

FRactal Geometry Concept in Physical Adsorption on Solids

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سوف تتّم في هذا البحث مراجعة الطرق التجريبية والنظرية المختلفة المستعملة لتحديد بُعد صورة النمطي الهندسي المتكرر (د) للمكثفات الصلبة. وسيُركز على طرق حساب المعامل (د) المستندة إلى نتائج قياس تكثيف فريد متساوي الحرارة. كما ستعرض كيفية جديدة لااشتقاق نظير صورة النمطي الهندسي المتكرر لمعادلة التكثيف المتساوي الحرارة (ف.ش.ش) ، ويُقترح نموذج جديد للتكثيف على المسام وعلى صور النمطي الهندسي المتكرر السطحي. وأخيراً سوف توضح بعض الطرق المقترحة في هذا البحث من خلال تطبيق نظم الحلول الحاسوبية الرقمية المطورة حديثاً من قبلنا.

ABSTRACT

The different experimental and theoretical methods of determining the fractal dimension (D) of solid adsorbents are reviewed. Attention is paid to the methods of calculation for D based on the results of a single adsorption isotherm measurement. A new derivation of the fractal analog of the FHH adsorption isotherm equation is given and a new model of adsorption on pore and surface fractals is proposed. Some of the methods are illustrated, applying our recently developed numerical algorithms.

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FRactal GEOMETRY CONCEPT IN PHYSICAL ADSORPTION ON SOLIDS

1. INTRODUCTION

Recently, significant progress has been made in the theoretical description of structural and energetic heterogeneity of porous solids. As 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 function can be obtained solving the linear Fredholm equation of the first kind defined as follows [1–9]:

$$\theta_t(p) = \int_{z_{\min}}^{z_{\max}} \theta_{\text{theor}}(z, p) f(z) dz \quad \text{for} \quad T = \text{const}, \quad (1)$$

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, and z_{\min} is the smallest and z_{\max} the largest value of the parameter considered in the analysis. Unfortunately, all such integral equations are ill-posed; even small changes in the data cause large changes in the obtained solution [10–24].

Fractal geometry [25, 26] has been widely applied in different studies on a great number of various porous solids providing an appropriate tool to study problems related to structure and scale [27–36]. The fractal dimension of the surface $2 \leq D < 3$ accessible for adsorption is a global measure of surface irregularity, and for highly porous systems “fractal behavior does not reflect the structure of the basic objects (such as pores or clusters) but their distribution” [37]. A relation between the shape of the pore-size distribution function and D was discussed by Ehrburger–Dolle and co-workers [38].

The fractal dimension D of the surface can be determined directly from the results of several methods. For example, **small-angle X-ray scattering (SAXS)** [39–41] has been recently used for the description of the fractality of metals [42], porous silicas [43], activated carbons and carbon blacks [44–52], and porous glass [53]; **small-angle neutron scattering (SANS)** for the study of sandstone and shale [54], graphites [55, 56], cements and rocks [57–59], and porous membranes [60]; **proton-induced x-ray emission (PIXE)** method for the determination of D of Portland cements (a good agreement was obtained with the values found by SANS and NMR) [61]; **atomic force microscopy (AFM)** for the determination of D of porous silicon [62]; **scanning electron microscopy (SEM)** for the determination of D of carbon fibers [63], and silicas [64]; **small-angle static light scattering** for the determination of D of microporous membrane filters [65]. Some other widely applied methods include **nuclear magnetic resonance (NMR)** [66, 67]; **dielectric response measurements** [68], or **thermogravimetry** [69]. D values can be also obtained from **mercury porosimetry** results [70]. This method was applied for the evaluation of D of chars, coals, and carbons [38, 71–76], rocks, marbles and soils [77–80].

Several procedures of estimating D on the basis of adsorption measurements have been presented so far [29, 81–107]. The simplest is the measurement of the adsorption of molecules of different size, where the fractal dimension is calculated from the slope of the line: monolayer capacity (n_m) (or volume adsorbed in pores) vs. molecular size, cross sectional area of adsorbates (σ) or their molar volume:

$$\ln(n_m) = (-D/2) \ln \sigma + \text{const}. \quad (2)$$

This pioneering procedure, proposed by Avnir, Pfeifer, and Farin [91, 108, 109] was adopted for the determination of D for silicas [110, 111], clays [112], carbonaceous materials [113–116], metals and metal oxides [117], polymers [118], zeolites [119], and soils and soil minerals [92].

