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Computer analysis of the effect of the type of activating agent on the formation of the porous structure of activated carbon monoliths

Mirosław Kwiatkowski [a],*, Diana Paola Vargas Delgadillo [b]

[a] AGH University of Science and Technology, Faculty of Energy and Fuels, al. A. Mickiewicza 30, 30-059 Krakow, Poland
[b] Departamento de Química, Facultad de Ciencias, Universidad del Tolima, Barrio Santa Helena Parte Alta, Código Postal Nro. 730006299, Ibagué, Tolima, Colombia

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ABSTRACT

The paper presents the results of an investigation into the effect of the type of activating agent on the formation of the microporous structure of activated carbon monoliths obtained by chemical activation involving calcium chloride, phosphoric(V) acid, and zinc chloride. The research into the microporous structure of the activated carbon monoliths subject to the analysis was based on the innovative method of porous structure analysis along with the unique fast procedure of multivariant identification of adsorptive systems. The analyses carried out with the use of the mentioned method were based on nitrogen, carbon dioxide, and methane adsorption isotherms. The research evidenced that a microporous structure analysis based on various adsorption isotherms and involving the method in question yields comprehensive and reliable information on the adsorptive properties of analysed materials, which is useful for technologists and designers alike.

1. Introduction

Recent decades have seen an increasing number of initiatives aimed at diversifying motor fuels in order to gain independence from the products of crude oil processing. Since the early 1980s, interest in natural gas as motor fuel for cars has been on the rise. Still, given the low energy density of that fuel under normal conditions, the ratio of the car's range to its fuel tank volume would be very low compared with petrol. Therefore, the usefulness of natural gas as motor fuel depends on the sufficient capacity of the corresponding tank. One of a variety of methods of natural gas storage that has a good chance of wide-ranging implementation consists in storing the mentioned fuel under the pressure of between 3.5 and 5 MPa in the beds of carbonaceous adsorbents [1–7].

At present, activated carbons, including in particular the monoliths thereof, occupy the most important position among other carbonaceous adsorbents as belonging to the category of materials that are the most appropriate for the processes of natural gas storage owing to their specific properties, the possibility of formulating their porous structure by choosing

the suitable precursor, selecting suitable production methods, controlling the conditions of the production process, and significant potential for modification of pore size and chemical properties of the surface [1–9].

The technology of active carbon production is based on two processes, i.e. carbonisation and its following process of activation during which a carbonaceous adsorbent with a developed microporous structure is obtained [10–15]. The carbonisation consists of heating input raw materials at the temperature below 800 °C with no air access or in a continuous stream of an inert gas atmosphere [10–15]. The porous structure of charcoal has large pores, due to which these materials cannot be used directly in adsorption technology. Therefore it must undergo the activation process to enlarge the diameters of the pores which were created during the carbonisation process and to create some new porosity, therefore resulting in the formation of a well-developed and readily accessible micropore structure with a very large specific internal surface area. The activation process is realized by two methods: oxidizing by gas or vapour leading to partial charcoal gasification called physical activation [10–15] or processing with chemical reagents called chemical activation [16–25].

Both processes mentioned above have a significant influence on the parameters of the obtained porous structure. As a result, one of the key questions related to the production of active carbons is the optimizing the production process conditions and selecting the optimal method and suitable reagents.

2. The characterisation of the microporous structure

The unique properties of carbonaceous adsorbents result from their well-developed microporous structure, and the most important aspect of the porous structure is that there are large numbers of the smallest pores having linear size comparable to the size of the adsorbed molecules, also known as micropores, which determine, among other things, the effectiveness of adsorption processes.

In microporous carbonaceous adsorbents, such as activated carbons and activated carbon monoliths, adsorption takes place mostly in the micropores, where the adsorption potential is substantially higher than in wider pores. The growth in potential is triggered by an overlap between the fields of adsorptive forces generated by micropore walls; consequently, the value of adsorption in the micropores is much higher than the total value of adsorption on the surface of larger pores, i.e. meso- and macropores.

