рукавцов

Исполнительный директор

В.П. Писарев

Исполнительный директор

Сертификат не применяется при обязательной сертификации

ДОБРОВОЛЬНАЯ СЕРТИФИКАЦИЯ ПРОДУКЦИИ

СЕРТИФИКАТ СООТВЕТСТВИЯ

№ РОСС КЗ.НП66.1.Н13398

Срок действия с 18.09.2020

до 17.09.2023

№ 0004020

ОРГАН ПО СООТВЕТСТВИЮ R.A.R.111(NB6)

Орган по сертификации ООО «ШТРИХ». Адрес: 153009, РОССИЯ, Нижегородская область, город Нижний, улица Козлова Хмельницкого, дом 14Б. Телефон +7 493272 145. Адрес электронной почты info@strich.ru

ПРОДУКЦИЯ Угли активированные из каменного угля маркировка «Шубарька» для аквариума (карбона и дробленый уголь: «АУ Шубарька», «АС Шубарька», «Обруч», «АУ Шубарька - КСВ», «АУ Шубарька - КСВ-1 Обруч», марки АГ - 3) Маркировка ТОО «Штритх» каменного угля и технологии. Сертификат выпуска.

Код ОКС
25.99.54.110

СООТВЕТСТВИЕ ТРЕБОВАНИЯМ НОРМАТИВНЫХ ДОКУМЕНТОВ
СТ РК 2246-2012 "Угли активированные. Общие технические условия"

Код ТН ВЭД
3812100000

ИЗГОТОВИТЕЛЬ Товарищество с ограниченной ответственностью «Штритх» каменного угля и технологии. Адрес: 010013, КАЗАХСТАН, город Нур-Султан, район Байконур, Проспект Ала-Фарби, здание 26, 308, 60Н1 127740914906, телефон: 8(7172) 48-77-36, адрес электронной почты: cootved@shk.ru.

СЕРТИФИКАТ ВЫДАН Товарищество с ограниченной ответственностью «Штритх» каменного угля и технологии. Адрес: 010013, КАЗАХСТАН, город Нур-Султан, район Байконур, Проспект Ала-Фарби, здание 26, 308, 60Н1 127740914906, телефон: 8(7172) 48-77-36, адрес электронной почты: cootved@shk.ru.

НА ОСНОВАНИИ

Протокол испытаний № 06215-18-09-20 от 18.09.2020 года, выданный Институтной лабораторией качества с ограниченной ответственностью "ТАНТАЛ" (аттестат аккредитации РОСС RU.11574.06.0038.01311)

ДОПОЛНИТЕЛЬНАЯ ИНФОРМАЦИЯ

Связь сертификата №

Руководитель органа

Эксперт

(Signature)
Подпись
Место

П.Г. Рухадени

В.П. Шаронов

Сертификат не применяется при обязательной сертификации

PRODUCTION OF ACTIVATED ADSORBENT BASED ON SEMICOKE FROM THE COAL SHUBARKOL DEPOSIT FOR GAS PURIFICATION

The production process of granulated activated carbons consists of several crucial stages, including thermo-treatment and activation, along with additional procedures involving the preparation of a paste-like mass from coke powder and binder, followed by the granulation of the resulting coal-tar composition. The properties of the obtained granules and the parameters of the granulation process are significantly influenced by the characteristics and composition of the raw materials.

Semi-coke fines (3-5 mm) from Shubarkol coal, grade D, Kazakhstan, were used as raw material. Their technical characteristics are: moisture content 7.71%, ash content 6.60%, and volatile matter 19.43%. To produce the activated adsorbent, the fines are crushed, fractionated, and introduced into a rotating drum furnace for steam activation at 700°C with a heating rate of 5-10°C/min, held at 700°C for 60 minutes, then cooled in a dry atmosphere.

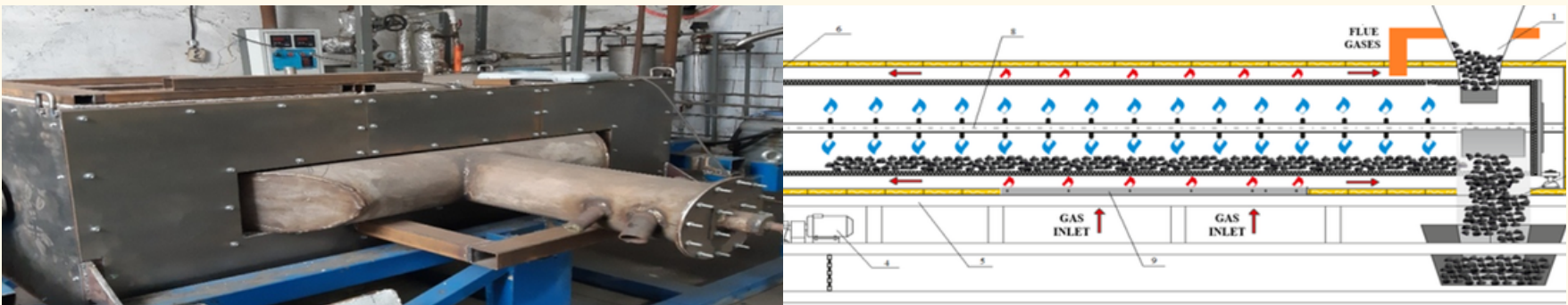


Figure 1 – Pilot pilot rotary drum furnace for carbonization and activation for the production of adsorbents

Table 1 - Gas composition of semi-coke fine (size 3-5 mm) activation at 700°C

T, C°	Composition of gases, %						
	O ₂	H ₂	CO ₂	N ₂	CH ₄	CO	H ₂ S
200	1.809	7.603	12.505	0.239	1.217	-	0.217
300	0.819	4.638	9.617	1.237	1.690	0.290	0.379
400	3.298	4.516	11.089	0.292	1.700	-	0.104
500	0.484	4.818	9.057	3.996	1.768	0.378	0.118
600	3.220	3.575	7.184	0.266	0.466	-	0.183
700	5.613	5.054	3.847	4.596	0.611	0.244	0.051

Table 2 - Material balance of the process of activation of semi-coke breeze (2-5 mm)

№	Name	Content	
		kg	%
1	Semi-coke breeze, incl.	15	100
	Total	15	100
1	Adsorbent	12,4	82,3
2	Resin+water	0,02	0,13
3	Gas	2,63	17,5
	Total	15	100

Table 3 - Physico-chemical characteristics of the adsorbent based on semi-coke fines

Semi-coke fines (3-5 mm)	W _{it} , %	A _r , %	V _d , %	V _{Эby water} , cm ³ /g	ρ _{bulk} , g/cm ³	pH _{aqueous extraction}	A _{M.O.} , mg/g	A _{M.G.} , mg/g	A _{Iodine} , %	S _{BET} , m ² /g
Initial	7.71	6.6	19.4	1.62	0.39	6	29.3	95	44.61	8.23
Activated	0.77	13.2	5.99	1.66	0.40	7.5	31.5	100	43.22	227

Table 4 - Elemental composition of the samples

Semicoke fines (fraction 3-5 mm)	Elemental composition, wt. %									
	C	O	Na	Mg	Al	Si	K	Ca	Fe	S
Initial	90.06	8.00	0.06	0.03	0.46	0.34	0.07	0.39	0.26	0.33
Activated	88.1	4.21	0.61	0.13	2.51	3.18	0.23	0.45	0.31	0.23

As a consequence of steam activation, there is a notable increase in the total pore volume due to water and the adsorption activities of the sample, as assessed by methylene orange, methylene blue, and iodine. Furthermore, the specific surface area of the sample experiences a substantial augmentation from 8.23 m²/g to 227.01 m²/g, representing an almost 28-fold increase. This phenomenon can be attributed to the liberation of volatile constituents during thermal treatment and steam activation, along with the emergence of additional microporous structures.

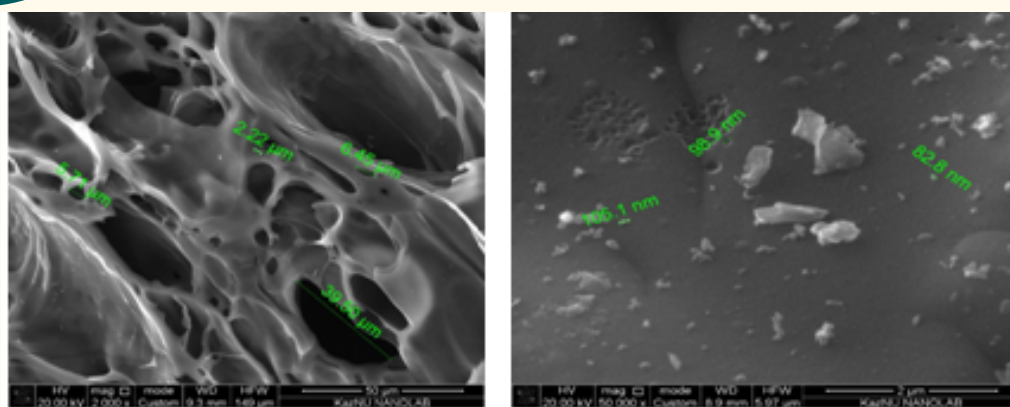


Figure 1 - Electron microscopic images of the original semi-coke breeze

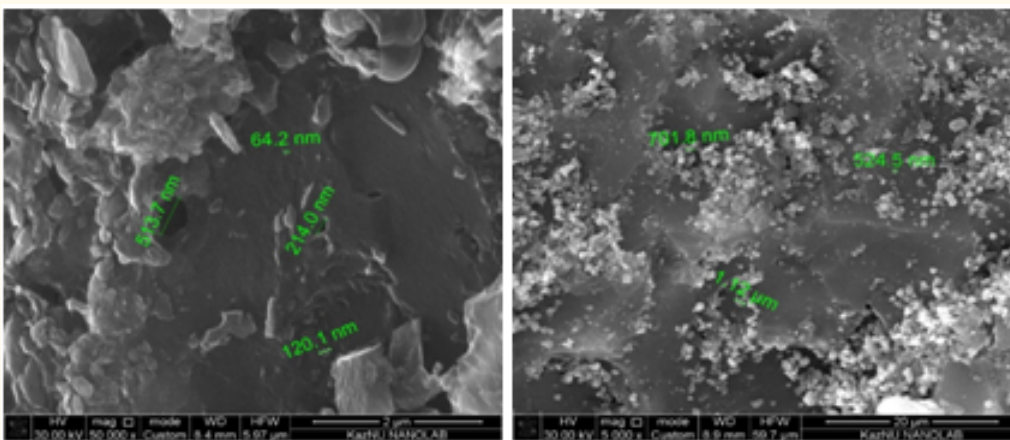


Figure 2 - Electron microscopic images of the activated semi-coke breeze

Table 5 - Test Results of Activated Semicoke Fines (fraction 3-5 mm)

No	Test Indicator	Name of Test Method Nominal	Value, %
1	Particle Size Distribution	ST RK 2405-2013	
	> 5 mm 8		8
	3-5 mm		57.9
	1-3 mm		31.9
	0.1-1 mm		1.9
	< 0.1 mm 0.3		0.3
	Total		100
2	Structural Strength, P _s	ST RK 2243-2012	93.86
3	Mass Fraction of Chlorine on Dry Fuel Basis, Cl ^d	GOST 9326-2002, (ISO 587-97)	0.1
4	Mass Fraction of Arsenic on Dry Fuel Basis, As ^d	GOST 10478-93, (ISO 601-81, ISO 2590-73)	0.0002
5	Mass Fraction of Total Sulfur on Dry Fuel Basis, S ^d	GOST 8606-93, (ISO 334-92)	0.23



Figure 3 – Activated coke breeze, crushed

An activated adsorbent based on semi-coke breeze has been tested for gas purification. An analysis of the kinetic characteristics and sorption capacity was carried out using gas chromatography for the retained volumes of nitrogen, oxygen, hydrogen, carbon monoxide, carbon dioxide, methane, propane, butane, sulfur oxides and nitrogen oxides. The sorption-kinetic characteristics of the adsorbent sample were determined by gas chromatography.

Table 6 - Results of studies of the specific retained volume of gases, selectivity coefficients for adsorbent separation

No	Defined indicators	Test results	Units
Specific retention volumes of gases (according to gas chromatography) at 30°C			
1	Nitrogen	2,27	cm ³ /g
2	Oxygen	3,47	cm ³ /g
3	Methane	7,84	cm ³ /g
4	Hydrogen	0,73	cm ³ /g
5	Carbon monoxide	3,90	cm ³ /g
6	Carbon dioxide	121,4	cm ³ /g
7	Propane (C ₃ H ₈) at T=140°C	5,4	cm ³ /g
8	Butane (C ₄ H ₁₀) at T=140°C	113,4	cm ³ /g
9	Sulfur dioxide SO ₂	complete absorption	cm ³ /g
10	Nitrogen dioxide NO ₂	complete absorption	cm ³ /g
Gas separation selectivity coefficient (ratio of retained volumes)			
1	CH ₄ /N ₂	3,4	-
2	CH ₄ /CO	2,0	-
3	CO/H ₂	5,3	-
4	CO ₂ /CH ₄	15,5	-

As the test showed, the presented adsorbent based on semi-coke breeze has developed porosity with the presence of micropores in the range of 0.3-2 nm. This is confirmed by the results of gas adsorption chromatography.

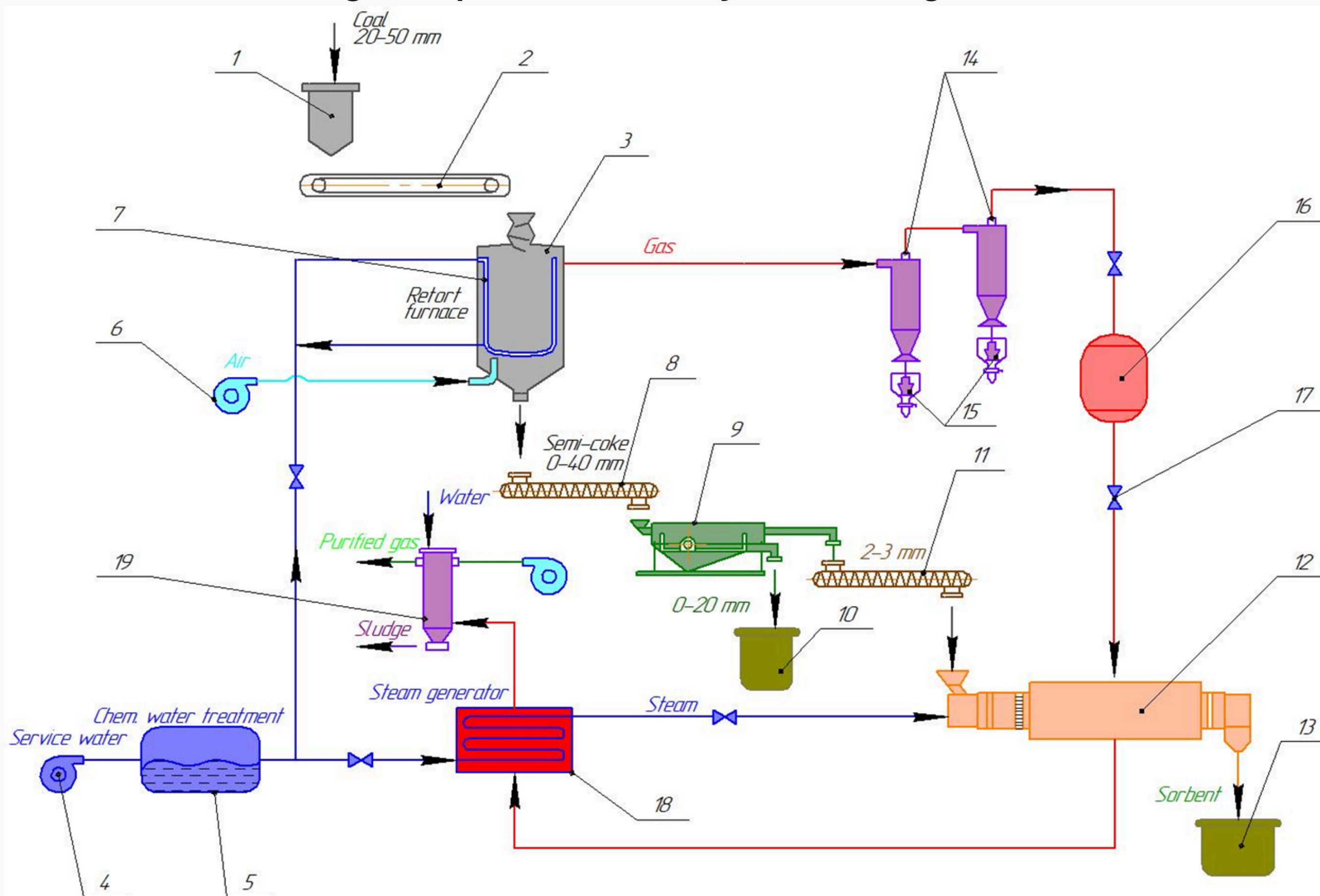
The sample "Activated semi-coke fines (fraction 3-5 mm)" conforms to the ST RK 2246-2012 classification. It is suitable for gas and liquid adsorption, manufacturing absorbents and catalysts, respiratory protection equipment (AG-2B), and recuperative activated carbons (AR-A, AR-B, AR-C) for capturing and recycling volatile solvent vapors at high concentrations.

The study indicates the potential for commercializing carbon adsorbents based on semi-coke breeze for air purification, flue gas capture, gas purification, ventilation, filters, and sorption plants. The research outcomes include enhanced energy efficiency, increased specific surface area, solid product yield, strength, porosity, and adsorption activity, with reduced volatility due to steam thermal activation.



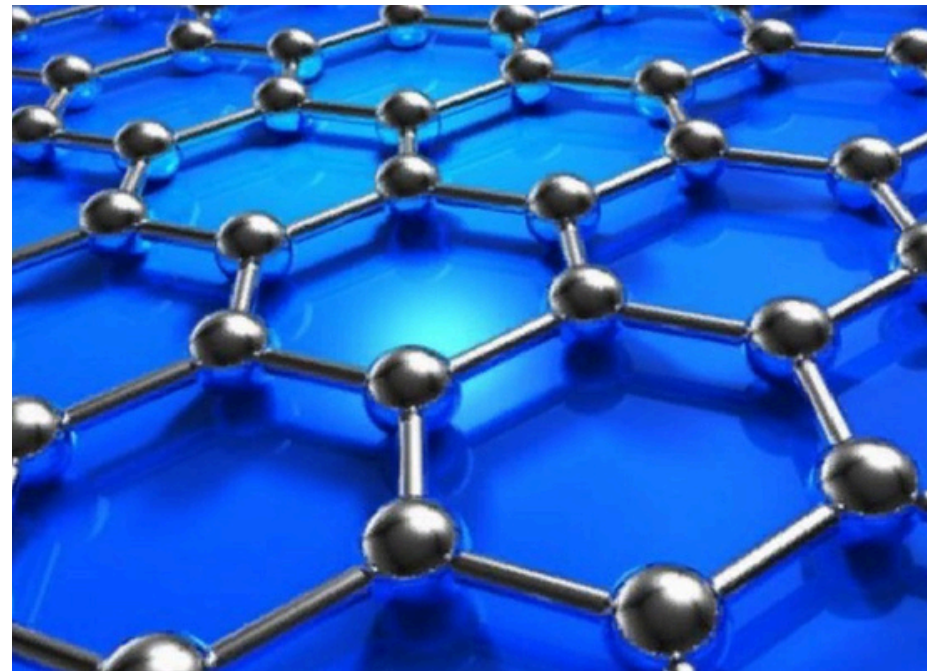
According to our calculations, from 1 ton of coal we obtain from 0.4 to 0.6 tons (depending on the feedstock) of the finished adsorbent product with a high specific surface area (400-1200 m²/g) and increased sorption capacity with a cost of 1000-1200 USD per 1 ton. The cost of the adsorbent ranges from 194.0 USD to 609.0 USD per ton, depending on the technology for obtaining the product, while the annual profitability of adsorbent production on average over 10 years will be in the range of 64% and higher, respectively, based on a productivity of 3 t/ hour. The forecast report on Cash Flow shows that, starting from the first year of operation of the Shop, there are no cash gaps; all cash flows, starting from the first year, are positive.

Hardware design of a production facility for obtaining activated adsorbents based on coke breeze



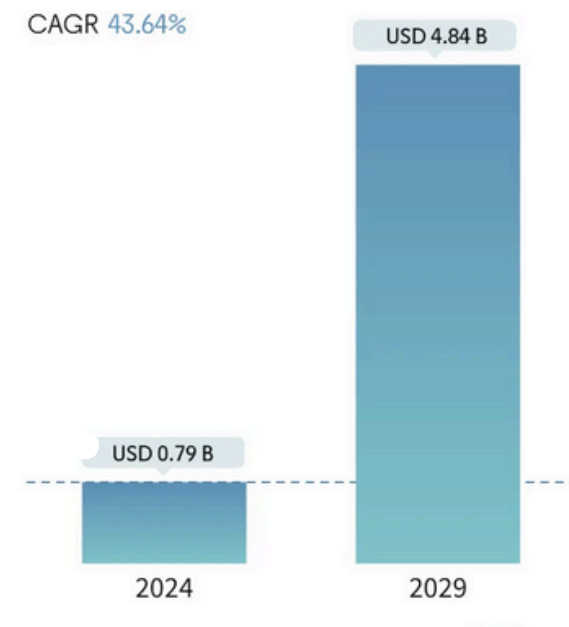
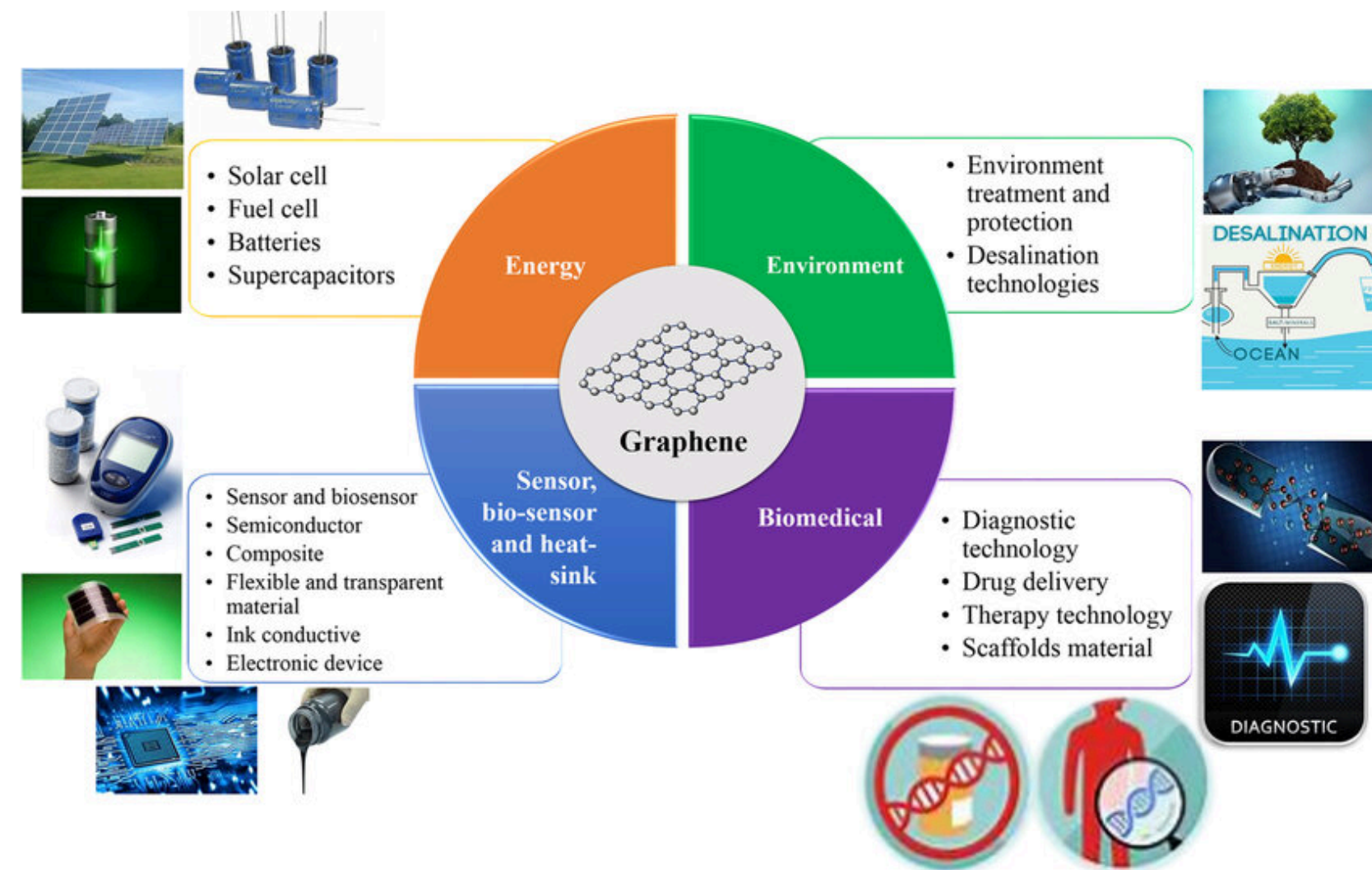
	Name
1	Loading hopper
2	Belt Conveyor
3	Retort oven
4	Feed water pump
5	Chemical water treatment unit
6	Fan
7	Water jacket
8	Coal screw conveyor (0-40 mm)
9	Bolt
10	Collection tank
11	Coal screw conveyor (2-3 mm)
12	Rotary kiln
13	Sorbent collection tank
14	Cyclones
15	Dust collectors
16	Receiver
17	Control valve
18	Steam generator
19	Wet scrubber

Preparation of graphene-like materials based on Kazakhstan coals



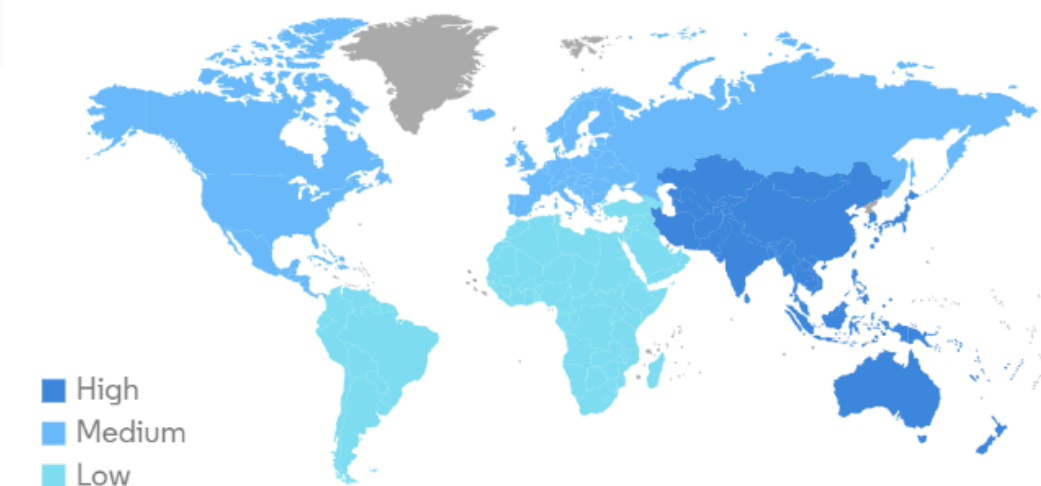
Graphene is a two-dimensional allotrope of carbon, consisting of a single layer of carbon atoms arranged in a hexagonal lattice. It is the basic building block of other carbon allotropes like graphite, carbon nanotubes, and fullerenes. a material that has a large specific surface area ($2630 \text{ m}^2\text{g}^{-1}$), high internal mobility ($200,000 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$), high Young's modulus ($\sim 1.0 \text{ TPa}$), thermal conductivity ($\sim 5000 \text{ W m}^{-1}\text{K}^{-1}$), optical transmittance ($\sim 97.7\%$).

