

**ҚАЗАҚСТАН РЕСПУБЛИКАСЫ БІЛІМ ЖӘНЕ ҒЫЛЫМ МИНИСТРЛІГІ
Л.Н. ГУМИЛЕВ АТЫНДАҒЫ ЕУАЗИЯ ҰЛТТЫҚ УНИВЕРСИТЕТІ**

**Химиктер күніне орай және кафедра профессорлары Тәшенов Әуезхан
Кәріпханұлы мен Рахмадиева Слукен Бигалиқызын еске алуға арналған
«Химиялық білім мен химия ғылымының өзекті мәселелері» атты
халықаралық ғылыми-практикалық конференция
МАТЕРИАЛДАРЫ
27 мамыр 2022 ж.**

МАТЕРИАЛЫ

**Международной научно-практической конференции «Актуальные
проблемы химического образования и химической науки», приуроченной
ко Дню Химика и посвященной памяти профессоров Ташенова Ауэзхана
Карипхановича и Рахмадиевой Слукен Бигалиевны
27 мая 2022 г.**



**ТАШЕНОВ АУЭЗХАН
КАРИПХАНОВИЧ
(04.04.1950-11.07.2021)**



**РАХМАДИЕВА СЛУКЕН
БИГАЛИЕВНА
(21.01.1952-11.07.2021)**

**27 мамыр 2022
Нұр-Сұлтан**

УДК 54

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G99 Химиктер күніне орай және кафедра профессорлары Тәшенов Әуезхан Кәріпханұлы мен Рахмадиева Слукен Бигалиқызын еске алуға арналған «Химиялық білім мен химия ғылымының өзекті мәселелері» атты халықаралық ғылыми-практикалық конференция=Международной научно-практической конференции «Актуальные проблемы химического образования и химической науки», приуроченной ко Дню Химика и посвященной памяти профессоров Ташенова Ауэзхана Карипхановича и Рахмадиевой Слукен Бигалиевны. – Нұр-Сұлтан: –б. - қазақша, орысша.

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Жинақта 2022 жылғы 27 мамырда Л.Н.Гумилев атындағы ЕҰУ-де (Нұр-Сұлтан қ.) өткен Химиктер күніне орай және кафедра профессорлары Тәшенов Әуезхан Кәріпханұлы мен Рахмадиева Слукен Бигалиқызын еске алуға арналған «Химиялық білім мен химия ғылымының өзекті мәселелері» атты халықаралық ғылыми-практикалық конференция материалдары жинақталған. Конференция материалдары химия ғылымы мен білім берудің әртүрлі мәселелеріне арналған және секцияларға бөлінген. Жинаққа ақымдағы мамандарға арналған.

Сборник содержит материалы Международной научно-практической конференции «Актуальные проблемы химического образования и химической науки», приуроченной ко Дню Химика и посвященной памяти профессоров Ташенова Ауэзхана Карипхановича и Рахмадиевой Слукен Бигалиевны, проходившей 27 мая 2022 г. в ЕНУ им. Л.Н.Гумилева (г.Нур-Султан). Материалы конференции посвящены различным проблемам химической науки и образования и распределены по секциям. Сборник предназначен для широкого круга специалистов.

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**Evaluation of adsorption properties of carbon material obtained from pine cone
in relation to nitrogen**

Abstract: The pine cone, solid waste was successfully converted into activated carbon using chemical agents H_3PO_4 . Their properties including porous structures, surface functional groups and morphology structures were carefully studied. The N_2 adsorption studies showed that the nitrogen isotherm exhibits Type IV, and the presence of hysteresis loop clearly shows the predominantly mesoporous characteristics. The values of correlation coefficient $R^2 = 0.9999$ represented the satisfactory pseudo-second-order model. The results show that pine cone activated carbon was effectively used as adsorbent.

Keywords: Carbon, plant waste, activation, adsorption.

