Description of the structural and energetic heterogeneities of solid surfaces in terms of fractal geometry.
A comparative analysis of the methods of estimation of fractal dimension from a single gas adsorption isotherm and some suggestions for the future research

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Different methods of the calculation of fractal dimension (D) of adsorbents are shortly reviewed. Freshly projected algorithms are applied to calculate D for two systems previously studied by Ehrburger-Dolle, and Rudziński et al., and the results are compared. Further a modification of the recently derived fractal analogue of the Dubinin – Astakhov adsorption isotherm equation is proposed to take into account the effect of multilayer adsorption. Numerical analysis of obtained “hybrid” isotherms is presented for some arbitrarily chosen parameters.

1. INTRODUCTION

Recently, a significant progress has been made in the theoretical description of structural and energetic heterogeneity of porous solids. As it was suggested by many authors, a quantitative measure of the structural and energetic heterogeneity of a porous solid is the pore and adsorption energy distribution function, respectively. From the mathematical point of view such a distribution

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function can be obtained by solving the linear Fredholm equation of the first kind defined as follows [1-9]:

$$\theta_i(p) = \int_{z_{\text{min}}}^{z_{\text{max}}} \theta_{\text{theor}}(z, p) f(z) \, dz \quad \text{for} \quad T = \text{const}$$

(1)

where $z$ describes the heterogeneity of an adsorbent related to one of the properties of the porous medium, $f(z)$ is the distribution function of the parameter $z$, $\theta_{\text{theor}}(z)$ is the local adsorption isotherm (i.e. kernel) that describes the adsorption process on a homogeneous "patch" of an adsorbent, $z_{\text{min}}$ is the smallest and $z_{\text{max}}$ is the largest value of the parameter considered in the analysis. Unfortunately, all integral equations formulated on the ground of adsorption science are ill-posed; even small changes in the data cause large changes in the obtained solution [10-24].

To overcome such difficulties, the problem of inverting the unstable linear Fredholm equation can be replaced by the classical non-linear optimisation method with constrains [25-31]:

Minimise \[ \left\| \theta_i(p) - \sum_{j=1}^{M} w_j \cdot \theta_{\text{theor}}(p, z = \text{const}) \right\|^2 \] with respect to $w_j \geq 0$

(2)

applying the normalisation condition, $\sum_{j=1}^{M} w_j = 1$, where $M$ is a number of local functions $\theta_i(p, z = \text{const})$, $w_i$ is the weight vector. In other words, the proposed procedure finds the weights of participation of the local functions (i.e. discrete kernel $\theta_i(p, z = \text{const})$) in relation to the experimentally measured global function $\theta_i(p)$.

In our recent papers [14, 24, 32, 33] the concept of a static penalty function was adopted to obtain a stable solution characterised by a clear physical meaning (i.e. the lack of both; the negative values of the distribution function and the strong oscillations of that function). Accepting the concept mentioned above, the functional defined by Eq. (2) can be expressed as follows:

Minimise \[ \left\{ \sum_{j=1}^{M} \left[ \theta_i(p_j) - \sum_{i=1}^{N} w_i \theta_{\text{theor}}(z_i, p_j) \right] \right\}^2 \quad \text{if} \quad \bar{w} \in \Xi \cap S \]

\[ \left\{ \sum_{j=1}^{M} \left[ \theta_i(p_j) - \sum_{i=1}^{N} w_i \theta_{\text{theor}}(z_i, p_j) \right] \right\}^2 + \sum_{i=1}^{M} C_i \delta_i \quad \text{otherwise} \]

(3)

with respect to $\bar{w} = (w_1, w_2, \ldots, w_N) \in R^N$
where
\[
\delta_i = \begin{cases} 
1 & \text{if constraint "i" is violated} \\
0 & \text{if constraint "i" is satisfied}
\end{cases}
\]

Here \( H \) is a number of constraints, \( \forall \in \Xi \cap S \). The set \( S \subseteq R^\nu \) defines a search space and the set \( \Xi \subseteq R^\nu \) defines a feasible search space. The search space \( S \) is defined as a \( N \)-dimensional rectangle in \( R^\nu \) (domains of variables defined by their lower and upper bounds):

\[
l_i \leq w_i \leq u_i, \quad 1 \leq i \leq N
\]