Graphene has high mechanical strength. It is the most durable material known to mankind. It can withstand enormous loads without collapsing. It is capable of transferring heat efficiently, making it potentially useful in a variety of thermal conduction applications. These unique characteristics make graphene a highly attractive material for a wide range of applications, from electronics and energy to medicine and materials science.

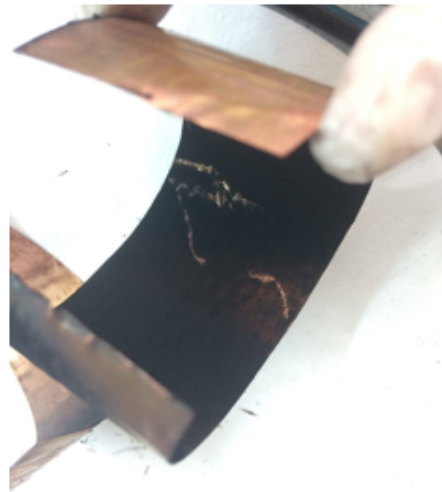
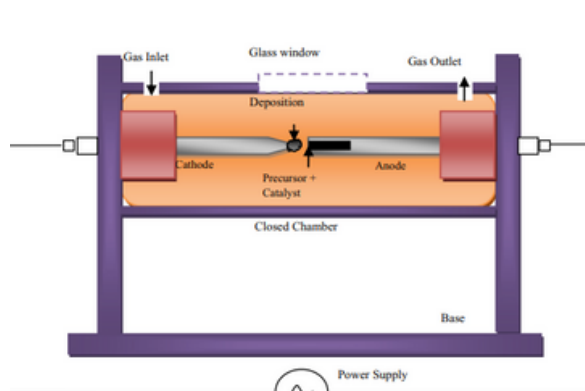


The graphene market size is valued at US\$0.79 billion in 2024 and is expected to reach US\$4.84 billion by 2029, growing at a CAGR of 43.64% during the forecast period (2024-2029).

Graphene Market - Growth Rate by Region



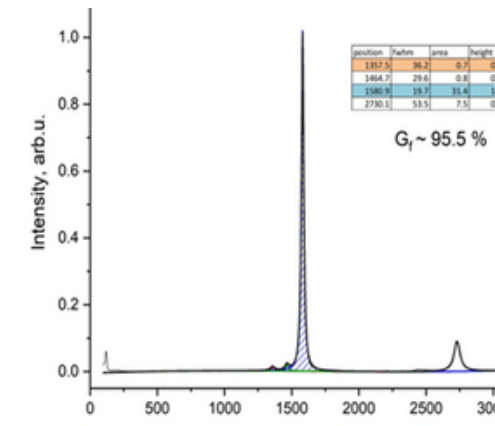
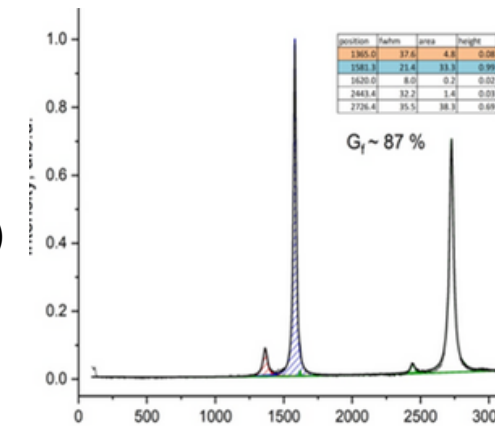
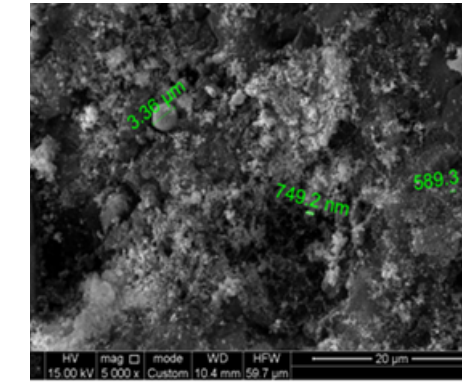
Production of high-quality graphene by electric discharge method



Arc discharge is the electrical breakdown of a gas to generate plasma. This technique of generating arc using electric current was first used by Iijima in 1991. A schematic of an arc discharge chamber. The chamber consists of two electrodes which are mounted horizontally or vertically; one of which (anode) is filled with powdered carbon precursor along with the catalyst and the other electrode (cathode) is usually a pure graphite rod.

Schematic of an arc discharge setup.

Element	Wt%	At%
C	78.91	89.47
O	8.20	6.98
Mg	0.32	0.18
Al	0.53	0.27
Si	0.52	0.25
S	0.36	0.15
Ca	1.45	0.49
Fe	5.25	1.28
Zn	4.45	0.93
Matrix	Correction	ZAF

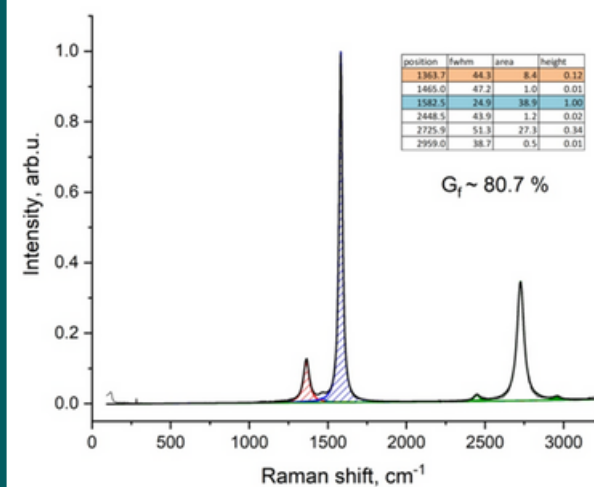
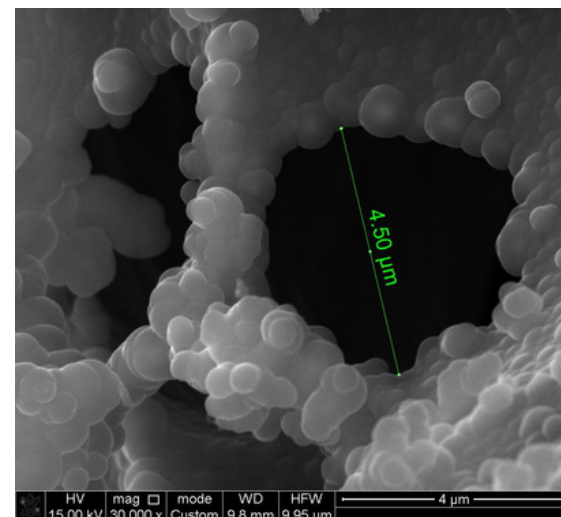


Based on "Shoptikol" coal

After the activated carbon "Shoptikol" electricity arc discharge 100A (reactor wall) Low-layer (less than 10 layers) graphene with a high-quality graphite structure with a graphitization ratio of 87-95.5%. The study of the dependence of electrical resistance on temperature shows that the material in the range of 293-333 K shows metal, 333-483 K - semiconductivity. The material is of interest in semiconductor technology.

Based on "Shubarkol" coal

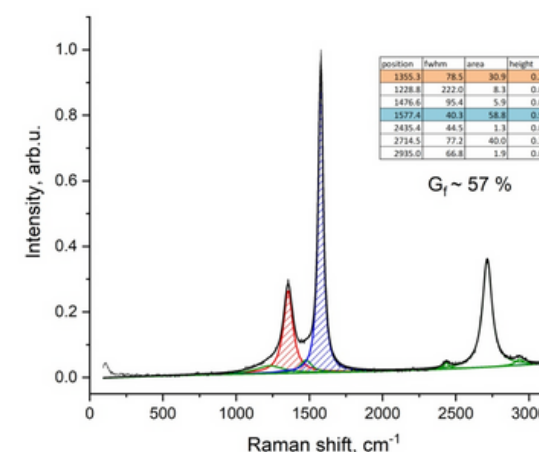
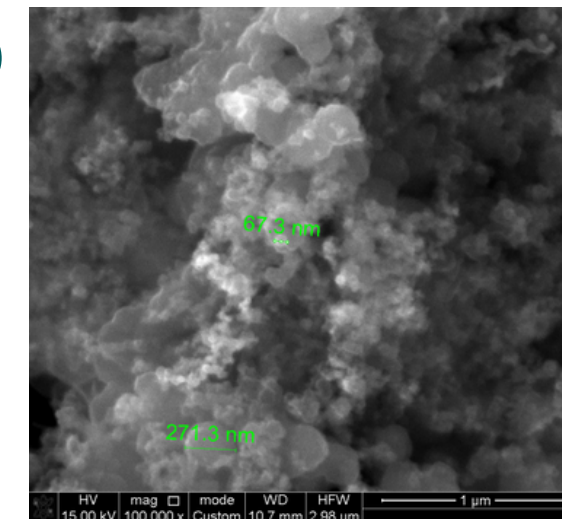
Element	Wt%	At%
C	87.21	90.40
O	11.75	9.15
Na	0.25	0.13
Al	0.36	0.16
Si	0.19	0.08
Ca	0.25	0.08
Matrix	Correction	ZAF



Nanomaterials obtained by the method of electric arc discharge on the reactor walls from Shubarkol activated carbon have graphene-like qualities. The degree of graphitization is 80.7%, $I(D)/I(G)=0.1$, $I(G)/I(2D)=2.9$

Based on "Shubarkol" coal

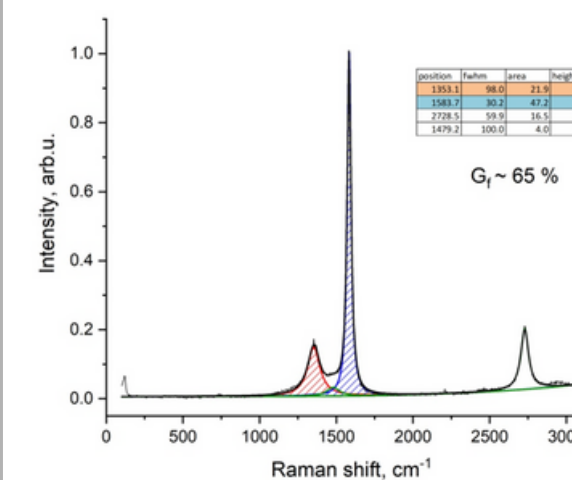
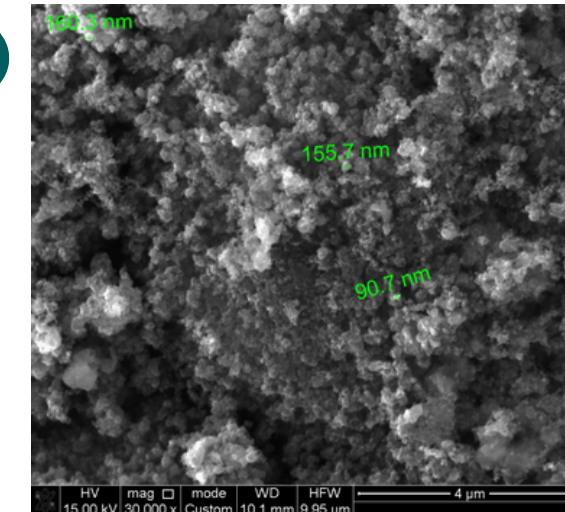
Element	Wt%	At%
C	71.70	85.89
O	6.51	5.86
Mg	0.18	0.11
Al	2.04	1.09
Si	7.68	3.94
S	0.20	0.09
Ca	0.25	0.09
Fe	11.42	2.94
Matrix	Correction	ZAF



Nanomaterials obtained by the method of electric arc discharge on the surface of an electrode from activated carbon "Shubarkol" The degree of graphitization is 57%, $I(D)/I(G)=0.3$, $I(G)/I(2D)=2.8$

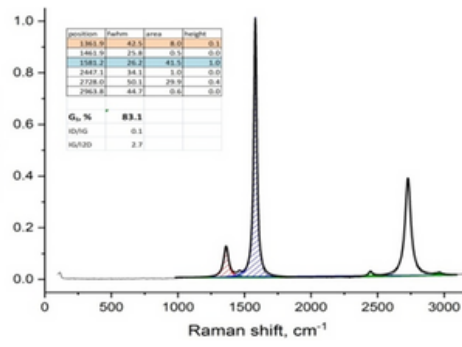
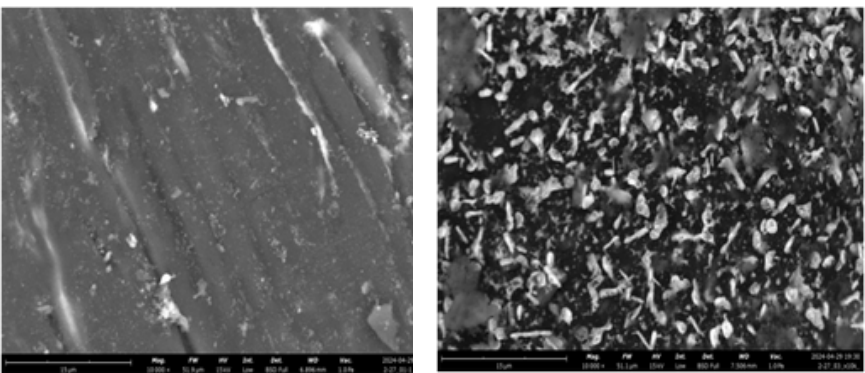
Based on "Bogatyr" coal

Element	Wt%	At%
C	77.82	87.56
O	8.43	7.12
Na	0.15	0.09
Mg	0.19	0.11
Al	2.05	1.03
Si	5.49	2.64
S	0.11	0.04
Ca	0.17	0.06
Fe	5.58	1.35
Matrix	Correction	ZAF



Nanomaterials synthesized by the method of electric arc discharge on the reactor wall from activated carbon "Bogatyr" The degree of graphitization is 65%. $I(D)/I(G)=0.1$, $I(G)/I(2D)=5.7$

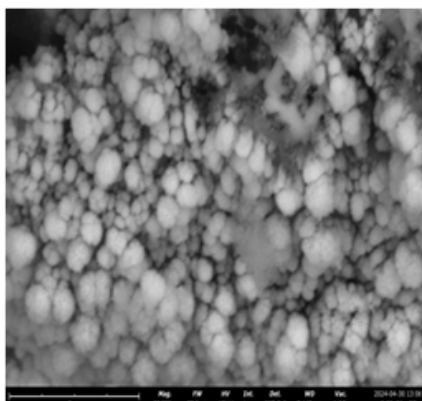
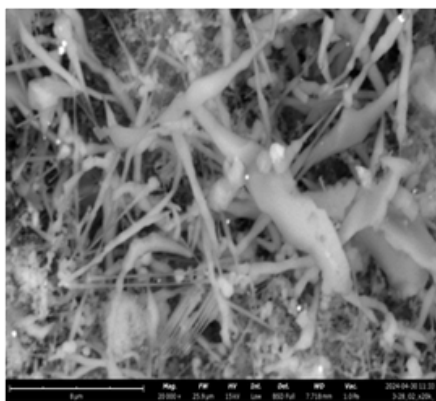
Activated carbon "Taldykol" after electric arc discharge 100A (reactor wall)



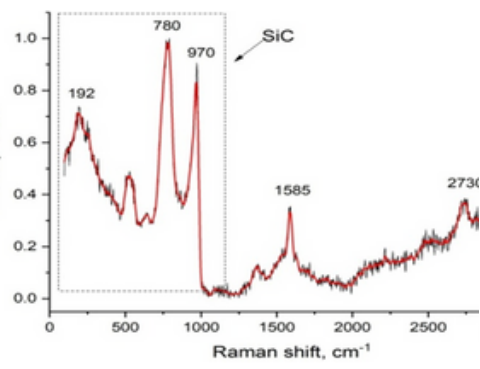
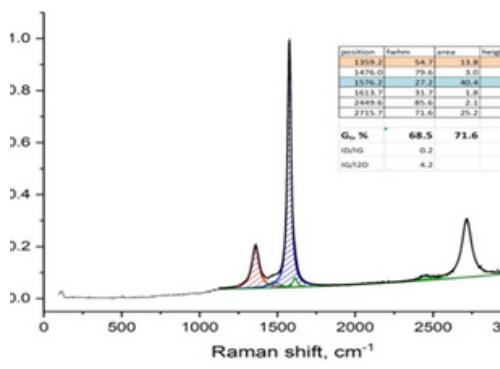
Element	Wt%	At%
C	25.807	15.485
O	37.743	30.170
Na	1.826	2.098
Mg	0.411	0.500
Al	3.855	5.195
Si	24.132	33.866
S	0.187	0.300
K	4.910	9.590
Ca	0.449	0.899
Fe	0.680	1.898
Matrix	Correction	ZAF

Graphite-like structure. Gf = 31.6%. ID/IG ratio 1.1; IG/I2D ratio is 9.2. Low-layer graphene (2-6 layers). The defect peak indicates the small lateral dimensions of graphene. Gf = 83.1%. ID/IG ratio 0.1; The IG/I2D ratio is 2.7.

Activated carbon "Taldykol" after electric arc discharge 100A (electrode surface)

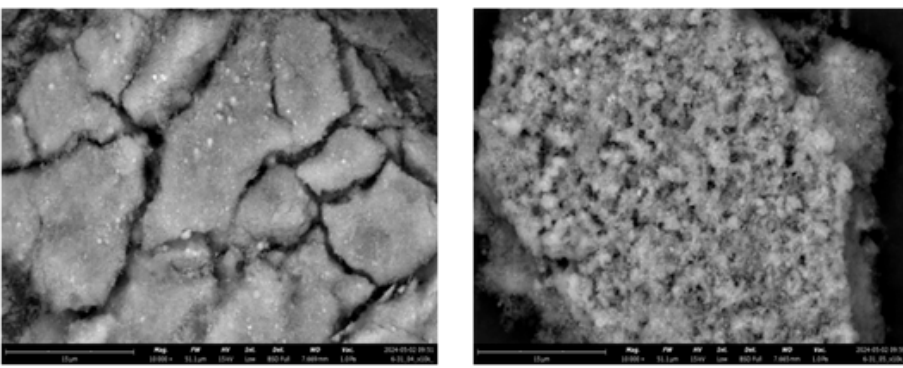


Element	Wt%	At%
C	89.986	84.300
O	7.372	9.200
Al	0.665	1.400
Si	0.776	1.700
S	0.480	1.200
K	0.721	2.200
Matrix	Correction	ZAF

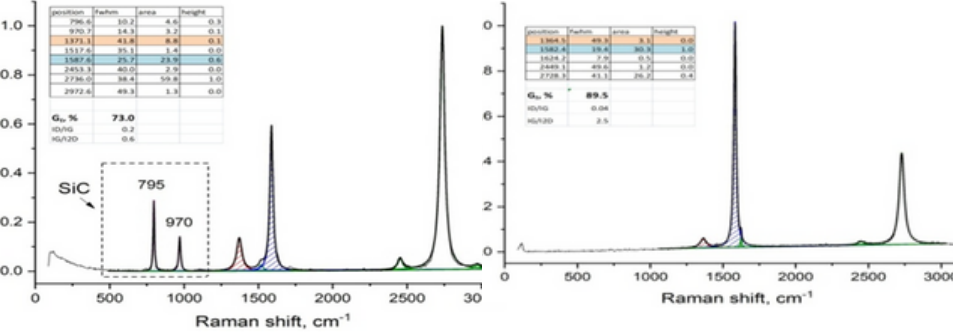


Structure of defective silicon carbide combined with graphitic and amorphous regions. Gf = 68.5%. ID/IG=0.2; IG/I2D=4.2.

Activated carbon "Taldykol" after electric arc discharge 200A (lower part of the reactor wall)

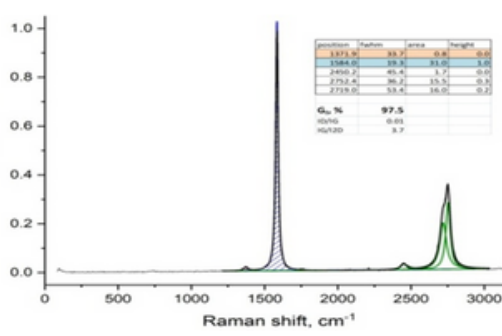
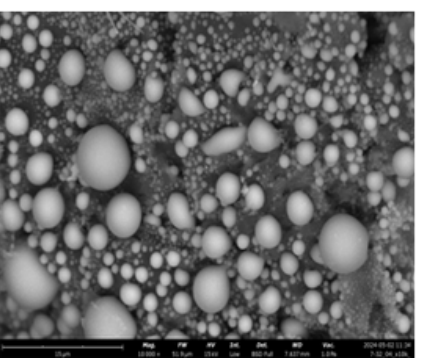


Element	Wt%	At%
C	8.196	4.995
O	59.061	47.952
Na	1.027	1.199
Mg	0.324	0.400
Al	15.037	20.579
Si	13.597	19.381
K	2.316	4.595
Ca	0.442	0.899
Matrix	Correction	ZAF



Silicon carbide and graphene (1-3 layers) Gf = 73.0% ID/IG=0.2; IG/I2D=0.6 High-quality low-layer graphene (5-10 layers). Gf = 89.5%. ID/IG=0.04; IG/I2D=2.5.

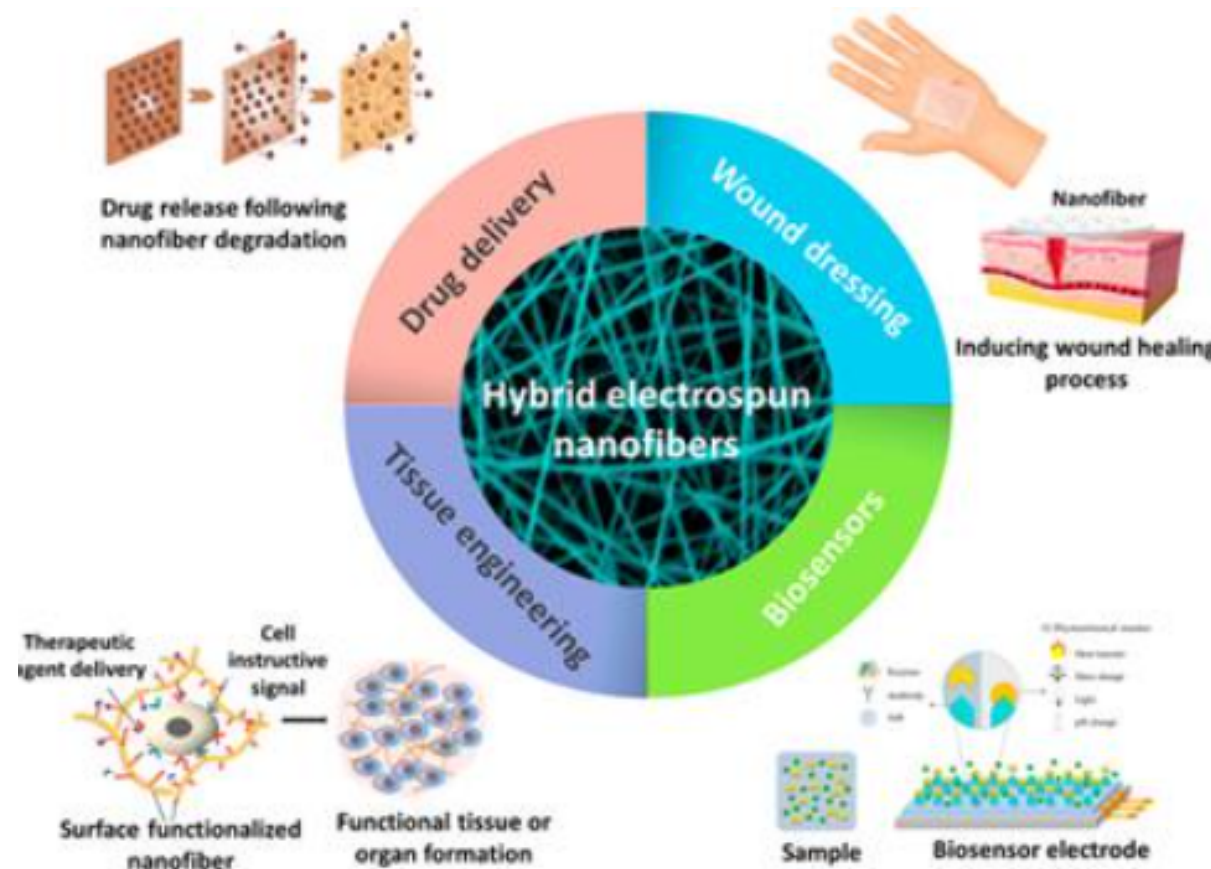
Activated carbon "Taldykol" after electric arc discharge 200A (electrode surface)



Element	Wt%	At%
C	29.340	20.259
N	13.009	10.479
O	35.801	32.934
Na	1.358	1.796
Mg	0.357	0.499
Al	5.664	8.782
Si	12.235	19.760
S	0.271	0.499
K	1.110	2.495
Ca	0.433	0.998
Fe	0.155	0.499
Zn	0.265	0.998
Matrix	Correction	ZAF

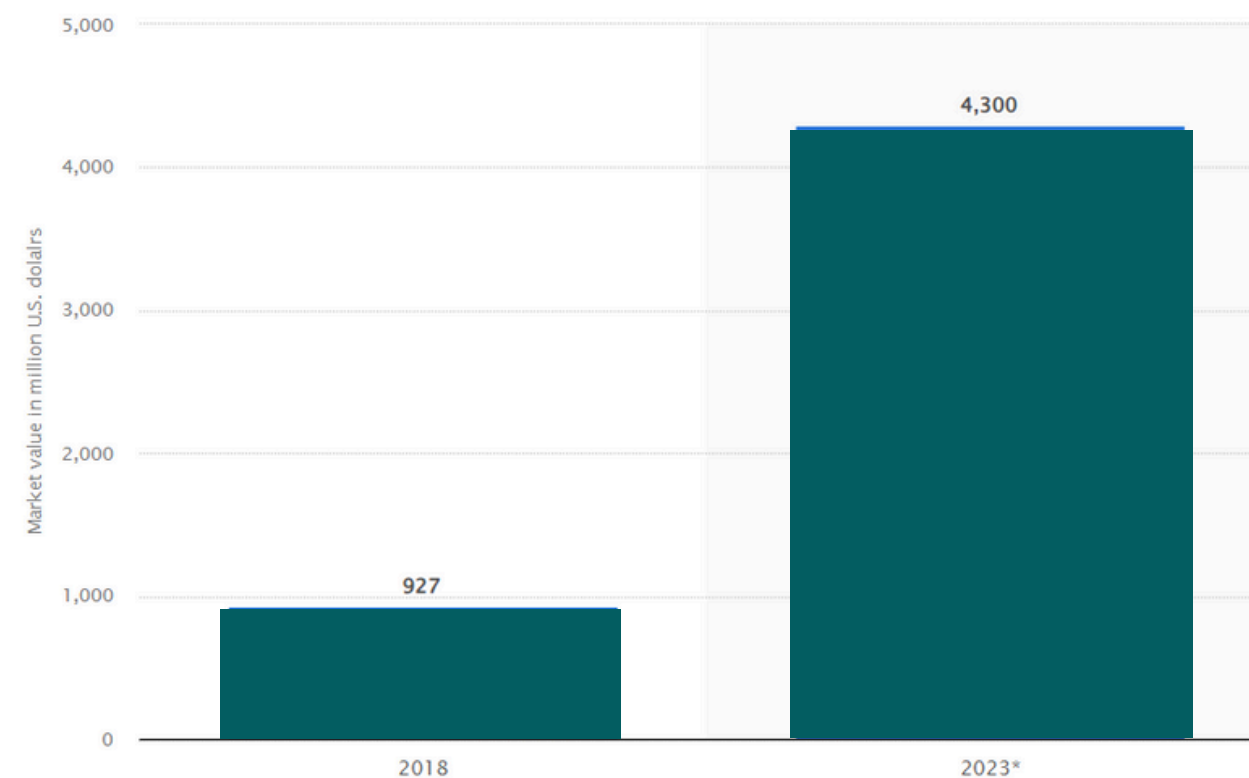
Silicon carbide and graphene (1-3 layers) Gf = 73.0%. ID/IG=0.2; IG/I2D=0.6 High-quality low-layer graphene (5-10 layers). Gf = 89.5%. ID/IG=0.04; IG/I2D=2.5.