1. Introduction

Activated carbons are widely used in a variety of applications, including separation, gas purification, removal of pollutants and odors, gas storage, catalysis, and catalyst supports, due to their large micropore volume and high internal surface area [1]. The most common way to make activated carbons now is to employ natural materials as a precursor, which include coal, petroleum, vegetables, and polymeric precursors. The pore structure and surface chemistry are affected by the nature of which, as well as the activation procedure and carbonization method, which impacts the adsorption capacities and hence application of the adsorbents. However, the demand for novel and less expensive precursors in the form of industrial and

agricultural leftovers with high valorization potential is expanding [2-4]. This research examines the chemical and physical properties of carbon-based material, as well as their adsorption capabilities and potential modifications. Bamboo, bean dreg, peanut shells, petroleum coke, and other natural woody materials have been utilized to make activated carbons for CO₂ adsorption. Pine cone shells are abundant in nature, and pine cone shells or pine cone shell-based activated carbons have been used to remove the anionic dye Congo red, Ni²⁺, Pb²⁺, Cr⁶⁺, phenol, and Cu²⁺ from aqueous solutions, or as an electrode material in some experiments. Pine cone is a commonly available biomass that is primarily made of cellulose and lignin [5]. It has a porous structure after being crushed, which is a great attribute. It can interact with various chemicals and capture them to optimize the final product's structure. In this study, a pine cone shell is used as an initial object to obtain carbon-rich material [6].

2. Materials and methods

According to [7], pine waste was impregnated by a solution of 10 mol·L⁻¹ of orthophosphoric acid at constant stirring and a temperature of 70°C. The weight ratio of initial mass to modifying agent was 1:5. The material slur was then subjected to evaporation until the wet residue was left. To this residue, metallurgical (1% by weight of the sorbent) was added, thermal treatment at the temperature of 300°C withholding the sorbent at final temperature for 120 min. After temperature treatment, the obtained carbonized material was washed with hot distilled water heated to 90°C (3 times), then dried at 105°C. Then obtained the product (active carbons) was used as sorbent in adsorption tests after argon treatment.

To characterize the carbon-based materials obtained following methods were used Infrared-Spectroscopy (FTIR), Energy-dispersive X-ray spectroscopy (EDS), Scanning Electron Microscopy (SEM), Brunauer-Emmett-Telle analysis (BET), Barrett-Joyner-Halenda analysis (BJH), Density-functional theory (DFT), Dubinin-Radushkevich (DR) method. Samples were placed on the Fourier spectrometer "TENSOR R27", manufactured by "BRUKER". Spectra were collected from 400 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹ by co-adding 32 individual scans. The elemental compounds were analyzed by EDS spectroscopy. Magnification was 2000, and the high voltage was 15.0 kV. SEM was used to analyze the surface properties and morphology of the prepared activated carbons. Samples were loaded onto a double-sided carbon tape attached to SEM tubs and then coated with a

gold/palladium using a sputter coater for 75 s at 18 mA to avoid charging effects. SEM images were acquired using a JEOL JSM-6510 mode Field Emission Scanning Electron Microscope. The acceleration voltage was set at 15 kV, and the images were magnified 4000 times. Determination of porosity, micro- and mesopores were acquired using Automatic physisorption micropore analyzer Autosorb IQ and the cell type is 9 ml with vial and rod, adsorbate gas is N₂, calibration gas is He. Under 77 K temperature, equilibrium time at each point of analysis is 2 minutes.

3. Results

Various functional groups determination on the carbon material surface were identified by FTIR (Fourier Transform Infrared Spectroscopy) analysis (Fig.1). Infrared transmission percentage signal at different wavelengths are mapped. From the nature of signal and wavelengths at which signals are obtained functional groups are identified [8].