The feasible search space was assumed outside the defined \( N \)-dimensional rectangle. Clearly, to extract global minima of the functional defined by Eq. (3) nontrivial numerical procedures should be applied. Most of them (i.e. genetic algorithms, evolutionary algorithms, simulated annealing, taboo search, stochastic hill climbing algorithms and others) belong to "special artificial intelligence techniques" [34-40]. In order to demonstrate the complexity of an optimisation problem, in Figure 1 we show the micropore size distribution functions (MPSD) of two microporous activated carbons (synthetic origin carbon B (the polymeric carbon obtained from polyfurfuryl alcohol carbonized in vacuum) and commercial Norit ROW 0,8 Supra (Norit, Amersoort, Holland)) obtained solving the well-known integral equation with Dubinin and Radushkevich formula as a kernel. It is seen, that the transformation of the ill-posed integral equation (MPSD was obtained by CONTIN algorithm [14, 16-22, 24]) to its discreet form does not influence the shape of obtained distribution function only for ASA (adsorption stochastic algorithm) and SASA (simple mutation algorithm) algorithms [34-40]. The two evolutionary algorithms are based on both mutation and relaxation procedures. The main idea of such minimisation algorithms is the sequential minimisation problem in one dimension, executed by means of mutation operators. The techniques determining all unknown weights simultaneously (represented in Figure 1 by advanced GABI evolutionary algorithm) give poor results.

Fractal geometry has been widely applied in different studies on a great number of various porous solids providing an appropriate mathematical tool to study problems related to structure and scale [41-68]. The fractal dimension of the surface \( 2 \leq D < 3 \) accessible for adsorption is a global measure of surface irregularity. Several procedures of estimating fractal dimension on the basis of single adsorption isotherm have been presented so far [41-68]. We want to point out that contrary to the mentioned above methods of the pore size distributions, the calculation of the fractal dimension is both faster and simpler.
Fig. 1. The micropore size distribution functions of two microporous activated carbons (i.e. synthetic carbon B and commercial Norit ROW 0.8 Supra one) obtained solving the integral equation (Eq. (1)) with DR isotherm as a kernel. CONTIN: the solution of the integral equation using Provencher modified algorithm; ASA, SASA: the solutions of the discreet form of the integral equation by the combination of mutation and relaxation procedures; GABI the solution of the discreet form of the integral equation by means of advanced evolutionary algorithm.
In the present study we discuss some of the most important methods of $D$ determination, together with a newest one developed by Rudziński and co-workers [41, 42]. We also propose the method of the modification of FRDA (fractal analogue of the Dubinin – Astakhov isotherm) equation [43-48], to take the effect of multilayer adsorption into account. In this case, the influence of the change in the shape of adsorption isotherms with the change in $D$ is also analysed numerically.

Some discussed methods are put to use and the results of different methods of $D$ calculations using standard static adsorption measurements are presented by means of the freshly projected new numerical algorithms. For the estimation of the fractal dimensions from a single adsorption isotherm, the well-known fractal analogues of FHH (Frenkel – Halsey – Hill) [49-53] and n-BET (Brunauer – Emmett – Teller) [54-57] equations are used, and the results are compared with those obtained from the very promising method recently developed by Rudziński and co-workers [41, 42].

2. THEORETICAL DEVELOPMENT

Fractal analogue of n-BET equation. Brunauer-Emmett-Teller (n-BET) model of adsorption is one of the most common and popular tool of surface analysis. Such a theoretical model is mainly used for measuring the surface area of non-porous and porous solids. The monolayer capacity of an investigated material is easily obtained from an adsorption isotherm in the range of the relative pressure $0.06 \leq x \leq 0.2$. The n-BET theory of adsorption is recommended by IUPAC [62] for the surface area estimation despite many well-known drawbacks (i.e. lack of regard of both energetic and geometric heterogeneity, overestimating of surface area and so on). The fractal analogue of n-BET (fn-BET) equation was developed by Fripiat and co-workers [54], and the details can be found in [55]. In the present paper the fractal analogue of n-BET equation obtained on the basis of the so-called molecular approach is used for describing the data of nitrogen adsorption isotherms. Thus, the surface coverage is defined as follows:

$$\frac{N}{N_{\text{mon}, \text{fn-BET}}} = \frac{C \sum_{i=1}^{n} 2^{-D} \left( \sum_{j=1}^{n} x^j \right)}{1 + C \sum_{i=1}^{n} x^i}$$