SYNTHESIS OF CARBON NANONFIBERS FROM CARBON-CONTAINING MATERIALS

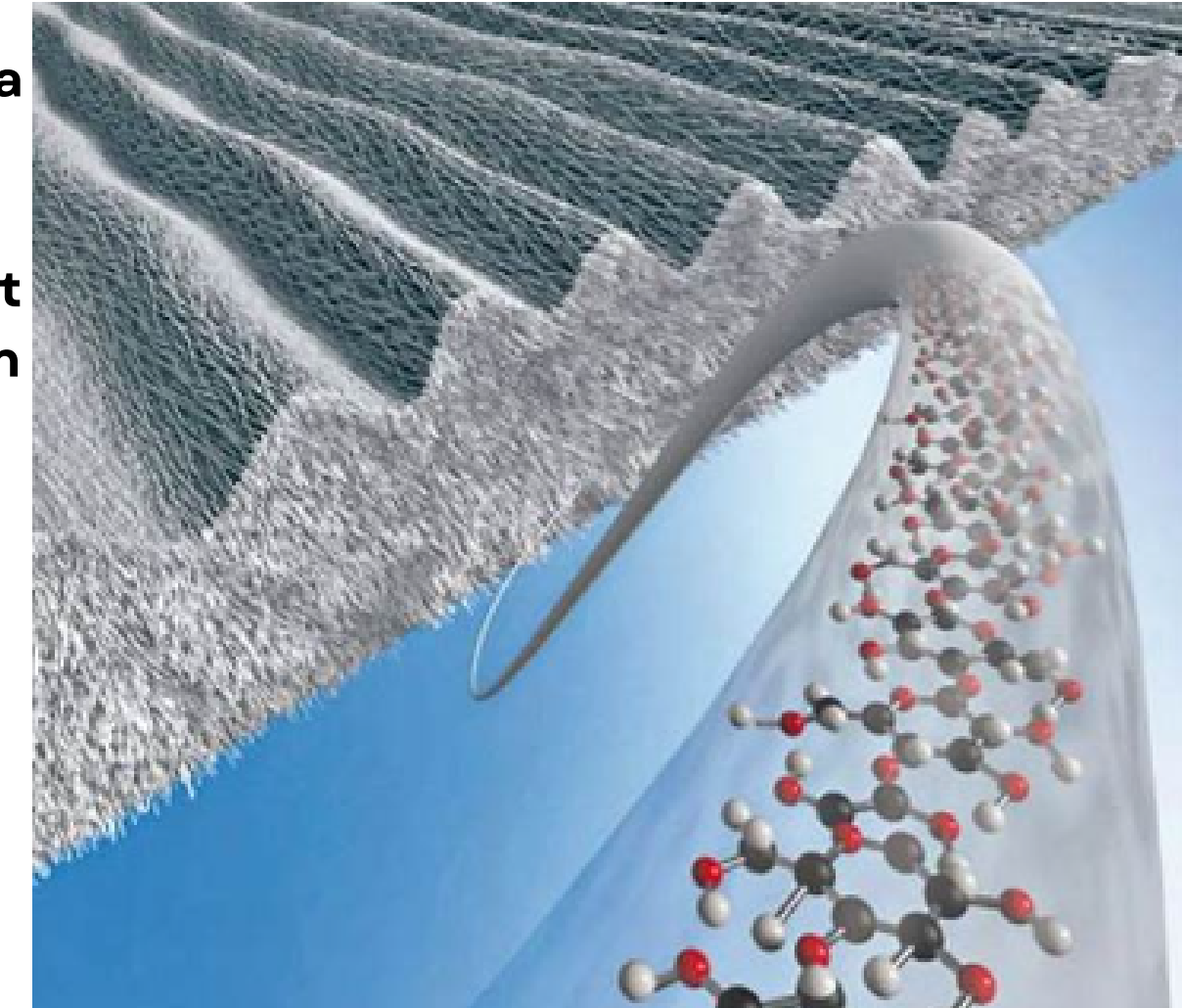


Nanofibers are used in current and emerging applications for building materials and structures (i.e., reinforced polymers, self-healing materials), energy generation, conversion, and storage (i.e., batteries, supercapacitors, fuel cells, and solar energy), environmental improvement, and defense (ie, ultra-high air filtration, wastewater treatment, and water treatment), biomedical applications (ie, drug delivery systems, blood purification, tissue engineering, wound healing), and other applications, including defense and security

This statistic shows the market value of nanofiber products worldwide in 2018, with a forecasted figure for 2023. Nanofibers are fibers with a diameter in the nanometer range. It is forecasted that the global market value of nanofiber products will be 4.3 billion U.S. dollars in 2023.

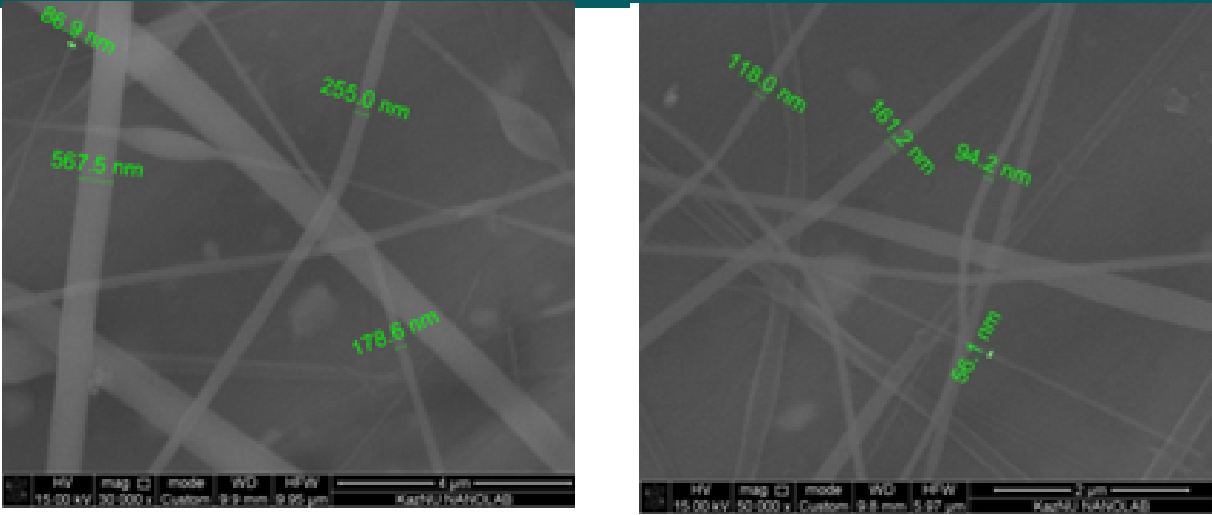


Market value of nanofiber products worldwide in 2018 and 2023(in million U.S. dollars)



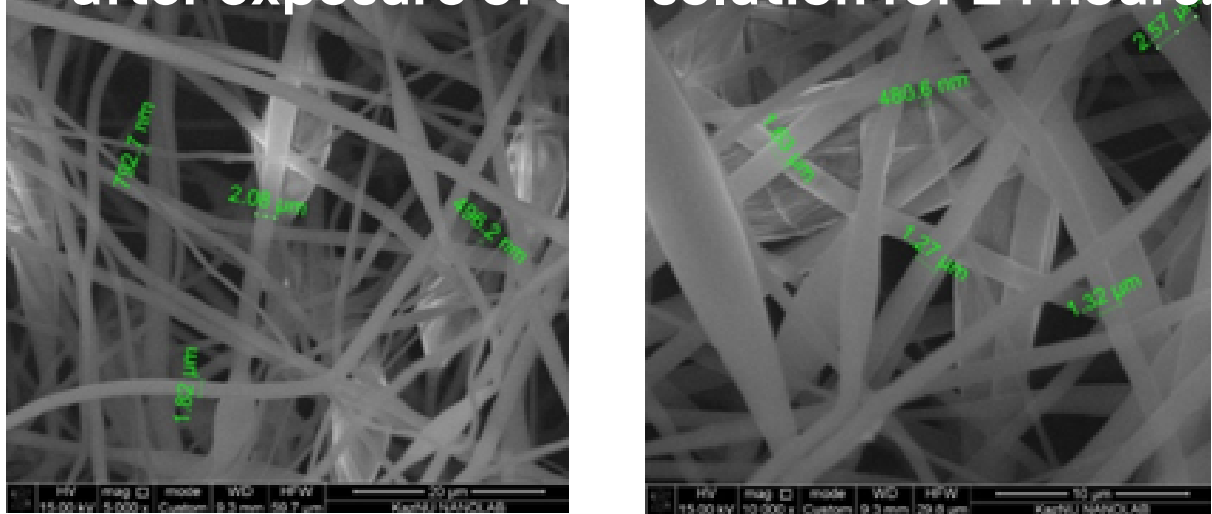
Carbon nanofiber (CNF) is another exciting material in the field of nanotechnology. It is a thin structure consisting of carbon nanotubes laid parallel to each other. These nanotubes can be either single-walled (single-walled) or multi-walled (multi-walled), depending on how many layers of carbon form the wall of the nanotube.

CNF coal tar+polymethyl methacrylate on fixed substrate



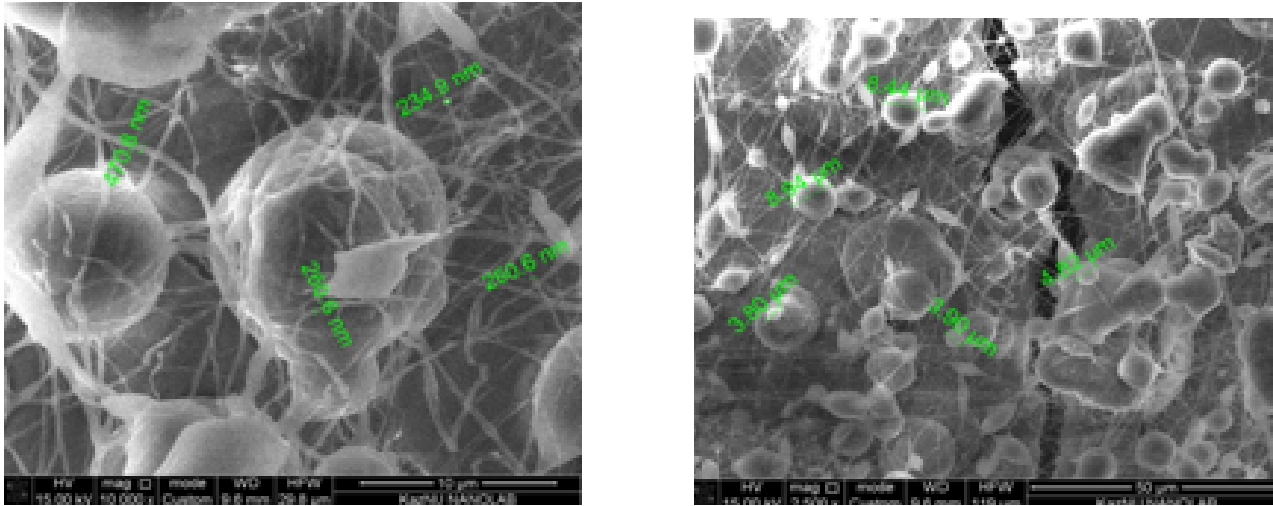
CNF particles with a diameter of 56.1 nm to 567.5 nm are visible, structural elements take the form of fibrils - filamentous formations, the length of which exceeds their diameter by more than a row.

CNF from Coal tar + polymethyl methacrylate after exposure of the solution for 24 hours.



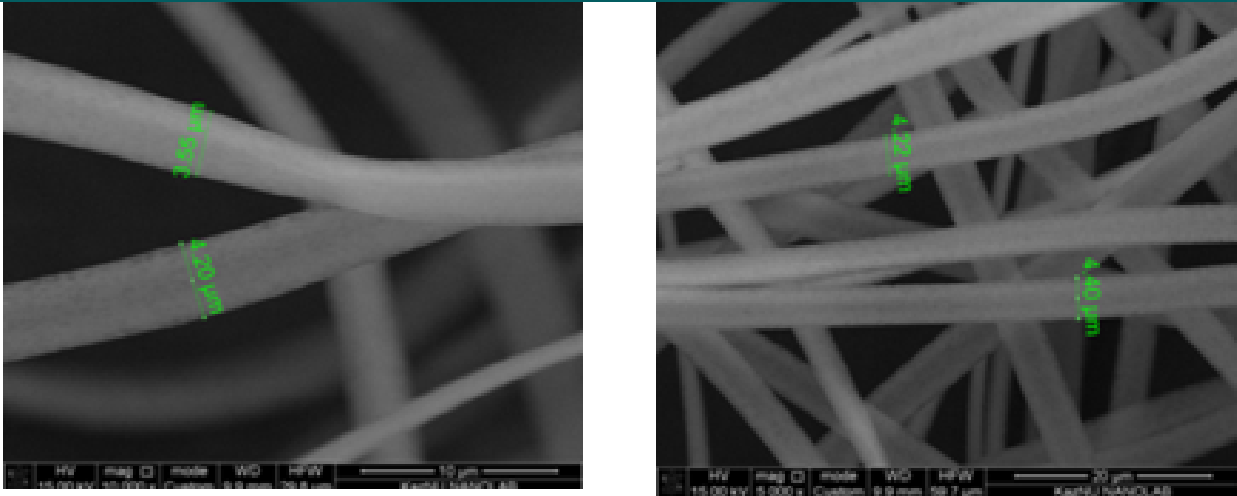
The figure clearly shows hydrocarbon particles with a diameter of 2.40 to 4.63 microns, structural elements take the form of fibrils - filamentous formations

CNF coal tar+polymethyl methacrylate on cone backing

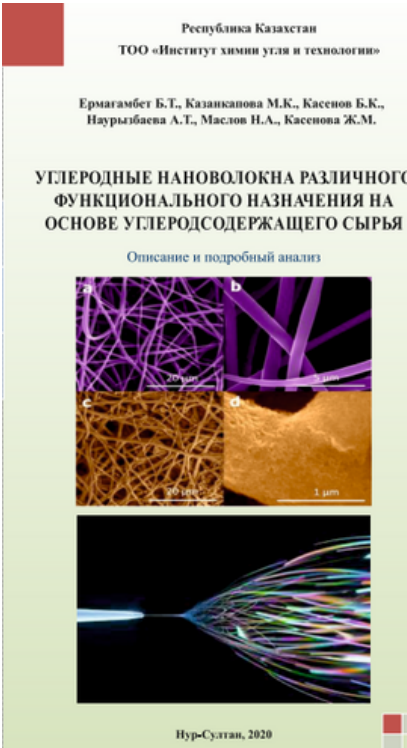


Particles of nanofibers with a diameter of 234.9 nm to 470.8 nm are visible, the adhesion of fibers during deposition and the formation of fiber agglomerates of various shapes during drying can be associated both with incomplete drying of the fibers and with the presence of undissolved residues of the fiber-forming polymer in the spinning solution, and also air bubbles.

CNF coal tar pitch+polymethyl methacrylate



The figure clearly shows CNF particles with a diameter of 480.6 nm to 2.57 μm. Due to the existence of pentagons and heptagons, structural defects, the formation of bridges and distortion of the cylindrical surface in the sample are observed.

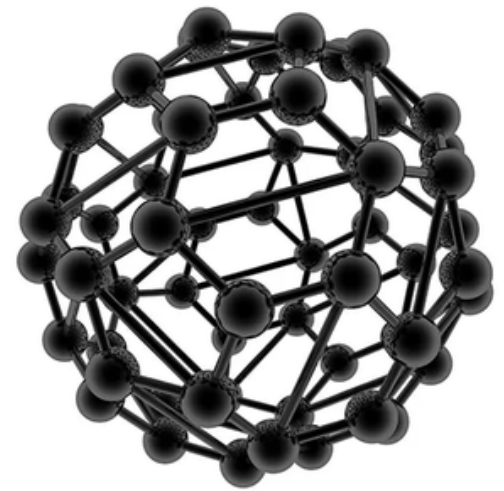
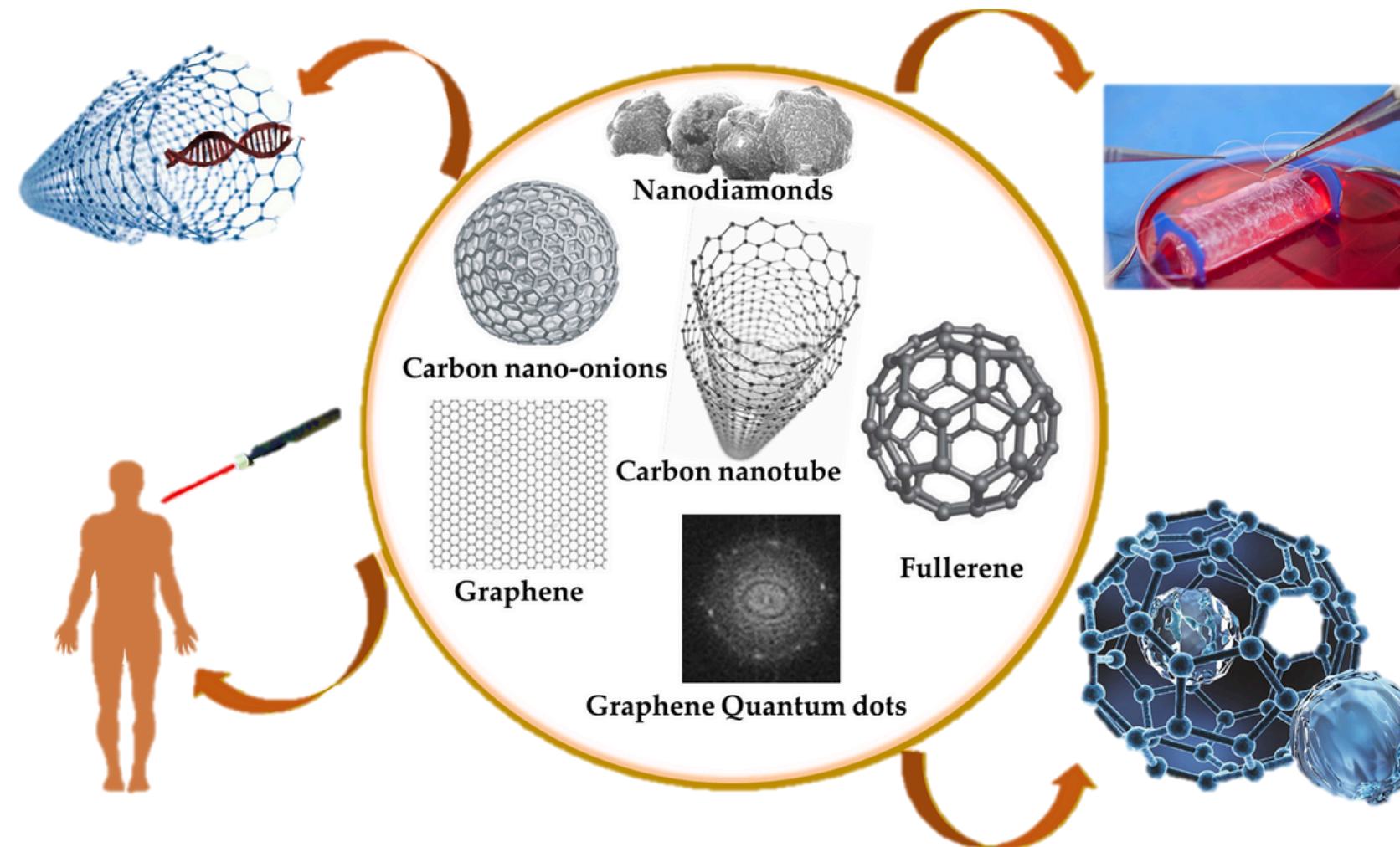


PRODUCING NANOMATERIALS BY CVD METHOD

Chemical Vapor Deposition (CVD) is a process used to produce solid materials, typically in the form of thin films, on a substrate through chemical reactions of vapor-phase precursors. For carbon nanomaterials, this involves the decomposition of a carbon-containing gas (like methane, acetylene, or ethylene) at high temperatures in the presence of a catalyst.

Chemical Vapor Deposition (CVD) is a process used to produce high-purity, high-performance solid materials by depositing a thin film from a vapor phase.

1. High Quality and Parameter Control
2. Scalability
3. Diverse Applications
4. Technological Innovations
5. Economic Efficiency



- Graphene: Single layer of carbon atoms arranged in a hexagonal lattice.
- Graphene Oxide (GO): Graphene with oxygen-containing groups.
- Reduced Graphene Oxide (rGO): Graphene oxide that has been chemically reduced to remove oxygen groups, improving conductivity.

THE PROCESS OF THE METHOD

Choosing a catalyst

Table I
Carbon solubility and the growth mechanism on typical metals for CVD graphene.

Metal (bulk)	Carbon solubility at 1000 °C (at)
Copper(Cu)	0.04
Cobalt (Co)	3.41
Platinum (Pt)	1.76
Nickel (Ni)	2.03
Palladium (Pd)	5.98
Iron (Fe)	7.89
Germanium (Ge) (semi-metal)	0.00

METHOD PROCESS IN 3 STEPS

1

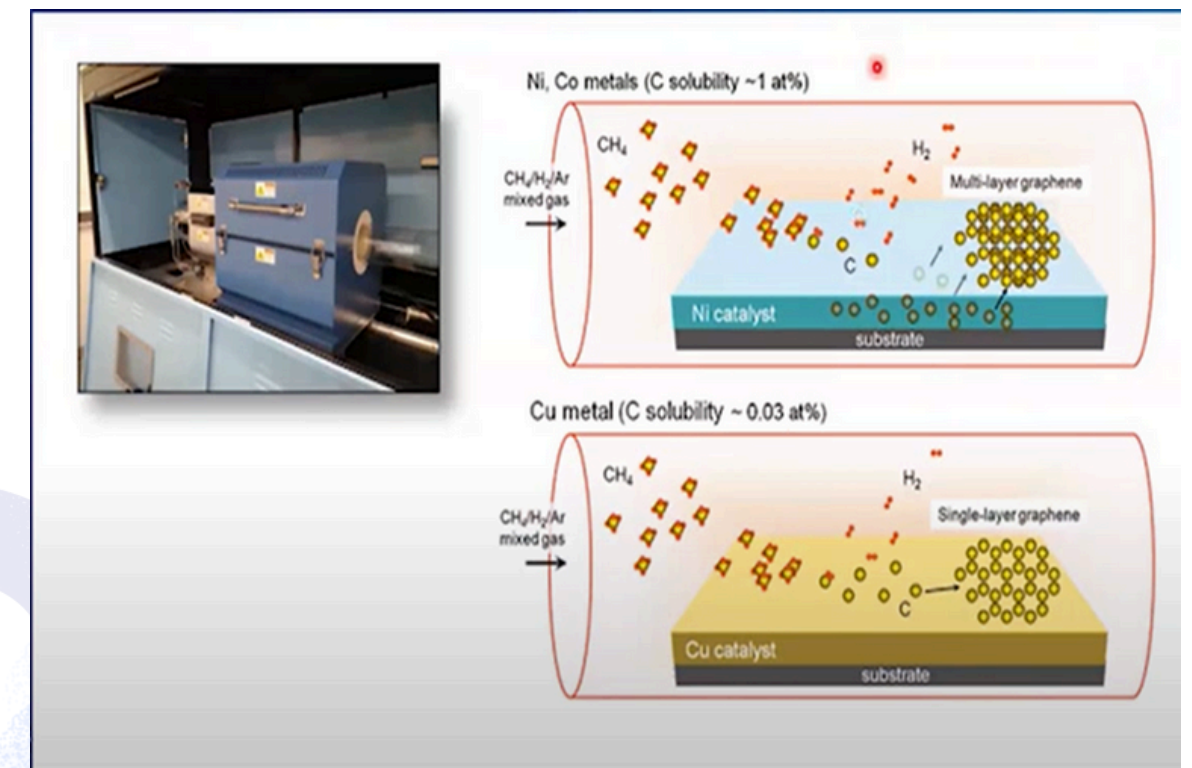
Preparation and Setup
Coat the selected substrate with a metal catalyst (e.g., nickel, iron, or cobalt).

2

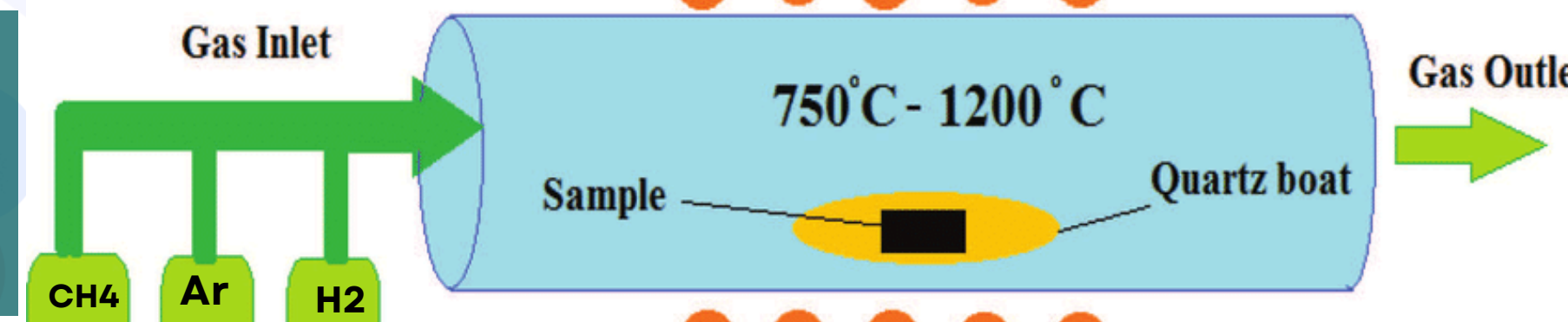
Deposition Process
Heat the reactor to high temperatures (500-1000°C), causing the gases to decompose and release carbon atoms.

3

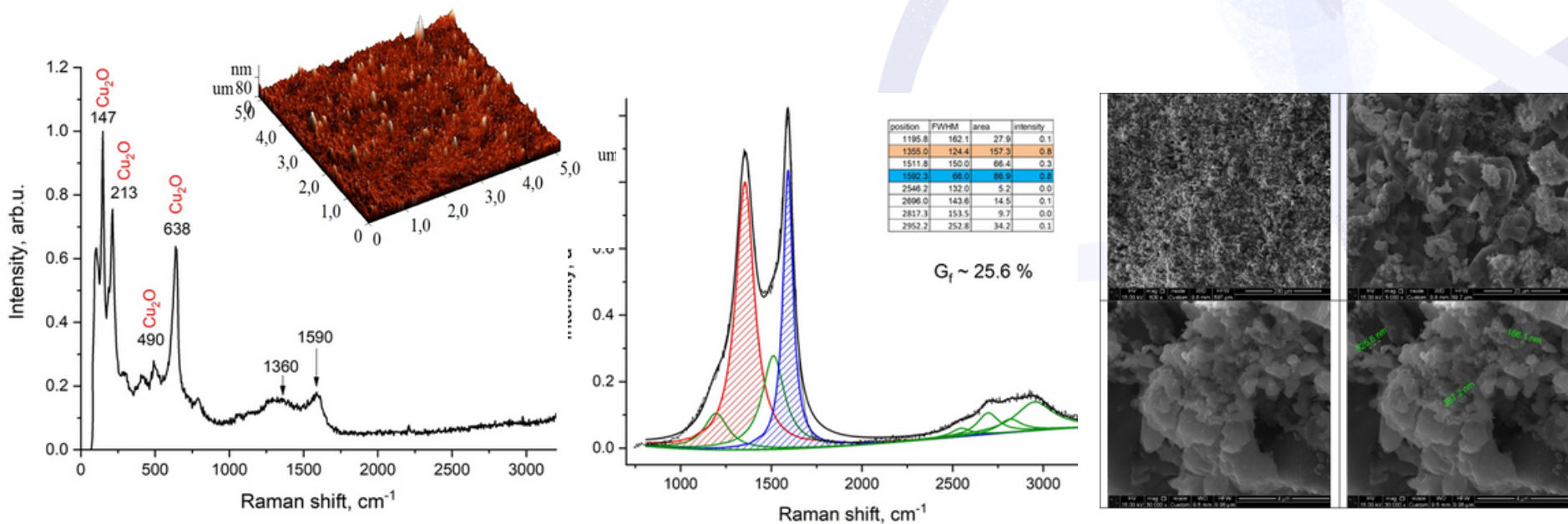
Post-Processing and Characterization
Gradually cool the reactor and turn off the gas flow.



