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STUDY OF PHYSICOCHEMICAL PROPERTIES OF ADSORBENTS BASED ON POTASSIUM HUMATE AND USE IN HYDROGEN STORAGE

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This research is based on the investigation of the physicochemical properties of adsorbents based on potassium humate. During this study, we evaluated the structure, characteristics, and adsorption capacity of these materials. Potassium humate served as the main starting material, and we used a series of high-temperature carbonization and activation processes to produce the adsorbents we were investigating.

We characterized the surface structure, porosity, and elemental composition of the resulting adsorbents using techniques such as cryogenic scanning probe microscopy and scanning electron microscopy (SEM). We determined the specific surface area of the adsorbents in terms of surface volume using gas absorption techniques, specifically the Brunauer-Emmett-Teller (BET) method.

The findings reveal a significant improvement in the porosity and adsorption properties of activated adsorbents. Most of these materials have a high specific surface area, which indicates their exceptional adsorption capacity.

These porous carbonaceous adsorbents, obtained through the methods described, are well-suited for purifying industrial wastewater and can act as effective gas adsorbents, including for hydrogen storage. Further research and experimentation hold promise for even greater improvements. Based on the results obtained through these methods, potassium Humate-derived adsorbents emerge as a versatile and technologically feasible raw material with wide-ranging applications.

Key words: adsorbent, potassium humate, adsorption properties, surface area, activation, storage, hydrogen.

КАЛИЙ ГУМАТЫ НЕГІЗІНДЕ АЛЫНҒАН АДСОРБЕНТТЕРДІҢ ФИЗИКА-ХИМИЯЛЫҚ ҚАСИЕТТЕРІН ЗЕРТТЕУ ЖӘНЕ СУТЕГІ САҚТАУДА ҚОЛДАНУ

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Бұл зерттеу калий гуматы негізіндегі адсорбенттердің физика-химиялық қасиеттерін зерттеуге негізделген. Осы зерттеу барысында біз осы материалдардың құрылымын, сипаттамаларын және адсорбциялық қабілетін бағаладық. Калий гуматы негізгі бастапқы материал ретінде қызмет етті және біз зерттеген адсорбенттерді алу үшін жоғары температуралы карбонизация және белсендіру процестерінің сериясын қолдандық.

Біз алынған адсорбенттердің беттік құрылымын, кеуектілігін және элементтік құрамын криогендік сканерлеу зондтарының микроскопиясы және сканерлеуші электронды микроскопия (SEM) сияқты әдістерді қолдана отырып сипаттадық. Біз адсорбенттердің бетінің нақты ауданын газды сіңіру әдістерін, атап айтқанда Брунауэр-Эмметт-Теллер (BET) әдісін қолдана отырып, бетінің көлемі бойынша анықтадық.

Нәтижелер белсендірілген адсорбенттердің кеуектілігі мен адсорбциялық қасиеттерінің айтарлықтай жақсарғанын көрсетеді. Бұл материалдардың көпшілігінің бетінің жоғары спецификалық ауданы бар, бұл олардың ерекше адсорбциялық қабілетін көрсетеді.

Сипатталған әдістер арқылы алынған бұл кеуекті көміртекті адсорбенттер өнеркәсіптік ағынды суларды тазартуға өте қолайлы және тиімді газ адсорбенттері, соның ішінде сутегін сақтау үшін әрекет ете алады. Әрі қарайғы зерттеулер мен эксперименттер одан да жақсартуға уәде береді. Осы әдістер арқылы алынған нәтижелерге сүйене отырып, Калий Гуматынан алынған адсорбенттер жаңжақты және технологиялық тұрғыдан мүмкін болатын шикізат ретінде пайда болады.

Түйін сөздер: адсорбент, калий гуматы, адсорбциялық қасиеттері, бетінің ауданы, активтенуі, сақталуы, сутегі.

ИЗУЧЕНИЕ ФИЗИКО-ХИМИЧЕСКИХ СВОЙСТВ АДСОРБЕНТОВ НА ОСНОВЕ ГУМАТА КАЛИЯ И ИСПОЛЬЗОВАНИЕ В ХРАНЕНИИ ВОДОРОДА

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Данное исследование основано на изучении физико-химических свойств адсорбентов на основе гумата калия. В ходе этого исследования мы оценили структуру, характеристики и адсорбционную способность этих материалов. Гумат калия служил основным исходным материалом, и мы использовали ряд процессов высокотемпературной карбонизации и активации для получения исследуемых адсорбентов.

Мы охарактеризовали структуру поверхности, пористость и элементный состав полученных адсорбентов, используя такие методы, как криогенная сканирующая зондовая микроскопия и сканирующая электронная микроскопия (SEM). Мы определили удельную поверхность адсорбентов в пересчете на объем поверхности, используя методы поглощения газа, в частности метод Брунауэра-Эмметта-Теллера (BET).

Полученные результаты свидетельствуют о значительном улучшении пористости и адсорбционных свойств активированных адсорбентов. Большинство из этих материалов имеют высокую удельную поверхность, что свидетельствует об их исключительной адсорбционной способности.

Эти пористые углеродсодержащие адсорбенты, полученные описанными способами, хорошо подходят для очистки промышленных сточных вод и могут выступать в качестве эффективных газовых адсорбентов, в том числе для хранения водорода. Дальнейшие исследования и эксперименты обещают еще большие улучшения. Основываясь на результатах, полученных с помощью этих методов, адсорбенты на основе гумата калия становятся универсальным и технологически приемлемым сырьем с широким спектром применения.

Ключевые слова: адсорбент, гумат калия, адсорбционные свойства, площадь поверхности, активация, хранение, водород.

Introduction. In light of the global trend towards renewable energy sources and the mounting environmental concerns, the development of highly efficient, sustainable, and environmentally friendly materials assumes paramount importance

The Relevance of the Study. Natural carbon-based materials, particularly humic substances such as potassium humate, have garnered significant attention due to their remarkable chemical reactivity, abundance, and potential for tailored modification [1].

These materials exhibit promising sorption properties, rendering them suitable for a wide range of applications, including water purification, gas adsorption, and hydrogen storage. However, a more in-depth exploration of their activation mechanisms, thermal stability, structural integrity, and textural characteristics is crucial to fully appreciate their scientific significance and practical utility.

The purpose of this research is to develop and investigate the properties of porous sorbents based on potassium humate. Specifically, we aim to analyze how different activation temperatures affect the structure, chemical composition, and sorption capacity of these materials, as well as their potential for hydrogen storage.

In order to accomplish this objective, several tasks were defined:

- To conduct carbonization and activation processes of potassium humate at various temperatures.

- To characterize the textural properties of the resulting materials using BET, Raman, and FTIR spectroscopy techniques, as well as scanning electron microscopy (SEM).

- To determine how heat treatment influences graphitization processes and the formation of microporous structures.

- To study the hydrogen sorption performance of these materials and compare it to that of CO_2 and N_2 sorbates.