(6)

where $x = p/p_0$ is a relative pressure; $C$ and $N_{\text{mon}, \text{fn-BET}}$ are fn-BET constant and monolayer capacity, respectively; $n$ is the limited number of forming adlayers, and the numerator in Eq. (6) is equal to:

$$\left[ \sum_{i=1}^{n} x^i + 2^{-D} \sum_{j=2}^{n} x^j + 3^{-D} \sum_{j=3}^{n} x^j + \ldots + n^{-D} x^n \right]$$

(7)
This equation for $D = 2$ reduces to the classical n-BET ones [54, 55]:

$$
\frac{N}{N_{\text{mono},n-BET}} = \frac{C \sum_{i=1}^{n} x^i}{1 + C \sum_{i=1}^{n} x^i} 
$$

Fripiat [54] suggested a simple method of the fractal dimension evaluation by the comparison of the shapes of experimental and theoretical isotherms (fn-BET). This procedure requires the knowledge of the n-BET constant $C$. The value of this constant can be simply obtained by fitting the classical n-BET equation to experimental data in the standard range of pressures (i.e. $0.06 \leq x \leq 0.2$). This method of $D$ finding [54 - 57] can be treated as a very rough approximation, therefore, in the current paper the modification of the simple genetic algorithm with real coding was applied for fitting the fractal analogue of n-BET equation to experimental adsorption isotherm data.

**Fractal analogue of FHH equation.** The first approach mentioned above bases on the argument that multilayer coverage induces progressive smoothing of the solid surface [49-53]. The fractal FHH equation (f-FHH) assumes that the substrate - adsorbate interactions dominate over the adsorbate-adsorbate interaction and are therefore non-negligible all the way out to the outermost layer of the film [49-53]. This is verified in the case of a pure Van der Waals (VdW) regime, in which the adsorbate surface tension can be neglected. In this regime, the fractal FHH equation has the following form [49-53]:

$$
\frac{N}{N_{\text{mono,f-FHH,VdW}}} = \kappa_{\text{f-FHH}} \left[ \ln \left( \frac{p_0}{p} \right) \right]^{1/m} \text{ and } m = 3/(3 - D) \tag{9}
$$

where $\kappa_{\text{f-FHH}}$ and $N_{\text{mono,f-FHH,VdW}}$ are f-FHH constant and monolayer capacity, respectively. In the case of a flat surface, $D = 2$ and $m = 3$, as it is expected from the classical FHH equation. For the larger substrate - adsorbate interaction the VdW regime is not valid. In such a case the so-called capillary condensation regime (CC) is applicable. Here the equation is transformed as follows [49-53]:

$$
\frac{N}{N_{\text{mono,f-FHH,CC}}} = \kappa_{\text{f-FHH}} \left[ \ln \left( \frac{p_0}{p} \right) \right]^{1/m} \text{ and } m = 1/(3 - D) \tag{10}
$$

This yields $m > 1$ for $D > 2$ and accounts for $m < 3$. 
Since this method is very simple, it has been widely used for the
determination of the surface fractal dimension of solids, particularly, in the case
of activated carbons and silicas. From the numerical point of view the fitting of
the parameters of the fractal FHH equation to experimental data is a very simple
problem. In the present study the modification of Needle and Mead algorithm
(simplex) was applied. To escape from local minima of the defined functional
the well-known multi start technique was adopted.

**Generalised fractal n-BET equation (GFNBET).** Recently developed by
Rudziński and co-workers [41, 42] the generalised fractal n-BET equation
(GFNBET) seems to be a very powerful tool for studying the both energetic and
geometric heterogeneity of porous solids. According to the mentioned authors,
real solid surfaces are never perfectly regular and never totally irregular
(fractal). Such surfaces are called "partially correlated" and represent an
intermediate state between the mentioned above two extreme models of solid
surfaces. Agreeing with those assumptions, the fractal pore size distribution can
be defined as follows:

$$\frac{\partial N}{\partial r} = \frac{C(3-D)r^{2-D}}{[1 + r^{3-D}]^3}$$

(11)

where C is a proportionality constant, D is the fractal dimension of the surface
accessible for adsorption and r is the radius of a (spherical) molecule. One
should notice that for small pores, i.e., in the limit \( r \to 0 \):

$$\lim_{r \to 0} \left( \frac{\partial N}{\partial r} \right) = C(3-D)r^{2-D}$$

(12)

a new fractal pore size distribution is transformed to the classical Pfeiffer and
Avnir fractal pore size distribution [59]. On the other hand, in the limit \( r \to \infty \):

$$\lim_{r \to \infty} \left( \frac{\partial N}{\partial r} \right) = C(3-D)r^{D-4}$$