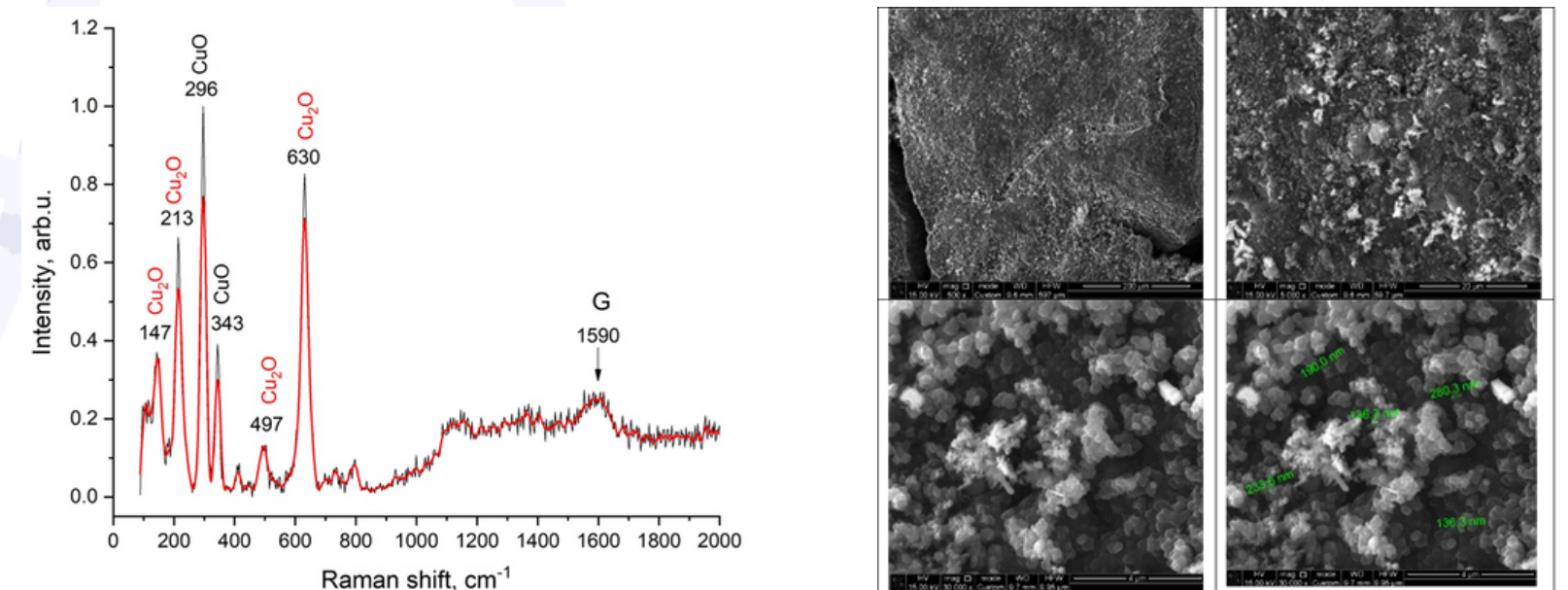
Chemical vapor deposition includes chemical precipitation, a reaction in which precursor molecules are activated and pass into a gaseous state, which is deposited on the substrate. The precursor may initially be in a solid, liquid or gaseous state. Substrates may have an amorphous, mono- or polycrystalline structure, in some cases in a molten state.

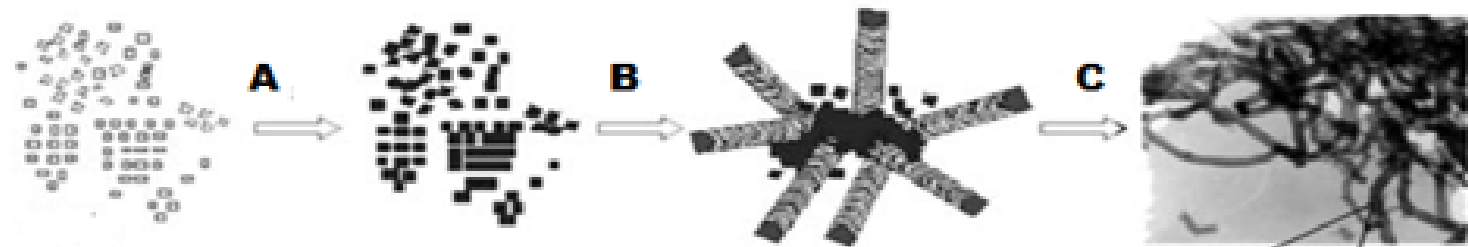


CVD reactor products 900°C H2-49 ml/min, Ar-20 ml/min, CH4

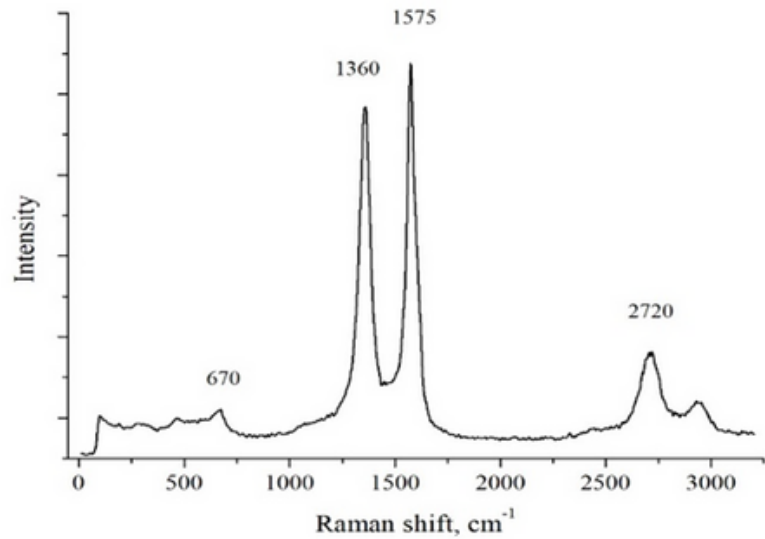
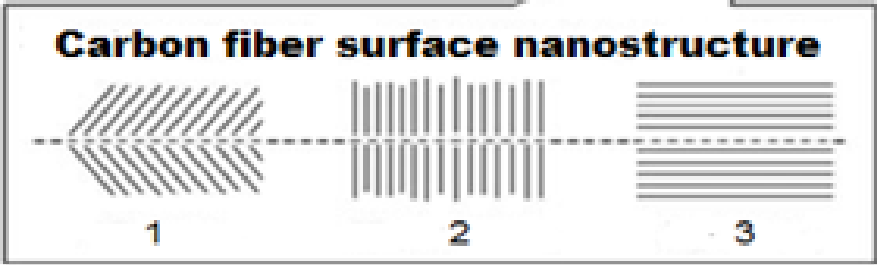


CVD reactor product 900°C without H2 with pump, Ar-20 ml/min, CH4



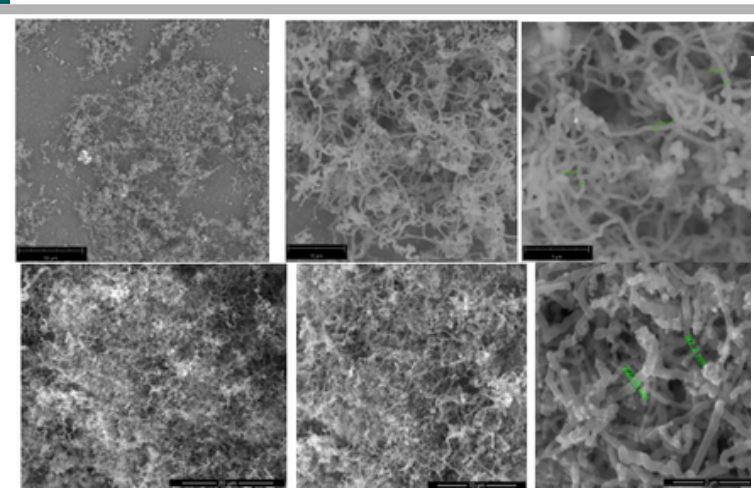
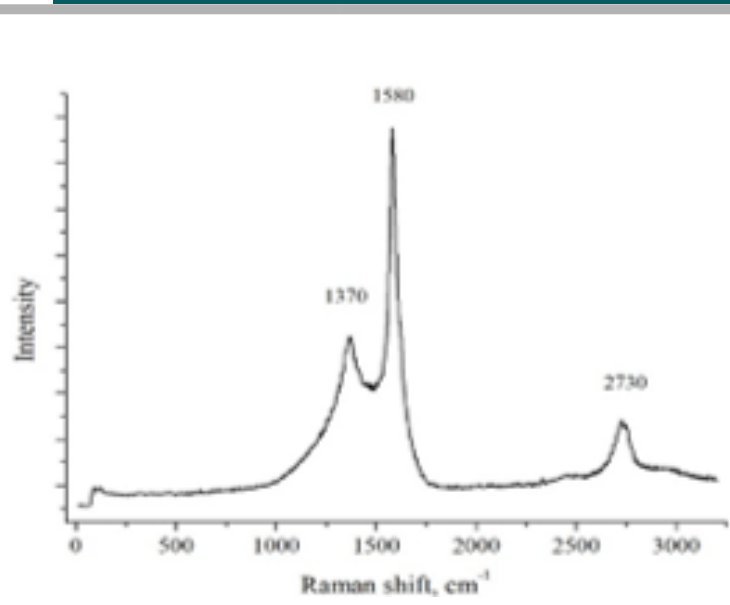


Scheme for the production of CFC based on Co-catalyst



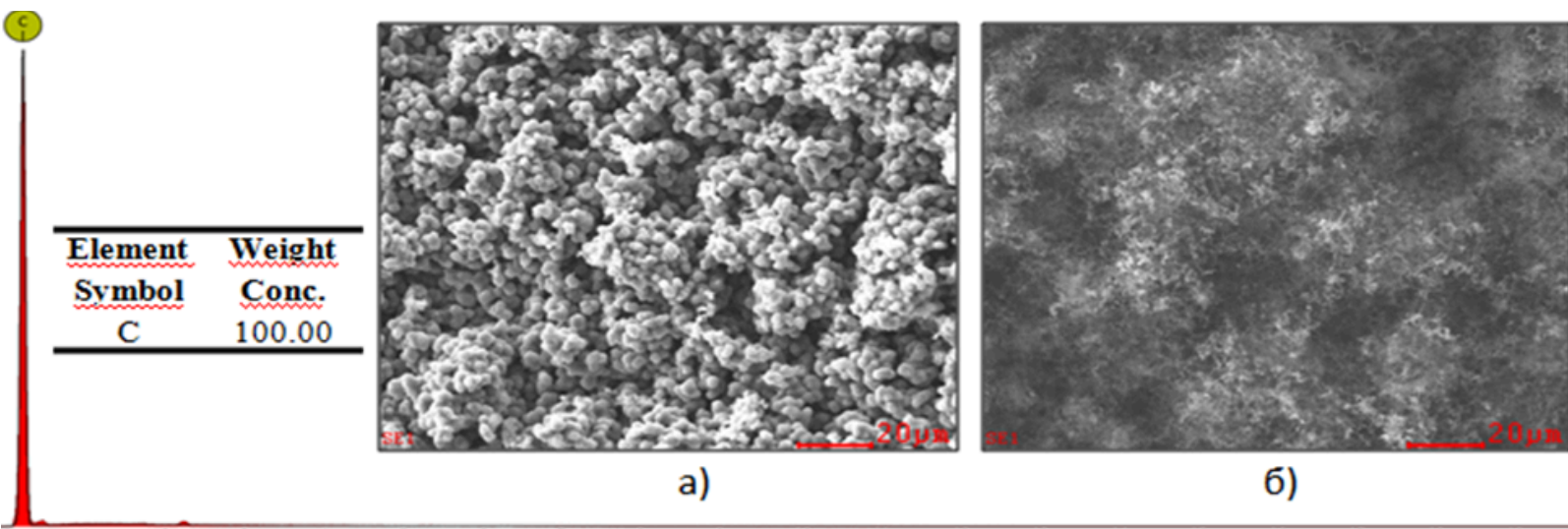
There are regions containing crystalline graphite structures (possibly carbon nanotubes), as evidenced by narrow peaks at 1360, 1575, 2720 and 2940 cm-1

Particles of CNT with diameters from 50 to 500 nm are clearly visible, which are folded into a single, seamless seam cylinder. The length of nanotubes can reach tens of micrometers, the end of such a tube can be an open or closed fullerene-like hemisphere. The cylindrical surface of the tubes is formed by hexagons. In real nanotubes, due to the existence of penta- and heptagons, structural defects, the formation of bridges and the sparking of a cylindrical surface are observed



Electron microscopic images of the film after synthesis at t = 120 min, on the device

After synthesis, carbon materials in the form of a film were formed on the walls of the reactor. The elemental composition of the carbon material showed the presence of 100% pure carbon

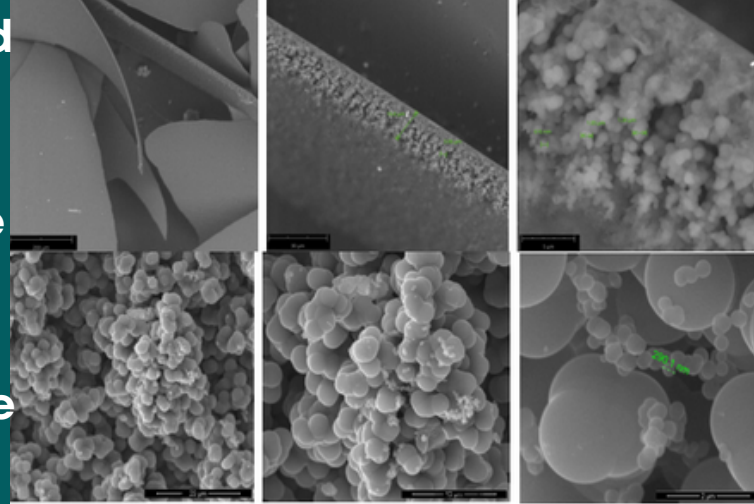


Elemental composition of the film after synthesis (T = 800C) with a holding time: a - 60 min; b - 120 min

Thus, the proposed method of carbon nanotubes is based on the method of chemical (catalytic) vapor deposition, which is the most promising method of industrial production and provides a product with a relatively high multilayeredness and homogeneity of the fraction, which determines the achievement of the strength characteristics required for structural materials. As a result of the high-temperature process, carbon nanotubes (CNTs) were obtained at 8000C (in an inert atmosphere) by the CVD method (chemical Vapor Deposition) with the decomposition of monoxide on the Co catalyst surface, where the hydrophobic ash of the Kendyrlik (Kazakhstan) based on soot. The optimum condition for obtaining CNTs by a catalytic method was established, where the holding time was 120 min at a pyrolysis temperature of 800 0C. The yield of carbon nanotubes per unit mass of catalyst was ~ 30%. The carbon nanotubes obtained by this method can be used as a power filler in the production of composite and heat-insulating materials.



Carbon material was formed as graphite sheets (also known as graphene), in which the carbon atoms are ordered into sheets with a thickness of 10 to 20 μm. As can be seen from picture the material consists of spherical forms of carbon with dimensions from 200 nm to 1.0 μm.



Electron microscopic images of the film after synthesis at t = 60 min, on the device

Analysis of wastewater “Astana su arnasy”

01

A production test of the obtained adsorbents for wastewater treatment of JSC “ASA”, Nur-Sultan, May-July 2018-2019 was carried out.

The obtained samples of carbon porous sorbents passed laboratory tests for the purification of gases and sewage water taken from the SUC "Astana su arnasy". Sampling point: distribution chamber after preliminary mechanical cleaning. Chemical analysis of wastewater before (control) and after treatment with adsorbents was carried out in an accredited analytical laboratory of sewage treatment facilities of the SUC "Astana su arnasy", in which the main indicators of wastewater treatment were determined. Analysis of the data obtained showed that after wastewater treatment, the values of all chemical indicators decrease, especially such indicators as BOD (76-88%), suspended solids (77.38-61.57%), iron (61.16-70, 87%) and oil products (96.52-97.22%), which are the highest degree of wastewater treatment (in terms of the number of indicators). Indicators such as pH, suspended solids, phosphates, oil products generally comply with ND standards.



The results of chemical analysis of wastewater "Astana su arnasy" before and after treatment with adsorbents

The name of indicators	Purification degree, in %							
	"Shoptyko I"	"Saryko I"	«Pyati metrovy»	«Sputnik»	«Nadezhda»	«Mamay»	«Oikaragay»	«Kushmurum»
pH	8,82	8,70	7,35	7,85	7,9	8,5	9,00	10,10
BOD, mgO / dm ³	86,31	72,63	87,77	70,00	88,44	84,44	36,84	84,24
COD, mgO / dm ³	61,53	34,23	52,75	57,14	68,29	52,75	14,61	29,43
Suspended substances, mg/dm ³	73,22	67,58	65,51	93,11	73,79	69,65	59,94	72,31
Chlorides, mg/dm ³	46,29	23,14	3,74	2,14	3,74	0,13	-	-
Ammonium nitrogen, mg/dm ³	63,74	56,99	10,88	14,23	22,04	11,72	48,16	89,81
Nitrites, mg/dm ³	57,61	58,27	35,03	13,63	29,92	42,33	45,03	42,22
Nitrates, mg/dm ³	79,62	64,81	21,42	18,75	12,5	30,35	40,74	47,61
Iron, mg/dm ³	81,74	76,58	56,31	66,11	76,69	61,16	22,61	56,52
Phosphate, mg / dm ³	22,52	46,92	33,93	35,68	47,65	65,34	79,87	93,32
Zinc, mg / dm ³	24,75	14,35	8,16	33,66	-	-	29,20	66,66
Copper, mg/dm ³	43,47	47,82	9,67	16,00	22,58	41,93	-	6,66
Synthetic surfactants, mg / dm ³	25,35	29,57	39,91	81,31	66,94	50,10	11,97	13,64
Oil products, mg/dm ³	65,25	56,16	88,19	94,73	95,13	92,36	55,84	18,00

The obtained activated adsorbents were tested for the treatment of sewage waste water taken from the State Enterprise "Astana su Arnasy" (Astana). Sampling point: distribution chamber after preliminary mechanical cleaning. Chemical analysis of wastewater before (control) and after treatment with adsorbents in laboratory adsorption plants was carried out in an accredited analytical laboratory of sewage treatment facilities of the SUC "Astana su arnasy", in which the main indicators of wastewater treatment were determined. The degrees of purification were also calculated according to the main indicators (for comparison of adsorption properties).

The analysis of the data obtained showed that after wastewater treatment, the values of all chemical indicators for all adsorbents decrease, especially such indicators as **BOD, suspended solids, phosphates, iron and oil products**. These results of the study show that the obtained samples based on carbon materials can be considered promising, in particular, as adsorbents for the purification of liquid media.

Tap water purification with the use of "Shoptykol" activated carbon of the Maikuben basin

Works were carried out to purify drinking water from the tap in special columns filled with PCM based on coals "Shoptykol" and "Shubarkol". Physicochemical and microbiological parameters of the source and treated water were studied in the laboratory "RSE "Center for Sanitary and Epidemiological Expertise" of the Medical Center of the Administration of the President of the Republic of Kazakhstan". The results of the study showed that in water after cleaning with adsorbents, the content of total hardness, residual chlorine, bicarbonate, COD decreased. In all respects, purified water complies with the SP "Sanitary and epidemiological requirement for water sources, water intake points for domestic and drinking purposes, domestic and drinking water supply and places of cultural and domestic water use and safety of water bodies", approved. By order of the Ministry of National Economy of the Republic of Kazakhstan No. 209 dated March 16, 2015 and TR "Requirement for the safety of drinking water for the population" approved. Decree of the Government of the Republic of Kazakhstan dated May 13, 2008 No. 456.

According to the obtained results, it can be seen that after water purification with the "Shoptykol" adsorbent, the concentration of chlorides, potassium, sodium, COD decreased



Purification of tap water using PCM based on coal "Shoptykol" and "Shubarkol"

Казакстан Республикасы Президентінің Іс басқармасы Медициналық орталығының «Санитарлық-эпидемиологиялық сараптама орталығы» шаруашылық жүргізу құқығындағы РМҚК РГП «Центр санитарно-эпидемиологической экспертизы» Медицинского центра Управления делами Президента Республики Казахстан на праве хозяйственного ведения

010000, Астана қ., Бейбітшілік көшесі, 93/А үй, телефон: (8 7172) 49-96-53, факс: (8 7172) 31-83-93

Казакстан Республикасы Президенті Іс басқармасы Медициналық орталығының 2016 жылғы 10 наурыздағы № 44 бұйрығымен бекітілген № 13/е нысаны медициналық құжаттама Медицинская документация Форма № 13/у Утверждено приказом Медицинского центра Управления делами Президента Республики Казахстан №44 от 10 марта 2016г.

ИЛАС-MRA NCA KZ.И.01.0570

Ауыз су үлгілерін зерттеу ХАТТАМАСЫ ПРОТОКОЛ санитарно-химического исследования питьевой воды № 781 от 16 ноября 2018г.

Сынама алынған орын (Место взятия пробы): ТОО «Институт химии угля и технологий»
Саны (Количество): на анализ 1 бут. х 5,0 л
Сынаманың алынған күні мен уақыты (Дата и время взятия пробы): 15.11.2018г.
Жеткізілген күні мен уақыты (Дата и время доставки): 15.11.2018г.
Зерттеудің басталу уақыты (Дата начала исследования): 16.11.2018г. аяқталуы (окончания): 16.11.2018г.
Қосымша мәліметтер (Дополнительные сведения): СП «Санитарно-эпидемиологические требования к водоемностям, местам водозабора для хозяйственно - питьевых целей, хозяйственно-питьевому водоснабжению и местам культурно-бытового водопользования и безопасности водных объектов», утв. приказом Министра национальной экономики РК №209 от 16.03.2015г.
Сынақ жүргізу шарттары (Условия проведения испытаний): ылғалдылық 46,0% Температурасы 23,0°C
Сынама алынған нүктелер (Точки отбора проб): 1. Вода после очистки адсорбентом из угля месторождения «Шоптыкол» (Май-кубенский бассейн).

ЗЕРТТЕУ НӘТИЖЕЛЕРІ
РЕЗУЛЬТАТ ИССЛЕДОВАНИЯ:

Көрсеткіштер аты (Наименование показателей)	Нәтижесі (Результат)	Рұқсат етілген нормалары (Допустимые нормы) (ПДК), не более	Единицы измерений	Зерттеу әдістеріне қолданылатын НК (НД на методы испытаний)
Запах при 20,0° С	2	2	баллы	ГОСТ 3351-74
Привкус	1	2	баллы	ГОСТ 3351-74
Цветность	15	20	град.	ГОСТ 3351-74
Мутность	0,52	1,5	мг/дм³	ГОСТ 3351-74
Общая жесткость	3,2	7,0	ммоль/дм³	ГОСТ 26449.1-85
pH	8,12	6,0-9,0	pH	ГОСТ 2874-82
Сульфаты	54,62	500,0	мг/дм³	СТ РК ИСО 10304-1-2009
Аммиак	0,0	2,0	мг/дм³	ГОСТ 33045-2014
Хлориды	53,98	350,0	мг/дм³	СТ РК ИСО 10304-1-2009
Нитраты	0,0	45,0	мг/дм³	СТ РК ИСО 10304-1-2009
Нитриты	0,0	3,3	мг/дм³	СТ РК ИСО 10304-1-2009
Медь	0,0	1,0	мг/дм³	СТ РК ГОСТР 51309-2003
Железо	0,0	0,3	мг/дм³	СТ РК ГОСТР 51309-2003
Калий	4,45	20,0	мг/дм³	СТ РК ГОСТР 51309-2003
Натрий	44,57	200,0	мг/дм³	СТ РК ГОСТР 51309-2003
Окисляемость перманганатная	1,3	5,0	мг/дм³	ГОСТ 23268.12-78
ХПК	6,7	15,0	мгО₂/дм³	ГОСТ 31859
Остаточный свободный хлор	0,09	0,3-0,5	мг/л	ГОСТ 18190

Зерттеу жүргізген адамдардың Т.А.Ә., лауазымы, қолы,
(Ф.И.О., должность, подпись, проводивших исследования):
химик-лаборант отд. санхимисследований РГП «ЦСЭЭ» МЦ УДП РК М. Байтантаева;
химик-лаборант отд. санхимисследований РГП «ЦСЭЭ» МЦ УДП РК И. Ишанова;
фельдшер-лаборант отд. санхимисследований РГП «ЦСЭЭ» МЦ УДП РК А.Б. Балтабаева;

Зертхана меңгерушісінің қолы, Т.А.Ә.
(Ф.И.О., подпись заведующего лабораторией):
зав. отд. санхимисследований РГП «ЦСЭЭ» МЦ УДП РК Г.Габбасова.

КОРЫТЫНДЫ (ЗАКЛЮЧЕНИЕ): Результаты анализа образцов соответствуют, не соответствуют (не нужно зачеркивать) требованиям СП «Санитарно-эпидемиологические требования к водоемностям, местам водозабора для хозяйственно - питьевых целей, хозяйственно-питьевому водоснабжению и местам культурно-бытового водопользования и безопасности водных объектов» утвержденный приказом Министра национальной экономики РК № 209 от 16.03.2015г.