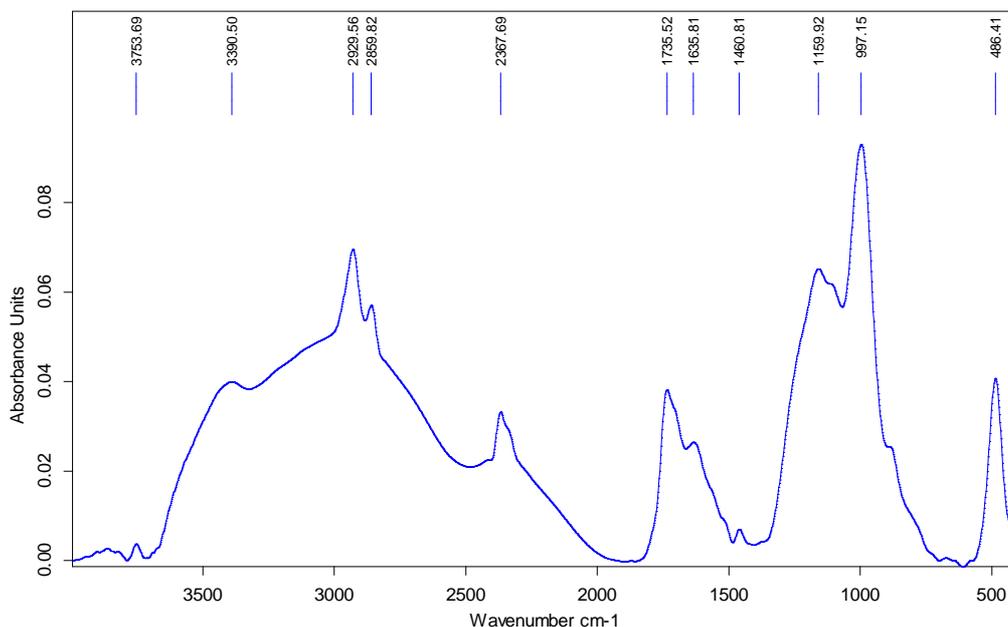


Figure 1. The FTIR spectra of pine cone shell-based activated carbon

A weak peak obtained at 3753.69—3390.50 cm⁻¹ indicates O—H stretching group. Spectra band observed at 2929.56 cm⁻¹ represents vibrations of (CH)_n especially due to C—CH and C—CH₂ bonds. A medium peak at wavelength 2859.82

cm^{-1} signify that there is C—H stretching and N—H stretching. The band at about 2367.69 cm^{-1} identifies the stretching vibrations of aliphatic groups $-\text{CH}_2-$. The peaks between 1735.52 — 1635.81 cm^{-1} correspond to C=O and vibration of C=C. The band at 1460.81 cm^{-1} corresponds to N—O. Spectra band between 1159.92 and 486.41 cm^{-1} may be assigned to organophosphorus compounds, respectively. As a result, huge functional groups exist on activated carbon for collecting pollutant ions. In the absorption of contaminating ions, these functional groups are involved.

In the EDS analysis of carbon-based on pine cone (Fig.2) obtained with argon treatment, a porous and rough surface, as well as some notches in each section of the surface, and porosity with low uniformity, were observed for the carbon. Porosity in the carbon structure can be attributed to additive activation and argon treatment. The carbon content (C) in the obtained material is 65.84% (Table 1), which is higher than the atomic carbon content for the material treatment in air. In terms of oxygen, its content was reduced due to the action of a mineral additive that improves the chemical properties of activated carbon [9].

