IRSTI 31.23

Sh.K. Amerkhanova[1], A.S. Uali[2], R.M. Shlyapov*, K. Yerkin[3]

L.N. Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan
(E-mail: [1]amerkhanovashk@gmail.com, [2]ualiaitolkyn@gmail.com, [3]karakat.erkin@mail.ru)
**Corresponding author: rustamshlyapow@gmail.com*

Evaluation of adsorption properties of carbon material obtained from a pinecone in relation to nitrogen

Abstract. *The pinecone, solid waste was successfully converted into activated carbon using chemical agents H3PO4. There were carefully studied properties including porous structures, surface functional groups, and morphology structures. The N2 adsorption studies showed that the nitrogen isotherm exhibits Type IV, and the presence of a hysteresis loop clearly shows the predominantly mesoporous characteristics. The values of correlation coefficient R2 = 0.9999 represented the satisfactory pseudo-second-order model. The results show that pinecone-activated carbon was effectively used as an adsorbent.*

Keywords: *carbon, plant waste, activation, adsorption.*

DOI: https://doi.org/10.32523/2616-6771-2022-139-2-7-17

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 the 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 materials, 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 CO_2 adsorption. Pinecone shells are abundant in nature, and pinecone shells or pine cone shell-based activated carbons have been used to remove the anionic dye Congo red, Ni^{2+}, Pb^{2+}, Cr^{6+}, phenol, and Cu^{2+} from aqueous solutions, or as electrode material in some experiments. Pinecone is 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 pinecone shell is used as an initial object to obtain carbon-rich material [6].

Materials and methods

According to [7], pine waste was impregnated with 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 a 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 physiosorption micropore analyzer Autosorb IQ and the cell type is 9 ml with vial and rod, adsorbate gas is N_2, calibration gas is He. Under 77 K temperature, equilibrium time at each point of analysis is 2 minutes.

Results

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

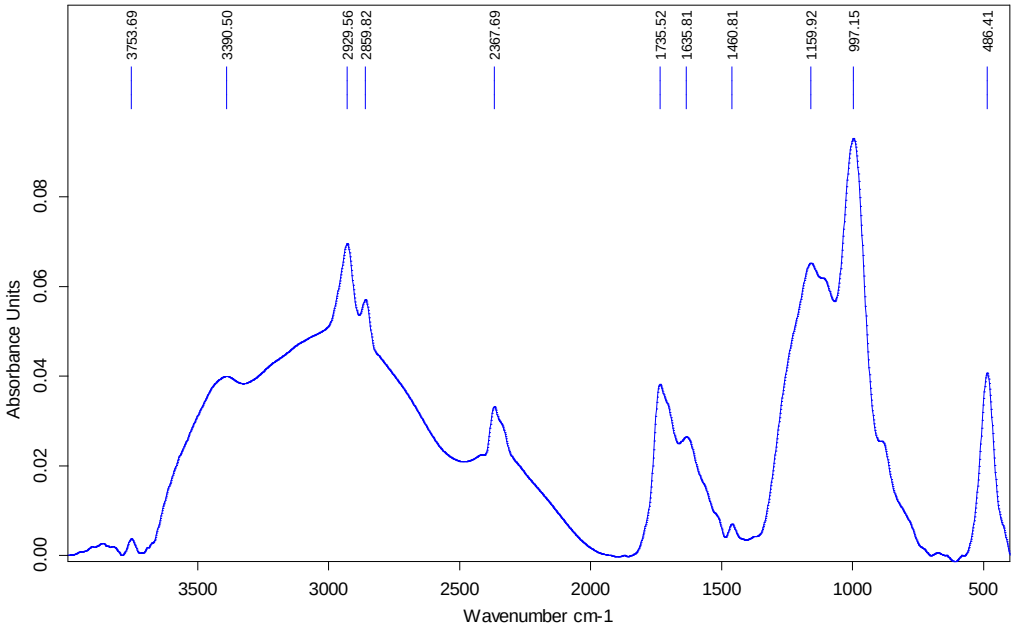

Figure 1. The FTIR spectra of pine cone shell-based activated carbon

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—CH_2 bonds. A medium peak at wavelength 2859.82 cm^{-1} signifies 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 –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 bands 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 a pine cone (Figure 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 the 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].