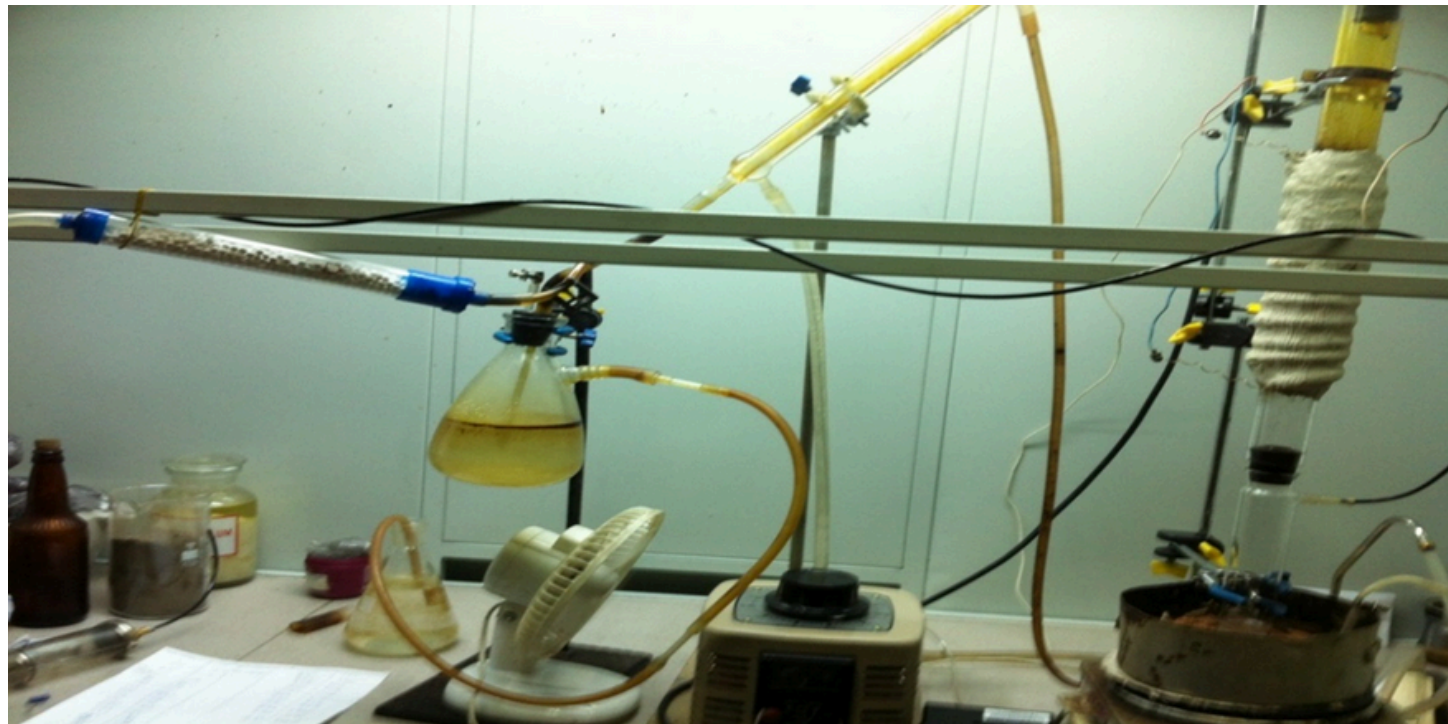
Т.А.Ә., лауазымы, қолы
(Ф.И.О., должность, подпись): директор РГП «ЦСЭЭ» МЦ УДП РК Е.Киясов
«16» ноября 2018 ж.(г.)

Хаттама сынақ жүргізілген үлгілерге ғана таратылады
(Протокол распространяется только на образцы, подвергнутые испытанию)
СО-ның рұқсатымен сынақ хаттамаларын бізге шығаруға тыйым салыныды. Хаттама 3 данада тастырылды
(Переводится протокол испытаний без разрешения ИЦ запрещается. Протокол составляется в 3-х экземплярах)

1 бет 1 из 1

Approbation of adsorbents for gas purification

In the laboratory of the Institute of Coal Chemistry and Technology, the resulting carbon nanoporous materials were tested for purifying gases (composition: H_2S , CO , CO_2 , CH_4 , N_2 , H_2) from harmful substances H_2S , CO_2 , N_2 to obtain predominantly flammable components CO , CH_4 , H_2 . The results of the elemental analysis before and after gas purification with determination of the degree of purification are presented in the table



Test report on gas cleaning with the activated Shoptykol adsorbent (No. 1) and the activated Shoptykol adsorbent hydroxy.: KOH (1: 1) (Kuzbass, Kemerovo)

КОЛИЧЕСТВЕННЫЙ АНАЛИЗ

1. Проба (образец):

№ п/п	Определяемые показатели	Результаты испытаний					Единицы измерения
	Удельные удерживаемые объёмы газов (по данным газовой хроматографии) при 30° С	№ 1 Акт.адсорбент "Шоптыколь с КОН"	№ 2 Акт.адсорбент "Шоптыколь с КОН" (облученный)	№ 3 Акт.адсорбент "Шубарколь с КОН"	№ 4 Акт.адсорбент "Шубарколь"	№ 5 Акт.коксовая мелочь "Шубарколь"	
1.	Азот	4,7	2,8	5,4	1,21	2,27	см³/г
2.	Кислород	5,0	3,40	5,2	2,14	3,47	см³/г
3.	Метан	13,7	11,4	26,10	3,01	7,84	см³/г
4.	Водород	0,59	0,51	0,46	0,42	0,73	см³/г
5.	Моноксид углерода СО	7,90	4,70	9,3	2,43	3,90	см³/г
6.	Углекислый газ	105,0	159,9	223,9	114,2	121,4	см³/г
7.	Диоксид серы SO₂	поглощение полное	поглощение полное	552,7	поглощение полное	поглощение полное	см³/г
8.	Диоксид азота NO₂	поглощение полное	поглощение полное	поглощение полное	поглощение полное	поглощение полное	см³/г
9.	Пропан (C₃H₈) при T=140°С	11,5	14	27,5	13,2	5,4	см³/г
10.	Бутан (C₄H₁₀) при T=140°С	26	46,5	139,2	74,1	113,4	см³/г
	Коэффициент селективности разделения газов (отношение удерживаемых объёмов)						
1.	CH₄/ N₂	2,9	4,1	4,8	2,5	3,4	
2.	CH₄/ СО	1,7	2,4	2,8	1,2	2,0	
3.	СО /H₂	13,4	9,2	20,2	5,7	5,3	
4.	СО₂ / CH₄	7,7	14,0	8,6	37,9	15,5	

Испытания проводили (должность, подпись, Ф.И.О.):

Инженер - аналитик лаборатории



Суняева Т.В.

Закключение: протокол проверен и оформлен правильно

Директор ООО «Сорбенты Кузбасса»



Бервено А.В.



ООО «СОРБЕНТЫ КУЗБАССА»

Испытательная лаборатория

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Банк: Банка ВТБ (ПАО) в г. Москва, ИНН/КПП 4205205648/420501001, ОГРН 1104205014011, ОКПО: 67691232, ОКАТО: 32401365000, ОКОПФ 12165, ОКТМО 32701000001, ОКОГУ – 4210014, ОКВЭД 73.10, 24.66.4, 24.14.2, 24.11, 24.7, 74.20.14, 74.20.15

Свидетельство о состоянии измерений в испытательной лаборатории:
№ 976/16 выдано ФБУ «Кемеровский ЦСМ» г. Кемерово

1. The samples of carbon sorbents from hard coals submitted by the Institute of Coal Chemistry and Technology LLP for testing have developed porosity, with the presence of micropores in the range of 0.3-2 nm, which is confirmed by the results of analyzes using gas adsorption chromatography (molecular probe method) using as adsorbates of nitrogen, oxygen, carbon monoxide, carbon dioxide, methane, hydrogen, sulfur dioxide, nitrogen dioxide, propane, butane, as well as gas mixtures.

2. The tests carried out prove the higher efficiency of carbon sorbent sample No. 3 in comparison with others for carbon dioxide, carbon monoxide, methane, propane and butane.

3. High specific retention volumes of gases and their separation coefficients on sample No. 3, determined by gas chromatography, suggest the prospects of commercializing the technology for the synthesis of carbon sorbents for their further use in air purification processes and flue gas capture, gas purification, ventilation, filters and sorption installations, and also recommend voluntary certification of samples No. 3 and No. 5 in accordance with GOST R for the possibility of further implementation in the territory of the Customs Union.



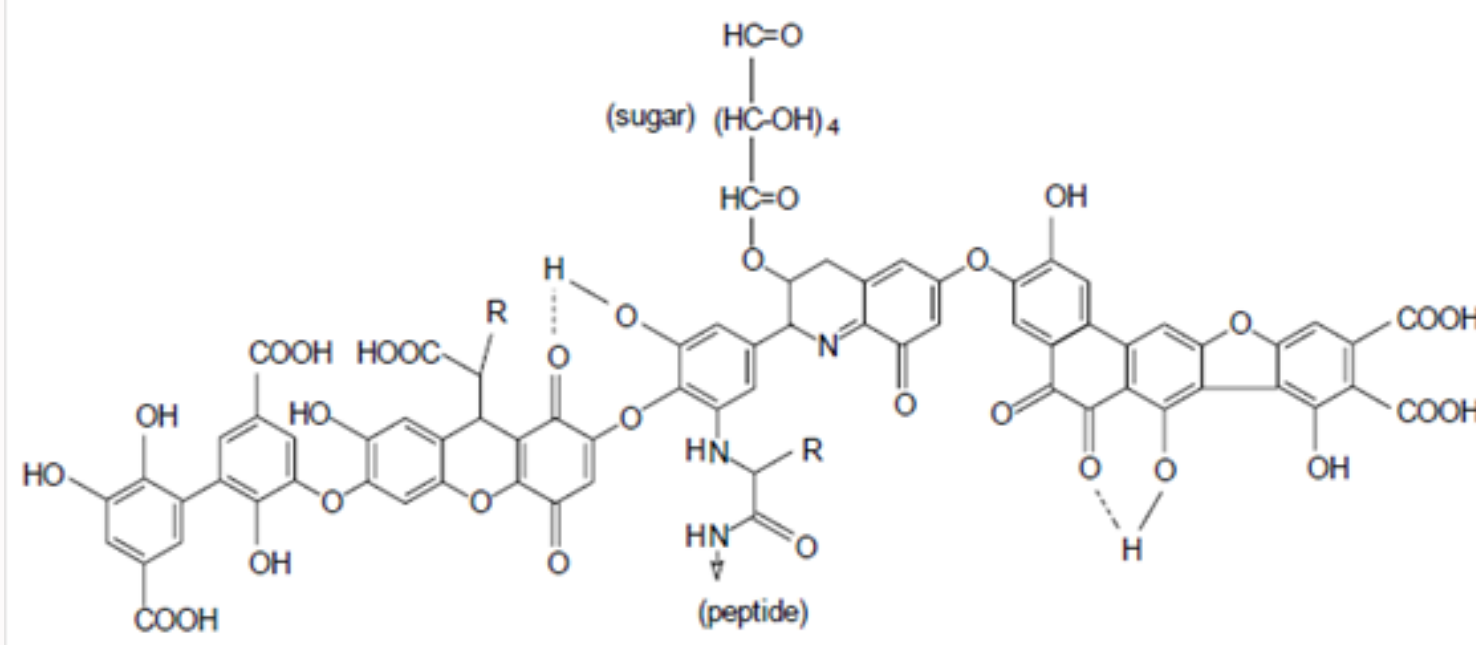
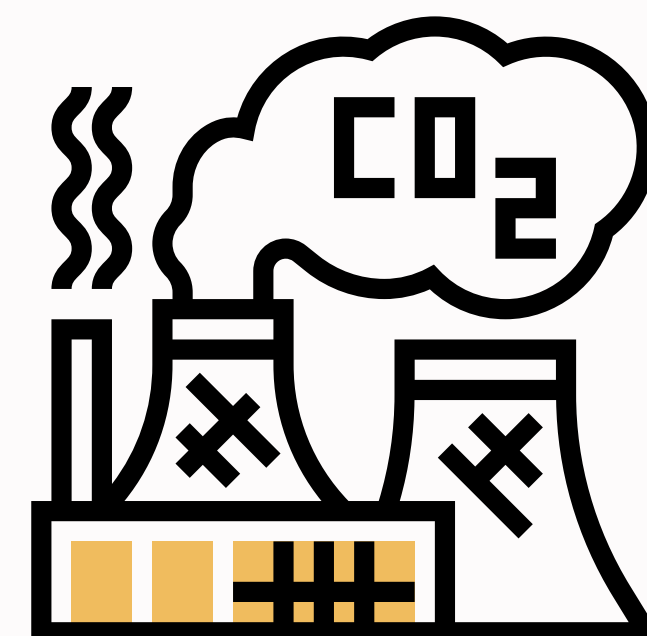
Characterization of humic acid salts and their use as a “green solvent” for CO₂ capture and utilization

Authors: Tomasz Spietz, Maira Kazankapova, Szymon Dobras, Zhanar Kassenova, Bolat Yermagambet, Andrey Y. Khalimon, Sławomir Stelmach

The EU aims to be climate neutral by 2050. To achieve such an ambitious goal, net greenhouse gas emissions should be reduced by at least 55% by 2030. CCUS technologies play an important role in the energy transition. Post-combustion CO₂ capture methods are essential to reduce CO₂ from the chemical industry, power generation and cement plants. A well-known method of CO₂ reduction is chemical absorption using amine solutions. While very effective, amine solutions can undergo degradation, are corrosive, and can be released into the atmosphere (along with the treated gas). A more environmentally friendly alternative may be humic acid salts (HAS).

In this work, a process for the preparation of humic acid salts of potassium (HmK) and ammonium (HmA) was described. Then, a detailed characterization of the obtained HAS was carried out (elemental analysis, granulometric and thermogravimetric analysis, ¹H-NMR and IR spectroscopy). Finally, the obtained materials were evaluated for use as absorbents for CO₂ capture and utilization.

Laboratory tests on the maximum absorption capacity and CO₂ absorption rate of HAS were conducted. It was shown that the absorption capacity was more than 10 times lower than that of a benchmark solution of 30% MEA. However, the concentration of active groups (carboxyl and hydroxyl) in the HAS solvent was much lower than in 30% MEA. The CO₂ absorption rate of a 30% HmA solution was close to that of 30% MEA. Nevertheless, HAS solutions may provide an environmentally friendly promising alternative to amine solutions.



Model structure of humic acid according to Stevenson, R can be alkyl, aryl or aralkyl.

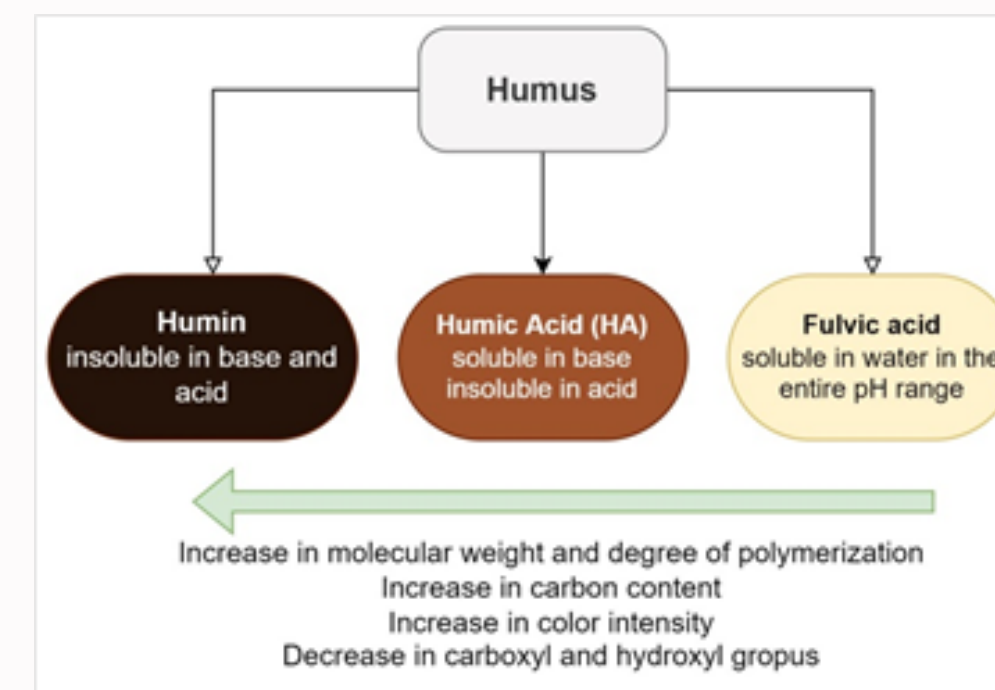


Table 1. Elemental analysis of obtained humic salts (HAS).

Solution	Technical specification, %			Content, %					Chemical formula	O/C	H/C	P ₂ O ₅ , %	K ₂ O, %
	W ^t	A ^d	V ^d	C	H	N	S	O					
Potassium humate, HmK	44.80	11.64	42.69	34.31	1.66	0.80	0.43	19.03	C ₂₉₀ H ₁₆₀ O ₁₂₀ N ₆ S	0.55	0.048	0.31	24.65
Ammonium humate, HmA	56.46	31.76	14.90	53.21	2.70	13.89	0.48	12.70	C ₄₄₀ H ₂₇₀ O ₈₀ N ₁₀ S	0.24	0.051	0.26	9.48

W^t - total moisture, A^d – ash content, V^d – volatile matter

Table 2. Chemical composition of obtained HAS.

Solution	The content of elements, wt. %											
	C		Na	Al	Mg	Si	K	Ti	Fe	S	F	Ca
Potassium humate	35.95		0.44	8.57	0.25	1.12	21.05	-	1.47	0.14	0.84	-
Ammonium humate	56.09		0.19	2.84	0.30	7.25	0.65	0.36	0.74	-	-	0.49

humate											
	Content of cations, mg/l					Content of anions, mg/l					
	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻			
Potassium humate	442.2	34.7	14 658.9	128.4	762.3	137.3	77.6	550.9			
Ammonium humate	375.1	7 144.7	1 722.7	134.4	674.4	135.9	28.4	227.9			

Table 3. Other parameters of prepared humic acid salts.

Solution	HA, dry basis %	TOC, %	pH	Conductivity mS/cm	Surface S _{BET} , m ² /g	The content of functional groups, mmol/g		Particle size, μm		
						carboxyl	Phenolic-hydroxyl	10 %	50 %	90 %
Potassium humate	81.48	2.82	12.33	20.44	0.55	0.241	0.549	0.02	0.36	3.57
Ammonium humate	80.70	17.36	10.94	12.18	3.96	0.304	0.126	0.69	7.21	296.00

TOC – total organic carbon

Table 4. pH of the HAS solutions.

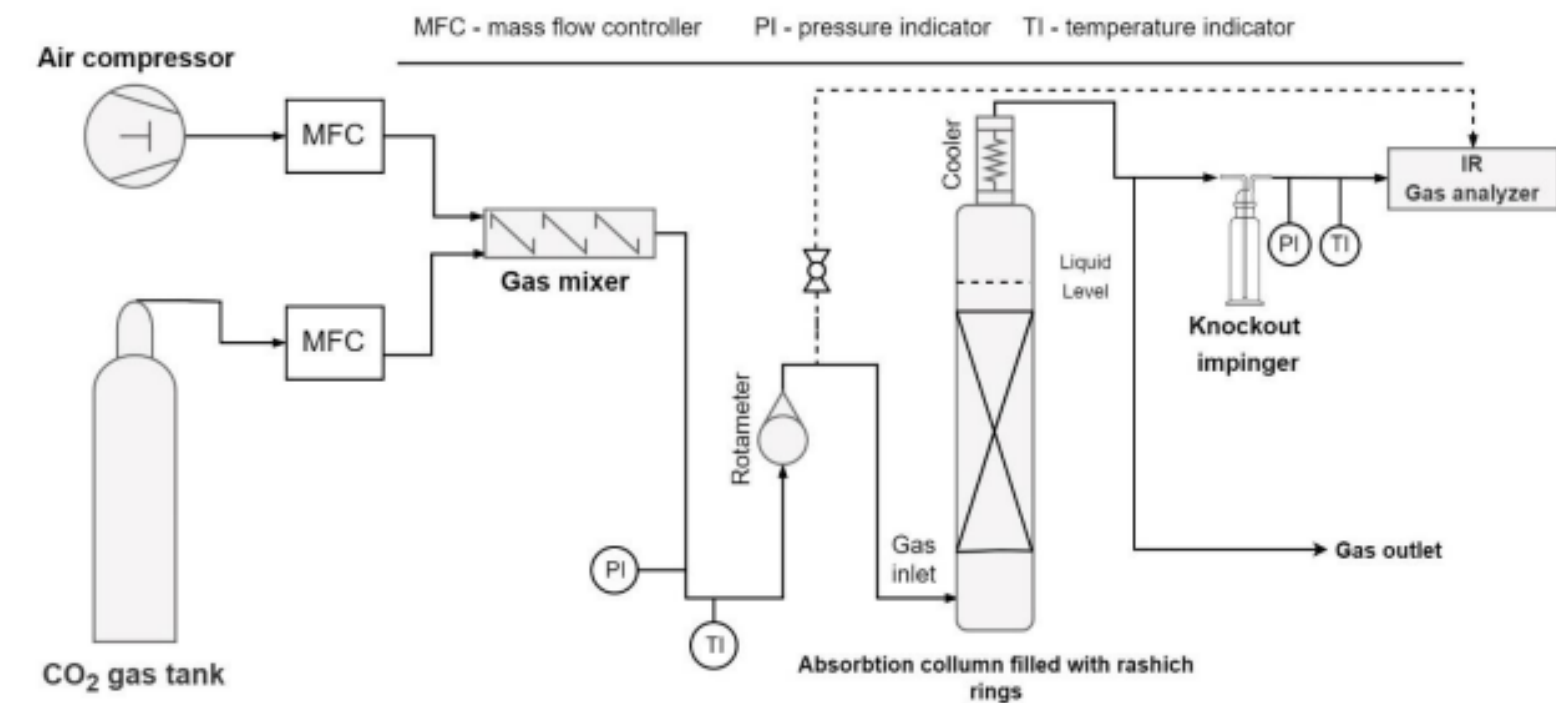
HmK		HmA	
% wt.	pH	% wt.	pH
50	10.975	50	10.202
30	10.915	30	9.927
10	10.757	10	9.722
1	10.249	1	9.421
0.1	9.409	0.1	9.048

Laboratory stand for CO₂ capture

The laboratory setup for studying CO₂ absorption (Fig. 12) consisted primarily of a glass-jacketed absorption column. The double wall of the absorber allowed its temperature to be controlled by a thermostat. To enhance the mass transfer process, the column was filled with glass Rashig rings (6 mm in diameter). The column had a total height of 1.2 m and a diameter of approximately 30 mm. An additional Graham condenser at the top of the column was provided to reduce evaporation of the solution. The scheme of the laboratory stand is shown in Fig. 13. It is worth noting that the main purpose of the installation is to conduct screening tests of absorbents and to estimate their practical absorption capacity.

The gas preparation section includes a CO₂ gas tank and an air compressor. Air and carbon dioxide were mixed in a gas mixer (bottle filled with glass balls) and the correct ratio was provided by two mass flow controllers (Beta-ERG, Poland). The total inlet gas flow was visually verified with a rotameter (Dwyer, Visi-Float, VFB series., 0.2-4 l/min, accuracy of 3% of the range). The accuracy of the equipment used is given in Table 5.

The CO₂ content in the inlet and outlet gas was measured with a portable gas analyzer GA-40 T-plus (Madur Electronics). The measuring method was based on NDIR and the measuring range of CO₂ was 0-100% vol.



The scheme of laboratory stand for CO₂ saturation of humic acid salts.

Results and Discussion

Absorption capacities

The tests were carried out by first increasing the salt concentration and then changing the temperature to obtain the best result. The results of the CO2 absorption tests are summarized in the Monoethanolamine (MEA) 30% of aqueous solution and distilled water were tested for comparison and to check the equipment used.

Table 6. Absorption capacity of the humic acid salts solutions studied.

Solution and concentration*	CO ₂ in the inlet gas % vol.	Temperature, °C	Absorbed CO ₂ g _{CO2} /kg	pH before/after the CO ₂ absorption
dw	13.5	25	0.34	6.75/ 6.17
1% HmK	13.5	25	0.60	10.25/6.74
10% HmK	13.6	25	1.22	10.76/6.83
30% HmK	13.5	25	2.69	10.92/6.81
50% HmK	13.5	25	4.69	10.98/7.07
50% HmK	13.5	40	4.18	10.98/7.68
50% HmK	13.5	60	3.76	10.98/8.38
1% HmA	13.6	25	0.89	9.42/6.64
30% HmA	13.6	25	7.12	9.93/7.41
50% HmA	13.6	25	10.90	10.20/7.43
30% MEA	13.4	25	100.82 (0.513 mol _{CO2} /mol _{MEA})	13.30/8.70
30% MEA	13.4	40	97.1 (0.493 mol _{CO2} /mol _{MEA})	13.30/8.78

HmA – ammonium humate, HmK – potassium humate, dw – distilled water, MEA – ethanolamine, * - The solution taken directly form the HAS production is considered 100%. This is not the direct content of HAS.

Carbon dioxide can react with the ammonium humate according to the following equations (3-5):



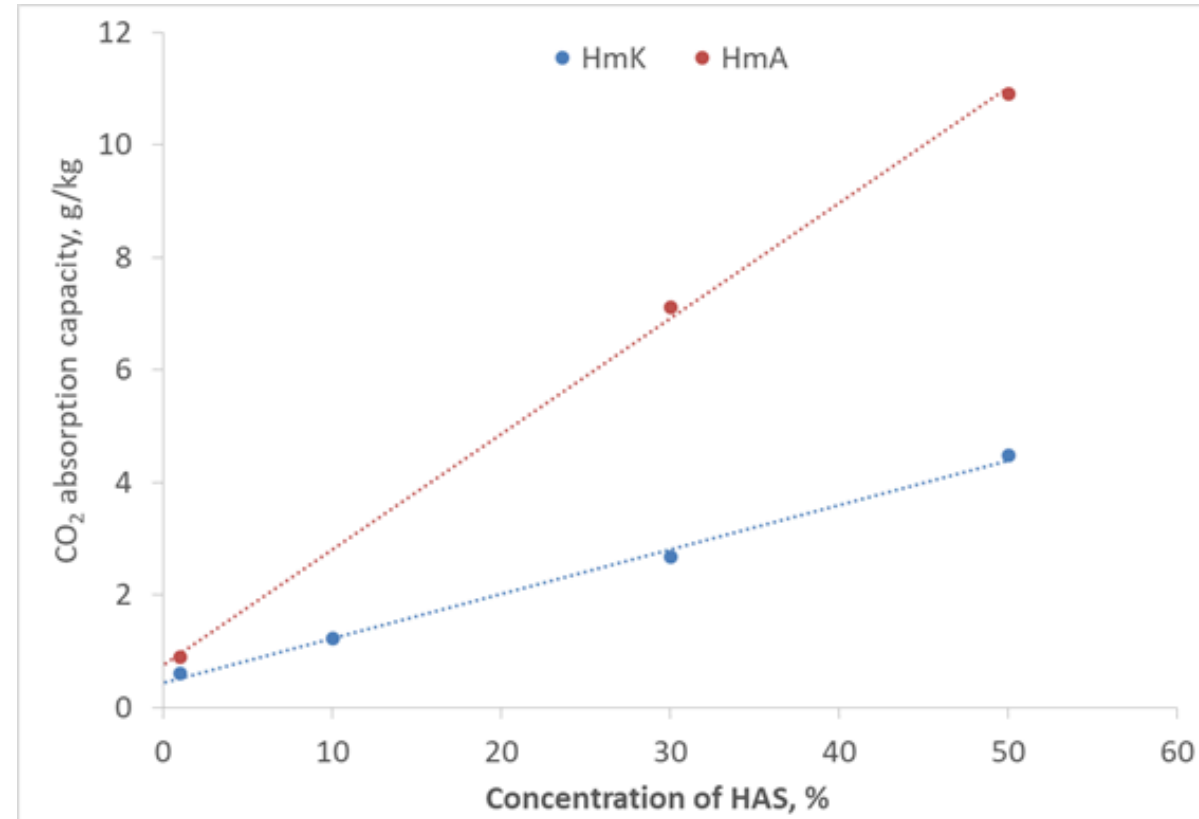
Potassium humate reacts in the following manner:



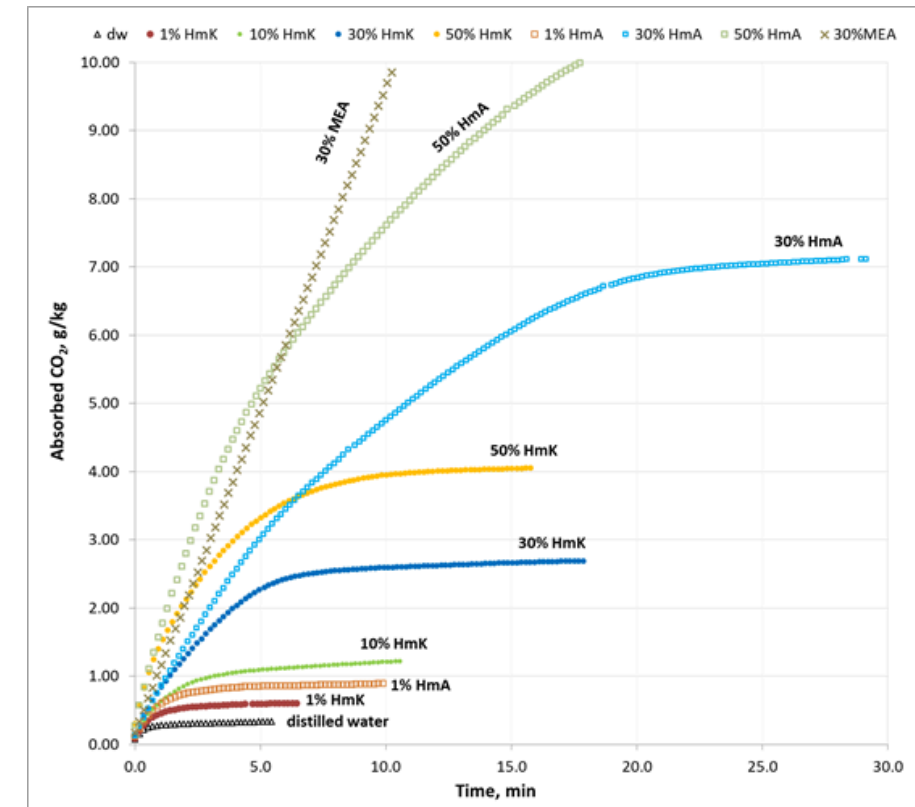
Where $[O^- - Hm - COO^- + 2NH_4^+]$ is HmA; $[O^- - Hm - COO^- + 2K^+]$ is HmK; $OH - Hm - COOH$ is humic acid;

The highest absorption capacity of 10.9 gCO2/kg was obtained for 50% HmA at 25°C. The highest absorption capacity for 50% HmK at 25°C was 4.69 gCO2/kg. The highest absorption capacity of HmA is almost 2.5 times higher. As can be seen, the absorption capacities of HAS were much lower than for benchmark 30% MEA. Even the best result (obtained for 50% AH) had about 10 times less maximum absorption capacity than 30% MEA.