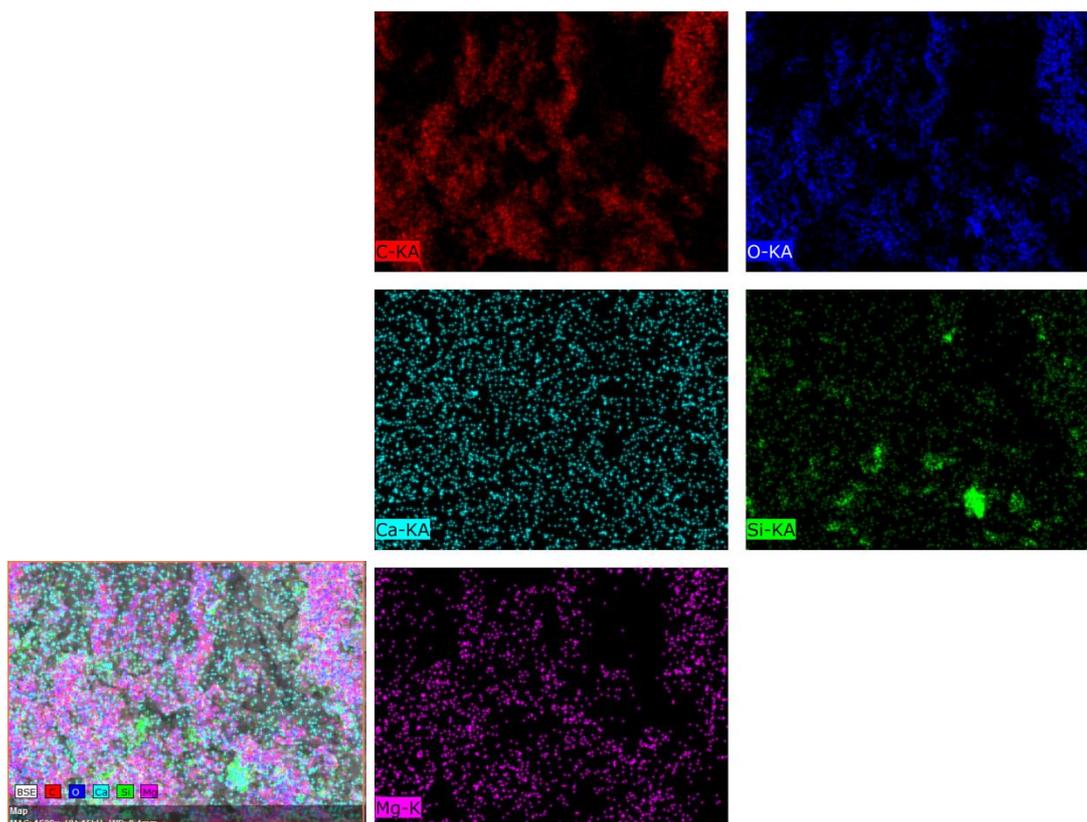


Figure 2. EDS spectra of pine cone shell-based activated carbon

Table 1 Elemental composition of pine cone-based activated carbon by EDS analysis

Element	Atom, %
C	65.84
O	32.04
Ca	0.92
Si	0.81
Mg	0.40

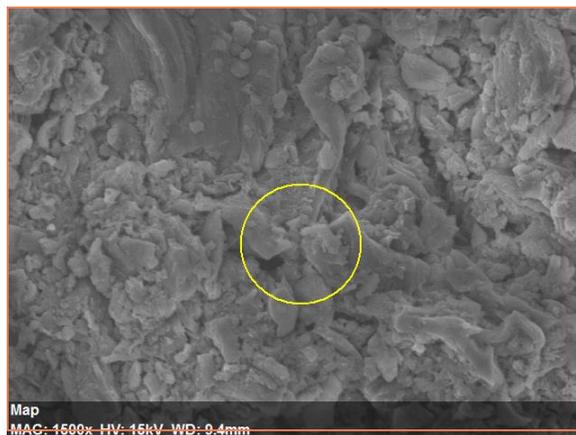


Figure 3. SEM images of pine cone-based activated carbon

The SEM images of the pine cone-based activated carbon (Fig.3) clearly show the availability of pores and internal surface [10].

According to the IUPAC classification of isotherms (or the Brunauer-Deming-Deming-Teller classification), this isotherm belongs to the second type (S-shaped). This form of isotherm indicates polymolecular adsorption (Fig.4). As a rule, this form of isotherm is characteristic of non-porous materials. There is also a hysteresis loop on the isotherm associated with a difference in the pore filling-release mechanism. This loop belongs to the H3 type (found in materials with slit-shaped pores). To understand the surface properties like specific surface area, pore volume, pore size, nature of pores BET and BJH isotherm models have been used here. The sample was tested in a Autosorb iQ BET analyser through nitrogen adsorption-desorption isotherm at 77 K temperature.