(13)

Taking into account both energetic and geometric heterogeneities of a solid
surface Rudziński and co-workers [41, 42] developed two new fractal equations
(GFNBET) defined as follows:

$$\ln \left[ \frac{N_i/(M\Phi)}{1 - N_i/(M\Phi)} \right] = A_i - A_i kT \ln X - A_i (kT)^2 \ln X^2$$

(14)
\[
\ln \left[ \frac{N_t}{M \phi} \right] = A_0 - A_k T \ln X - A_x (kT)^2 \left[ \ln X \right]^2
\]  
(15)

where unknown polynomial coefficients are defined by the following formulas:

\[
A_0 = \varepsilon_o (\alpha - \beta e_o)
\]  
(16)

\[
A_1 = 2 \beta e_o - \alpha
\]  
(17)

\[
A_2 = \beta
\]  
(18)

here \(\phi(x)\) is a function describing multilayer formation on the fractal surfaces proposed by Fripiat [54, 55]:

\[
\phi(x) = \frac{1}{X} \sum_{m=1}^{N_i} \sum_{j=0}^{2-D} x_j
\]  
(19)

where \(X = \sum_{m=1}^{N_i} x_i\); \(k\) is a Boltzmann constant; \(T\) is temperature; \(M\) is a monolayer capacity; \(N_i\) is a value of adsorption; and \(\alpha, \beta, \varepsilon_o\) are the energetical parameters characterising energetic heterogeneity of an investigated porous material. The adsorption energy distributions on fractal surfaces corresponding to Eqs. (14) and (15), respectively, are defined by:

\[
\chi(\varepsilon) = (3-D) \cdot \left[ \left( \frac{\partial F}{\partial \varepsilon} \right)_{\varepsilon_o} + \left( \frac{\partial^2 F}{\partial \varepsilon^2} \right)_{\varepsilon_o} (\varepsilon - \varepsilon_o) + \ldots \right] \times \frac{1}{r_0} \cdot \exp \left[ (3-D) \cdot \left( \frac{\partial F}{\partial \varepsilon} \right)_{\varepsilon_o} (\varepsilon - \varepsilon_o) + \frac{3-D}{2} \cdot \left( \frac{\partial^2 F}{\partial \varepsilon^2} \right)_{\varepsilon_o} (\varepsilon - \varepsilon_o)^2 + \ldots \right]
\]  
(20)

\[
\chi(\varepsilon) = (3-D) r_0 \cdot \left[ \left( \frac{\partial F}{\partial \varepsilon} \right)_{\varepsilon_o} + \left( \frac{\partial^2 F}{\partial \varepsilon^2} \right)_{\varepsilon_o} (\varepsilon - \varepsilon_o) + \ldots \right] \times \exp \left[ -(3-D) \cdot \left( \frac{\partial F}{\partial \varepsilon} \right)_{\varepsilon_o} (\varepsilon - \varepsilon_o) - \frac{3-D}{2} \cdot \left( \frac{\partial^2 F}{\partial \varepsilon^2} \right)_{\varepsilon_o} (\varepsilon - \varepsilon_o)^2 + \ldots \right]
\]  
(21)
where

\[ \alpha = \left( 3 - D \frac{\partial F}{\partial \varepsilon} \right)_{\varepsilon_0} \quad \beta = \frac{3 - D}{2} \frac{\partial^2 F}{\partial \varepsilon^2} \quad r_0 = \exp(-\varepsilon_0) \quad (22) \]

and \( F(\varepsilon) \) is a function of \( \varepsilon \) describing the individual features of the studied adsorption system.

Obviously, fractal pore size distribution can be obtained on the basis of Eq. (11) or by simple relations:

\[ \frac{\partial V}{\partial r} = -\chi(\varepsilon) \frac{d\varepsilon}{dr} \quad (23) \]

\[ r = \exp\left\{-F(\varepsilon_0)-\left(\frac{\partial F}{\partial \varepsilon}\right)_{\varepsilon_0}(\varepsilon-\varepsilon_0) - \frac{1}{2}\left(\frac{\partial^2 F}{\partial \varepsilon^2}\right)_{\varepsilon_0}(\varepsilon-\varepsilon_0)^2 - \cdots\right\} \quad (24) \]

In the present study a special hybrid algorithm was constructed for the fitting of GFnBET equation to the experimental data. Such a two step algorithm consists of classical Monte Carlo (i.e. pure random search method) and evolutionary searching procedures. The first method was used for the global penetration of searching space. The second method starts with the best solution obtained by Monte Carlo method and sequentially approaches to the global minima of defined functionals (i.e. objective function, fitness function, and so on). Such an iterative improvement technique includes new "intelligence" powerful numerical methods.