Scientific breakthrough. In the course of our research, we conducted experiments aimed at producing porous carbon that was activated at elevated temperatures of 800 and 900 degrees Celsius. By comparing their physicochemical properties, we were able to observe their characteristics. With an increase in processing temperature, we observed an enhancement in the quality attributes of the adsorbent and a corresponding increase in its adsorption capacity. Potassium humate can be added to the list of environmentally and economically viable adsorbents.

In the current context of various processes involving man-made waste contamination, as well as the purification of contaminated wastewaters and gases, adsorbents play a crucial role as part of composite materials in the realm of medicine.

In light of these features and advantages, research into the development of porous materials based on humic substances is gaining momentum. The structure of potassium humate, the primary component of adsorbents, exhibits remarkable complexity. Due to the presence of diverse functional groups, it demonstrates rapid reactivity with a wide range of metals and simple substances, indicating its high chemical activity [2,3].

Within this functional structure, carboxyl, phenolic, and hydroxyl groups can be identified [4]. Studies have demonstrated that modifications to humates, such as carbonization and activation, significantly enhance their specific surface area, porosity, and selective adsorption capabilities.. The activation of humates through physicochemical methods, such as thermal treatment, exposure to water vapor, carbon dioxide or chemical reagents, can result in the formation of a highly porous structure with exceptional adsorption capacity. Potassium humate, a specific type of humic substance, holds significant potential in agriculture due to its capacity to enhance the physical and chemical characteristics of soil, promote root system development, and bolster plant resilience against abiotic stressors. The utilization of potassium

humate fosters more efficient nutrient absorption, allowing for a reduction in mineral fertilizer application without compromising crop yield [5]. Moreover, the use of granular forms of potassium humate has been demonstrated to enhance soil water-holding capacity and stimulate microbiological processes.. Humic substances (HS), which are formed through the process of humification and carbonization of natural organic materials such as lignite, brown coal, Leonardite, and peat, play a crucial role in soil ecosystems [6,7]. They constitute the dominant component of soil organic matter, accounting for 60–80% of the total organic matter and 50–80% of dissolved organic matter in water, with a concentration of 25% in groundwater.

These substances contribute to soil water retention, regulate the formation of soil aggregates, facilitate carbon sequestration, and impact the dynamics of soil microorganisms. However, extracting HS from natural organic materials presents significant challenges due to their tendency to bind with humins, polyvalent cations, and heavy metals, rendering them insoluble and less accessible for agricultural use [8].

Research has shown that materials based on humates effectively remove heavy metals and organic contaminants from aqueous solutions, while other studies have explored the use of humic sorbents in gas separation and air purification processes.. The study conducted by [9] highlights the advantages of humic sorbents, such as their lower cost and upgradeability compared to activated carbon. Furthermore, research [10] has explored various methods for activating humic substances, including treatments with CO_2, steam, and ozone, allowing for precise control over the structure of the material [11]. However, optimizing activation conditions and enhancing mechanical strength remains a challenging task.

A number of investigations have demonstrated that adsorbents based on potassium humate can effectively eliminate heavy metals, organic contaminants, petroleum products, and other toxic substances from aqueous solutions, as reported in [12] and [13]. In the study [14], it was demonstrated that treating humates in a CO_2 atmosphere increases their surface area and forms a mesoporous structure, enhancing their capacity to absorb metal ions such as Pb^{2+} and Cd^{2+}. Further investigations suggest the potential application of humate-laden adsorbents for capturing gases such as CO_2 and H_2C, thereby paving the way for their utilization in gas separation processes and air purification procedures [15]. Moreover, adsorbents based on humic substances exhibit similar advantages to activated carbon when compared to conventional sorbents, owing to their affordability, renewable nature, and capacity for chemical modification of their structure to enhance sorption performance [16].

Nevertheless, there remain unresolved challenges related to optimizing activation methods, enhancing the mechanical durability of the resulting materials, and investigating their regenerative capabilities [17]. In this study, we delve into the physicochemical characteristics of adsorbents derived from potassium humate, examining their structure, porosity, and sorption efficacy.

Materials and methods. In order to conduct this research, we employed state-of-the-art laboratory instruments and equipment, including a quartz reactor, a rotary tube furnace, a gas chromatograph, a shaker-incubator, and a spectrophotometer, as well as a microscope equipped with a pH meter, a centrifuge, an ultrasonic bath, and an electron quantum scanning device.

The process of carbonization and activation to produce potassium humate-based carbon adsorbents occurred under laboratory conditions in a nitrogen-filled environment at a temperature of 500 degrees Celsius. Carbonization serves the purpose of eliminating volatile components and establishing a porous structure in the material. For activation, water vapor was employed, which facilitated the development of a microporous framework.

Various methods were employed to investigate the physicochemical characteristics of the resulting adsorbents. X-ray diffraction analysis was conducted using an X-ray diffractometer equipped with Cu Ka radiation, spanning a range from 5 to 90 degrees of diffraction angle, to examine the phase composition and crystal structure.. The analysis of infrared (IR) spectra was conducted in

the laboratories of «Nazarbayev University» using a Nicolet iS10 Fourier transform infrared (FTIR) spectrometer. To evaluate the porous structure and specific surface area of the materials, gas adsorption was employed using the Brunauer-Emmett-Teller (BET) method. Scanning electron microscopy (SEM) allowed us to investigate the morphology and surface structure of the adsorbents, while the adsorption properties were explored using methyl orange, enabling the determination of the materials'https://doi.org/10.58805/kazutb.v.2.27-884 activity in solutions containing organic pollutants.

The elemental composition of the materials was analysed using a Quanta 3D 200i scanning electron microscope equipped with an energy dispersive X-ray analyser (EDAX detector). Additionally, the pH levels of aqueous solutions containing the adsorbents were measured using a pH meter, providing insights into their acid–base properties. All experiments were conducted multiple times.

Results and discussion. The gas chromatographic analysis revealed the primary composition of gases emitted during the processes of carbonization and activation of potassium humate.

At a temperature of 800°C, the concentration of oxygen was 38.033%, hydrogen - 27.612%, carbon dioxide - 6.966%, nitrogen - 1.532%, and methane - 9.767%.

During pyrolysis at a temperature of 900°C, oxygen concentration decreased to 7.39%, while hydrogen increased to 17.68%. The concentration of carbon dioxide remained relatively stable at 5.58%. Nitrogen concentration rose to 69.35%, indicating a significant increase in its proportion. Carbon monoxide was also detected in the gas mixture.

Detailed information on the composition of gases and material balance during carbon activation is provided in Tables 1-4, which showcase the elemental composition of the released gases.

At the initial stage of the thermal processing of potassium humate, there is a process of dehydration, accompanied by the release of water and volatile compounds with a low molecular weight. As the temperature continues to rise, the decomposition of carboxyl, phenolic, and other oxygen-containing functional groups commences, resulting in the emission of CO_2, CO, and a minor amount of volatile organic compounds.