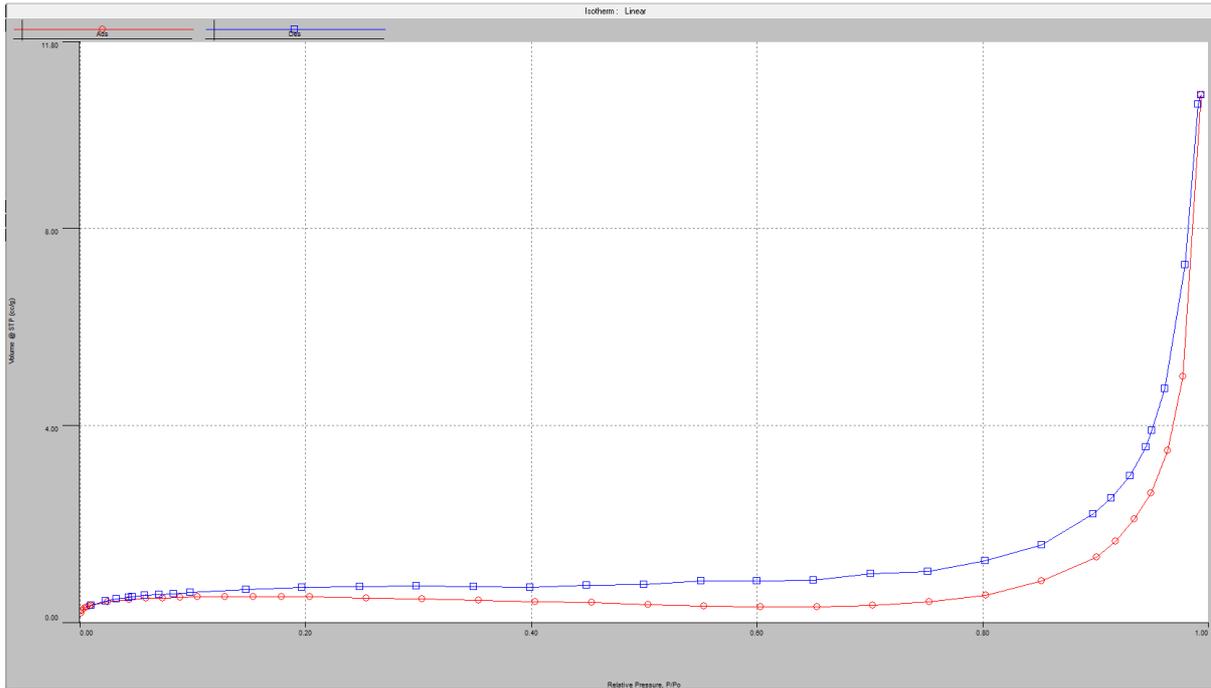


Figure 4. Adsorption-desorption isotherm of pine cone-based activated carbon

Prior to that, the sample was degassed at 170 °C to remove all impurities. The obtained surface properties of the carbon material by BET analysis are presented in Table 2. Pore volume, pore diameter, and pore nature was determined from BJH. From this analysis, the porosity of the surface can be identified either microporous, mesoporous, or macroporous. The size of micropore is <2 nm, mesopore 2–50 nm, and macropore > 50 nm [11].

As claimed by Fig.5, when carbon material is treated with inorganic acid H_3PO_4 , the acid solutions create many micropores on the surface of the biomass and penetrates in it because of its corrosive nature. As the micropores increased on the surface the overall surface area increase significantly that has been evident in this investigation from BET analysis and is in agreement with the results reported by Wedja et al., 2021 [12].

Table 2 BET summary

Slope	1656.187
Intercept = 6.638e+00	6.638e+00
Correlation coefficient	0.999957
C constant	250.488