The value of adsorption in the macropores is very low – it is assumed to be close to zero – and these pores perform the function of transport channels for the adsorbate molecules travelling in the direction of micro- and mesopores [1–4]. It has to be pointed out that the mechanism of physical adsorption in the micropores, whose size is comparable to the size of the adsorbed molecules, differs from the corresponding mechanism in larger micropores, since the proximity of pore walls implies an increase in the interaction of the mutual adsorbent-adsorbate forces. As a consequence, adsorption energy surges and the pores are filled with molecules adsorbed physically at low relative pressures. Micropores are also the source of struc-tural and energetic heterogeneity of carbonaceous materials, such as activated carbons, hence the inseparable link between the discussion of adsorption on the heterogeneous surface of the mentioned materials and the description of their microporosity. Despite the complex and diverse character of heterogeneous surfaces, there are some striking similarities in their adsorptive properties. They are determined by the parameters of the heterogeneous structure, and attempts have been made to correlate these with the experimental isotherms of vapour and gas adsorption.

The proper selection of the conditions for the process of producing microporous carbonaceous adsorbents and optimizing their structure to the specific application conditions requires precise description of the microporous structure.

In the 20th century, various theories and mathematical tools were developed for the analysis the porous structure of adsorbents and the adsorption processes which occur on their surface. Many equations describing the relation between the amount of adsorbed gas or vapour and the relative pressure of the adsorbed substances in the volatile phase were derived as well. Originally, these formulas had the form of empirical equations, although with the development of science and the growing knowledge of the adsorption process parameters, the thermodynamic models with parameters having a clearly definite physical interpretation were developed.

The author and his research team also undertook to develop a new theory, based on the basic assumptions behind the BET theory and aimed at the description of the process of multilayer adsorption on the surface of microporous carbonaceous adsorbents [26]. The work on the new theory, which was called uniBET, drew on the fundamental presupposition that it is not possible to unambiguously and reliably determine either the distribution of energy on the surface of the adsorbate or the structure of the porous material, yet the mathematical description of the adsorption process should account for the anticipated geometrical properties of the material and the energy properties of its surface [26–29]. The above mentioned theory was the basis for developing the LBET models used in this research along with a unique procedure of fast multivariant identification of adsorption systems called jointly as the LBET method. To enable the application of the LBET equations to near and supercritical temperatures, an original fluid state model was elaborated, fitted with high accuracy compression factor data [27].

3. Materials and methods

A paper by Vargas et al. [30] presents the results of a study which yielded activated carbon monolithsfrom African palm shell by chemical activation with calcium chloride $CaCl_2$, phosphoric(V) acid H_3PO_4, and zinc chloride $ZnCl_2$. The monoliths formed into cylinders of about 1.5 cm in diameter and 8 cm in height, each with seven parallel channels of 3 mm in diameter along the cylindrical axis [30]. The adsorptive properties of those activated carbon monoliths were analysed on the basis of nitrogen adsorption isotherms determined at the temperature of 77 K and used to identify the following: the specific surface area S_{BET} based on the Brunauer–Emmett–Teller equation [31], the volume of micropores V_{micro}, using the

Table 1 – A compilation of the results of microporous structure analyses carried out on the basis of adsorption isotherms using the LBET method: LBET No., the number of the best-fitted LBET class model; V_{hA}, volume of the first adsorbed layer determined from the LBET equation; Q_A/RT, energy parameter for the first layer; B_C, energy parameter for the higher layers; Z_A, effective contact correction factor; h, surface heterogeneity parameter; α, the geometrical parameter of the porous structure determining the height of the adsorbate molecule clusters; β, the parameter of the porous structure determining the width of the adsorbate molecule clusters; σ_e, the value of the fitting error dispersion; w_{id}, the identifiability index [26].

Adsorbate	LBET No.	V_{hA} [cm^3/g]	Q_A/RT	B_C	Z_A	h	α	β	σ_e	w_{id}
M/CaCl$_2$										
N$_2$	19	0.654	−9.38	6.95	0.446	3	0.45	1.05	0.01	0.08
CO$_2$	27	0.679	−6.37	2.75	0.601	7	0.69	3.20	0.15	0.15
CH$_4$	15	0.722	−9.18	0.92	0.930	9	0.85	3.02	0.017	0.31
M/H$_3$PO$_4$										
N$_2$	22	0.616	−9.57	6.95	0.451	0	0.81	1.00	0.46	0.21
CO$_2$	29	0.457	−5.93	2.81	0.576	9	0.49	3.40	0.054	0.34
CH$_4$	30	0.694	−7.59	1.30	0.785	9	0.90	3.61	0.013	0.16
M/ZnCl$_2$										
N$_2$	16	0.330	−6.88	1.00	0.380	0	0.15	1.00	0.89	0.01
CO$_2$	29	0.723	−5.93	1.00	0.569	9	0.97	1.43	0.069	0.05
CH$_4$	15	0.422	−7.69	0.67	0.774	9	0.39	3.30	0.012	0.14