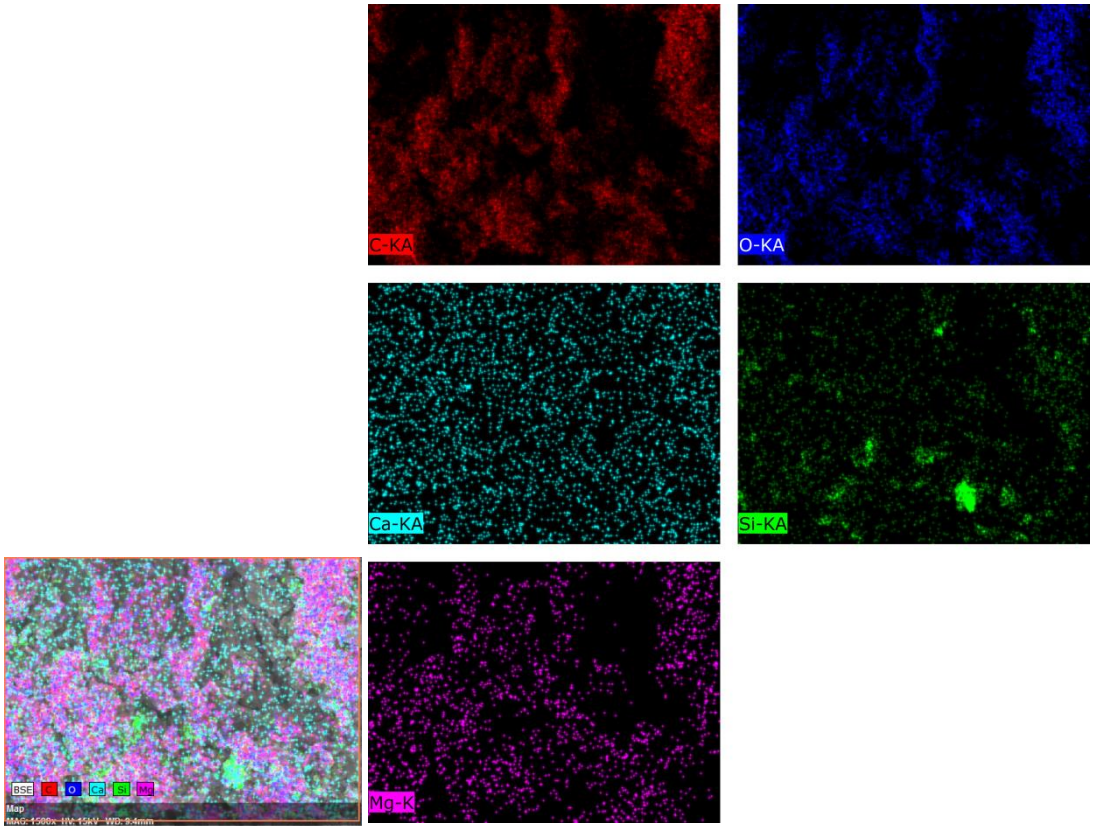

Figure 2. EDS spectra of pine cone shell-based activated carbon

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

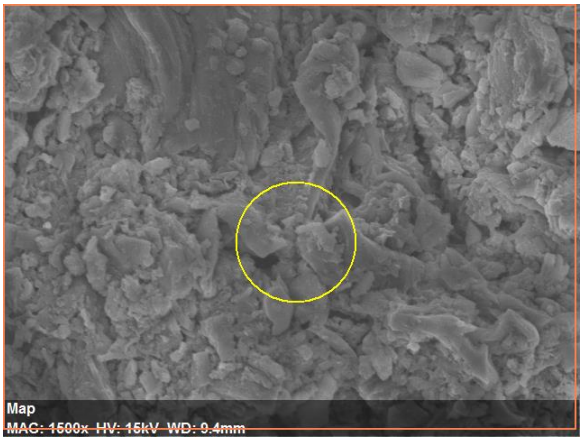

Figure 3. SEM images of pine cone-based activated carbon

The SEM images of the pine cone-based activated carbon (Fig.3) clearly show the availability of pores and internal surfaces [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 analyzer through nitrogen adsorption-desorption isotherm at 77 K temperature.