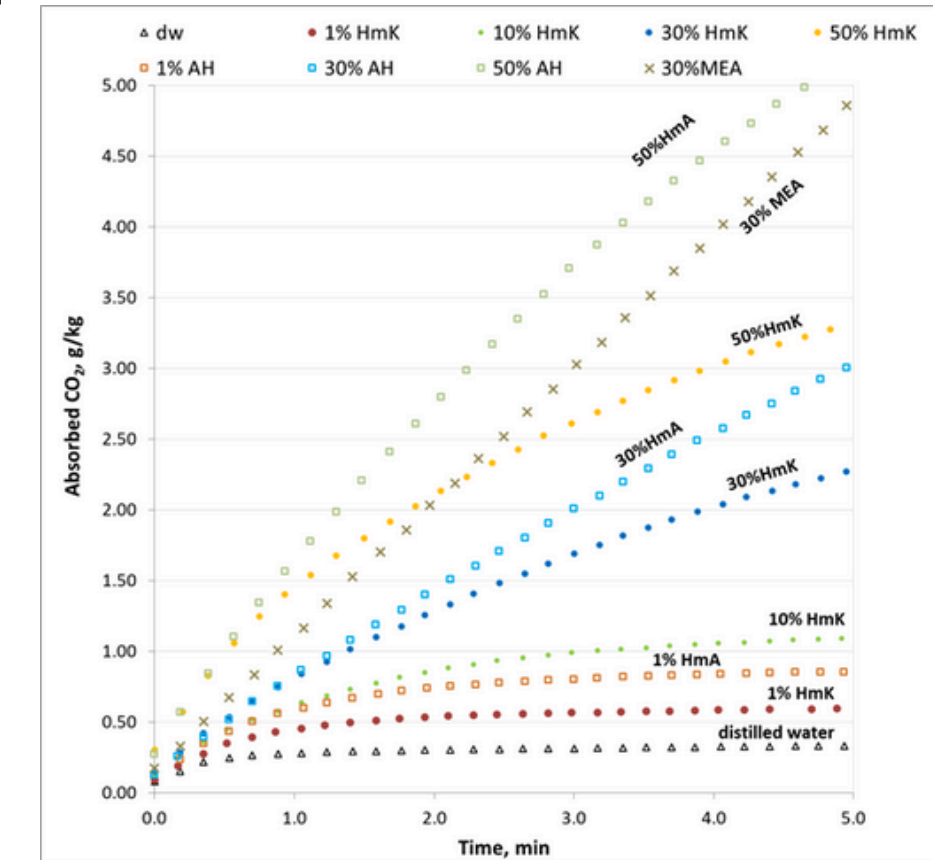
Results and Discussion



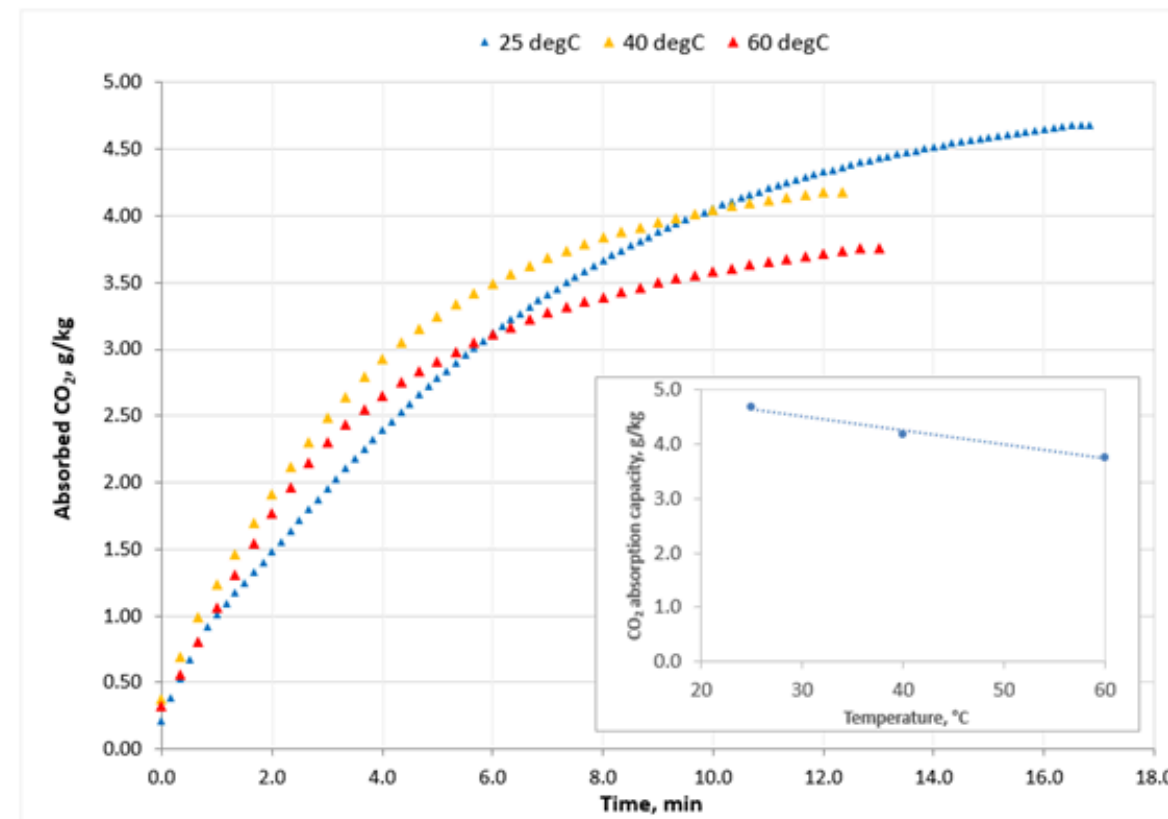
The effect of HAS concentration on the CO₂ absorption capacity



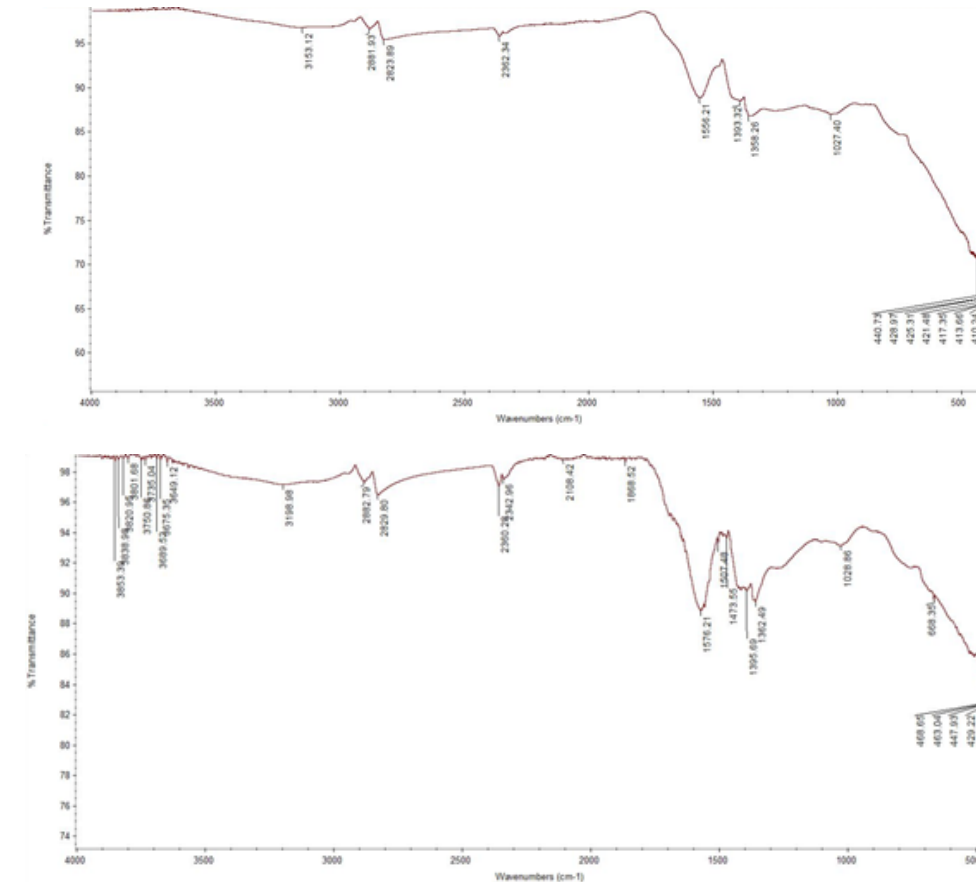
CO₂ absorption rate in studied solutions (at 25°C).



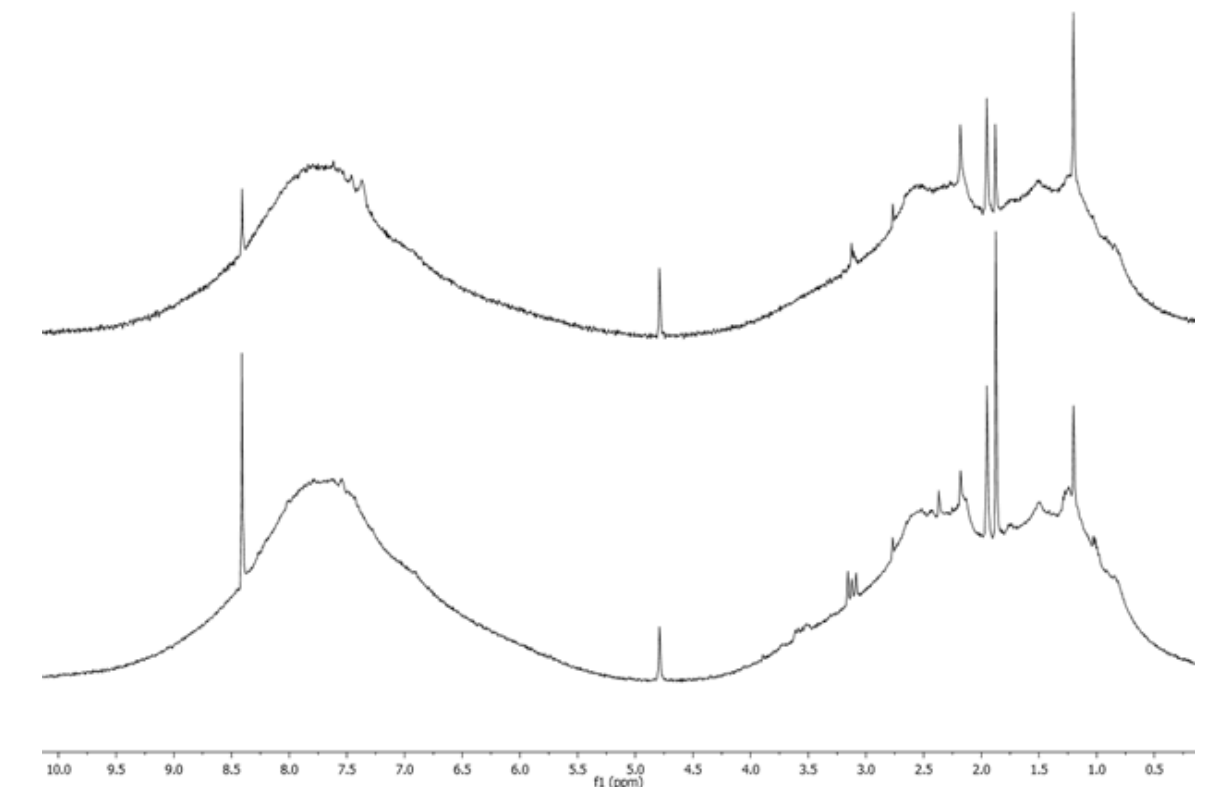
Close-up on the CO₂ absorption rate



The effect of temperature on the CO₂ absorption in 50% HmK



IR spectra of HmA (obtained from 50% solution in H₂O) in Nujol before (A) and after (B) CO₂ absorption at 25 °C



Comparison of ¹H-NMR spectra (in D-₂O) for 50% AmH before CO₂ absorption (bottom) and after CO₂ absorption at 25 °C (top)

The results showed that the studied HAS solutions can absorb CO₂ in the range of 0.6-10.90 g CO₂/kg of the solvent. More concentrated HAS solutions absorbed more CO₂ and the best results were obtained for 50% HmA , which was 10.90 gCO₂/kg. In contrast, 50% potassium humate absorbed 4.69 gCO₂/kg and. From the point of view of further scaling up of the process, it should be mentioned that there was intense foaming of the solution during the absorption.

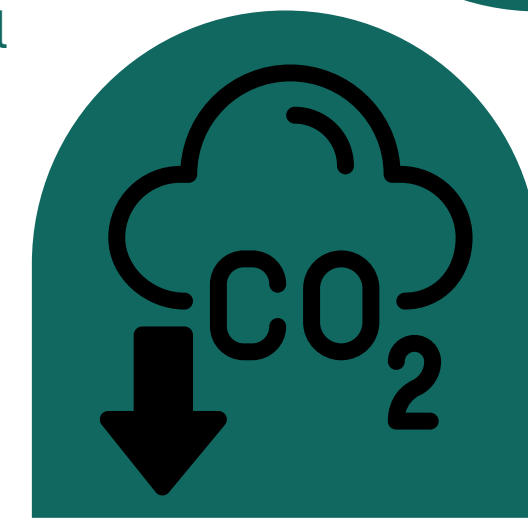
Theoretical calculations of absorption capacities on the basis of conducted analyses (IC, number of functional groups) and their comparison with experimental results showed that the CO₂ absorption capacity of HAS cannot be precisely determined only on the basis of reactions of carboxyl and phenolic groups to bicarbonate and carbonate. In particular, the greatest discrepancy of results in this regard was obtained for HmK.

The solutions of humates (HmA and HmK) after CO₂ absorption were analyzed by elemental analysis, IR and NMR spectroscopy. Whereas elemental analysis showed an increase in carbon content and TOC, both NMR and IR spectra revealed the retention of the general HAS structure with only minor changes in acetate, acetoacetate, N-alkylamine/N-alkylamide and/or polysaccharide-like functionalities. Although the CO₂ absorption capacity of HAS is quite low, these solutions have a certain advantage. The solutions after CO₂ absorption can be widely used in agriculture as an organic fertilizers saturated with K₂CO₃ or (NH₄)₂CO₃. Chemically bound CO₂ can be used by plants. Thus, the presented method can be considered as a potent method for CO₂ capture and utilization.

Overall, humic substances have unique physical and chemical properties that make them a promising candidates for the development of environmentally friendly and effective methods for CO₂ capture and utilization.

Acknowledgments

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Adsorption of organochlorinated pesticides

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Adsorption of organochlorinated pesticides: Adsorption kinetic and adsorption isotherm study

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ABSTRACT

Adsorption of organochlorine pesticides (OCPs) on 4 contrasted activated carbons (ACs) and biochars (BCs) and 5 different basic substances of soil organic matter (SOM) in aqueous media was investigated using adsorption kinetic and isotherm study. This study was performed with emphasis on relationship between adsorption capabilities and physical-chemical properties of the OCPs and above-mentioned sequestration materials (SMs). A kinetic batch study revealed that adsorption efficiency of the SMs-OCPs is time- and dose dependent. Adsorption process between different OCPs and SMs showed diverse fitting to Freundlich isotherm model (R^2 ranked between 0.567 and 0.995). Interestingly, that Freundlich constants such as adsorption capacity and adsorption intensity of all SMs revealed a very similar uptake behavior for dichlorodiphenyltrichloroethane (DDT) metabolites ($P < 0.0001$). The principal component analysis (PCA) demonstrated that adsorption of porous SMs was driven by high carbon content and surface porosity, and adsorption of non-porous SOM-type samples was explained by richness of elemental composition and functional groups. In addition, DDT and metabolites, hexachlorocyclohexane isomers (HCHs) and chlordane (CLD) showed a different degree of affinity and adsorption to the SMs indicating an obvious molecular effect, which in case was explained by difference in molecular weight, stereochemistry and hydrophobicity. Generally, results of this study revealed the list of adsorbents which could be effectively applied in further investigations focused on sequestration of OCPs in environmental matrices.



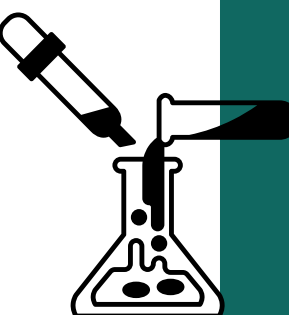
Therefore, **the aim of the study** was to investigate the adsorption behavior and physical-chemical properties of several sequestration materials (SMs) which could be a potential candidate to sequester OCPs and being applied as sequestrants in remediation of contaminated soil or water in perspective. The current study explored adsorption of OCPs with different hydrophobic nature, on 4 contrasted porous adsorbents (ACs and BCs) and 5 different basic substances of soil organic matter (SOM) in aqueous media using kinetics and isotherm batch studies with emphasis on relationship between adsorption capabilities and physico-chemical properties.

Organochlorine pesticides (OCPs) are highly toxic synthetic chemicals, most of which have been classified as persistent organic pollutants (POPs) (Stockholm Convention, 2019). These pesticides have been used due to their effectiveness against pests and insects on agricultural crops up to the 1970s (ATSDR, 2021, 2020, 2019, 2005) but have been withdrawn due to their toxic adverse effects on health such as cancer, but also different disorders of the reproductive, nervous and hormonal systems (Gomaa et al., 2008; X. Jin et al., 2014; X. T. Jin et al., 2014). In addition, OCPs characterized by their high persistency in the environment, especially in soil, as this media is a powerful reservoir of different contaminants. The OCP half-lives in soil varied from 60 days to 15 years (Jayaraj et al., 2016). In this context, soil is a huge storage reservoir for many POPs, and at the same time it's the key element in many food chains as well as its play an important role for water management systems. Therefore, soil could be the main vector for the transfer of POPs to agricultural animals through the oral soil ingestion (Collas et al., 2019; Healy, 1968; Jurjanz S. et al., 2012; Jurjanz, 2011), and, accordingly, to the food products they produce (meat, milk, eggs) (Amutova et al., 2021; MacLachlan and Bhula, 2009; Maervoet et al., 2004; Weber et al., 2018).

Materials and methods

Nine OCPs with different hydrophobic properties, α -HCH, β -HCH, γ -HCH, δ -HCH (log Kow 3.8–4.1) chlordane (log Kow 4.5), 2,4-DDD, 4,4-DDE, 4,4-DDD, 4,4-DDT (6.5–6.9) were selected to investigate the adsorption behavior of nine adsorbents (AC DARCO, AC Shubarkol, BC oak tree, BC Japanese knotweed, peat, potassium humate, humic acid, fulvic acid and black coal Shoptkyol). Assessment of adsorption was based on 2 batch studies:

- 1) Adsorption kinetic study, which allows one to determine the time needed to reach equilibrium between OCPs and adsorbents.
- 2) Adsorption isotherm study, which allows determining OCPs adsorption behavior for different SM at equilibrium in constant time and temperature.



Characterization of SMs

The adsorption capacity K_F ($\mu\text{g/g}$ ($\mu\text{g/L}$)^{1/n}) of studied couples of OCPs-SMs determined by the Freundlich equation.

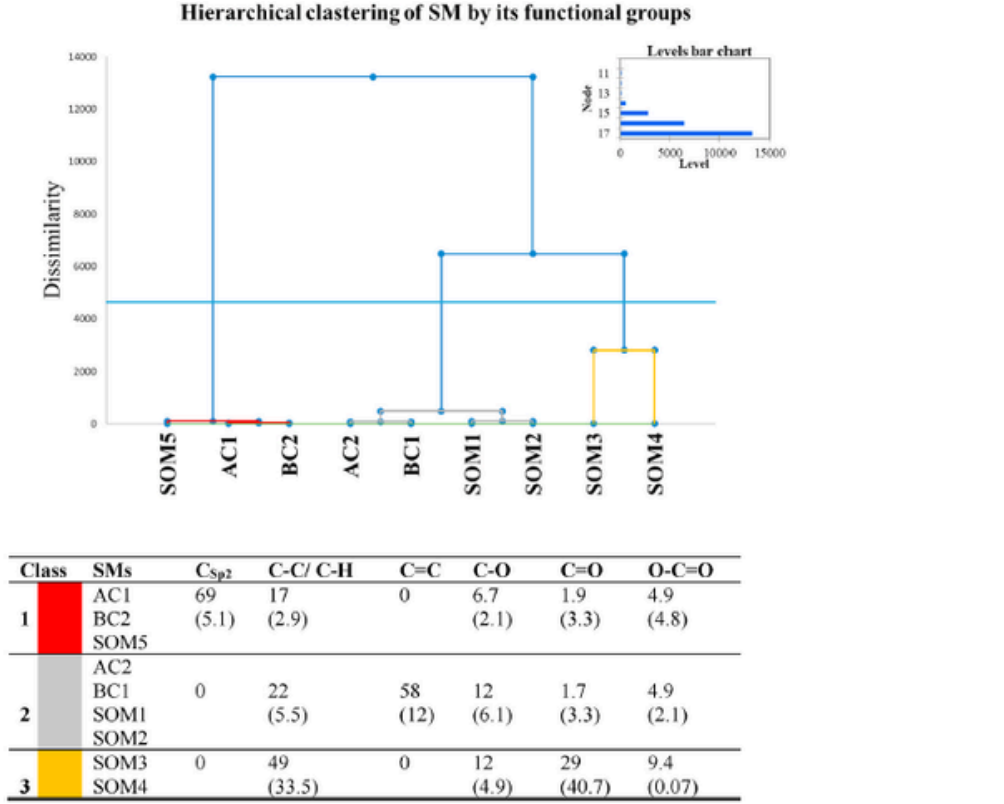
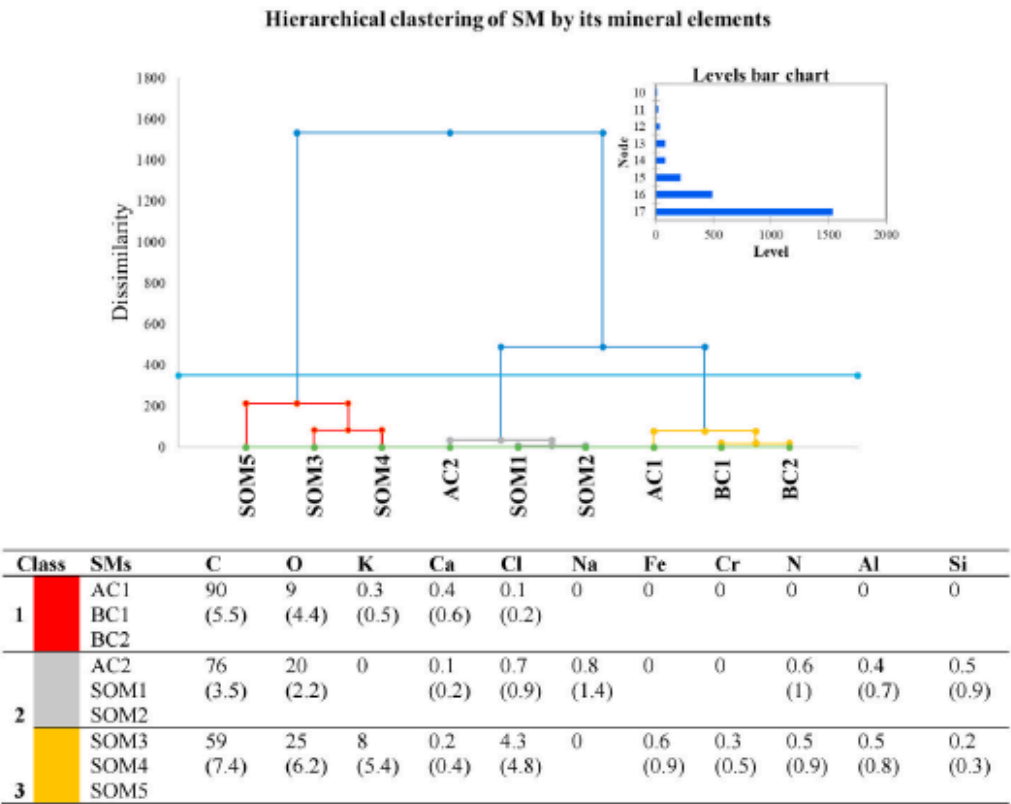
SMs	α -HCH	β -HCH	γ -HCH	δ -HCH	2,4-DDD	4,4-DDD	4,4-DDE	CLD
AC1	0.000028	0.00001	5.80E-13	7.70E-06	2.10E-07	2.30E-15	1.30E-19	2.25
AC2	1.20E-06	0.12	0.52	3.33	12.8	13.48	62.24	0.02
BC1	1.10E-26	1.50E-06	4.50E-08	0.02	0.07	0.09	0.02	0.0002
BC2	4.40E-13	0.21	1.24	0.63	1.18	1.28	1.2	1.16
SOM1	2.70E-13	4.70E-06	1.49	0.00023	22.9	19.8	154.3	0.33
SOM2	3.20E-15	1.50E-08	7.00E-15	1.40E-04	2.70E-09	4.00E-12	2.60E-12	0.002
SOM3	6.30E-10	1.10E-07	0.39	4.70E-19	0.23	1.99	3.99	0.002
SOM4	4.70E-09	6.90E-33	2.40E-02	2.50E-67	0.0003	0.0007	0.0003	1.90E-36
SOM5	0.73	5.80E-11	2.00E-11	4.40E-06	1.50E-08	3.10E-11	3.80E-17	2.70E-14

AC1- DARCO, AC2-Shubarkol, BC1-Oak tree, BC2-Japanese knotweed, SOM1-Peat, SOM2- Humic acid, SOM3- Fulvic acid, SOM4- Potassium humate, SOM5- Shoptykol.