In the present review we discuss some historically most important methods of D determination based on single adsorption isotherm measurements. Since this subject has been already partially discussed by others [27–34] we only pay

attention to papers published in the late 80's and later concentrating on pore and surface fractal dimension. The results of different methods of D calculation using standard static adsorption measurements are presented by means of new numerical algorithms. For the estimation of the fractal dimensions from a single adsorption isotherm, well-known fractal analogs of FHH (Frenkel–Halsey–Hill) [29, 96–99], n-BET (Brunauer–Emmett–Teller) [92–95], FRDA (Fractal Analogue of Dubinin–Astakhov equation) [100–105, 121–126], and GFnBET (Generalized Fractal n-BET) [106, 107, 126] equations are used.

The calculation of the fractal dimension is fast and simple, and D is a very convenient measure of the comparative analysis of surface irregularity of the adsorbents.

2. METHODS OF DETERMINING THE FRACTAL DIMENSION OF SOLIDS FROM SINGLE ADSORPTION ISOTHERM DATA

2.1. Fractal Analogue of n-BET Equation (fn-BET)

The Brunauer–Emmett–Teller (n-BET) model of adsorption is one of the most common and popular tools for surface analysis. This 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 [85] for surface area estimation despite many well-known drawbacks (*i.e.* lack of consideration of both energetic and geometric heterogeneities, overestimation of surface area, and so on). The fractal analogue of the n-BET (fn-BET) equation was developed by Fripiat and co-workers [95], the details can be found in [94]. In the present paper the fractal analogue of the n-BET equation obtained on the basis of the molecular approach is used for describing the data of nitrogen adsorption isotherms. Thus, the surface coverage is defined as:

$$\frac{N}{N_{\text{mono, fn-BET}}} = \frac{C \sum_{i=1}^n i^{2-D} \left(\sum_{j=1}^n x^j \right)}{1 + C \sum_{i=1}^n x^i} \quad (3)$$

where $x = p/p_0$ is relative pressure; C and $N_{\text{mono, fn-BET}}$ are the fn-BET constant and monolayer capacity, respectively; n is the limited number of adlayers formed. The numerator in Equation (3) is equal to:

$$\left[\sum_{j=1}^n x^j + 2^{2-D} \sum_{j=2}^n x^j + 3^{2-D} \sum_{j=3}^n x^j + \dots + n^{2-D} x^n \right]. \quad (4)$$

For $D = 2$ this equation reduces to the classical n-BET form [94, 95]:

$$\frac{N}{N_{\text{mono, n-BET}}} = \frac{C \sum_{i=1}^n x^i}{1 + C \sum_{i=1}^n x^i}. \quad (5)$$

A detailed analysis of the applicability and properties of the fractal analogues of the BET and FHH adsorption equations was given by Pfeifer and co-workers [127]. They also showed that the fractal analogue of the BET equation should be applied for so-called “mass fractals”, as also pointed out by others [31, 128]. Equation (3) assumes that all adsorption sites have the same energy, and, simultaneously, geometric irregularities exist. This is far from reality, therefore, some authors tried to modify the fractal BET equation assuming that Equation (3) can be treated as a kernel in the GAI (‘global adsorption isotherm’) formula (Equation (1)) [93, 129] and linking it with different energy distribution functions to arrive to, for example, Langmuir–Freundlich or Dubinin–Radushkevich adsorption isotherm equations.

Fripiat [95] suggested a simple method of the fractal dimension evaluation by comparing 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 relative pressures (*i.e.* $0.06 \leq x \leq 0.2$). As an example, Figure 1 shows the application of this method for experimental nitrogen ($T = 77.5$ K) adsorption data measured on two systems: TN330 carbon black, and A200 silica (experimental details can be found in [81, 82, 106, 107, 126]).