Dubinin–Radushkevich equation [32], the total pore volume V_t from the amount adsorbed at a pressure P/P$_0$ of 0.99, and the mesopore volume V_{meso} based on the difference between the total pore volume and the micropore volume. As part of the study in question, carbon dioxide and methane adsorption measurements were also carried out at 298 K until the pressure of 4.500 kPa was reached. The research evidenced a significant potential for using activated carbon monoliths in the processes of gas fuel storage and testified to a correlation between the results of analyses of the adsorptive properties of the monoliths by means of different methods.

However, the BET [31] and DR [32] methods applied in the studies as well as simple analyses based on adsorption isotherms may prove insufficient to reliably and accurately assess the adsorptive properties of microporous carbonaceous adsorbents and, consequently, choose the optimal methods and conditions of the process of producing activated car-

bons that are intended for a specific use. Considering the above, a new series of studies was commenced to analyse the adsorptive properties of carbonaceous adsorbent monoliths M produced by way of activation with, successively, CaCl$_2$, H$_3$PO$_4$ and ZnCl$_2$, with a particular focus on the assessment of the effect of activator type on the formation of the microporous structure of activated carbon monoliths.

The analyses with the LBET method [26–29] conducted under this study were based on three adsorption isotherms, i.e. those of the adsorption of nitrogen, carbon dioxide, and methane, determined for the particular activated carbon monoliths, which is a unique approach to porous structure analysis.

This approach offers a substantial advantage over using only nitrogen adsorption isotherms in the analysis, because analysing isotherms of specific adsorbates, namely, in this case, methane, for the adsorption of which the analysed
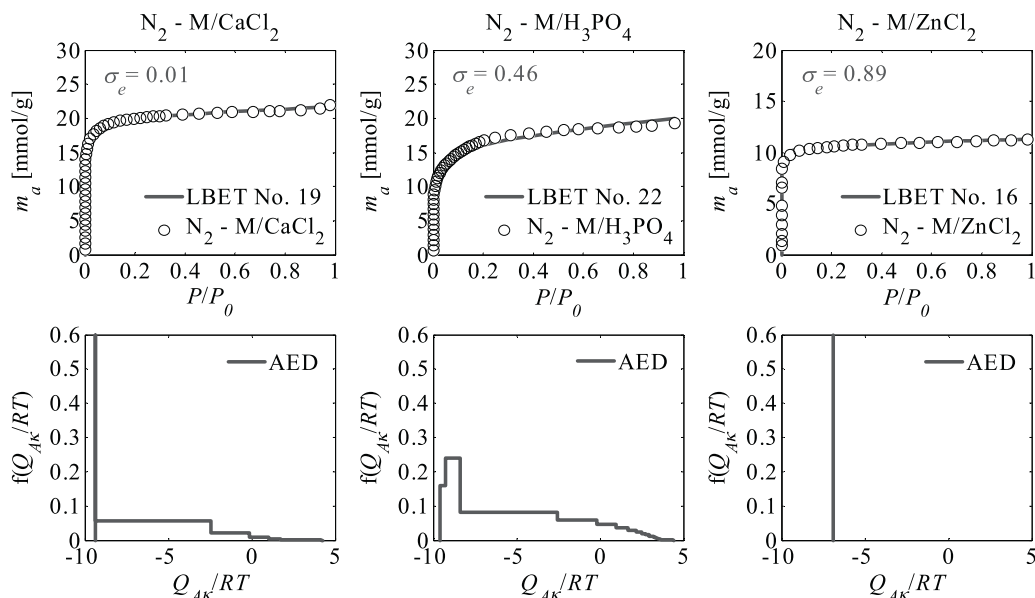

Fig. 1 – Results of the analyses of nitrogen adsorption isotherms carried out using the LBET method.