**Fractal analogue of the Dubinin – Astakhov adsorption isotherm equation (FRDA), and modifications.** The fractal analogues of Dubinin – Astakhov (FRDA) and Dubinin – Radushkevich (FRDR) adsorption isotherm equations were developed [43-48] basing on the concept of global adsorption isotherm equation (GAI), where the Pfeiffer – Avnir function [59] and DR or DA isotherm equations [1-9] were applied. Integration of GAI in the finite limit of microporosity (the real system is finite: \( \Omega \in \langle x_{\min}, x_{\max} \rangle \)) leads to the following equation:

\[ \theta = \frac{\rho}{n} (\mu A)^{\frac{D-2}{n}} \left[ \gamma \left( \frac{3-D}{n}, x_{\min} \mu A \right) - \gamma \left( \frac{3-D}{n}, x_{\max} \mu A \right) \right] \quad (25) \]
where $\theta$ is the degree of micropore filling, $A = -\Delta G = RT \ln(p_o/p)$ and $R$ is the universal gas constant, $T$ is temperature, $p_o$ and $p$ are the saturation vapour pressure and the equilibrium pressure of the adsorbate, respectively, $\gamma$ is an incomplete gamma function and $n$ is an equation parameter. Moreover:

$$\rho = \frac{3 - D}{x_{\text{max}}^{3-D} - x_{\text{min}}^{3-D}}$$  \hspace{2cm} (26)$$

and

$$\mu = (\beta \kappa)^{-n}$$  \hspace{2cm} (27)$$

where $D$ is the pore fractal dimension for pores with minimal and maximal slit half-widths between $x_{\text{min}}$ and $x_{\text{max}}$, $\beta$ is the affinity coefficient and $\kappa$ is a constant.

As it was shown previously if $n = 2$ the fractal DR equation is obtained. The main properties of the both fractal analogues (FRDR and FRDA) together with the application for the description of experimental adsorption data and related thermodynamic formulas have been shown elsewhere [43-48]. It was also presented [46] that for strictly microporous carbons the description of the nitrogen adsorption isotherm data by the typical DA isotherm can lead to the evaluation of the pore fractal dimension of micropores by the application of the relation:

$$D = \frac{E_0(15.3897 - 3.6083 \times 10^4 n_{\text{DA}}) - 283.3356 + 6.3019 \times 10^4 n_{\text{DA}}}{E_0(0.9396 + 0.1054 n_{\text{DA}}) + 1.0557 - 1.8407 n_{\text{DA}}}$$  \hspace{2cm} (28)$$

where $E_0$ and $n_{\text{DA}}$ are the parameters obtained from fitting experimental nitrogen adsorption data by typical DA equation.

FRDA formula has been widely applied for the characterisation of the heterogeneity of carbonaceous surfaces [61, 62]. On the other hand, for carbons possessing relatively wide pore size distribution, i.e. containing the meso or macropores, some problems concerning multilayer adsorption occur; i.e. it is obvious that FRDA isotherm equation does not take into account the adsorption on the surface of larger pores. To overcome this difficulty in the following study we propose taking into account the fact of polymolecular adsorption by adding to the FRDA isotherm (Eq. (25)), the terms referring to the presence of larger pores (i.e. Eqs. (6) and/or Eq. (9)). The both new equations are valid for pure fractal carbonaceous solids, while for partially correlated the isotherm proposed by Rudziński and co–workers [41, 42] is still suitable. Figure 2
shows the properties of the modified FRDA equation, taking into account f-FHH (Eq. (10)) and/or fn-BET (Eq. (6)) type multilayer adsorption.
Fig. 2. “Pure” (FRDA – Eq. (25)) and “hybrid” models (FRDA (Eq. (25)) + fn-BET (Eq. (6)) and FRDA (Eq. (25)) + f-FHH (Eq. (10))) – the effect of the fractal dimension value. The following parameters were taken for the calculation (nitrogen at the temperature \( T = 77.5 \) K): FRDA (Eq. (25)) - \( x_{\text{min}} = 0.15 \) nm, \( x_{\text{max}} = 1.0 \) nm, \( n = 2 \), \( W_0 = 1 \) cc g\(^{-1}\), \( \kappa = 12 \) kJ nm/mole; \( \beta = 0.32 \); f-FHH (Eq. (10)) – \( N_{\text{mono,f-FHH}} = 0.3 \) cc g\(^{-1}\), \( \kappa_{\text{FHH}} = 1.5 \); fn-BET (Eq. (6)) - \( N_{\text{mono,fn-BET}} = 0.5 \) cc g\(^{-1}\), \( C = 30 \), \( n = 20 \).