Surface Area	2.094 m ² /g
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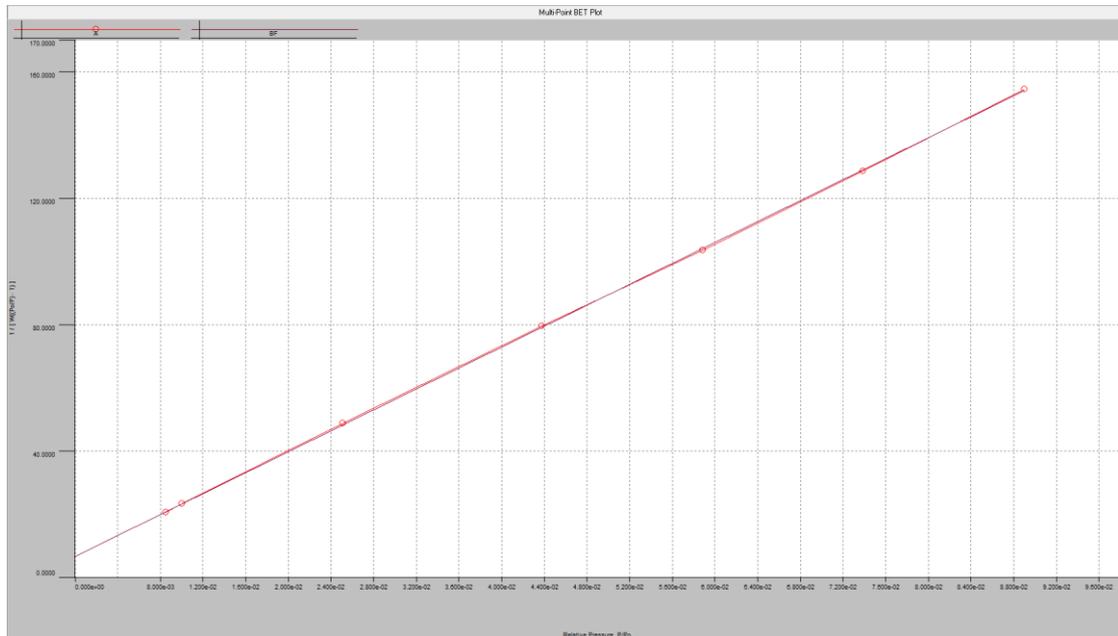


Figure 5. BET analysis of pine cone-based activated carbon

Figure 6 shows the Barrett–Joyner–Hanlenda (BJH) shape for the distribution of radius pores started from 17 to 1208 Å. Corresponding the great development of mesoporous structures based on the IUPAC classification: micropores (8 to 100 Å), mesopores (100–500 Å) and macropores (>500 Å), pore radius equals to 191.559 Å. The total pore volume was estimated to 0.017 cc/g [13]. The average pore diameter was estimated from the surface area and total pore volume. According to measurements of adsorption isotherms of the activated carbon, we obtained a great surface area equals to 1.678 m²/g.