	S_{BET} [m²/g]	V_{micro} [cm³/g]	V_t [cm³/g]	V_{meso} [cm³/g]
M/CaCl$_2$	1700	0.43	0.64	0.21
M/H$_3$PO$_4$	1368	0.32	0.48	0.16
M/ZnCl$_2$	924	0.36	0.37	0.01

carbonaceous adsorbents are intended yields the most reliable information as to the adsorptive properties, microporous structure, heterogeneity and adsorption energy distribution on the first adsorbed layer, as well as the shape and size of micropores. Used in the research into the microporous structure of the activated carbon monoliths, methane is also a gas which will eventually be stored in the mentioned materials.

4.   Results and discussion

The results of analyses carried out using the LBET method have been compiled in Table 1 and in Figs. 1–3. Additionally, the results of earlier analyses, carried out using the BET and the DR methods, have been compiled in Table 2.

The results of the analyses of nitrogen, carbon dioxide, and methane adsorption isotherms determined for the obtained monoliths of activated carbons have been presented in a set of two figures. In the top right-hand figure, the dots '◦' mark the spots of the fitted empirical adsorption isotherm, while the solid line '-' marks the theoretical isotherm plotted according to the best-fitted variant of the LBET class model. The heading of the top figure gives the name of the adsorbate and the symbol of the adsorbent. The area of the top chart also contains the value of the fitting error dispersion σ_e. The second figure presents adsorption energy distribution on the adsorbent surface, determined on the basis of the given adsorption isotherm.

Based on the results of analyses of the nitrogen adsorption isotherm determined for the activated carbon monolith obtained by activation with CaCl$_2$ and labelled M/CaCl$_2$, where the analyses were carried out using the LBET method (and the results have been presented in Table 1), a conclusion can be drawn that the material in question displays limitations to nitrogen particle cluster growth related to the geometrical limitations of pores, as evidenced by the number of the best-fitted LBET class model. Interestingly, the parameter concerning the volume of the first adsorbed layer V_{hA} is relatively high, denoting a prevalence of micropores in the structure of the analysed material with a significant share of mesopores. These observations are further confirmed by the value of the energy parameters Q_A/RT and B_C. Moreover, drawing on an analysis of the isotherm of adsorption of nitrogen on the activated carbon monolith M/CaCl$_2$, it has been evidenced that the surface of the analysed material is relatively heterogeneous, with medium-sized and unbranched clusters of nitrogen particles formed in its micropores. It is particularly interesting that the LBET model very fitted the empirical data, as reflected by the value of the fitting error dispersion, yet the identifiability of the system is merely average, as evidenced by the value of the identifiability index w_{id}.

The results of analyses of the energy distribution diagram laid out for the N$_2$-M/CaCl$_2$ adsorption system point to a prevalence of adsorption sites with a very narrow range of adsorption energy. Consequently, it can be concluded that the micropores that prevail in the analysed material are comparable in size to the size of the adsorbed particles, and there also occurs a fraction of pores with a wide range of adsorption energy, namely large-sized micropores and mesopores. As can be observed, the results obtained using the LBET method cor-
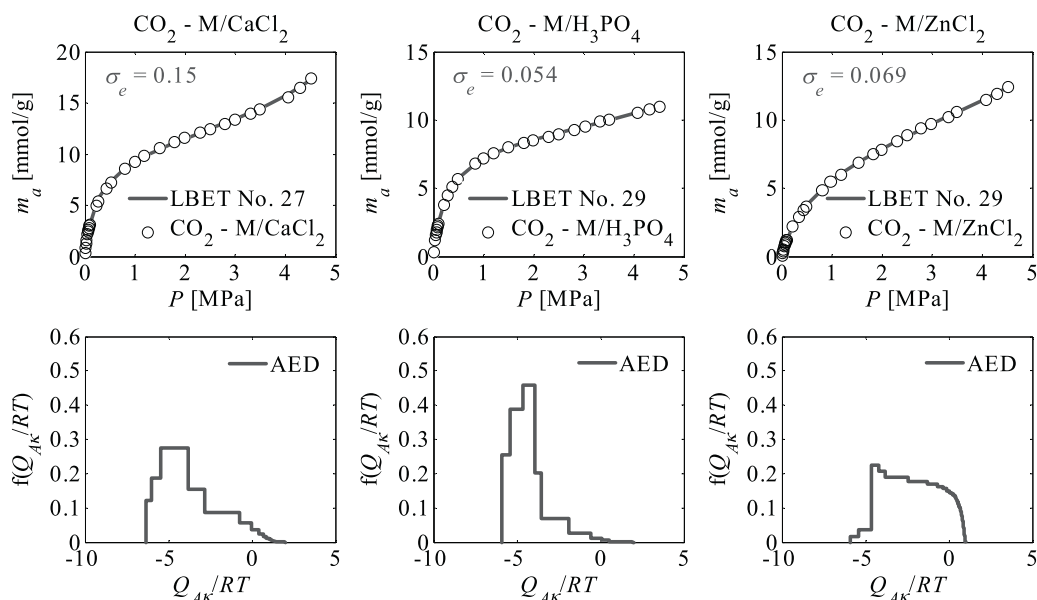