It is seen that the differences in the change of isotherm shapes are observed, in dependence on the model chosen for the description of adsorption in the multilayer region. Both groups of isotherms show the same behaviour at low relative pressures, i.e. adsorption increases with the rise in the value of \( D \) (this increase is smaller when fn-BET model is added to the FRDA one), contrary to the situation observed at larger pressures. Since both equations describe adsorption on carbons containing micropores (and these materials have not been
analysed in this paper) the applicability of them for the description of experimental data will be the subject of our forthcoming studies.

3. EXPERIMENTAL

To estimate fractal dimensions by some of the mentioned above methods, two adsorption systems have been chosen. The analysed adsorption isotherms carefully measured in the range of the relative pressure c.a. $10^{-6}$ (p/p$_s$), up to the unity, were previously studied by Ehrburger-Dolle [67, 68] and Rudziński and co-workers [41, 42]. Following Rudziński et al. [41, 42], the activated carbon TN330 and aerosil A200 silica were the objects of the present study. A200 is fume silica obtained by phyrohydrolysis of SiCl$_4$, produced by Degusa. The remaining system was nitrogen adsorbed by carbon black TN330, produced by Tokai Carbon. The values of the parameters characterising both materials are summarised in Table 1.

4. RESULTS AND DISCUSSION

Figure 3 shows the adsorption isotherms on both investigated materials in the classical and logarithmic co-ordinates. One should notice that such isotherms differ significantly from each other not only in the values of adsorption capacity but also in the shape. Both materials are characterised by a short initial step of adsorption, suggesting their mesoporous nature. The results of the calculation of a pore size distribution function for TN300, applying the method proposed recently by Nguyen and Do [19, 24, 26-34] are shown in Figure 4. It can be noticed that the total volume of micropores contributes c.a. 1.5 % to the total pore volume, therefore the solid can be considered as strictly mesoporous (the volume of mesopores is equal to 0.0204 cm$^3$/g). The results of the fitting by classical and fractal n-BET equations (in the case described above a new numerical algorithm, which is the modification of a simple genetic algorithm (SGA [35, 69]) with real coding, was applied) in the range of the pressure $0.06 \leq x \leq 0.2$ are presented in Figure 5. Both systems are described by the models very well, especially the data for the carbon black TN330 (see Table 1). Moreover, the values of some equation parameters obtained during the minimisation process are similar (see Table 1). Fractal n-BET shows that adsorption on the surface of TN330 carbon black is characterised by the value of the fractal dimension close to 2.0. In a case of A200 silica the value of the surface fractal dimension is greater than for TN300, and is equal to 2.13.
Tab. 1. The values of the parameters characterizing the pore structures of TN330 and A200 adsorbents, calculated from nitrogen adsorption/desorption isotherms