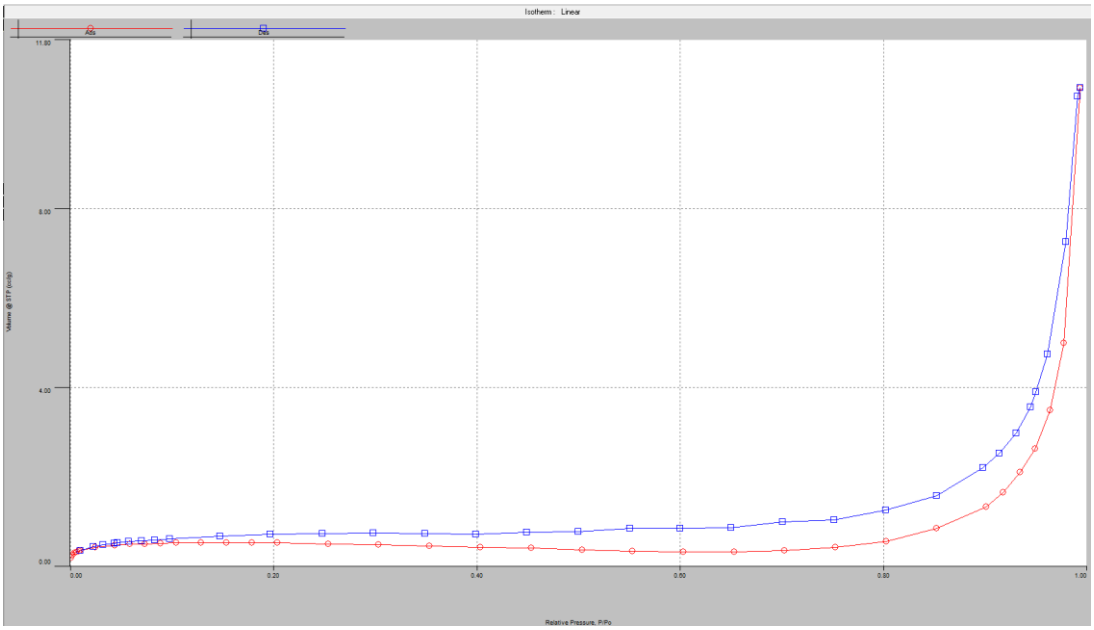

Figure 4. Adsorption-desorption isotherm of pine cone-based activated carbon

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 were determined from BJH. From this analysis, the porosity of the surface can be identified either microporous, mesoporous, or macroporous. The size of micropores is <2 nm, mesopores 2–50 nm, and macropores> 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 penetrate in it because of its corrosive nature. As the micropores increased on the surface the overall surface area increase significantly which has been evident in this investigation from BET analysis and agrees 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