The absorption intensity N (dimensionless) of studied couples OCPs-SMs determined by the Freundlich equation.

SMs	α -HCH	β -HCH	γ -HCH	δ -HCH	2,4-DDD	4,4-DDD	4,4-DDE	CLD
AC1	0.24	0.22	0.11	0.2	0.15	0.09	0.06	0.48
AC2	0.18	0.46	0.7	0.92	0.97	0.92	0.35	0.4
BC1	0.06	0.2	0.19	0.5	0.39	0.37	0.24	0.28
BC2	0.1	0.48	0.78	1.22	2.19	2.33	3.37	0.66
SOM1	0.09	0.21	0.99	0.27	0.95	1	0.9	0.5
SOM2	0.1	0.15	0.1	0.26	0.11	0.09	0.07	0.28
SOM3	0.14	0.17	0.8	0.08	0.46	0.66	0.43	0.32
SOM4	0.16	0.05	0.07	0.02	0.2	0.22	0.14	0.04
SOM5	0.93	0.12	0.13	0.2	0.11	0.09	0.05	0.1

AC1- DARCO, AC2-Shubarkol, BC1-Oak tree, BC2-Japanese knotweed, SOM1-Peat, SOM2- Humic acid, SOM3- Fulvic acid, SOM4- Potassium humate, SOM5- Shoptykol.



Sequestration Materials	Type	Origin	Production	BET method	t-plot method			
				Surface area (m ² /g)	Total surface (m ² /g)	Microporous surface (m ² /g)	Non- microporous surface (m ² /g)	Mesoporous volume (cm ³ /g)
DARCO	AC1	Lignite ^a	n/s	793.8 ± 14.5 ^b	829.9 ^b	486.8 ^b	382.1 ^b	-
Shubarkol	AC2	Lignite ^b	900°C ^b	722.8 ± 5.4	744.0	314.1	450	0.30
Oak tree	BC1	<i>Quercus ilex</i> ^c	500°C ^c	144.4 ± 7.8 ^c	-	76.6 ^c	79.0 ^c	-
Japanese knotweed	BC2	<i>Reynoutria japonica</i> ^d	700°C ^d	190.0 ± 7.2	198.5	99.3	105.6	0.08
Peat	SOM1	<i>Sphagnaceae</i> ^d	n/s	na	na	na	na	na
Humic acid	SOM2	Humic acid ^e	Soil extract ^e	na	na	na	na	na
Fulvic acid	SOM3	Fulvic acid ^e	Humate extract ^e	na	na	na	na	na
Potassium humate	SOM4	Potassium humate ^e	Lignite ^e	na	na	na	na	na
Shoptykol	SOM5	Lignite ^e	n/s	4.55 ± 0.8	-	-	-	0.01

Abbreviations: AC-activated carbon, BC- biochar, SOM- soil organic matter.

Concentration of chemical elements (%) presented for studied sequestration matrices.

Sequestration materials	O (1s)	C (1s)	O/C (1s)	K (2p)	Ca (2p)	Cl (2p)	Na (1s)	Fe (2p)	Cr (2p)	N (1s)	Al (2s)	Si (2p)
AC1	4.2	95.8	0.04	-	-	-	-	-	-	-	-	-
AC2	22.5	72.2	0.31	-	-	0.4	-	-	-	-	1.2	1.5
BC1	9.8	90.2	0.11	-	-	-	-	-	-	-	-	-
BC2	12.8	84.8	0.15	0.9	1.1	0.3	-	-	-	-	-	-
SOM1	19.3	78.9	0.24	-	-	-	-	-	-	1.8	-	-
SOM2	18.3	77.1	0.23	-	0.3	1.8	2.5	-	-	-	-	-
SOM3	20.3	61.0	0.33	2.8	0.7	9.7	-	1.7	0.8	1.6	1.4	-
SOM4	23.8	66.0	0.36	8.9	-	0.6	-	-	-	-	-	0.6
SOM5	32.4	51.4	0.65	13.6	-	2.6	-	-	-	-	-	-

AC1- DARCO, AC2-Shubarkol, BC1-Oak tree, BC2-Japanese knotweed, SOM1-Peat, SOM2- Humic acid, SOM3- Fulvic acid, SOM4- Potassium humate, SOM5-Shoptykol.

Surface functional groups (peak area, %) of studied SMs

SMs	C _{1s}	C-C/C-H	C=C	C-O	C=O	-O-C=O
AC1	74.0	20.5	-	5.4	-	-
AC2	-	25.1	64.1	7.6	-	3.2
BC1	-	15.7	72.3	8.4	-	3.6
BC2	69.8	16.1	-	9.13	-	4.9
SOM1	-	21.1	46.0	21.0*	6.7	5.1
SOM2	-	28.4	51.6	12.2	-	7.8
SOM3	-	24.9	-	8.1	57.6	9.4
SOM4	-	72.3	-	15.1	-	9.3
SOM5	63.9	15.1	-	5.5	5.7	9.7

* – functional groups including C-O, C-N

AC1- DARCO, AC2-Shubarkol, BC1-Oak tree, BC2-Japanese knotweed, SOM1-Peat, SOM2- Humic acid, SOM3- Fulvic acid, SOM4- Potassium humate, SOM5-Shoptykol.

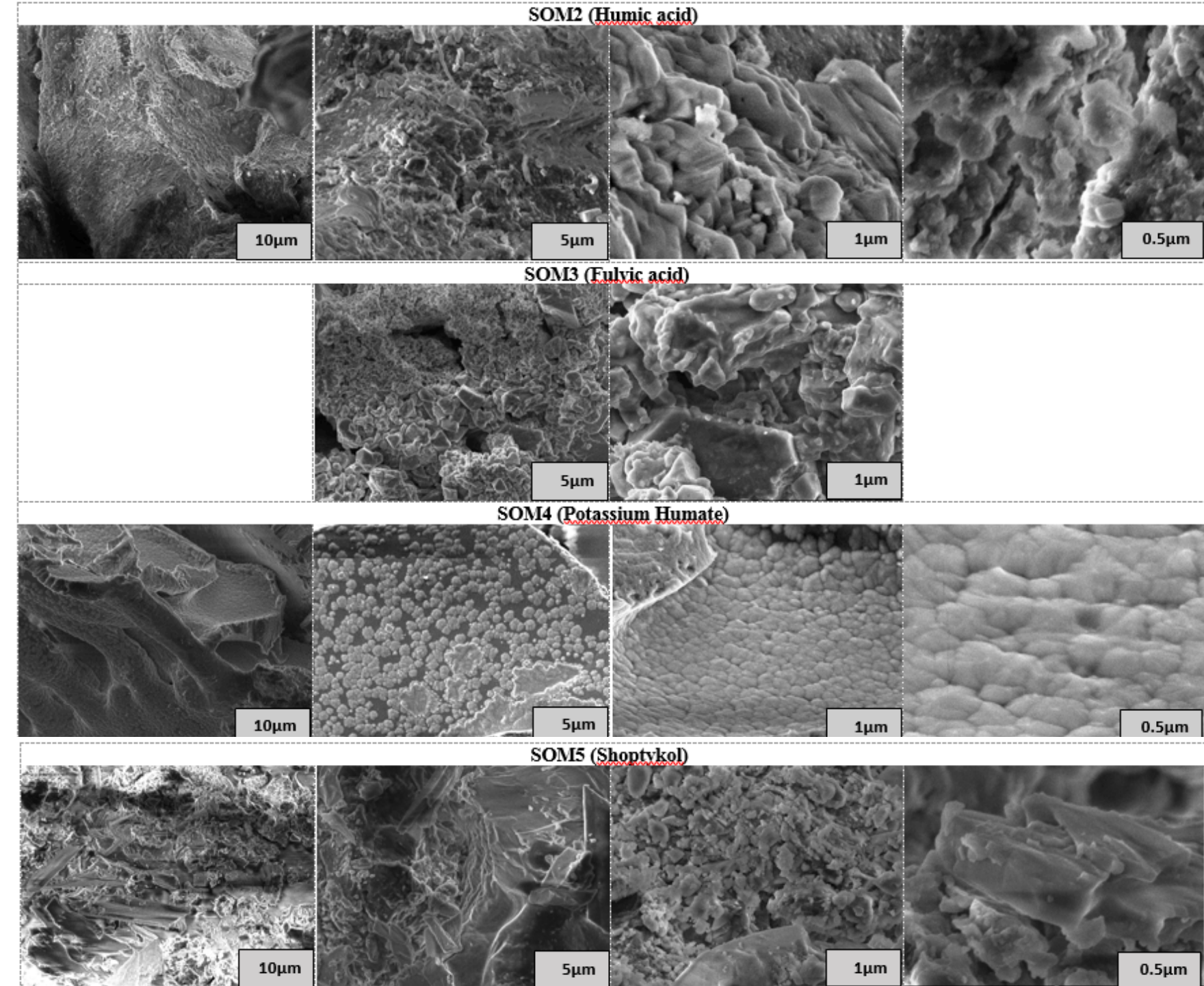


Figure S1 - Scanning electron microscopy (SEM) images of surface of studied SMs with magnification 10, 5, 1 and 0.5 μm (from left to right)

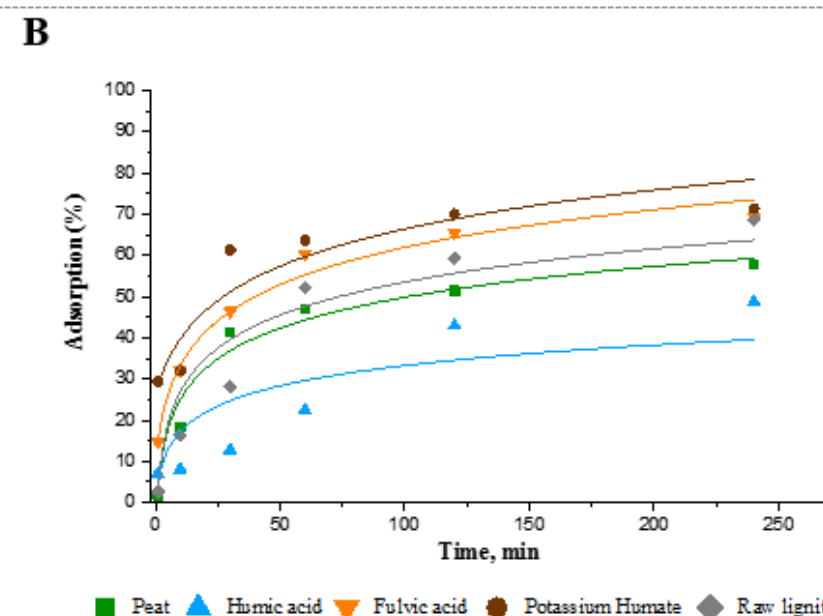
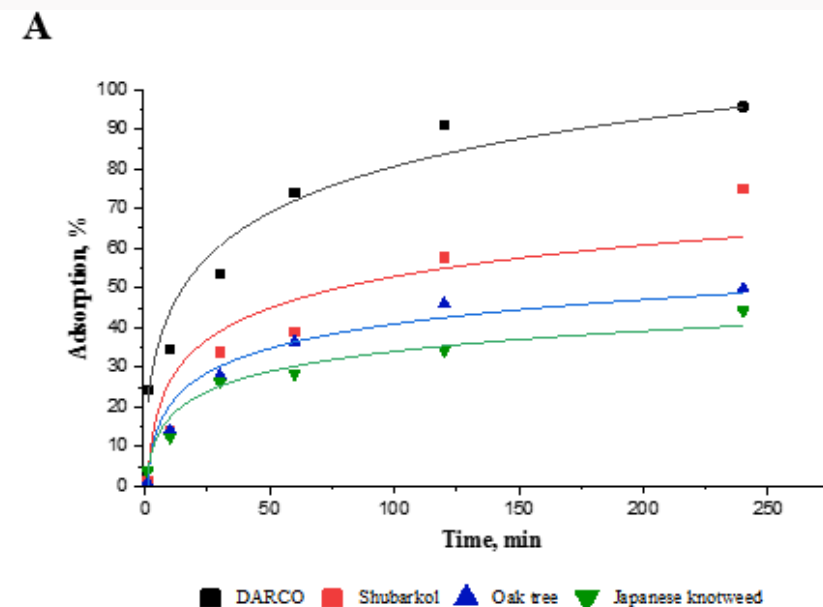


Figure 1 – Effect of contact time on 4,4-DDT adsorption on activated carbons and biochars (fig. 1A) and on soil organic matter (Fig.1B). Pesticide and sequestrant concentrations were 50 µg/L and 0.13 g/L, respectively. Results based on 2 replicates.

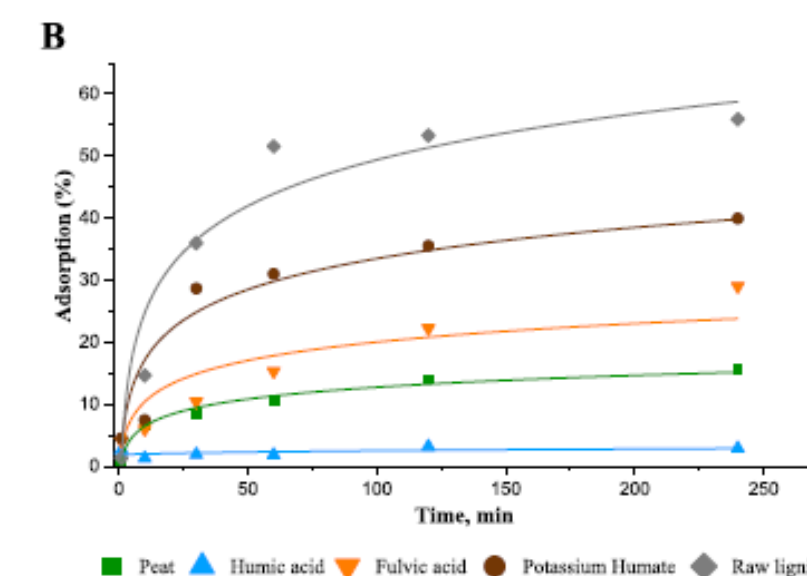
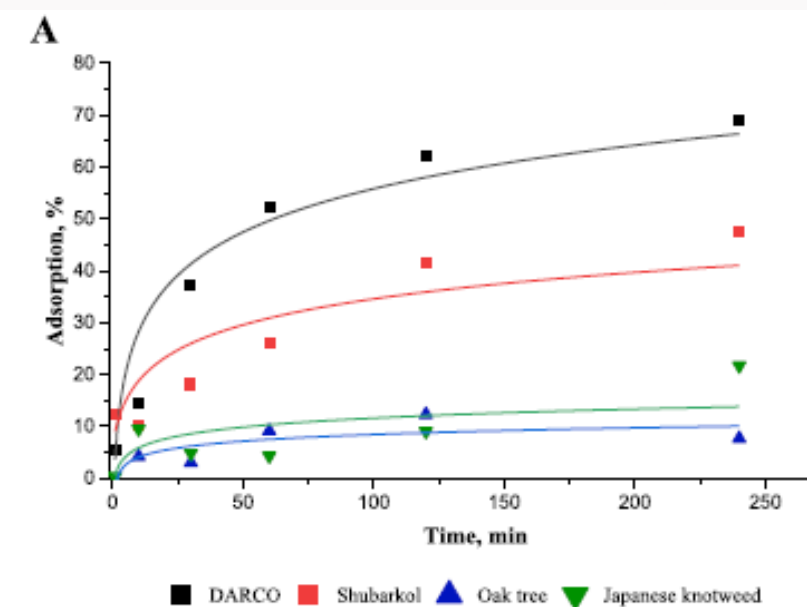
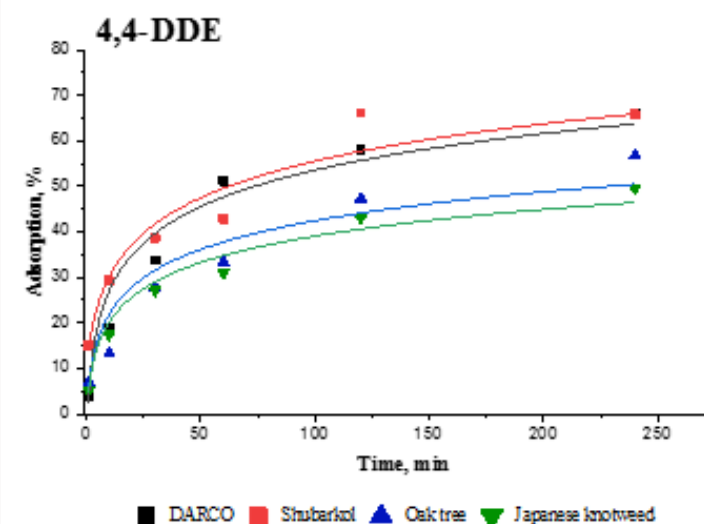
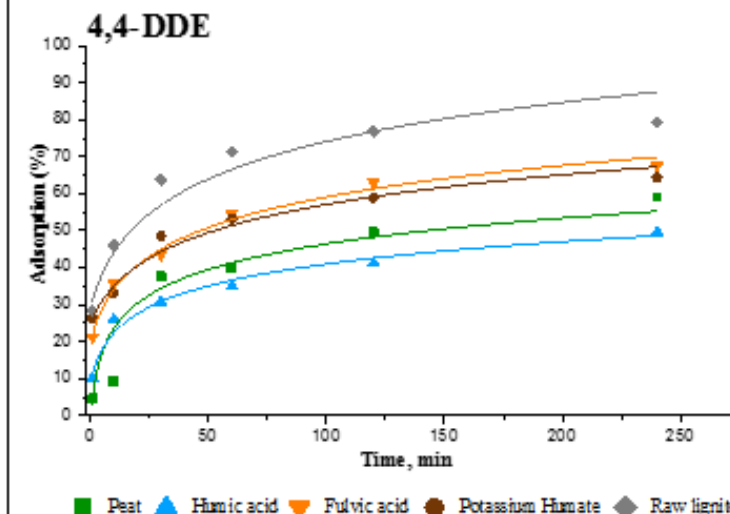


Fig. 2. Effect of contact time on α-HCH adsorption on activated carbons and biochars (Fig. 2A) and on soil organic matter (Fig. 2B). Pesticide and sequestrant concentrations were 50 µg/L and 0.13 g/L, respectively. Results based on 2 replicates.



Adsorption kinetic and adsorption isotherm studies have been shown to be an efficient tool to investigate adsorption behavior of OCPs to different contrasted SMs. The classification of SMs in ACs, BCs and SOMs allows a better understanding of adsorption mechanisms. Indeed, a very high proportion of carbon in ACs and BCs allowed them a high adsorption degree, especially on hydrophobic OCPs even if other physico-chemical characteristics as the presence of functional groups make vary the degree of adsorption. The most effective SM which could effectively adsorb all studied compounds were mainly AC1, AC2, BC1, BC2, SOM1 and SOM2. This study demonstrated that SMs parameters, which favorably affected on adsorption of OCPs were porosity, i.e SSA and mesoporosity (porous SMs), mineral elements (especially carbon) and functional groups (SOM type samples). Other factors as competition between different OCPs present in soil or between OCPs and soil compounds should be included to improve the prediction of adsorption. Finally, the proportion of amended SM on soil and by consequence the amount of available adsorption surface should be pathways to reduce the OCP availability in contaminated soils.

The data presented allow to conclude that above mentioned SMs could be effectively used in sequestration strategy studies as amendment which could immobilize OCPs in contaminated soil and water.

№. AR19577512 “DEVELOPMENT OF SCIENTIFIC AND TECHNICAL BASES FOR OBTAINING MICROPOROUS CARBON NANOMATERIALS FOR HYDROGEN SEPARATION AND STORAGE”

Project Manager: PhD in Philosophy, assoc. professor, member correspondent of the KazNANS, Leading Researcher – Kazankapova M.K.

01 Objective of the project.

The main goal of this project is to create, and develop carbon materials with a microporous structure and a high specific surface area for hydrogen separation and storage, characterized by greater capacity, low weight and high stability.

02 Project tasks.

1. Development of optimal methods for obtaining microporous carbon nanomaterials for hydrogen separation and storage.
2. Conducting experiments on the separation and storage of hydrogen with nanomaterials.
3. Optimization of the process of hydrogen separation and storage by carbon-containing nanomaterials.

Table 1. Comparison of hydrogen and other energy resources for electricity generation and their transport costs

	Price				
	tce/ton	dollars/ton	USD/tce	Efficiency preob, %	Fuel costs for electricity, dollars/MWh
Coal	0,626	20	31,9	40%	9,8
Natural gas	1,4	80	58,1	45%	15,9
LPG	1,6	90,0	57,3	45%	15,7
Fuel oil	1,4	338	245,0	40%	75,3
Gasoline	1,5	438,9	294,6	40%	90,6
Diesel fuel	1,5	457,0	315,2	40%	96,9
Hydrogen "gray"	4,1	1500	366,1	60%	75,0
Hydrogen is green	4,1	3702,3	903,5	60%	185,2

Table 2. Experimentally measured hydrogen capacity of activated carbon

Adsorbent	Hydrogen storage(mass%)	Conditions-Temp.(K)/Pressure (MPa)
AC	0.67	303K, 10MPa
AC	1.4	77K, 0.1MPa
AC	1.6	296K, 13MPa
AC	4.5	77.4K
AC	5.7	77K, 3MPa
AC(KOH)	6.6	77K, 4 MPa
AC(Ni)	1.8	77K, 0.1MPa
AC(Pt)	2.3	298K, 10MPa
AC(Pd)	5.5	298K, 8MPa

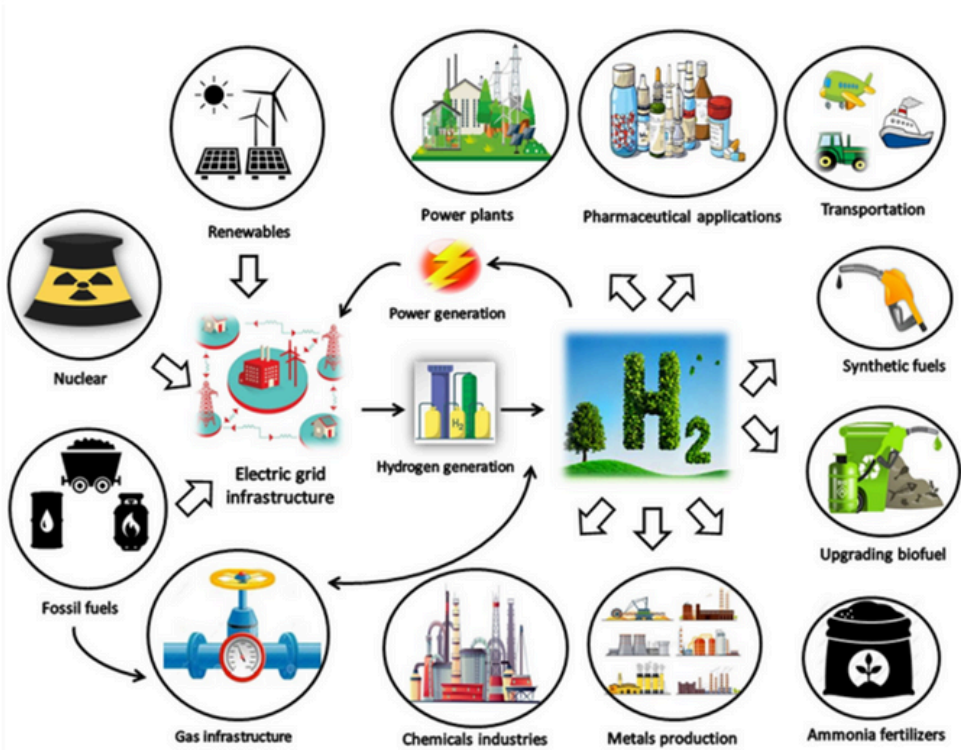
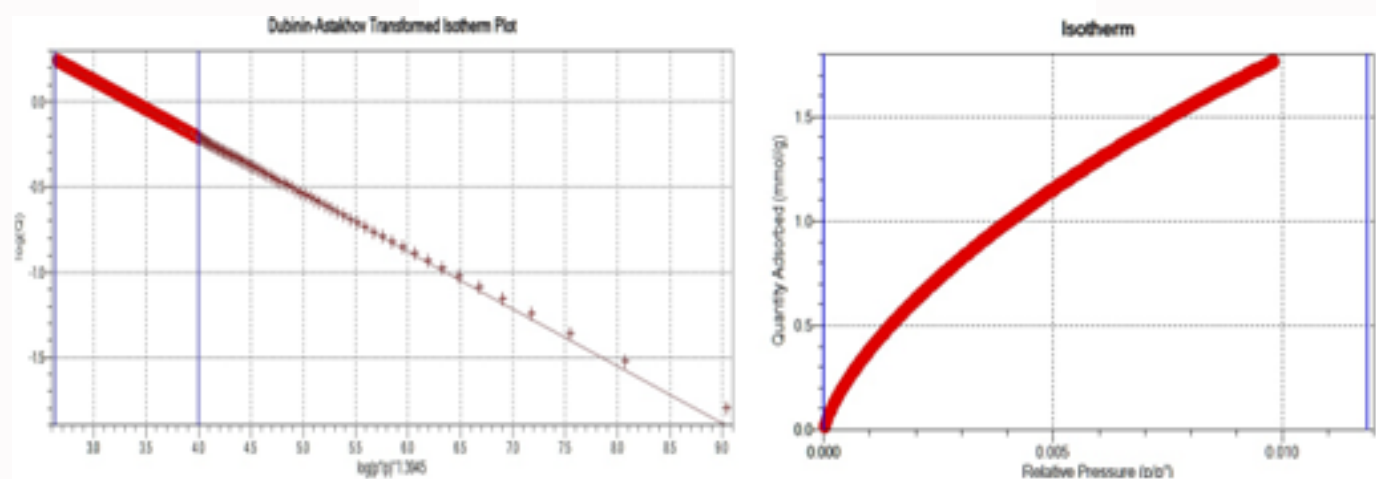
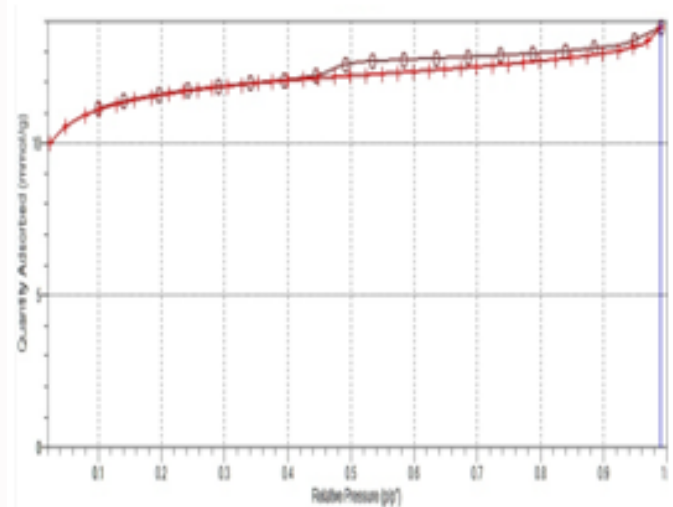


Fig. 1 Hydrogen production routes, including renewables, fossil fuels and nuclear, with hydrogen being produced in power plants, pharmaceutical applications, synthetic fuels or their upgrades in transportation, ammonia synthesis, metal production or chemical industry applications

At room temperature, the mass density for carbon nanotubes or graphite nanofibers ranges from 0.5-4.5 wt.% at 3-11 MPa, with 4.5 wt.% at ~11 MPa. Effective hydrogen storage requires further study of hydrogen's interaction with carbon nanostructures, including spillover and intercalation in graphene and graphite nanofibers.