<table>
<thead>
<tr>
<th>Adsorption isotherm equation</th>
<th>Adsorbent</th>
<th>Parameter</th>
<th>TN330</th>
<th>A200</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>fn</em>-BET 0.06 &lt; ( \frac{p}{p_s} ) &lt; 0.2</td>
<td></td>
<td>( N_{\text{mono,} fn\text{-BET}} ), mmol g(^{-1})</td>
<td>0.714</td>
<td>2.28</td>
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<tr>
<td></td>
<td></td>
<td>( n )</td>
<td>6</td>
<td>5</td>
</tr>
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<td></td>
<td></td>
<td>C</td>
<td>169.8</td>
<td>72.4</td>
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<td></td>
<td></td>
<td>D</td>
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<td>2.125</td>
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<td></td>
<td></td>
<td>SSD</td>
<td>2.316e-6</td>
<td>1.173e-4</td>
</tr>
<tr>
<td><em>n</em>-BET 0.06 &lt; ( \frac{p}{p_s} ) &lt; 0.2</td>
<td></td>
<td>( N_{\text{mono,} n\text{-BET}} ), mmol g(^{-1})</td>
<td>0.708</td>
<td>2.224</td>
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<td></td>
<td></td>
<td>( n )</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
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<td></td>
<td>C</td>
<td>186.464</td>
<td>83.145</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SSD</td>
<td>2.427e-6</td>
<td>3.01e-4</td>
</tr>
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<td>( GfnBET ) ( \frac{p}{p_s} &lt; 0.48 ) (for TN330) ( \frac{p}{p_s} &lt; 0.82 ) (for A200)</td>
<td></td>
<td>Surface area, m(^2) g(^{-1})</td>
<td>67.95</td>
<td>213.57</td>
</tr>
<tr>
<td>( f\text{-FHH} ) 0.17 &lt; ( \frac{p}{p_s} ) &lt; 0.91</td>
<td></td>
<td>( N_\alpha ), mmol g(^{-1})</td>
<td>0.917</td>
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<td></td>
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<td>( n )</td>
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<td>( \alpha_0 )</td>
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<td></td>
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<td>D</td>
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<td>2.999</td>
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<td></td>
<td>SSD</td>
<td>0.014</td>
<td>0.0098</td>
</tr>
<tr>
<td>( f\text{-FHH} ) 0.2 &lt; ( \frac{p}{p_s} ) &lt; 0.92</td>
<td></td>
<td>( \kappa_{\text{FHH}} )</td>
<td>1.491</td>
<td>1.432</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D</td>
<td>2.615</td>
<td>2.617</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SSD</td>
<td>0.013</td>
<td>0.014</td>
</tr>
<tr>
<td>( f\text{-FHH} ) 0.38 &lt; ( \frac{p}{p_s} ) &lt; 0.94</td>
<td></td>
<td>( \kappa_{\text{FHH}} )</td>
<td>1.431</td>
<td>1.417</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D</td>
<td>2.579</td>
<td>2.606</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SSD</td>
<td>0.117</td>
<td>0.051</td>
</tr>
<tr>
<td>( f\text{-FHH} ) 0.4 &lt; ( \frac{p}{p_s} ) &lt; 0.96</td>
<td></td>
<td>( \kappa_{\text{FHH}} )</td>
<td>1.349</td>
<td>1.414</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D</td>
<td>2.539</td>
<td>2.605</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SSD</td>
<td>0.382</td>
<td>0.047</td>
</tr>
<tr>
<td>( f\text{-FHH} ) 0.54 &lt; ( \frac{p}{p_s} ) &lt; 0.98</td>
<td></td>
<td>( \kappa_{\text{FHH}} )</td>
<td>0.950</td>
<td>1.358</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D</td>
<td>2.379</td>
<td>2.578</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SSD</td>
<td>4.123</td>
<td>0.205</td>
</tr>
</tbody>
</table>
Fig. 3. The experimental adsorption isotherms of nitrogen on the TN330 carbon black and A200 silica adsorbents measured at 77.5 K.

In Figure 6, the results for ten runs of algorithm are shown. In order to illustrate the method of Fripiat and co-workers [54, 55] we decided to generate the fractal n-BET isotherms for different values of the surface fractal dimension (basing on the classical n-BET equation parameters, Figure 7).
Fig. 4. Differential and cumulative pore size distributions calculated for TN300 carbon black applying the method of Nguyen and Do
Fig. 5. The experimental (points) and theoretical (lines) data obtained by fitting of the n-BET (Eq. (8)) and fractal n-BET (Eq. (6)) equations to nitrogen adsorption data on the TN330 carbon black and A200 silica.
The comparison of generated adsorption isotherms with experimental ones (especially in logarithmic co-ordinates) leads to the conclusion that for TN330 carbon black a small value of D is probable. In the case of A200 silica the comparative analysis is difficult since the generated adsorption isotherms converge. However, Fripiat’s comparative method suggests rather a smaller value of D equal to c.a. 2.3.

The fractal FHH analysis (Figure 8) leads to larger values of D for the both tested materials than those obtained from fn-BET equation. In the case of A200 silica f-FHH equation predicts the value of D around 2.6. We want to point out that here D value is practically independent of the chosen relative pressure range (see Table 1 and Figure 8). On the contrary, for TN330 carbon black the value of D is larger and it depends on the assumed relative pressure range (it changes between 2.38-2.62 (see Table 1 and Figure 8)).