Table 1 - Material balance of potassium humate activation at 800°C

	Name	Massa, g	Compound, %
Original	Potassium humate	270.0	90.0
	Water	30.00	10.00
	Total	300.00	100.00
Product	Solid residue (adsorbent)	172.00	57.30
	Generator gas	97.40	32.50
	Liquid product (water + resin)	30.60	10.20
	Total	300.00	100.0

Table 2 - Material balance of potassium humate activation at 900°C

	Name	Massa, g	Compound, %
Original	Potassium humate	200.00	66.67
	Water	100.00	33.33
	Total	300.00	100.00

Product	Solid residue (adsorbent)	68.40	22.80
	Generator gas	201.66	67.22
	Liquid product (water + resin)	29.94	9.98
	Total	300.00	100.00

Table 3 - Gas composition of carbonization and humate activation at 800℃

Process	T, C°	Gas composit vol., %				
		O_2	H_2	CO_2	N_2	CO
Carbonization	200	53.94	0.07	-	46.05	-
	300	37.52	0.71	9.45	22.34	27.83
	400	50.99	5.98	15.39	29.69	-
	500	30.17	6.73	19.43	45.77	-
	600	28.03	17.61	6.96	47.53	-
Activation	700	22.31	19.56	7.89	42.31	-
	800	19.14	16.37	7.93	57.25	-

Table 4 - Gas composition of carbonization and humate activation at 900℃

Process	T, C°	Gas composit vol., %			
		O_2	H_2	CO_2	N_2
Carbonization	200	8.79	2.18	-	89.03
	300	12.62	31.07	0.40	55.91
	400	10.89	8.16	0.47	80.48
	500	8.29	9.91	4.07	77.73
	600	5.68	10.44	5.24	78.64
Activation	700	2.96	4.93	5.89	86.31
	800	10.42	13.12	4.21	72.25
	900	7.39	17.68	5.58	69.35

Table 5 - Elemental composition of the initial and activated samples

Name	Content of elements, wt. %								
	C	O	Na	Mg	Al	Si	S	K	Fe
Initial potassium humate	42.94	26.16	0.62	0.21	1.27	0.48	0.26	25.92	2.14
Activated potassium humate 800℃	51.06	27.69	0.81	0.21	0.95	0.37	0.24	16.71	1.96
Activated potassium humate 900℃	29.45	31.22	3.86	0.08	0.56	0.25	0.18	34.07	0.33

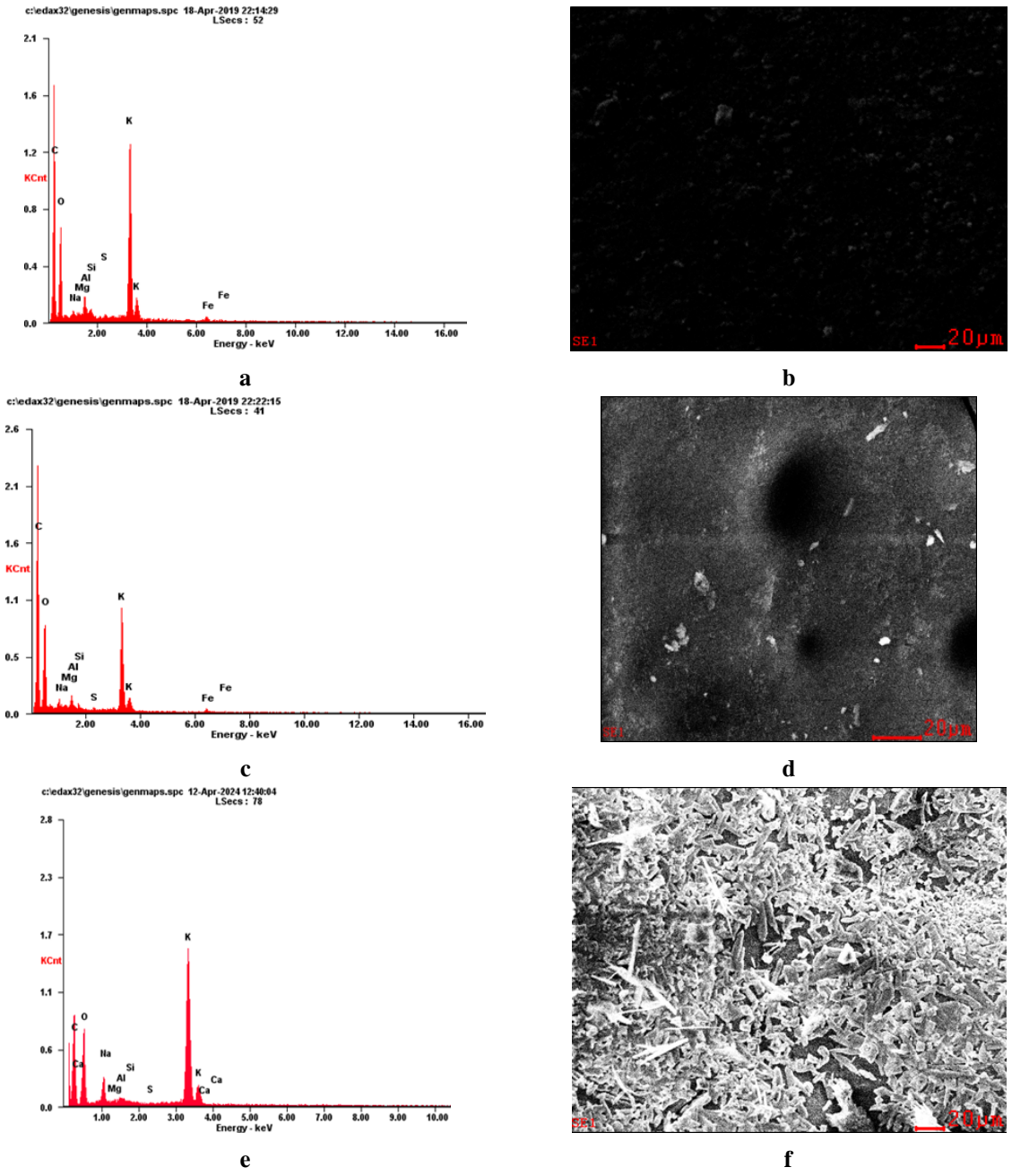


Fig.1 - Elemental composition of samples (a, b – initial potassium humate; c, d - activated potassium humate 800℃; e, f - activated potassium humate 900℃)

With an increase in temperature, aromatic and aliphatic components of the humate structure undergo destruction, leading to the formation of resinous intermediate products. These substances can participate in structural reorganization processes, contributing to the creation of more thermodynamically stable carbon systems.

At higher temperatures ranging from 600 to 700 degrees Celsius, carbonization and condensation reactions become predominant, resulting in the production of a carbonaceous residue with a highly porous structure.. The presence of potassium in a given environment promotes the catalytic breakdown of organic constituents, thereby facilitating the creation of microporous carbon materials. This process is of utmost significance in the manufacturing of activated carbon and sorbent materials. The findings regarding the elemental

composition of the examined samples are detailed in Table 5 and illustrated in Figure 1.

Based on the table data, the original potassium humate contains 42.94% C, 26.16% O_2, 0.62% Na, 0.21% Mg, 1.27% Al, 0.48% Si, 0.26% S, 25.92% K and 2.14% Fe.

