Numerical analysis of the effect of the kind of activating agent and the impregnation ratio on the parameters of the microporous structure of the active carbons

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Abstract. The paper presents the results of the research on the application of the LBET class adsorption models with the fast multivariant identification procedure as a tool for analysing the microporous structure of the active carbons obtained by chemical activation using potassium and sodium hydroxides as an activator. The proposed technique of the fast multivariant fitting of the LBET class models to the empirical adsorption data was employed particularly to evaluate the impact of the used activator and the impregnation ratio on the obtained microporous structure of the carbonaceous adsorbents.

1. Introduction
A range of activities have been undertaken in recent years with the aim of reducing the propagation of environmental pollution, while adsorptive processes and porous materials have been gaining in importance in the newly developed technologies. Carbonaceous adsorbents are among the most popular and commonly used groups of materials, mainly because their porous structure can be shaped in a number of ways, depending on the raw material chosen to make them and the production method applied as well as in terms of the control of the production process conditions and a substantial scope of modifying the chemical properties of their surface [1,2].

Carbonaceous adsorbents are usually produced by the carbonization and activation of materials of organic origin that are rich in carbon. Carbonization consists in the thermal processing of the raw material at about 500 to 800°C in the absence of air and without the involvement of chemical agents in the atmosphere of inert gases. As the process progresses, the organic matter is decomposed and the gaseous components are removed. As a result, an adsorptively inactive half-finished carbonization product is obtained, referred to as the carbonizate. The porous structure of the carbonizate is inadequate; in order to have it properly developed, the material must undergo activation [3].

Two types of activation are distinguished, namely physical activation and chemical activation. Physical activation consists in partially gasifying the remains of the carbonization process with oxidizing gases, namely carbon dioxide and water vapour, at increased temperatures [3-5]. The production of carbonaceous adsorbents by chemical activation consists in a one-off reaction of the raw material with any of the following activating agents: H₃PO₄, HNO₃, H₂SO₃, ZnCl₂, MgCl₂, KOH, or NaOH [6-9]. In that group, potassium hydroxide and sodium hydroxide are particularly noteworthy
for their effect on the production of carbonaceous materials characterized by substantially developed porosity and a large real surface [10-12].

Chemical activation using potassium and sodium hydroxides proves to be highly beneficial as compared with physical activation with the use of steam or carbon dioxide, its major advantages being greater efficiency of the process and the fact that it is carried out in a single stage, lower temperatures and shorter time of the process, as well as a significantly enhanced development of the porous structure and the possibility to obtain a porous structure with a limited range of pore width. The disadvantages of chemical activation using potassium and sodium hydroxides include substantially higher process costs as compared with physical activation, the requirement to add the rinsing stage, and considerable corrosion of the hydroxides applied to the process.

The right choice of the activation process conditions for the given raw material which would ensure the production of microporous carbonaceous adsorbents suitable for the particular adsorptive process requires laborious tests and experiments. Still, for the experimental work to yield the anticipated results, mathematical tools have to be used with which the microporous structure of carbonaceous materials obtained under different conditions can be reliably verified. The tool in question should not only enable accurate evaluation of the structural parameters, but also permit an analysis of the microporous structure independently of the adsorbate used and an evaluation of the reliability of the parameters determined. Looking to meet these expectations, the author and his research team developed a group of mathematical adsorption models derived from uniBET theory, which is their antecedent universal adsorption theory [13-15]. Within the scope of the research presented in this paper, the said models were used to analyse the effect of the type of activating agent and the impregnation ratio on the parameters of the obtained porous structure of carbonaceous adsorbents.

2. The adsorption LBET class models

In the presented approach the adsorption is viewed as a clusterization of adsorbate molecules in pores of different shapes. Each cluster starts at a place (primary site) on a pore wall producing a local minimum of adhesion energy. Further molecules (the layers \( n > 1 \)) are joined due to cohesive and adhesive forces [15-24]. The maximum number of layers \( k \) (referred to as the cluster size) is determined by a space preassigned to another cluster (competitive clusterization - 1st type) or by a geometry of pore (2nd type). Possible branching of clusters is taken into account that is expressed quantitatively by the pore shape factor \( \beta \). It can significantly affect adsorption isotherms. The clusters have only one molecule in the first layer, i.e. only one original adsorption site on the surface can begin its formation, and each adsorbate molecule which belongs to the layer \( n > 1 \) can fill only one location on the layer \( n - 1 \). The areas assigned to the clusters are divided into classes in a way that the energy profiles within each class required to place a molecule on the successive layers \( n = 1, 2,... \) are identical. Each place available on the layer \( n - 1 \) of given class can be occupied with the same probability, regardless of the condition of occupying the remaining places in the system - this way the interactions between particular cluster layers are taken into account.