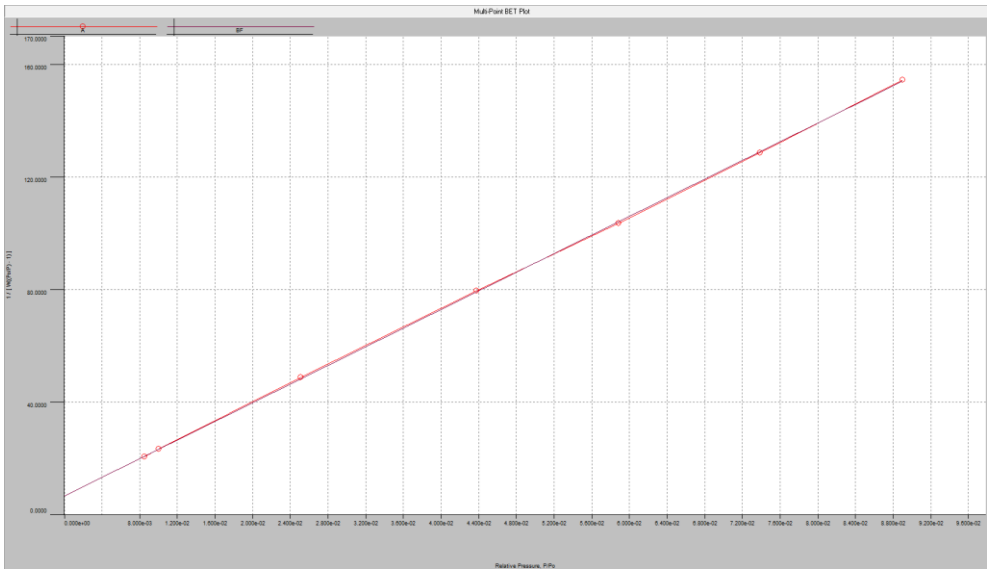

Figure 5. BET analysis of pine cone-based activated carbon

Figure 6 shows the Barrett–Joyner–Hanlenda (BJH) shape for the distribution of radius pores starting from 17 to 1208 Å. Corresponding the great development of mesoporous structures based on the IUPAC classification: micropores (8 to100 Å), mesopores (100–500 Å), and macropores (>500 Å), pore radius equals to 191.559 Å. The total pore volume was estimated to be 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 equal to 1.678 m^2/g.

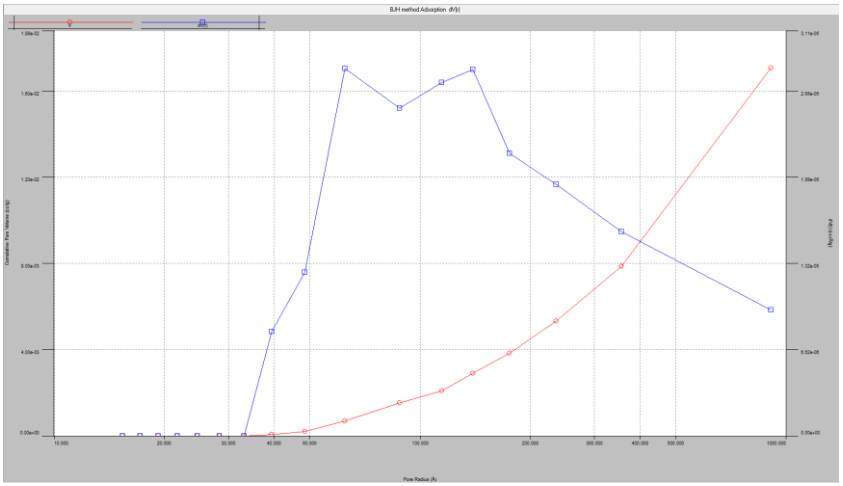

Figure 6. BJH analysis of pine cone-based activated carbon

From the data presented in Figure 6, it can be seen that the pine cone shell-based activated carbon produced predominantly mesoporous structures. Previous work reported that the preparation of activated carbon using chemical activation with $ZnCl_2$ has produced activated carbon with microporous characteristics, while with H_3PO_4 resulted in a 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 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 m^2/g. This result indicates that H_3PO_4 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 fillin 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.

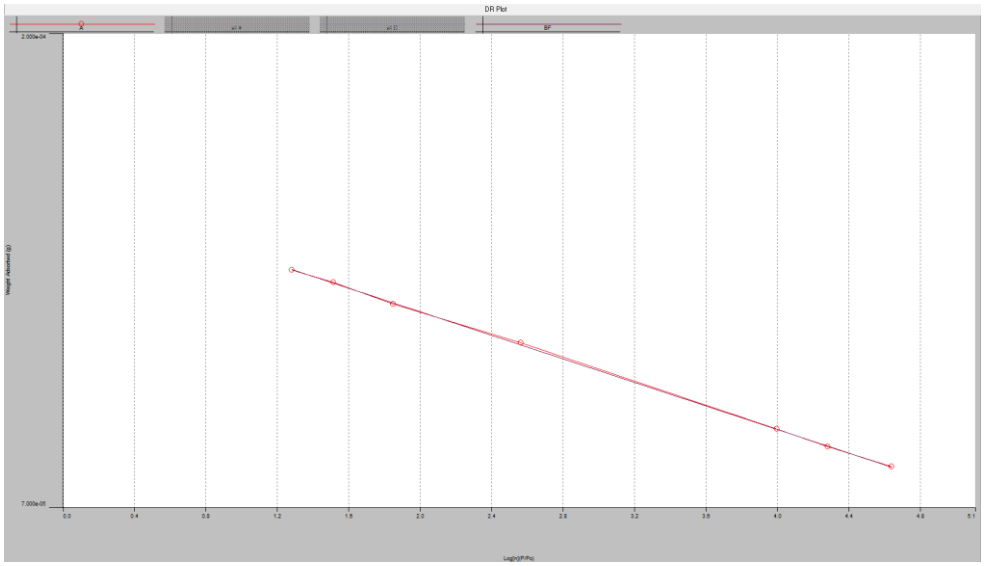

Figure 7. Micropore analysis by DR method (Dubinin-Radushkevich model) of pine cone-based activated carbon

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 the growth of the adsorbed film, followed by a single-phase transition at the capillary condensation pressure.