Following activation at a temperature of 800 degrees Celsius, the carbon content rises to 51.06 percent, oxygen to 27.69 percent, sodium to 0.81 percent, while magnesium remains unchanged at 0.21 percent. Aluminium decreases to 0.95 percent, silicon to 0.37 percent, sulphur to 0.24 percent, potassium content declines to 16.71 percent, and iron to 1.96 percent.

Upon activation at 900 degrees Celsius, the carbon content of the material significantly decreases to a level of 29.45 percent, while the oxygen content rises to 31.22 percent. The sodium concentration diminishes to 3.86 percent, magnesium to 0.08 percent, aluminum to 0.56 percent, silicon to 0.25 percent, and sulfur to 0.18 percent. Conversely, the potassium content rises to a value of 34.07 percent, while iron content decreases to 0.33 percent.

The presence of potassium within the humate framework serves as a catalyst, activating thermal decomposition reactions and promoting the expansion of the overall porous structure.. At temperatures exceeding 700 degrees Celsius, the process of active micropore formation commences, resulting in a substantial increase in the specific surface area of the material. The precise pore structure is contingent upon the conditions of heat treatment: at lower temperatures, mesopores dominate, providing exceptional sorption capacity for larger molecules, while high-temperature activation between 900 and 1000 degrees Celsius leads to the formation of well-developed micropores, further enhancing the specific surface area and rendering the material highly effective as a sorbent for both gases and smaller molecules.

The micrographs of both the original and activated samples can be seen in Figure 2. Upon analyzing the morphology of these adsorbents, it became evident that the dimensions of the particles exhibit a non-homogeneous structure. The adsorbent treated with potassium humate and subsequently dried at 900 degrees Celsius exhibited dimensions ranging from 295.4 to 548.2 nanometers, while the adsorbent treated with the same potassium humate but at 800 degrees Celsius had dimensions ranging between 41.2 and 71.1 nanometers.

As seen in Figure 2, the formation of carbon nanotubes is observed at 800 °C, where at 900 °C, other carbon materials are predominantly formed. The pores in the structure of potassium humate are formed as a result of heat treatment and chemical activation, which helps to increase the specific surface area and improve the adsorption properties of the material. These pores have different sizes, which allows potassium humate to effectively interact with gases and liquids.

The presence of some large particles and large pores is also observed, which may indicate the initial stage of structural changes in the material. The structure of potassium humate appears to be quite loose and porous, which determines its high activity and potential for use in various applications, such as adsorption or catalysis. FTIR is an effective analytical method used to study the chemical structure and composition of potassium humate. This material, a salt of humic acids obtained as a result of the decomposition of organic substances in soil and peat, undergoes significant structural changes when exposed to high-temperature activation. A comparison of the spectra obtained at 800 ℃ and 900 °C shows the evolution of functional groups during heat treatment.

Both spectra exhibit characteristic absorption bands associated with humic substances. The wide band around 3438-3445 cm^{-1} corresponds to the stretching fluctuations of hydroxyl (O-H), which indicates the presence of water, alcohol, or phenolic groups. The range of ~1630 cm^{-1} reflects fluctuations in carbonyl (C=O) and unsaturated C=C bonds, usually extending from aromatic rings. The 1404 cm^{-1} peak is caused by bending vibrations of C–h and deformation of O-H in humus structures. Ranges of 1010-1125 cm^{-1} show fluctuations in the stretching of C-O, which suggests the presence of alcohol or phenolic functions important for metal

bonding. The area of approximately 830 cm^{-1} and 700 cm^{-1} confirms the structures of aromatic rings, bending beyond the C–H plane. The ranges of ~2610 and 2950 cm^{-1} are associated with asymmetric and symmetrical C–H stretching fluctuations, usually observed in aromatic and aliphatic groups (Table 6).

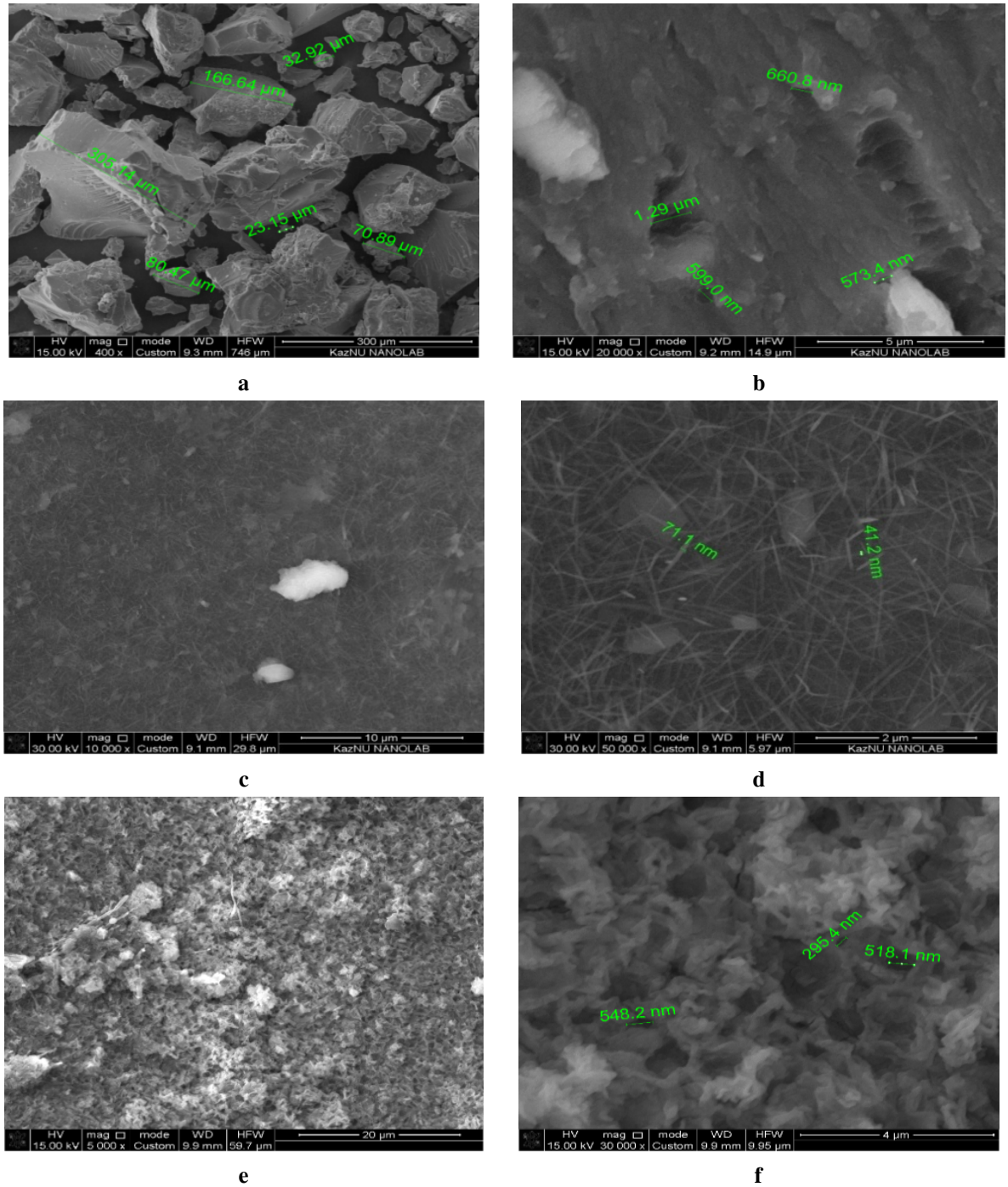


Fig.2 - SEM images of samples (a, b - initial potassium humate; c, d - activated potassium humate 800℃; e, f - activated potassium humate 900℃)

Figure 3 shows the IR spectra of potassium Humate activated at different temperatures-800°C and 900°C, showing changes in the composition of functional groups as a result of heat treatment.