In the proposed models, there exists a distinction between the two types of models. The first model type refers to the adsorption system in which the limitation in the number of layers results from competing physical adsorption. The second model type describes the systems in which limitations of cluster size result from pores size. Upon derivation of the LBET class models the following assumptions were taken into account [15-24]:

a) the layers \( n > 1 \) are homogeneous and energetic parameters \( B_c \) are the same for \( n > 1 \):

\[
B_c = \exp \left( U_p (1 - 2 \cdot Z_{pp}) - Z_c \cdot Q_{sp} / RT \right),
\]

where \( Q_{sp} \) is the molar adhesion energy in ideal adsorbent-adsorbate contacts, \( U_p \) is the molar cohesion energy of adsorbate and \( Z_{pp}, Z_c \) are the correcting factors.

The number of primary adsorption sites is expressed by the formula given below [15-24]:

\[
m_{hm,k} = m_{ha} (1 - \alpha) \alpha^{k - 1},
\]
where $\alpha$ is the geometrical parameter of the porous structure, $\alpha \in (0,1)$, $m_{ht}$ is the amount of primary sites for the $k^{th}$ type clusters
c) the first layer physical adsorption energy is expressed in the following form:

$$Q_{Ak} = U_p - Z_{Ak} \cdot Q_{cp},$$

(3)

where $Z_{Ak}$ is the factor uniformly distributed over a range depending on $k$, $\kappa$ counts $k^{th}$ type clusters of identical energy profile across the layers $n = 1, \ldots, k$, $Q_{Ak}$ is the molar energy contributed by placing an adsorbate molecule at first layer of $k^{th}$ class clusters $Q_{A} = \min\{Q_{Ak}\}$, $Q_{A}$ is the the first layer physical adsorption energy and $Z_{A}$ is the correcting factor of adsorbent-adsorbate contacts.
c) the distribution function related to the energetic parameter $B_{Ak} \in (B_{Ak}, B_{Bk})$ is:

$$B_{Ak} = \exp \left( \frac{Q_{Ak}}{RT} \right), B_{Bk} = \exp \left( \frac{Q_{Bk}}{RT} \right), Z_{A}^{(1-\zeta_{A})}.$$

(4)

The energetic parameters $B_{Ak}$ and $B_{Bk}$ do not depend on $k$, at least for $k > 1 + d$, where $d = \{0,1\}$ is the binary variable where its value 1 provides for a more accurate variant of the model, with bimolecular clusters treated separately.
e) the coverage ratios $\theta_{kj}$ are the same for all $k > 1 + d$, $n > 1 + d$.

The heterogeneous adsorption model derived using the above assumptions assumes the following mathematical form, called the $LBET$ class model [15-24]:

$$m_{a} = \frac{m_{ht}}{\alpha} = \left[1 - \frac{1}{\ln(B_{A} / B_{f1})} \cdot \ln \left( B_{A} + \pi \right) \right] +$$

$$+ d \cdot \alpha (1 - \alpha) \left[1 + \frac{1}{\ln(B_{A2} / B_{f2})} \cdot \ln \left( B_{A} (1 - \theta_{2})^{\beta} + \pi \right) \right].$$

(5)

where: $m_{a}$ is total adsorption [mmol/g], $m_{ht}$ is total number of the adsorption primary sites, $m_{ht} = V_{ht} / V_{a}$, $V_{ht}$ is the first adsorption layer capacity [mm$^3$/g], $V_{a}$ is the molar volume of adsorbate [mm$^3$/mmol], $\theta_{kj}$ and $\theta_{2}$ are the coverage ratio of $k$-th - layer at $k$-th - type cluster and mean coverage ratio of layers $n > 1$ respectively, $\pi$ is the relative pressure $p/p_{th}$, $\alpha$ and $\beta$ are parameters of the geometrical and pore shape porous structure respectively. $B_{Ak}$, $B_{Bk}$ are both energetic parameters, $Q_{A}$ is the first layer adsorption energy [J/mol] and $B_{c}$ is the energetic parameter for adsorption layer $n > 1$ [15-24].