Comparison of the 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 case of A200 silica the comparative analysis is difficult since the generated adsorption isotherms converge. However, Fripiat's comparative method suggests a rather small value of D equal to ca. 2.3. Therefore, Fripiat's method of finding D [92–95] is a very rough approximation. The problems associated with the application of this method can be circumvented by fitting the fractal analogue of n-BET equation to experimental adsorption isotherm data using a genetic algorithm developed by us [126, 130–135]. Results of fitting by classical and fractal n-BET equations in the range of the pressure $0.06 \leq x \leq 0.2$ are presented in Figure 2 and in Table 1.

Both systems are described by the models very well,

Table 1. The Values of the Parameters Characterizing the Pore Structures of TN330 and A200 Adsorbents, Calculated from Nitrogen Adsorption/Desorption Isotherms.

Adsorption isotherm equation	Parameter	Adsorbent	
		TN330	A200
fn-BET $0.06 < p/p_s < 0.2$	$N_{\text{mono, fn-BET}}$, mmol g ⁻¹	0.714	2.28
	N	6	5
	C	169.8	72.4
	D	2.048	2.125
	SSD	2.316×10^{-6}	1.173×10^{-4}
n-BET $0.06 < p/p_s < 0.2$	$N_{\text{mono, n-BET}}$, mmol g ⁻¹	0.708	2.224
	n	20	20
	C	186.464	83.145
	SSD	2.427×10^{-6}	3.01×10^{-4}
	Surface area, m ² g ⁻¹	67.95	213.57
GFnBET $p/p_s < 0.48$ (for TN330) $p/p_s < 0.82$ (for A200)	N_t , mmol g ⁻¹	0.917	1.45
	n	4	34
	A_0	1.366	0.607
	A_1	-0.139	-0.113
	A_2	0.061	0.037
	D	2.061	2.999
	SSD	0.014	0.0098
f-FHH $0.17 < p/p_s < 0.91$	κ_{FHH}	1.491	1.432
	D	2.615	2.617
	SSD	0.013	0.014
f-FHH $0.2 < p/p_s < 0.92$	κ_{FHH}	1.481	1.433
	D	2.607	2.618
	SSD	0.034	0.013
f-FHH $0.38 < p/p_s < 0.94$	κ_{FHH}	1.431	1.417
	D	2.579	2.606
	SSD	0.117	0.051
f-FHH $0.4 < p/p_s < 0.96$	κ_{FHH}	1.349	1.414
	D	2.539	2.605
	SSD	0.382	0.047
f-FHH $0.54 < p/p_s < 0.98$	κ_{FHH}	0.950	1.358
	D	2.379	2.578
	SSD	4.123	0.205

especially carbon black TN330. Moreover, the values of some equation parameters obtained during the minimization process are similar (see Table 1). Fractal n-BET shows that the adsorption on the surface of TN330 carbon black is characterized by a fractal dimension close to 2.0. In the case of A200 silica the value of the surface fractal dimension is greater than for TN330, and it is 2.13. In Figure 3, results for ten runs of the algorithm are shown.