In contrast to fractal n-BET and FHH equations, the generalised fractal n-BET equation (GFnBET) proposed by Rudziński and co-workers [41, 42] leads to larger differences in D values for investigated samples. In the case of TN330 carbon black the shape of the isotherm suggests a very smooth surface. However, for A200 silica Rudziński’s method predicts D approaching to 3.0 (i.e. strong irregularity of the surface of this material). The obtained results are very similar to those published by Rudziński and co-workers (see Table 2). It is obvious since we used the same pressure range for fitting the generalised fractal n-BET equation (see Table 1).
Fig. 7. Application of the Fripiat’s method – data generated on the basis fn-BET equation (Eq. (6)) for nitrogen adsorption isotherms on the TN330 carbon black and A200 silica, and for different values of D
Fig. 8. Application of the fractal FHH (Eq. (10)) equation for the analysis of the experimental data of nitrogen adsorption on TN330 carbon black and A200 silica. The computations were performed for different pressure ranges

The differences for A200 sample are caused by different forms of functionals applied for minimization (i.e. we optimise one parameter ($N_t$) more than Rudziński’s group). As one can see from Figures 9 and 10, proposed in the
current study new algorithm for fitting GFnBET equation to experimental data leads to very stable results especially in the case of TN330 carbon black. Rudziński and co-workers proposed classical exhaustive searching algorithm for estimation of the GFnBET equation parameters.

Fig. 9. The changes of objective function during the minimisation process (GFnBET equations – Eqs. (14) and (15), and the new algorithm described in the text) for the both investigated materials (i.e. TN330 carbon black and A200 silica). The computations were repeated ten times
On the other hand, our procedure is based on both exhaustive search method and parabolic approximation. The obtained results are shown as contour plots in Figure 11. One can also see that TN330 carbon black is characterised by a well-developed single global minimum. Such a minimum is characterised by a very low value of both fractal dimension (i.e. $D \to 2.0$) and the finite number of adsorption layers (i.e. $n \approx 4$). In the case of A200 silica the contour plot is characterised by a completely different features. First of all, the minimum is broader and not so clearly visible, but it is placed at a larger value of the fractal dimension (i.e. $D \to 3.0$) and larger number of adsorption layers (i.e. $n \approx 20$). Table 2 shows the parameters of the energy distribution calculated using Eq. (20). Since the results are almost the same as published by Rudziński and co-workers the graphical representation will be omitted in the current study.

Fig. 10. Application of GFnBET equations (i.e. Eqs. (14) and (15)) to correlate the experimental data on the TN330 carbon black (solid line) and A200 silica (broken line)
Fig. 11. Searching of the minima of GFnBET equations (Eqs. (14) and (15)) the for both considered systems by the proposed in this study novel algorithm (based on the both, exhaustive search method and parabolic approximation)
Table 2. The energetic parameters found by solving the equation system (Eqs. (16) – (18)). The value of the parameters published by Rudziński and co-workers is shown in parenthesis.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>( \alpha ), kJ mol(^{-1} )</th>
<th>( \beta ), (kJ mol(^{-1} ))(^2 )</th>
<th>( \varepsilon_0 ), kJ mol(^{-1} )</th>
<th>( \varepsilon_l ), kJ mol(^{-1} )</th>
<th>SSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>TN330</td>
<td>0.594 (0.505)</td>
<td>0.061 (0.069)</td>
<td>3.728 (3.41)</td>
<td>-1.139 (-0.025)</td>
<td>0.014 (0.014)</td>
</tr>
<tr>
<td>A200</td>
<td>0.32 (0.199)</td>
<td>0.037 (0.038)</td>
<td>2.803 (1.145)</td>
<td>-1.524 (-1.49)</td>
<td>0.0098 (0.011)</td>
</tr>
</tbody>
</table>

Finally, we want to state that the main advantage of the method proposed by Rudziński et al. [41, 42] is that the proposed fractal isotherm equation offers the possibility to obtain simultaneously the adsorption energy distribution function. The verification of this method for experimental systems remarkably differing in porosity as well as the comparison with the results obtained by modified in the current study FRDA isotherm (hybrid models) will be the subject of our forthcoming study.

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REFERENCES