An increase in the activation temperature from 800°C to 900°C leads to small but significant edits in the FTIR absorption bands, especially in the carbonyl and C–O regions, which indicates continuous decomposition or rearrangement of organic functional groups. The loss of the 510 cm^{-1} band at 900°C means a possible rupture of metal-organic interactions or complexes. Despite the thermal stress, the aromatic structures remain quite unchanged, which is expressed in the preservation of peaks below about 830 cm^{-1} and 700 cm^{-1}. In general, the Humate activated at 900°C is structurally stabilized and enriched with aromatic content, the volatile and unstable functional groups are reduced. The results of Raman spectroscopy of potassium Humate activated at 800 °C indicate the presence of peaks D (1359 cm^{-1}) and G (1575.8 cm^{-1}). The degree of graphitization for a given sample is 22.13%, which is determined using spectroscopic methods such as Gaussian decay of the spectrum. The intensity ratio of peaks D and G is I//I = = 0.86, and the obrat inverse ratio I / / I calculated by the Gaussian method is 1.15.

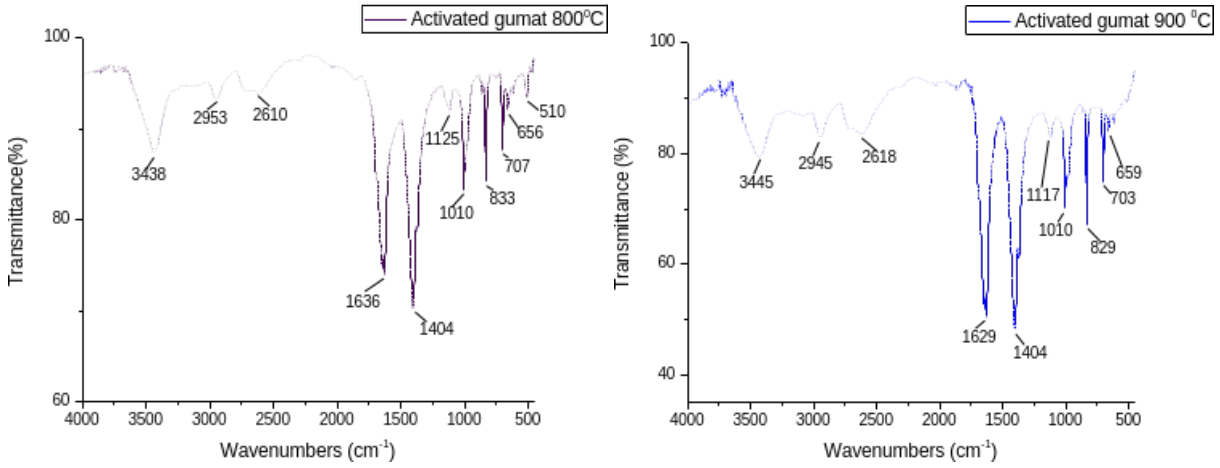


Fig.3 - IR spectra of potassium humate at 800°C (a) and 900°C (b)

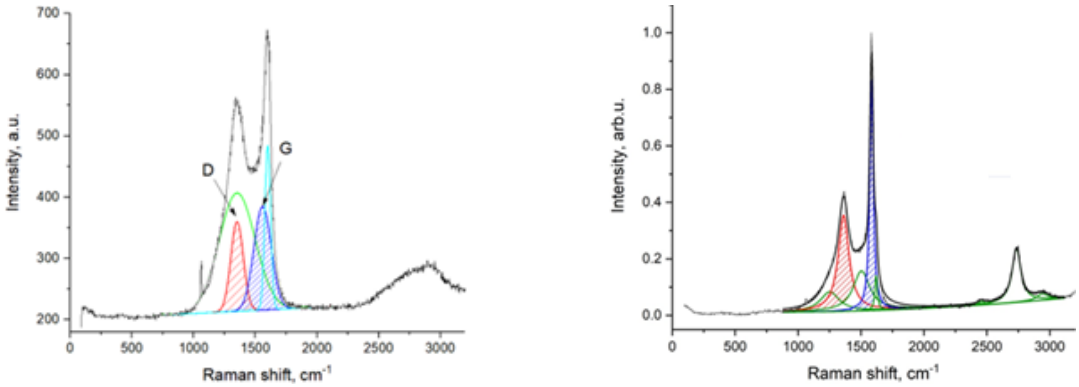
With an increase in the activation temperature to 900°C, the structure of the carbon material undergoes significant changes. In this sample, the degree of graphitization decreases compared to potassium Humate activated at 800°C, which may be due to the redistribution of carbon phases and changes in the structure defect. As a result, its adsorption properties and catalytic activity can be affected.

Thus, heat treatment at different temperatures significantly affects the degree of graphitalization of potassium Humate, as well as its structural and functional characteristics. An increase in the activation temperature leads to an increase in the defect of the carbon material, which is confirmed by a change in spectral characteristics.

Table 6 - Key Differences at 800 °C and 900 °C Spectr

Spectral Region	800 °C	900 °C	Interpretation
O–H Stretching	3438 cm^{-1}	3443 cm^{-1}	Slight shift, possibly due to changes in hydrogen bonding or moisture content.

C=O / C=Stretch C	1635 cm^{-1}	1626 cm^{-1}	A downward shift indicates the weakening or rearrangement of carbonyl/aromatic groups.
C–O Stretch	1125 - 1010 cm^{-1}	1118 - 1010 cm^{-1}	A slight decrease in wavenumber may be due to the breaking or structural rearrangement of ether/phenolic bonds.
C-H Aromatic Bend	833 cm^{-1}	827 cm^{-1}	A very small shift indicates a stable aromatic character.
C–H Out-of-Plane Bend	706 - 656 cm^{-1}	702 - 659 cm^{-1}	Minimal changes confirm the preservation of aromatic ring systems.
Low Frequency Vibration	510 cm^{-1}	Abs	A disappearance may indicate the decomposition of organometallic complexes at 900°C.
Asymmetric Stretch C-H	2611 cm^{-1}	2614 cm^{-1}	A slight shift towards magnification indicates changes in the local environment of aromatic/aliphatic C–H bonds.
Symmetric Stretch C-H	2952 cm^{-1}	2945 cm^{-1}	A slight decrease towards magnification indicates a slight structural rearrangement of organic structures.