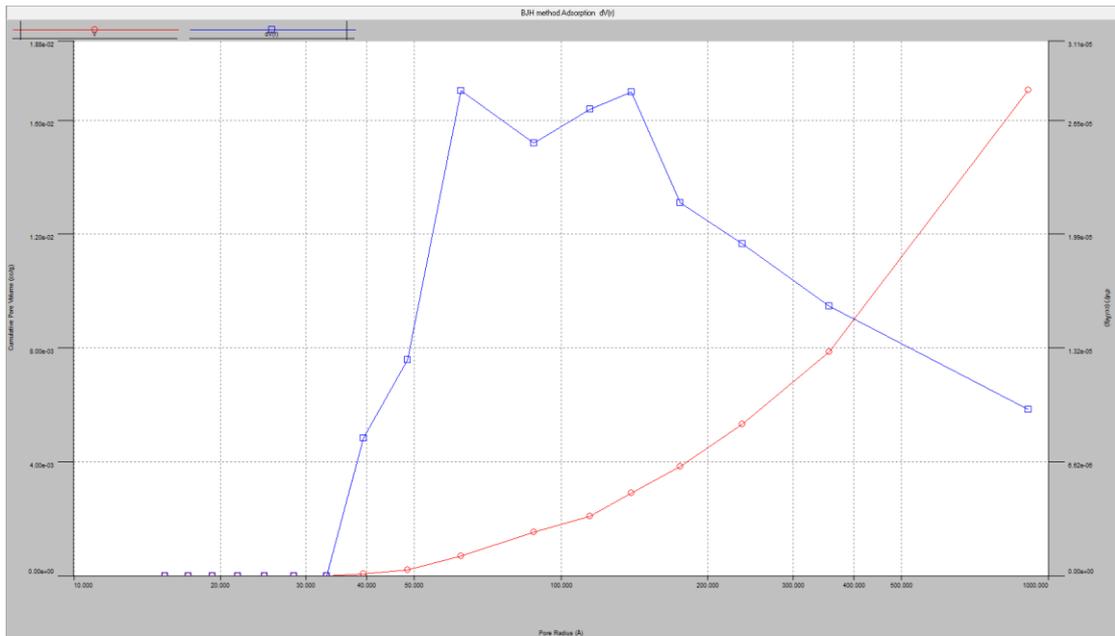


Figure 6. BJH analysis of pine cone-based activated carbon

From the data presented in the Figure 6, it can be seen that the pine cone shell-based activated carbon produced the predominantly mesoporous structures. Previous work reported that preparation of activated carbon using chemical activation with $ZnCl_2$ have produced activated carbon with microporous characteristics, while with H_3PO_4 resulted mesoporous structure. Therefore, due to the effect of H_3PO_4 , the pores have shifted from microporous to mesoporous structures [14]. The magnitude of E is useful for estimating the type of adsorption process. The magnitude of E is 12.431 kJ/mol. It is accepted that when the adsorption energy is below the 8 kJ/mol, the type of adsorption can be defined as physical adsorption (Table 3). According to the calculated mean free energy the type of adsorption of carbon material on the activated carbon was described as chemical adsorption [15].

Table 3 DR method summary

Slope	Intercept	Correlation Coefficient	Average Half pore width	Adsorption energy	Micropore volume	Micropore surface area
-5.662e-02	1.402e-04	0.9999	10.458 Å	12.431 kJ/mol	0.001 cc/g	2.559 m ² /g

Figure 7 presents the plots of Dubinin–Radushkevich isotherm model for the adsorption of activated carbon. From the correlation coefficient value is 0.9999, the adsorption process of the activated carbon was found to follow the Dubinin–Radushkevich isotherm model with the monolayer adsorption capability of 2.559 m²/g. This result indicates that H₃PO₄ molecules form monolayer coverage on the prepared activated carbon, which is homogenous in nature. This also means that every adsorption sites of the activated carbon have the same adsorption energy.

The DFT isotherms for nitrogen adsorption at 77 K in pores are presented in Fig.8. The lines divide the pore size distribution into many regions, which form the basis for choosing discrete pore sizes for study by simulation respectively. The pore size distribution was determined from the adsorption isotherm using the density functional theory method which has been shown to be more reliable for small pores than semiempirical methods [16]. In the micropores, the pores fill in a single step, whereas, in the mesopores, condensation is preceded by the formation of a monolayer, and, in the larger slit pores, condensation is preceded by wetting of one or more additional adsorbed layers.

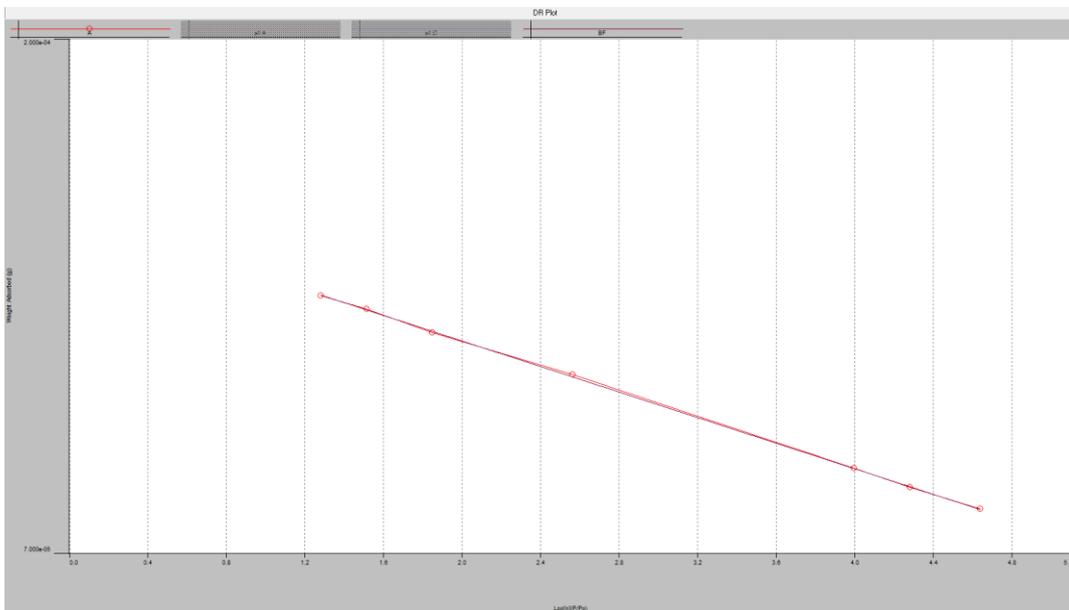


Figure 7. Micropore analysis by DR method (Dubinin-Radushkevich model) of pine cone-based activated carbon