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 H_3PO_4-treated pinecones showed microporous characteristics. We also can conclude the highest BET surface area did not result in the highest N_2 adsorption capacity. We infer that the most likely reason for the result is that the different properties of the pore size distribution of pinecone shell-based activated carbons. The contribution of the additives to the absorption properties of the carbon is expected to continue the study. Currently, it is carried out more detailed studies of the improved description of the adsorption mechanism.

References

1. Yobouet Y.A., Yao K.B., Goné D.L., Trokourey A. Investigation of dye adsorption onto activated carbon from the shells of Macoré fruit // Journal of Environmental Management. – 2015. – Vol. 156. – P. 11.

2. Bernardo M., Lapa N., Matos I., Fonseca I. Critical discussion on activated carbons from bio-wastes-environmental risk assessment // Bol. Grupo. Esp. Carbon. – 2016. – Vol. 40. – P. 18-21.

3. Piai L., Dykstra J.E., Adishakti M.G., Blokland M., Langenhoff A.A.M., Wal A.V.D. Diffusion of hydrophilic organic micropollutants in granular activated carbon with different pore sizes // Water Res. – 2019. – Vol. 162. – P. 518-527.

4. Bromic P.C., Supong A., Baruah M., Pongener C., Sinha D. Pine Cone biomass as an efficient precursor for the synthesis of activated biocarbon for adsorption of anionic dye from aqueous solution // Isotherm, kinetic, thermodynamic and regeneration studies. – 2018. – Vol. 10. – P. 41-49.

5. Swenson, H., Stadie, N.P. Langmuir S. Theory of adsorption: A centennial review. Langmuir. – 2019. – Vol. 38. – P. 9-11.

6. John L., Gennady Y.G. Alexander V.N. Density functional theory methods for characterization of porous materials // Colloids and Surfaces A: Physicochemical and Engineering Aspects. – 2013. – Vol. 437. – P. 3-32.

7. Amerkhanova Sh.K., Shlyapov R.M., Uali A.S. The active carbons modified by industrial wastes in the process of sorption concentration of toxic organic compounds and heavy metals ions // Colloids and Surfaces A: Physicochemical and Engineering Aspects. – 2017. – Vol. 532. – P. 36-40.

8. Ning J., Li S.M., Ma M.J., Zhu J.F., Sun R.C. Synthesis and characterization of cellulose-silica composite fiber in ethanol/water mixed solvents // Bioresources. – 2011. – Vol. 6. – P. 5.

9. Tuba U., Filiz U.N. Preparation and Characterization an Active Carbon Adsorbent from Waste Mandarin Peel and Determination of Adsorption Behavior on Removal of Synthetic Dye Solutions // Springer Nature Switzerland. – 2020. – Vol. 231. – P. 11.

10. Mustafa T.Y., Tushar K.S., Sharmeen A. Fixed-bed dynamic column adsorption study of methylene blue (MB) onto pine cone // Desalination and Water Treatment. – 2015. – Vol. 55. – P. 9.

11. Kaimin L., Tian S.C., Jiang J.G., Wang J.M., Chen X.J., Yan F. Pine Cone Shells-Based Activated Carbon Used for CO_2 Adsorption // Journal of Materials Chemistry. – 2016. – Vol.14. – P. 4-6.

12. Wedja T. et.al. Activated carbon from macauba endocarp (Acrocomia aculeate) for removal of atrazine: Experimental and theoretical investigation using descriptors based on DFT // Journal of Environmental Chemical Engineering. – 2021. – Vol. 9. – P. 6.

13. Allwar and Syamsurzal. Removal of 2-chlorophenol Using Rice Husk Activated Carbon Prepared by $ZnCl_2/H_3PO_4$ Activation // ORIENTAL JOURNAL OF CHEMISTRY. – 2017. – Vol. 33. – P. 2-4.