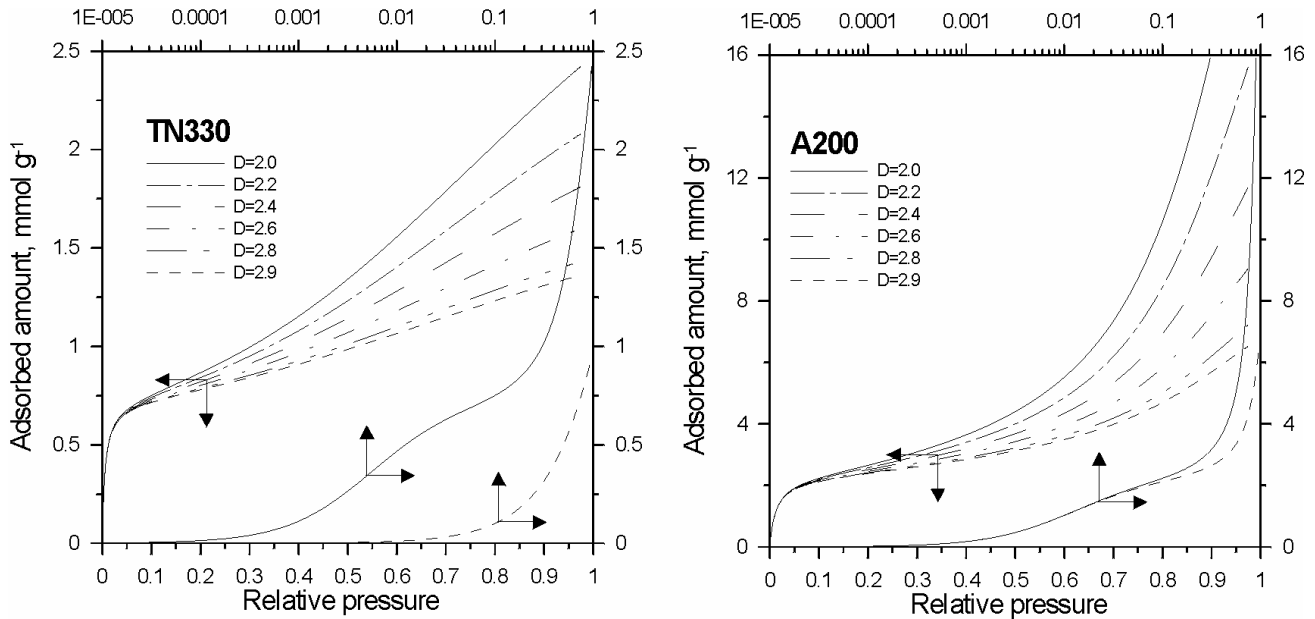


Figure 1. Application of Fripiat's method [94, 95] - data generated on the basis of fn-BET (Equation (3)) for nitrogen adsorption isotherms on the TN330 carbon black and A200 silica, and for different values of D .

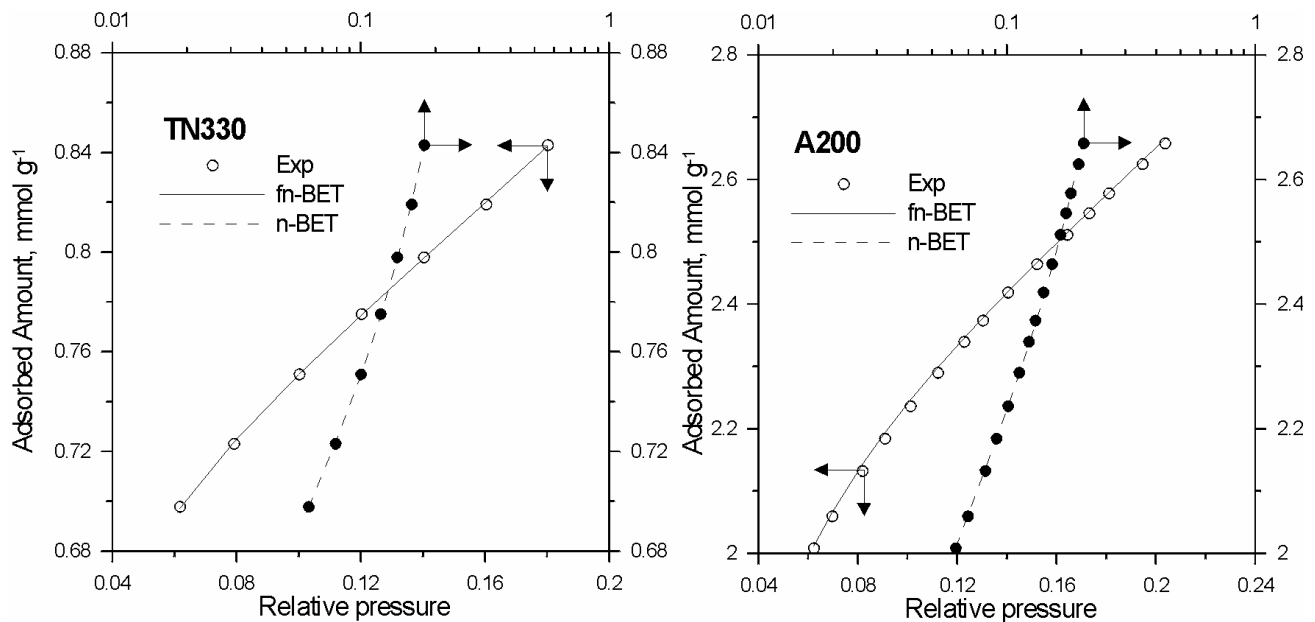


Figure 2. Experimental (points) and theoretical (lines) data obtained by fitting of the n-BET (Equation (5)) and fractal n-BET (Equation (3)) equations to nitrogen adsorption data on the TN330 carbon black and A200 silica.