Fig. 2 – Results of analyses of carbon dioxide adsorption isotherms carried out using the LBET method.
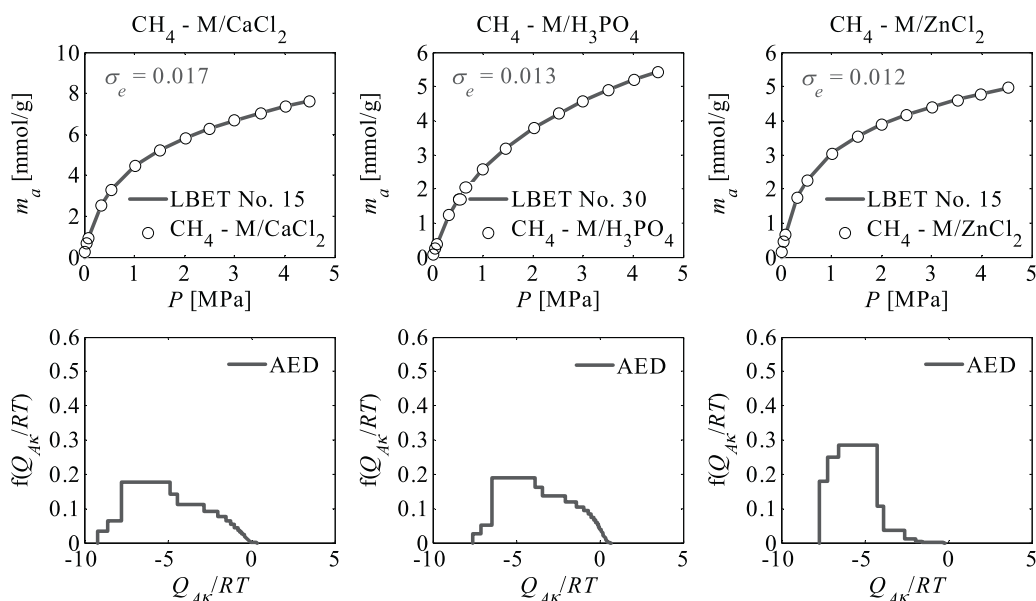
Fig. 3 – Results of analyses of methane adsorption isotherms carried out using the LBET method.

relate with those that were obtained with the BET and the DR methods which indicate that the analysed material is microporous with a prevalence of micropores and the presence of mesopores.

Another adsorption isotherm subject to the analysis was the N_2 - M/H_3PO_4 isotherm defined for the activated carbon monolith produced by way of chemical activation with phosphoric(V) acid. As can be concluded from the results of analyses compiled in Table 1, unlike in the case of the analysed material referred to above, the surface of the M/H_3PO_4 sample is homogeneous, and the adsorbate particle clusters formed in its micropores are about twice the size of the clusters in the above material. Unfortunately, though, the value of the fitting error dispersion σ_e is average, the same as the quality of identification defined by the parameter w_{id}, which implies that the results should be approached with reserve. By reference to the results of analyses carried out using the BET and DR methods, the reason could be a substantial share of mesopores in the structure of the activated carbon monolith M/H_3PO_4. In materials of this type, the LBET method may yield results that are not always reliable. What testifies to this conclusion is the shape of the adsorption energy distribution on the first layer, showing that the analysed material displays a wide range of energy of primary adsorption sites, while the sites with a relatively narrow distribution of adsorption energy prevail to a little extent.