14. Boukmouchea N., Azzouza N., Bouchamaa L., Chopartb J.P., Bouznit Y. Activated carbon derived from marine Posidonia Oceanica for electric energy storage // Arabian Journal of Chemistry. – 2014. – Vol. 7. – P. 347-354.

15. Dilek A., Kose T.E., Ugur S. Production and characterization of activated carbon prepared from safflower seed cake biochar and its ability to absorb reactive dyestuff // Applied Surface Science. – 2013. – Vol. 280. – P. 705-710.

16. Uthen T., Sakda L., Nicharat M., Sujitra W., Thanyalak C. Tuning pore characteristics of porous carbon monoliths prepared from rubber wood waste treated with H_3PO_4 or NaOH and their potential as supercapacitor electrode materials // Journal of Materials Science. – 2017. – Vol. 52. – P. 11.

Ш.К. Амерханова, Р.М. Шляпов, А.С. Уали, К. Еркін

Л.Н. Гумилев атындағы Еуразия ұлттық университеті, Нұр-Сұлтан, Қазақстан

Қарағай бүршіктерінен алынған көміртекті материалдың азоты бойынша адсорбциялық қасиеттерін бағалау

Аннотация. Қарағай бүршіктері, қатты қалдықтар H_3PO_4 химиялық реагенттері арқылы белсендірілген көмірге табысты түрде түрлендірілді. Кеуекті құрылымды, беткейлік функционалды топтарды және морфологиялық құрылымды қоса алғанда материалдың қасиеттері мұқият зерттелді. N2 адсорбциялық зерттеулер азот изотермасы IV типке жататынын көрсетті, ал гистерезис ілмегінің болуы мезопоралардың басым екенін анық көрсетеді. R2 = 0.9999 корреляция коэффициентінің мәндері екінші ретті жалған модельдің қанағаттанарлық сәйкестігін көрсетеді. Нәтижелер қарағай бүршіктерінен белсендірілген көмір адсорбент ретінде тиімді пайдаланылғанын көрсетеді.

Кілт сөздер: көміртек, өсімдік қалдықтары, активация, адсорбция.

Ш.К. Амерханова, Р.М. Шляпов, А.С. Уали, К. Еркин
Евразийский национальный университет им. Л. Н. Гумилева, Нур-Султан, Казахстан

Оценка адсорбционных свойств по азоту углеродного материала, полученного из сосновых шишек

Аннотация. Сосновые шишки, твердые отходы были успешно преобразованы в активированный уголь посредством химических реагентов H_3PO_4. Были тщательно изучены свойства материала, включая пористую структуру, поверхностные функциональные группы и морфологическую структуру. Исследования адсорбции N2 показали, что изотерма азота относится к типу IV, а наличие петли гистерезиса четко указывает на преобладание мезопор. Значения коэффициента корреляции R2=0,9999 указывают на удовлетворительное соответствие модели псевдовторого порядка. Результаты показывают, что активированный уголь из сосновых шишек эффективно использовался в качестве адсорбента.

Ключевые слова: углерод, растительные отходы, активация, адсорбция.