a b

Fig.4 - Raman spectr of activated potassium humate at 800℃ (a) and at 900℃ (b)

Potassium Humate interesting sorption properties that can be studied by adsorbing nitrogen. Nitrogen adsorption isotherms for potassium Humate show characteristic features of a microporous structure, which is confirmed by the fact that isotherms belong to type I. That is, potassium Humate has a high surface area, mainly consisting of micropores with a diameter of no more than a few nitrogen molecules. The process of nitrogen adsorption in potassium Humate is accompanied by saturation of the micropores of the material with nitrogen molecules, which leads to the formation of a horizontal site in the isotherm, where adsorption occurs at low pressure values. This suggests that the material is capable of effectively capturing gas molecules in microporous space. With increasing pressure, nitrogen fills the existing pores, but at higher pressure values, adsorption reaches

saturation, which is confirmed by the presence of a horizontal site in the isotherm. Potassium Humate also exhibits a type IV hysteresis cycle, which may indicate the presence of slit-like pores in its structure, typical of organic materials with a multilayer porous mesh. This allows potassium Humate to interact effectively with various gases, including nitrogen, making it useful in a variety of sorption and catalytic applications.

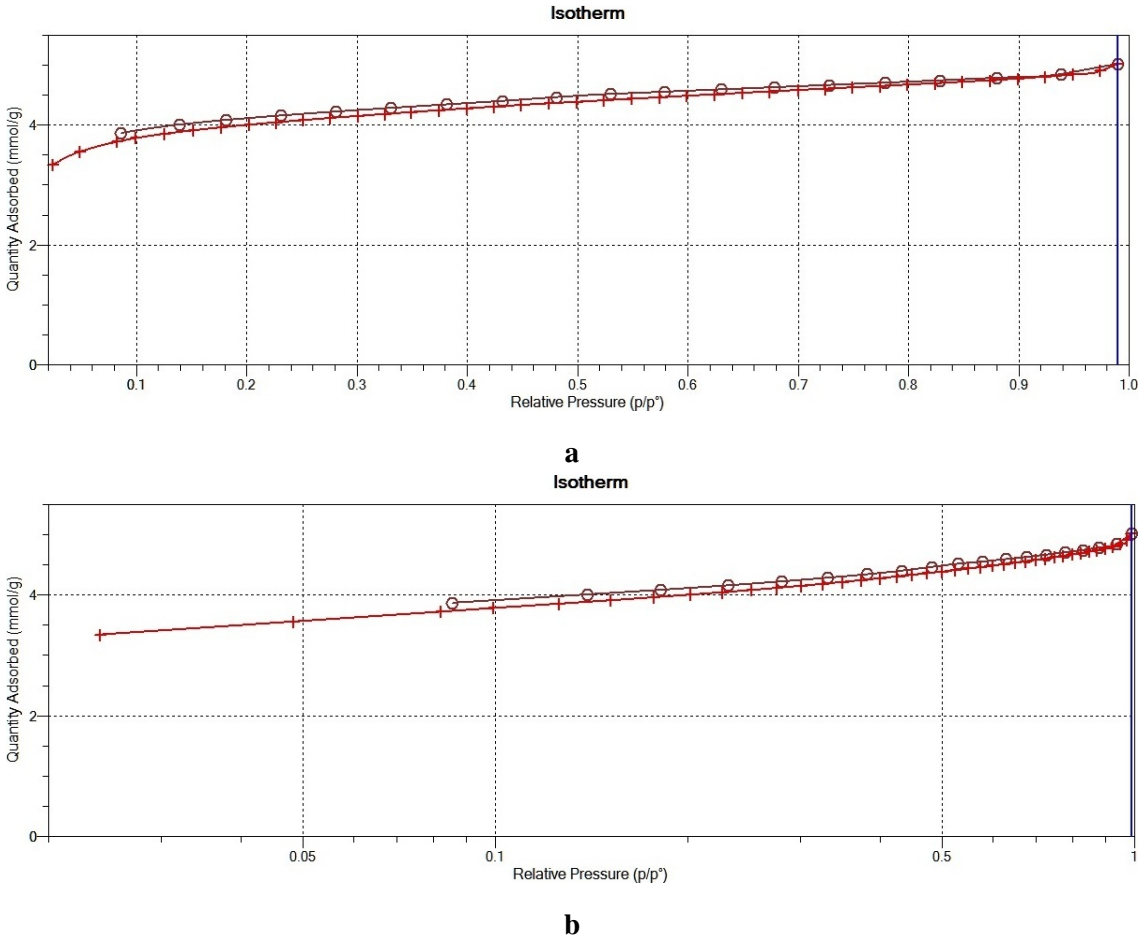


Fig.5 - Adsorption of activated adsorbents a-800°C, b-900°C (N_2, by BET method)

The results of the analysis of the pore structure show that the activation of potassium Humate at different temperatures significantly affects its texture characteristics.

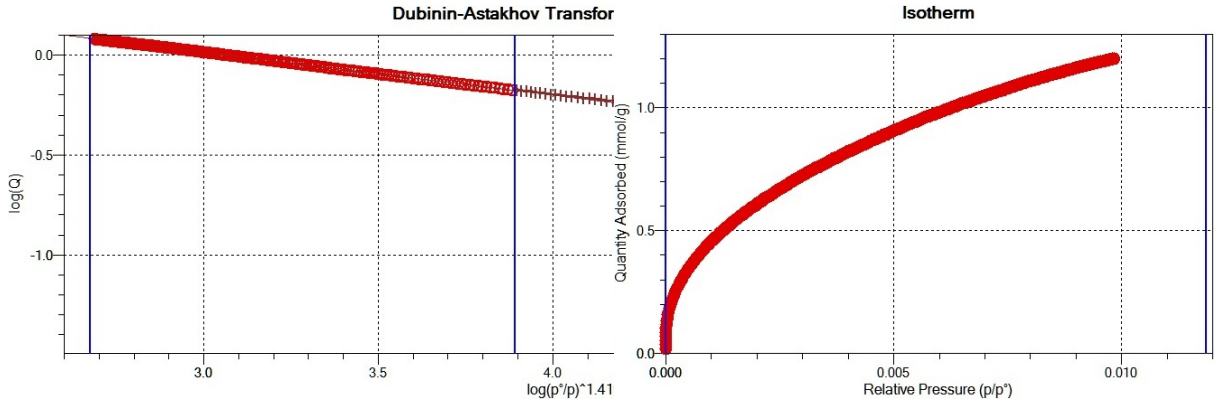
For a sample activated at 800°C, the specific surface area according to bat (S_{BET}) is 320.993 m^2/g, the total pore volume is 0.174 cm^3/G, including 0.116 cm^3/G - micropores, 0.052 cm^3/G - mesopores and 0.006 cm^3/G - macropores. For pores with a width of 17,000 Å to 3,000,000 Å, the actual surface area calculated by BJH is 68.8307 m2/g, while the average width of adsorption pores according to BJH (4V/A) is 36.72 Å.