The $LBET$ models involves five parameters: $V_{ht}$, $Z_{A}$, $\alpha$, $\beta$, $B_{c}$ which can be adjusted by fitting Eq. (5) to empirical adsorption isotherm, with a chosen variant of the surface energy distribution function [15-24].

4. Numerical calculations

The aim of the research was to analyse the possibilities of applying $LBET$ class models and the fast multivariate procedure of adsorption system identification to perform a comparative evaluation of the effect of the activating agent and the impregnation ratio on the parameters of the microporous structure of carbonaceous adsorbsents obtained by way of chemical activation. The calculations were carried out with the use of data taken from subject literature, namely the isotherms of adsorption of nitrogen on UA active carbons obtained from Spanish anthracites [12]. The fitting of the theoretical isotherm to the isotherms of adsorption of nitrogen on UA active carbons was performed using the method of non-linear optimization with limitations, which minimizes the smallest square fitting error. The presented analysis was carried out using the 30-variant version of the $LBET$ class models in the calculations and the reliability of identification was assessed based on residual dispersion [15-24].

The results of the numerical analyses carried out for the isotherms of adsorption of nitrogen on the active carbons UA [12] were presented in a set of two figures. In the top right-hand figure, the grey dots ‘●’ mark the spots of the fitted empirical adsorption isotherm, while the black solid line ‘-’ marks
the theoretical isotherm plotted according to the best-fitted variant of the LBET class model. The dotted line represents the theoretical coverage of the first adsorption layer. The heading of the top figure gives the name of the adsorption system, i.e. the name of the adsorbate (N\textsubscript{2}) and the symbol of the adsorbent (UA); the subscript at the adsorbent symbol points to type of the activating agent used and the impregnation ratio. Next the name and number of the best-fitted LBET class model is given, preceded by a slash. The area of the top chart contains the parameters \(Q_A[J/mol]\), \(B_C\), \(Z_A\) and the fitting error dispersion \(\sigma_e\). The second figure presents adsorption energy distribution on the adsorbent surface; it contains the value of the volume of monolayer \(V_{hA}[\text{mm}^3/\text{g}]\), the values of the geometrical parameters \(\alpha, \beta\) and the value of the parameter of heterogeneity \(h\).

5. Discussion of the obtained results
The results obtained during calculations carried out using computerized LBET class adsorption models for the isotherms of adsorption of nitrogen on active carbons produced from Spanish anthracites with sodium and potassium hydroxides as the activating agents [12] point to substantial discrepancies between the parameters of the microporous structure produced using the said activating agents at different impregnation ratios. As regards the analysis of active carbons obtained with the use of sodium hydroxide, it can be observed that an increase in the impregnation ratio results in an expansion of the volume of the first adsorption layer \(V_{hA}\) and a rise in the value of the geometric parameter \(\alpha\), which defines the height of the agglomerates of adsorbate particles formed in the micropores of the analysed material. Also, an increase in the impregnation ratio triggers a rise in the value of the energy parameter for the successive layers \(B_C\).

![Fig 1. Multivariant identification of the isotherms of adsorption of nitrogen on UA activated carbon obtained from Spanish anthracite with varying NaOH to anthracite mass ratio [12].](image-url)
Moreover, it can be seen that a microporous structure with a lesser degree of heterogeneity, namely with the heterogeneity parameter $h = 7$, was obtained for the ratio of the mass of the activating agent to the mass of the activated substance, i.e. the impregnation ratio, exceeding 1:1. A material with the largest volume of the first adsorption layer was obtained for the NaOH impregnation ratio of 3:1. High, stack-like adsorbate particles are formed in the said material, which points to the occurrence of long and narrow micropores in it. When comparing the above results of analyses carried out for carbonaceous materials produced by way of chemical activation with sodium hydroxide (Figure 1) with the results obtained for active carbons produced by way of chemical activation with potassium hydroxide (Figure 2), one glance is enough to conclude that evidently larger volume parameters of the first adsorption layer were obtained for active carbons produced by way of chemical activation using potassium hydroxide. Also, for the active carbon obtained by way of chemical activation with the Spanish anthracite to potassium hydroxide ratio of 3:1 a microporous structure was formed that had the highest degree of homogeneity of all the analysed materials ($h = 5$) and the largest volume of the first adsorption layer, namely $V_{hA} = 1231 \text{[mm}^3/\text{g}]\).
The instruments presented in the article prove highly advantageous when compared with well-known and popular methods of microporous structure description by providing a wider range of information on the analysed microporous structure and offering unique possibilities of evaluating reliability of the obtained information on the analysed structure.

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