An analysis of the microporous structure of another activated carbon monolith, i.e. $M/ZnCl_2$, produced by way of chemical activation with zinc chloride, showed that, judging from the nitrogen adsorption isotherm plotted using the LBET method, the surface of the material in question is heterogeneous. However, it is interesting to note that the parameter value of the volume of the first adsorbed layer V_{hA} is nearly half of the corresponding parameters of the analysed samples referred to above. What is more, the values of energy parameters, i.e. Q_A/RT and B_C, are also smaller, which is particularly

evident with the energy parameter for the second layer and the higher ones B_C, testifying to unfavourable energy conditions for the development of adsorbate particle clusters. These conclusions are further confirmed by the values of the geometrical parameters α and β.

As in the case analysed above, it is interesting to note the merely acceptable quality of the fitting between the theoretical model and the empirical data, and an average degree of identifiability of the system. The diagram of adsorption energy distribution on the first layer (see Fig. 1) permits a conclusion that the structure of the analysed material is dominated by micropores with a very narrow distribution of adsorption energy, i.e. pore sizes virtually comparable to the size of particles.

Analyses carried out based on carbon dioxide adsorption isotherms pointed to very high heterogeneity of the surface of the analysed activated carbon monoliths and a general formation of higher and significantly branched carbon dioxide particle clusters compared with nitrogen particle clusters. It is also interesting to note that, in all the analysed samples, the energy parameters for the first adsorbed layer and the successive ones are generally lower, whereas the values of the coefficients of effective adsorbate/adsorbent contact are evidently higher. Moreover, the shapes of the diagrams of adsorption energy distribution on the first adsorbed layer laid out based on carbon dioxide adsorption isotherms point to the occurrence of a wide range of adsorption energy on the surface of the analysed materials, with a clearly marked beginning and end of the distribution.

The subsequent analysis was concerned with methane adsorption isotherms determined for the analysed monoliths of activated carbons. The results of that analysis have been presented in Table 1 and in Fig. 3.

The results were found to be very close to the results of carbon dioxide adsorption isotherms. In particular, the results of the analysis of methane adsorption isotherms car-

ried out using the LBET method showed that the surface of the analysed monoliths of activated carbons was highly heterogeneous. The adsorbate particle clusters formed in the pores of the activated carbon monoliths M/CaCl$_2$ and M/H$_3$PO$_4$ were high and branched, whereas in the case of the monolith M/ZnCl$_2$ the occurrence of evidently smaller methane particle clusters was evidenced. The limitations to methane particle cluster growth in the analysed monoliths result from competitive adsorption in the neighbouring adsorption sites and the expansion of neighbouring clusters. The methane adsorption isotherms brought about the determination of generally lower values of energy parameters with regard to the first adsorbed layer and the successive ones, as well as evidently higher values of the coefficients of effective adsorbate/adsorbent contact obtained for all the analysed samples. It is also interesting to note that the energy parameters for the second layer B_C are very small for all the analysed monoliths of activated carbons on the basis of methane adsorption isotherms. Moreover, it has been evidenced that the limitations to methane cluster growth in the monoliths M/CaCl$_2$ and M/ZnCl$_2$ result from geometrical limitations related to the size of micropores. Also, the limitations to the growth of methane particle clusters in the monolith M/H$_3$PO$_4$ result from competitive adsorption and the expansion of neighbouring clusters.

5. Conclusions

The paper presents the results of research consisting in an analysis of the microporous structure of activated carbon monoliths produced by chemical activation with the use of CaCl$_2$, H$_3$PO$_4$ and ZnCl$_2$ as activating agents. Special attention has been paid to the assessment of the effect of the type of activating agent on the formation of the microporous structure and to the comparative analysis of the analytical results obtained with different adsorbates, namely nitrogen, carbon dioxide and methane. As has been evidenced from the results, an analysis of the porous structure based on the isotherms of adsorption of different adsorbates, i.e. nitrogen, carbon dioxide and methane, provides comprehensive information on the properties of adsorption systems. Moreover, the research has shown that carbon dioxide and methane adsorption isotherms yield comparable analytical results with the use of the LBET method, yet these results depart significantly from the results obtained based on nitrogen adsorption isotherms. The LBET method used in the research enables, among other things, an analysis of the porous structure of adsorbents based on the isotherms of adsorption of the substances to be eventually adsorbed by these materials. As a consequence, it is possible to determine with accuracy the adsorptive properties of the analysed materials and, subsequently, select with great precision the methods and conditions of the process of producing adsorbents, taking into account its economic aspects, which enhances the cost-effectiveness and competitiveness of the adsorption methods compared with other solutions.

Conflicts of interest

The authors declare no conflicts of interest.

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