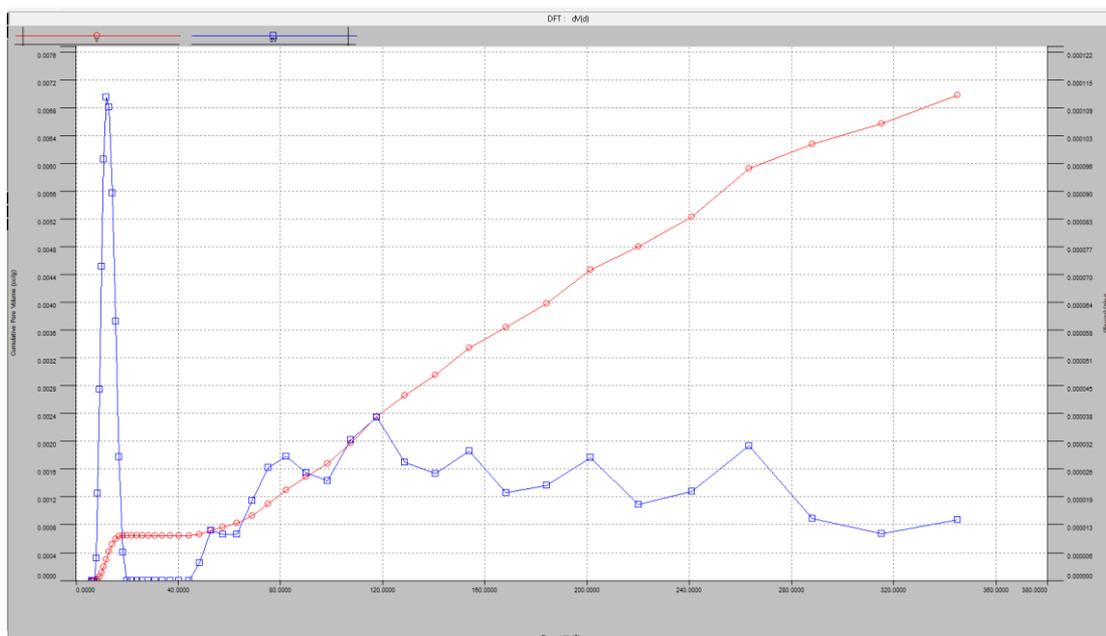


Figure 8. The DFT isotherms of pine cone-based activated carbon

The reference carbon also exhibited a small hysteresis loop of type H3, indicating that the material had slit-shaped pores, as is often found in many carbon materials. In addition, The presence of the small hysteresis loop was a result of the capillary condensation of nitrogen molecules in some mesopores in the reference carbon. In the nitrogen adsorption model, the isotherms of the micropores smaller than 10 Å are continuous. In the pores larger than 14 Å, the nitrogen model predicts continuous pore filling during growth of the adsorbed film, followed by a single phase transition at the capillary condensation pressure.

4. Conclusion

The structure and composition of the products obtained in the synthesis process of pine wastes have been investigated. It was shown that the porous carbon samples prepared from H₃PO₄-treated pine cone showed microporous characteristics. We also can conclude he highest BET surface area did not result in the highest N₂ adsorption capacity. We infer that the most likely reason for the result is that the different property of pore size distribution of pine cone shell-based activated carbons. Ehe contribution of the additives to the absorption properties of the carbon is expected to continue the study. More detailed studies of the improved description of the adsorption mechanism are currently being carried out.

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**"Натрий олеаты-мыс-молибден кені" жүйесіндегі адсорбция
кинетикасы және тепе-теңдігі**

Аннотация: Мыс-молибден кенінің бетіндегі натрий олеаты