References

1. Yobouet Y.A., Yao K.B., Goné D.L., Trokourey A. Investigation of dye adsorption onto activated carbon from the shells of Macoré fruit, Journal of Environmental Management, 156, 11 (2015).
2. Bernardo M., Lapa N., Matos I., Fonseca I. Critical discussion on activated carbons from bio-wastes-environmental risk assessment, Bol. Grupo. Esp. Carbon., 40, 18-21 (2016).
3. Piai L., Dykstra J.E., Adishakti M.G., Blokland M., Langenhoff A.A.M., Wal A.V.D. Diffusion of hydrophilic organic micropollutants in granular activated carbon with different pore sizes, Water Res. 162, 518-527 (2019).
4. Bromic P.C., Supong A., Baruah M., Pongener C., Sinha D. Pine Cone biomass as an efficient precursor for the synthesis of activated biocarbon for adsorption of anionic dye from aqueous solution, Isotherm, kinetic, thermodynamic and regeneration studies, 10, 41-49 (2018).
5. Swenson, H., Stadie, N.P. Langmuir S. Theory of adsorption: A centennial review. Langmuir, 38, 9-11 (2019).
6. John L., Gennady Y.G. Alexander V.N. Density functional theory methods for characterization of porous materials, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 437, 3-32 (2013).
7. Amerkhanova Sh.K., Shlyapov R.M., Uali A.S. The active carbons modified by industrial wastes in the process of sorption concentration of toxic organic compounds and heavy metals ions, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 532, 36-40 (2017).
8. Ning J., Li S.M., Ma M.J., Zhu J.F., Sun R.C. Synthesis and characterization of cellulose-silica composite fiber in ethanol/water mixed solvents, Bioresources, 6, 5 (2011).
9. Tuba U., Filiz U.N. Preparation and Characterization an Active Carbon Adsorbent from Waste Mandarin Peel and Determination of Adsorption Behavior on Removal of Synthetic Dye Solutions, Springer Nature Switzerland, 231, 11 (2020).
10. Mustafa T.Y., Tushar K.S., Sharmeen A. Fixed-bed dynamic column adsorption study of methylene blue (MB) onto pine cone, Desalination and Water Treatment, 55, 9 (2015).
11. Kaimin L., Tian S.C., Jiang J.G., Wang J.M., Chen X.J., Yan F. Pine Cone Shells-Based Activated Carbon Used for CO_2 Adsorption, Journal of Materials Chemistry, 14, 4-6 (2016).
12. Wedja T. et.al. Activated carbon from macauba endocarp (Acrocomia aculeate) for removal of atrazine: Experimental and theoretical investigation using descriptors based on DFT, Journal of Environmental Chemical Engineering. 9, 6 (2021).

13. Allwar and Syamsurzal. Removal of 2-chlorophenol Using Rice Husk Activated Carbon Prepared by $ZnCl_2/H_3PO_4$ Activation, ORIENTAL JOURNAL OF CHEMISTRY, 33, 2-4 (2017).

14. Boukmouchea N., Azzouza N., Bouchamaa L., Chopartb J.P., Bouznit Y. Activated carbon derived from marine Posidonia Oceanica for electric energy storage, Arabian Journal of Chemistry, 7, 347-354 (2014).

15. Dilek A., Kose T.E., Ugur S. Production and characterization of activated carbon prepared from safflower seed cake biochar and its ability to absorb reactive dyestuff, Applied Surface Science, 280, 705-710 (2013).

16. Uthen T., Sakda L., Nicharat M., Sujitra W., Thanyalak C. Tuning pore characteristics of porous carbon monoliths prepared from rubber wood waste treated with H_3PO_4 or NaOH and their potential as supercapacitor electrode materials, Journal of Materials Science, 52, 11 (2017).

Information about authors:

Амерханова Ш.К. – Химия ғылымдарының докторы, профессор, *Л*.Н. Гумилев атындағы Еуразия ұлттық университетінің химия кафедрасының профессоры., Қажымұқан 13, Нұр-Сұлтан, Қазақстан.

Шляпов Р.М. – Химия ғылымдарының кандидаты, доцент, *Л*.Н. Гумилев атындағы Еуразия ұлттық университетінің химия кафедрасының доцент, Қажымұқан 13, Нұр-Сұлтан, Қазақстан.

Уали А.С. – Химия ғылымдарының кандидаты, доцент, *Л*.Н. Гумилев атындағы Еуразия ұлттық университетінің химия кафедрасының доцент, Қажымұқан 13, Нұр-Сұлтан, Қазақстан.

Еркін К. – *Л*.Н. Гумилев атындағы Еуразия ұлттық университетінің химия кафедрасының магистранты, Қажымұқан 13, Нұр-Сұлтан, Қазақстан.

Amerkhanova Sh.K. – Prof., Doctor of Chem. Sciences, , Professor of the Department of chemistry, L.N. Gumilyov Eurasian National University, 13 Kazhimukan str., Sultan, Kazakhstan.

Shlyapov R.M. – candidate of chemistry sciences, Associate Professor, Associate Professor of the Department of chemistry, L.N. Gumilyov Eurasian National University, 13 Kazhimukan str., Sultan, Kazakhstan.

Uali A.S. – candidate of chemistry sciences, Associate Professor, Associate Professor of the Department of chemistry, L.N. Gumilyov Eurasian National University, 13 Kazhimukan str., Sultan, Kazakhstan.

Yerkin K. – Master student of the Department of chemistry, L.N. Gumilyov Eurasian National University, 13 Kazhimukan str., Sultan, Kazakhstan.