Adsorbents based on Kazakhstan coal for hydrogen storage

The figure shows the nitrogen adsorption-desorption isotherms of the samples. These isotherms characterize the porous structure of the material and help determine its properties. The isotherms belong to type I, indicating a microporous material, and exhibit a type IV hysteresis loop, typical of a microporous material with slot-like pores, characteristic of the layered structure of coals.



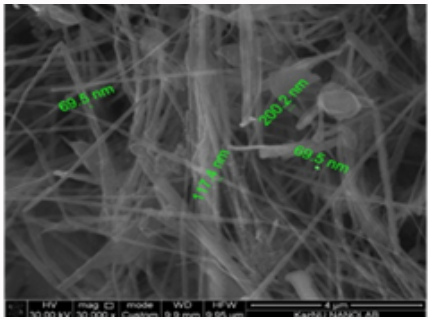
Adsorption curves of activated adsorbent (according to Dubinin-Astakhov, CO₂)



Analyzer 3Flex,
Micromeritics

Name	S _{BET} , m ² /g	Total pore volume, cm ³ /g	Microspores, cm ³ /g	Mesopores, cm ³ /g	Macropores, cm ³ /g	S _{BJH} , for pore widths from 17,000 Å to 3,000,000 Å, m ² /g	Average adsorption pore width BJH (4V/A), Å
Activated carbon-based adsorbent Shoptykol	1145.076	0.624	0.390	0.187	0.047	224.234	40.833

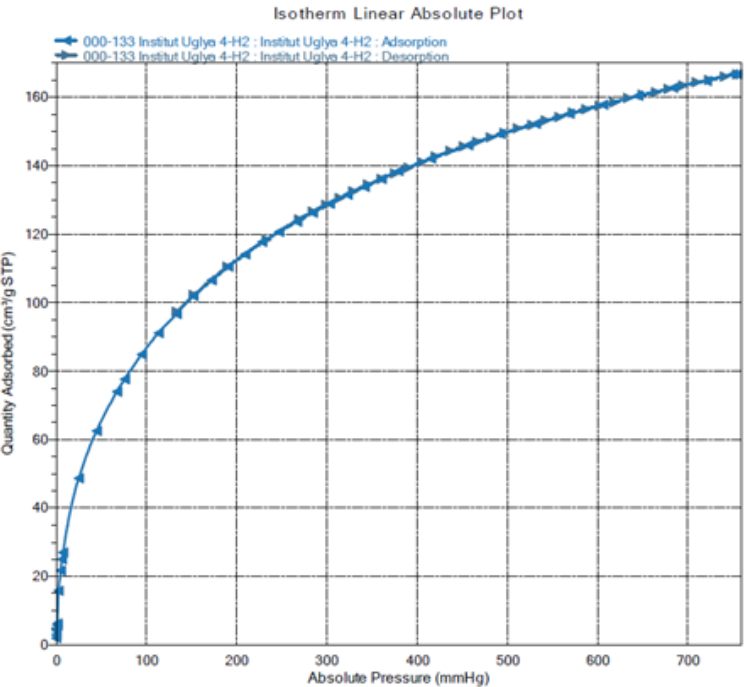
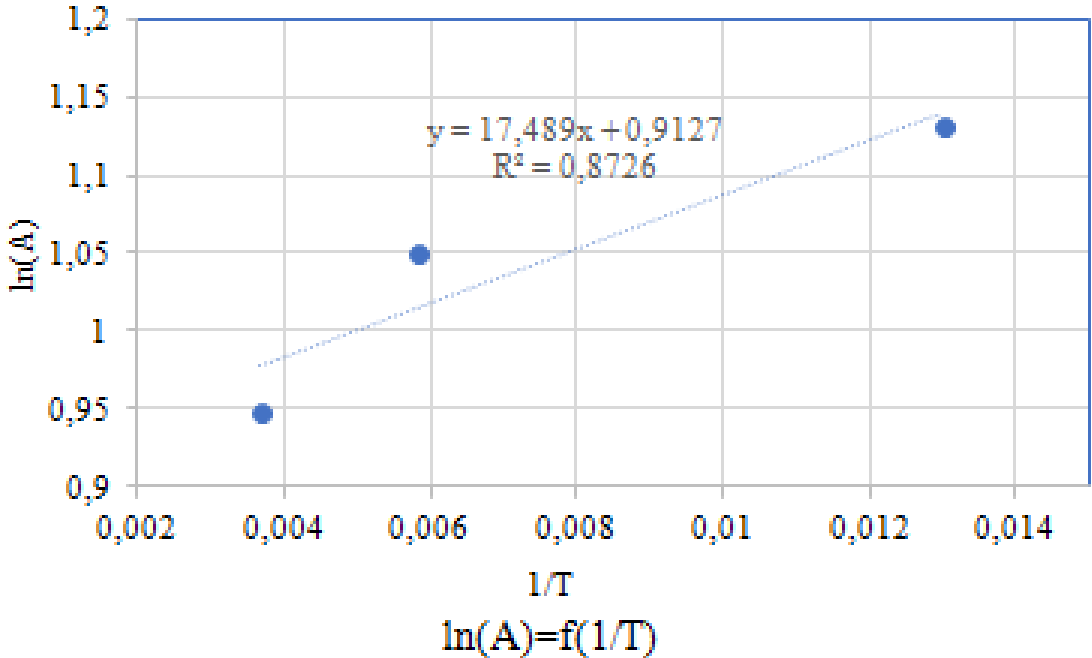
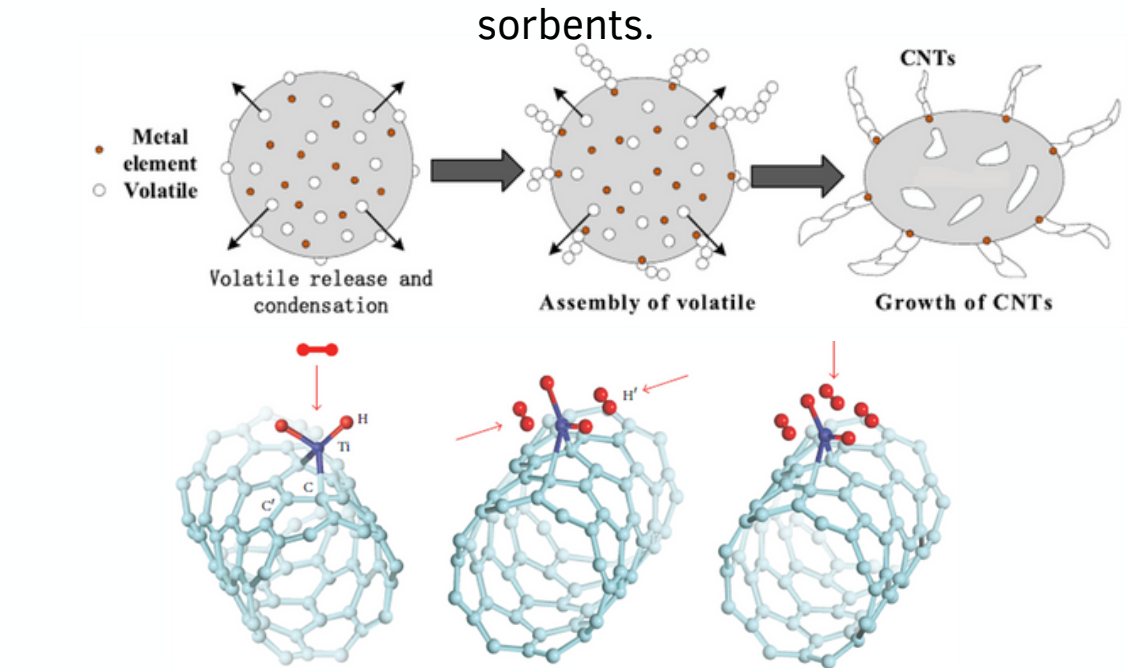
Name	Dubinin-Radushkevich			Dubinin-Astakhov			
	Limiting micropore capacity, mmol/g	Limiting micropore volume, cm ³ /g	Equivalent surface area, m ² /g	Maximum micropore capacity, mmol/g	Limiting micropore volume, cm ³ /g	Equivalent surface area, m ² /g	Average equivalent pore width, Å
Activated carbon-based adsorbent Shoptykol	6,499	0,309	665,376	13,676	0,652	1822,318	14,310



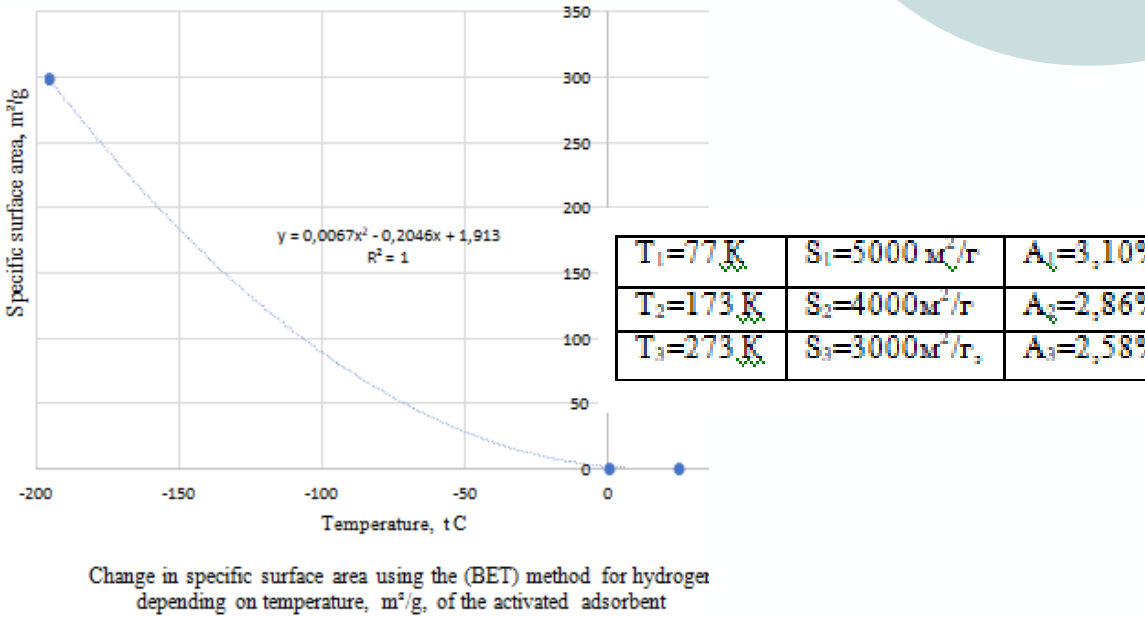
Electron microscopic
images of activated
adsorbent

ADSORBENTS BASED ON KAZAKHSTAN COAL FOR HYDROGEN STORAGE

Hydrogen can be stored in solid form through physical adsorption in carbon materials, which have high storage capacity due to their porous microstructure, high specific surface area, and low bulk density. Carbon sorbents are widely used in chemical, food, metallurgical, oil and gas processing, medicine, agriculture, water purification, and environmental protection industries. Their unique properties include high capacity, stable sorptive capability, minimal catalytic impact, sufficient strength, and hydrophobicity. Various carbon-containing materials can be used to produce these sorbents.



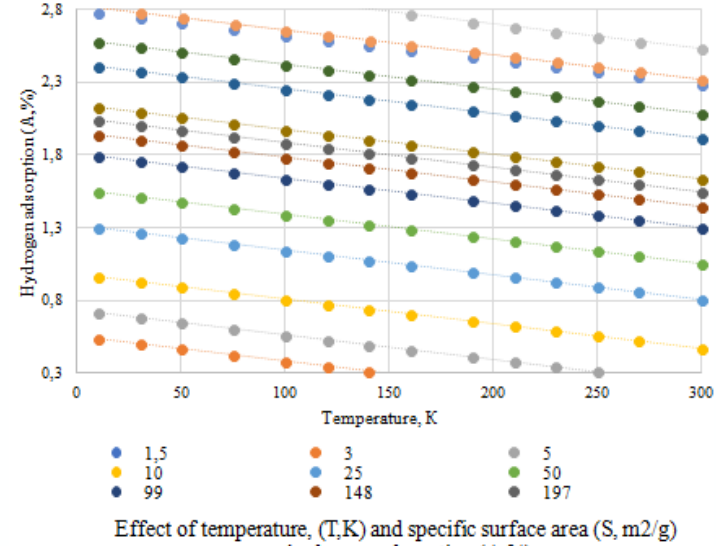
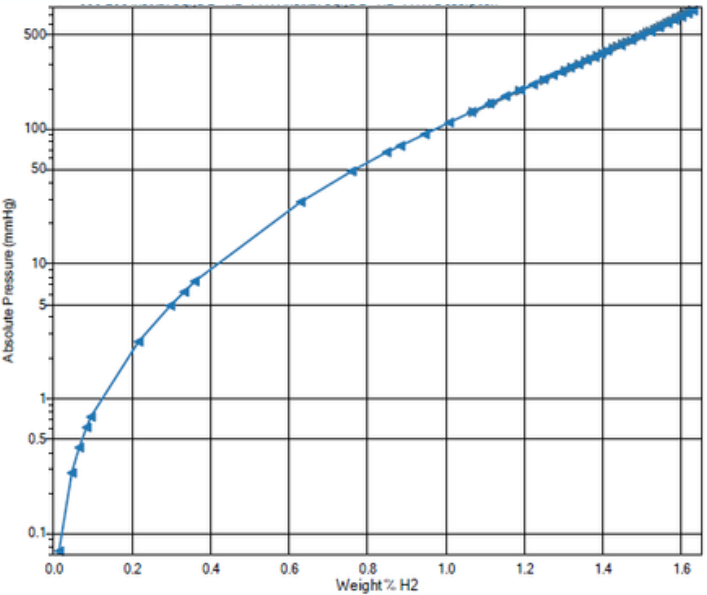
Name	Activated carbon-based adsorbent Shoptykol
$S_{(DFT)}$ specific, m^2/g	1165.97
mass H_2 , % 77 K	1.49
mass H_2 , % 273 K	0.017
mass H_2 , % 298 K	0.0076



Sections of the curves belong to type 1 isotherm, characteristic of the Langmuir isotherm. The table shows the sample has good hydrogen sorption capacity. As expected, increasing temperature significantly reduces hydrogen sorption. The capacitance values at three different temperatures can be used to determine the heat of adsorption of hydrogen molecules.

We can obtain data for hydrogen adsorption at different temperatures (77 K, 173 K, 273 K) and specific surface areas (S) up to 3000 - 5000 m^2/g . Let's calculate the percentage of adsorption (A) and plot the dependence of $\ln(A)$ on the reciprocal temperature ($1/T$).

The activation energy (E_a) value of 145.4 J/mol indicates that the hydrogen adsorption process on the material has a moderate energy barrier. A lower E_a value signifies more favorable conditions for adsorption in the system.



Name	Amount of adsorbed H_2 gas %
Activated carbon Taldykol/KOH, 1/0,5	1,62

ADSORBENTS BASED ON KAZAKHSTAN COAL FOR HYDROGEN STORAGE

Table 3. General Characteristics of Coal from the Shoptykoly Deposit

Parameter Name	Value
Moisture	12,02 %
Ash Content, Ad	10,4 %
Volatile Matter Yield	40,8 %
Phosphorus Content	0,037 %
Total Nitrogen Content, Ndaf	0,95 %
Total Sulfur Content, Sdt	0,50 %
Total Carbon Content on Dry Basis, Cdaf	74,86 %
Total Hydrogen Content on Dry Basis, Hdaf	5,35
Oxygen Content, Odaf	18,34 %
Heat of Combustion on As-Received Basis, kcal/kg	5570
True Density, g/cm3	1,47

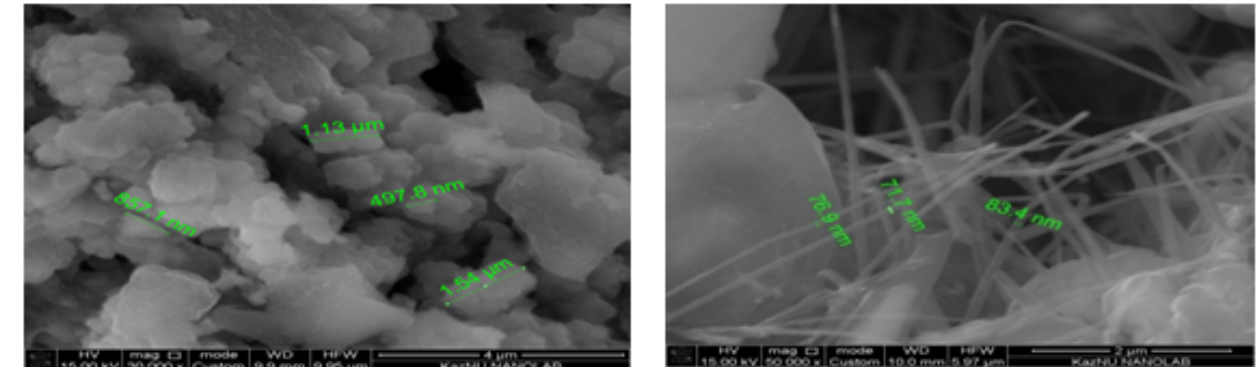


Figure 1. Electron microscopic images of samples: initial (a) and activated (b).

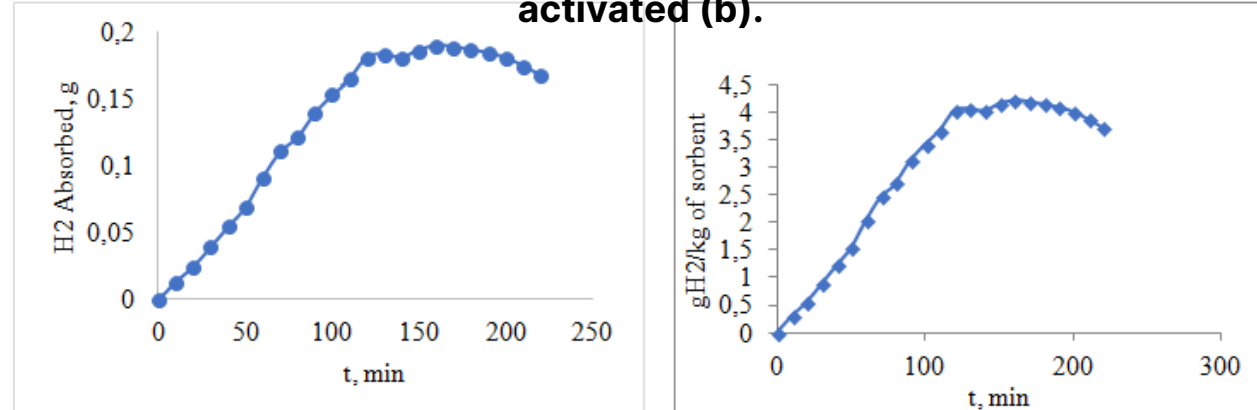


Figure 2. Hydrogen adsorption curves over time

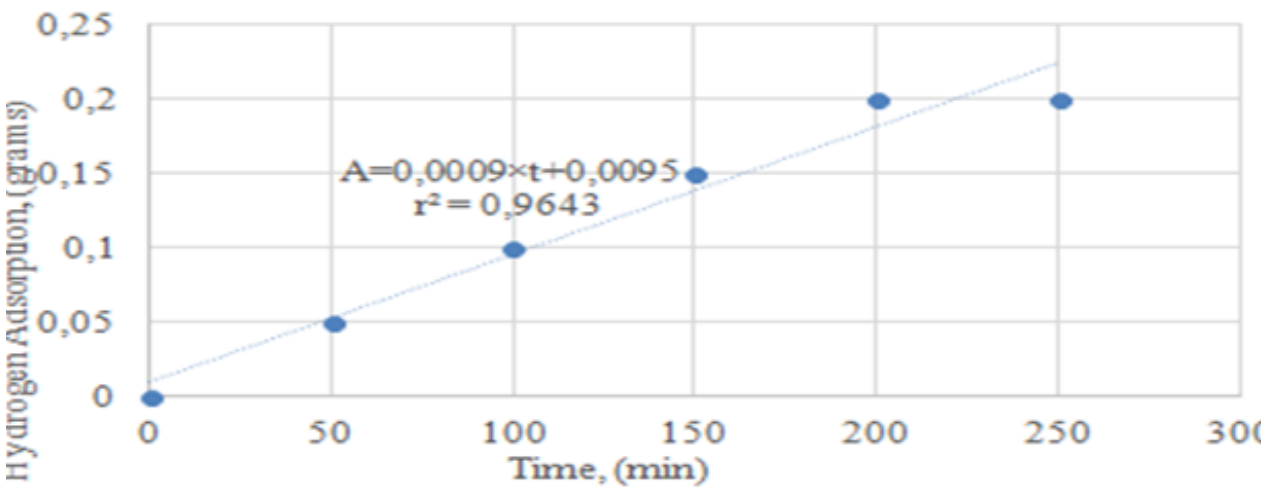


Figure 3. Hydrogen Adsorption vs. Time

Table 4. Results of Hydrogen Adsorption

Test Time, (min)	H ₂ % Volume Output	H ₂ Input - H ₂ Output, % vol.	Amount of Absorbed H ₂ , dm ³	Integral Calculation (sum of H ₂), dm ³	H ₂ Absorbed, g	gH ₂ /kg of sorbent
10	2,84	2,16	0,001	0,008	0,01	0,302
20	3,96	1,04	0,001	0,014	0,02	0,553
30	3,4	1,6	0,001	0,022	0,04	0,880
40	3,14	1,86	0,001	0,031	0,05	1,215
50	3,31	1,69	0,001	0,039	0,07	1,541
60	3,24	1,76	0,001	0,052	0,09	2,038
70	1,44	3,56	0,002	0,063	0,11	2,467
80	3,96	1,04	0,001	0,069	0,12	2,706
90	3,52	1,48	0,001	0,079	0,14	3,111
100	2,17	2,83	0,001	0,087	0,15	3,405
110	4,69	0,31	0,000	0,093	0,16	3,664
120	2,56	2,44	0,001	0,102	0,18	4,023
130	3,63	1,37	0,001	0,103	0,18	4,063
140	5,92	-0,92	0,000	0,102	0,18	4,020
150	4,52	0,48	0,000	0,105	0,19	4,139
160	4,23	0,77	0,000	0,107	0,19	4,213
170	5	0	0,000	0,107	0,19	4,191
180	5,22	-0,22	0,000	0,105	0,19	4,142
190	5,29	-0,29	0,000	0,104	0,18	4,088
200	5,27	-0,27	0,000	0,102	0,18	4,009
210	5,55	-0,55	0,000	0,099	0,17	3,874
220	5,84	-0,84	0,000	0,095	0,17	3,722
230	5,73	-0,73	0,000	0,095	0,17	3,722

The study investigated hydrogen adsorption dynamics on porous carbon at 296 K. The amount of adsorbed hydrogen over time was measured to assess the process's speed and efficiency. Initially, the adsorption rate increased, peaking at around 70 minutes, then gradually decreased, stabilizing at a higher level, suggesting surface saturation and fewer available active sites.

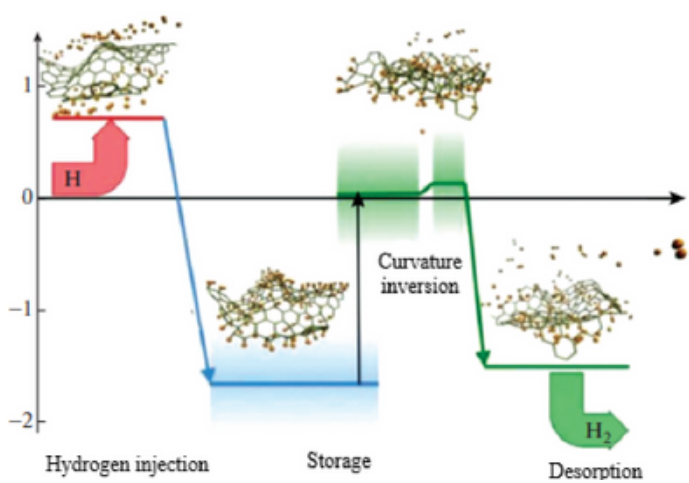


Figure 4. Adsorption-desorption during hydrogen gas storage

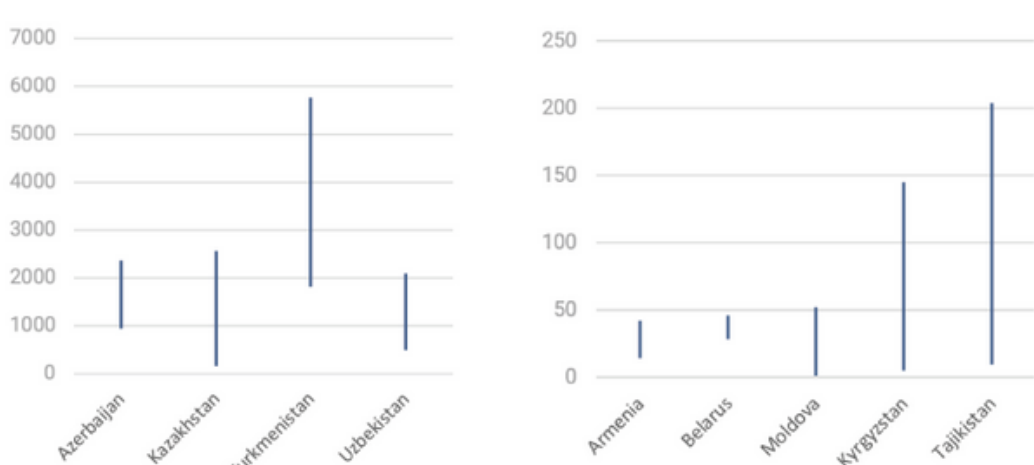


Figure 6. Low-carbon hydrogen production potential by 2040: volume (thousand tonnes of hydrogen per year)

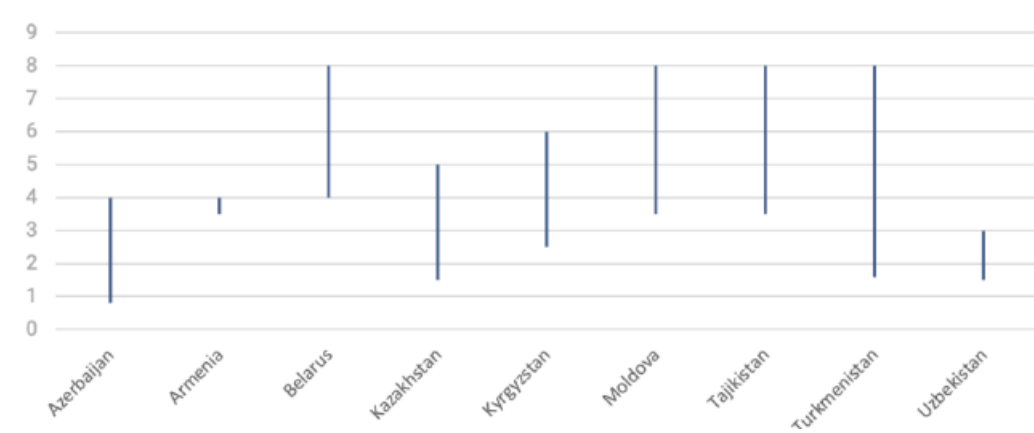


Figure 7. Low-carbon hydrogen production potential till 2040: a financial analysis



Figure 5. Laboratory device for hydrogen storage



WE BELIEVE THAT IF WE JOIN FORCES WITH COAL MINING COMPANIES, AND WITH THE SUPPORT OF GOVERNMENT AGENCIES, WE INVEST IN DEVELOPMENTS IN A PILOT-INDUSTRIAL MODE, WE WILL NOT BE FAR FROM CREATING THE SAME BATTERIES FROM COAL, THE SAME SENSORS FROM GRAPHENE, OR THE SAME NANOMATERIALS FROM COAL.

THANK YOU FOR YOUR ATTENTION



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