When the activation temperature rises to 900 °C, the specific surface of the SBET increases to 349.775 m^2/g, but the total pore volume decreases to 0.166 cm^3 / g. in this case, the volume of micropores remains practically unchanged (0.117 cm^3 / G), and the volume of mesopores decreases to 0.029 cm^3 / G, and the proportion of macropores increases to 0.020 cm^3/ G. the specific surface of BJH decreases to 28.9376 m^2 / g, and the average width of BJH adsorption pores decreases to 28.025 Å. Thus, an increase in the activation temperature leads to an increase in the specific surface and redistribution of porosity, which is accompanied by a decrease

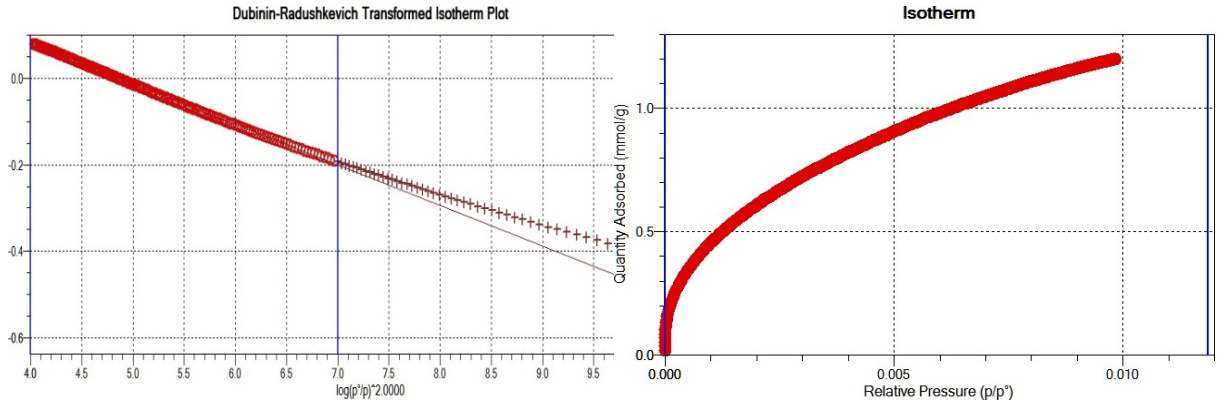
in mesopores and an increase in the proportion of macropores, which can affect the adsorption properties of the material.

Table 7 - Adsorption characteristic of samples (N_2)

Name	SBET, m^2/g	Total pore volume, cm^3/g	Micro-pores, cm^3/g	Meso-pores, cm^3/g	Macro-pores, cm^3/g	SBJH, for pore width from 17,000 Å to 3,000,000 Å, m^2/g	Average wid of adsorption pores BJH (4V/A), Å
Activated potassium humate 800℃	320.993	0.174	0.116	0.052	0.006	68.8307	36.720
Activated potassium humate 900℃	349.775	0.166	0.117	0.029	0.020	28.9376	28.025



a



b

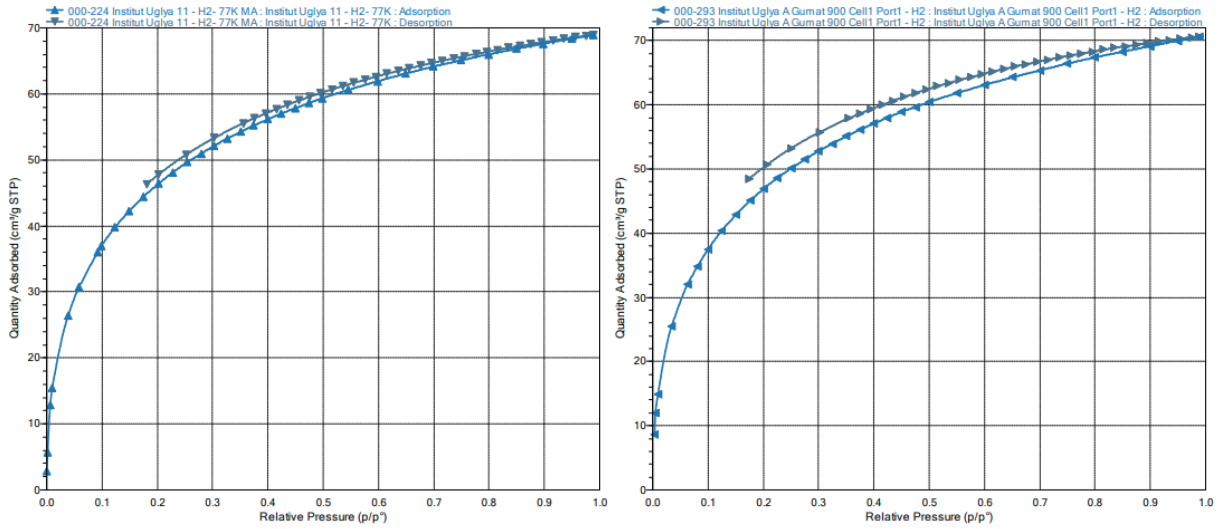
Figure 5 - Adsorption curves of activated potassium humate adsorbent a-800℃, b-900℃ (according to Dubinin-Astakhov, CO_2)

Table 8 shows the results of calculating the porous characteristics using the Dubinin-Radushkevich and Dubinin-Astakhov methods, showing changes in the micropore structure of activated potassium humate with an increase in the activation temperature.

For the sample activated at 800°C, the maximum micropore capacity using the Dubinin-Radushkevich method is 2.8628 mmol/g, and the maximum micropore volume is 0.136467 cm^3/g. The equivalent surface area reaches 293.08 m^2/g. According to the Dubinin-Astakhov method, the maximum micropores capacity is high - 4.56696 mmol/G, and the micropores volume limit is 0.217702 cm^3 / G. when using this method, the equivalent surface area is significantly higher and is 675.86 m2/g, and the average equivalent pore width is 1.88 Å.

Table 8 - Results of the study of sorption of PUM (by CO_2)

Name	Dubinin-Radushkevich			Dubinin-Astakhov			
	Maximum capacity of micropores, mmol/g	Maximum volume of micropores, cm^3/g	Equivalent surface area, m^2/g	Maximum capacity of micropores, mmol/g	Micropore volume limitation, cm^3/g	Equivalent surface area, m^2/g	Average equivalent pore width, Å
Activated potassium humate 800℃	2.8628	0.136467	293.084348	4.56696	0.217702	675.861223	1.884422
Activated potassium humate 900℃	2.2484	0.107183	230.192239	6.57723	0.408868	803.156566	1.303239



a **b**

Fig.6 - Adsorption curve of Activated potassium humate a-800℃, b-900℃ (H_2)

When activated at a temperature of 900°C, the maximum capacity of micropores decreases according to the Dubinin-Radushkevich method, to 2.24848 mmol / G, and the maximum volume

of micropores decreases to 0.107183 cm^3/g. accordingly, the equivalent surface area decreases to 230.19 m^2 / g. however, according to the Dubinin-Astakhov method, the maximum capacity of micropores increases to 6.57723 mmol / G, A micropores volume limit increases to 0.408868 cm^3 / G. the equivalent surface area reaches 803.16 m^2/g, the average equivalent pore width decreases to 1.30 Å.

A comparison of the data shows that with an increase in the activation temperature, the volume of micropores and their equivalent width decreases, but with the Dubinin-Astakhov method, the maximum capacity of micropores increases. This indicates the development of a fine porous structure, which can affect the adsorption properties of the material and its ability to hold molecules of different sizes. The adsorption curves of the activated adsorbent for hydrogen are shown in Figure 6.

The adsorption of hydrogen in activated potassium Humate is due to its developed porous structure with micropores and mesopores. The main contribution to the retention of H_2 is physical adsorption on the carbon surface, which is enhanced by the presence of narrow pores that contribute to an increase in retention forces due to capillary condensation at low temperatures (77 K). An increase in the activation temperature of potassium Humate leads to a slight increase in its actual surface area and redistribution of porosity, which ultimately contributes to an increase in hydrogen capacity.

Table 9 - Results of the study of hydrogen sorption with potassium humate

Name	Specific surface area $S_{(DFT)}$, m^2/g	Mass of H_2, % (77 K)	Maximum amount of adsorbed H_2, (cm^3/g)
Activated potassium humate 800℃	130.4471	0.6154	68.9271
Activated potassium humate 900℃	130.9283	0.6305	70.6192

The findings obtained from calculating the specific surface area and hydrogen adsorption at a temperature of 77 kelvin suggest that the activation of potassium humate at higher temperatures leads to a slight improvement in sorption characteristics.

Using the DFT technique, we determined the specific surface area for a sample that was activated at 800 degrees Celsius to be 130.4471 square meters per gram. The mass fraction of hydrogen adsorbed at 77 degrees Kelvin is 0.6154 percent, with a maximum amount of absorbed H_2 of 68.9271 cubic centimeters per gram.

Upon increasing the activation temperature to 900 degrees Celsius, the specific surface area marginally increases to 130.9283 square meters per gram. Correspondingly, the mass fraction of absorbed hydrogen rises to 0.6305 percent, while the maximum amount of H_2 adsorption reaches 70.6192 cubic centimeters per gram.

Consequently, despite a minor increase in the specific surface area, activation at 900 °C leads to an enhancement in hydrogen adsorption, which can be attributed to changes in the pore structure and the redistribution of micropore fractions. Table 7 provides comparative values for the calculated specific surface areas $S_{(BET)}$ related to the adsorption of N_2, CO_2, and H_2.

The investigation into the sorption characteristics of activated potassium humate under a temperature of 77 K revealed a correlation between the activation temperature and the pore structure as well as the gas adsorption capacity of the material.

Specifically, for a sample that was activated at 800 °C, the specific surface area was determined using the Brunauer-Emmett -Teller (BET) method with nitrogen (N2) and amounted to 320.993 m^2/g. The equivalent specific surface area computed using the Dubinin-Radushkevich approach with carbon

dioxide (CO2) was calculated to be 293.084 m^2/g, while the Dubinin-Astakhov approach yielded a value of 675.861 m^2/g. Density functional theory (DFT) computations with hydrogen (H2) estimated the specific surface to be 130.4471 m^2/g.

Under 77 K, the amount of adsorbed hydrogen reached 0.6154% corresponding to a volume of 68.9271 cm^3/g.

With an increase in activation temperature to 900 °C, the specific surface area determined by the Brunauer–Emmett–Teller (BET) method increases to 349.775 m^2/g. Conversely, the equivalent specific surface area calculated using the Dubinin–Radushkevich method decreases to 230.192 m^2, while the equivalent specific area determined by Dubinin–Astakhov increases to 803.156 m^2.

Table 10 – Comparative table of specific surface area $S_{(BET)}$ for N_2, CO_2 and H_2

Temp-erature, K	S(BET), m^2/g (based on N2)	Equivalent specific surface area (S), m^2/g (based on CO2)		Specific surface area S(DFT), m^2/g (based on H2)	Amount of adsorbed H2 gas	
		Dubinin-Radushkevich	Dubinin-Astakhov		%	cm^3/g
Activated potassium humate (800^0C)						
77	320.993	293.084348	675.861223	130.4471	0.6154	68.9271
-						
77	349.775	230.192239	803.156566	130.9283	0.6305	70.6192

According to density functional theory (DFT), the specific surface remains virtually unchanged at 130.9283 m^2. The quantity of adsorbed hydrogen rises to 0.6305%, or 70.6192 cm^3/g.

Thus, an increase in activation temperature leads to an increase in specific surface area and a re-distribution of porosity. This positively affects the adsorption properties of humic substances, particularly with regard to hydrogen adsorption. This may be attributed to alterations in the micropore structure, resulting in an increase in narrow pores that effectively retain hydrogen through van der Waals interactions.

Conclusion. The investigation into the adsorption and structural properties of activated potassium humate subjected to different thermal treatments at 800°C and 900°C has shown that an increase in the activation temperature leads to substantial alterations in the porous structure of the material. These modifications affect the specific surface area, the distribution of pore sizes, and the sorption characteristics of the substance.

A comprehensive analysis of the composition reveals that at 900°C, there is a decrease in the carbon content (from 51.06% to 29.45%) accompanied by an increase in oxygen content (from 27.69% to 31.22%). Additionally, there is a notable rise in the concentration of sodium and potassium, which can be attributed to a redistribution of mineral constituents within the structure of humate.

Raman spectroscopy analysis revealed a decline in the degree of graphitization as the activation temperature increased, with a 27.6% decrease at 800°C and a 22.13% decrease at 900°C. This was confirmed by an increase in the intensity ratio of the D and G peaks, indicating a rise in structural defects, which could potentially affect adsorption properties.

The porous characteristics showed a slight increase in specific surface area according to the Brunauer-Emmett-Teller (BET) method, from 320.99 m^2/g at 800 °C to 349.77 m^2/g at 900 °C, while total pore volume remained relatively constant.

Pore structure analysis using the Dubinin–Radushkevich and Dubinin–Astakhov models revealed changes in maximum micropore volume

and average pore size at 900 °C. Maximum micropore volume decreased, equivalent surface area increased, and average pore diameter decreased.

The sorption characteristics of hydrogen demonstrated a slight enhancement in the specific surface area, calculated using the DFT method with H2, ranging from 130.45 to 130.93 square meters. The adsorption capacity of hydrogen also increased from 0.6154% to 0.6305%.

This increase may be attributed to a reconfiguration of microporous structures and the emergence of novel active sites. An increase in the activation temperature for potassium humate resulted in an expansion of the specific surface area and a redistribution of porosity, affecting its adsorption capabilities. At 900°C, there was a reduction in graphitization degree and an enhancement in hydrogen sorption capacity. These findings indicate that humates could be employed as effective adsorbents for hydrogen storage in gas systems.

This study confirms the promising potential of potassium humate as an adsorbent. It opens up opportunities for the development of cost-effective and environmentally friendly carbon-based materials for applications in hydrogen storage, water treatment, and gas capture technologies.

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