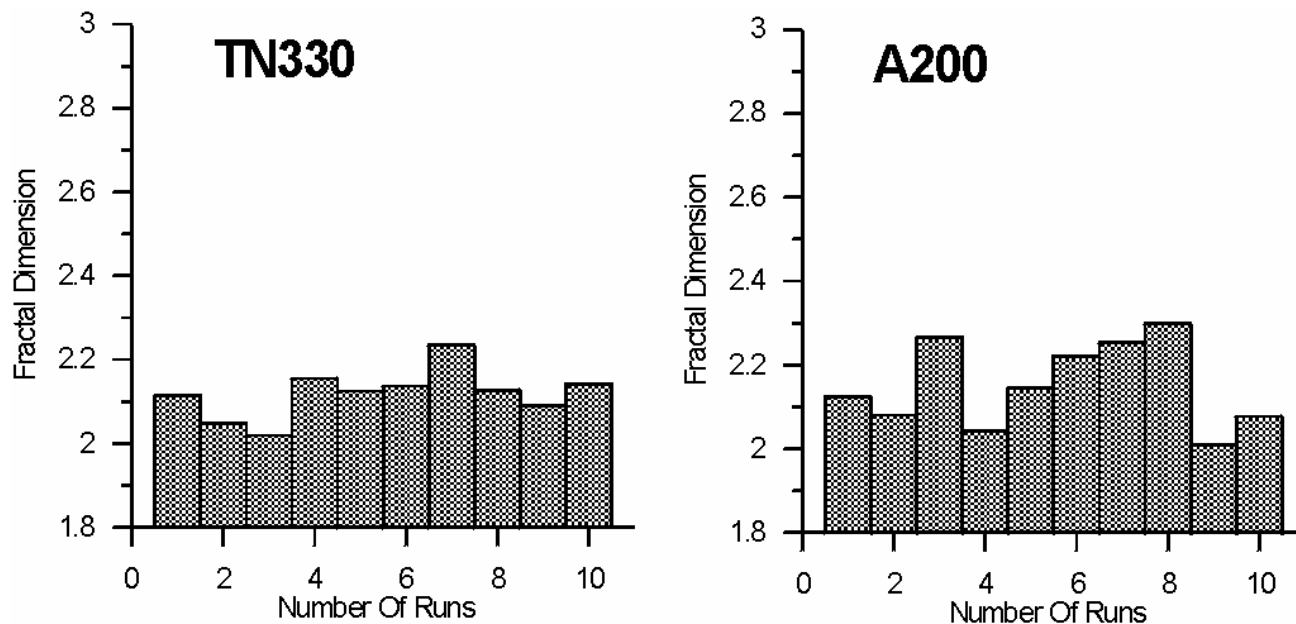


Figure 3. Estimated values of the fractal dimensions on the basis of the fractal *n*-BET equation (Equation (3)), applying the SGA algorithm (the program was started ten times for each system).

2.2. Fractal Analogue of FHH Equation (f-FHH)

The first approach, mentioned above, is based on the argument that multilayer coverage induces progressive smoothing of the solid surface [96–99]. 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 [96–99]. This is verified in 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 form [96–99, 136]:

$$\frac{N}{N_{\text{mono, f-FHH, VdW}}} = \kappa_{\text{FHH}} [\ln(p_0/p)]^{-1/m} \quad \text{and} \quad m = 3/(3 - D), \quad (6)$$

where κ_{FHH} and $N_{\text{mono, f-FHH, VdW}}$ are f-FHH constant and monolayer capacity, respectively. In case of a flat surface, $D = 2$ and $m = 3$, as is expected from the classical FHH equation. For larger substrate–adsorbate interactions the VdW regime is not valid. In such a case, the so-called capillary condensation regime (CC) is applicable and Equation (6) is transformed as [96–99]:

$$\frac{N}{N_{\text{mono, f-FHH, CC}}} = \kappa_{\text{FHH}} [\ln(p_0/p)]^{-1/m} \quad \text{and} \quad m = 1/(3 - D). \quad (7)$$

This yields $m > 1$ for $D > 2$.

Equation (7) was developed by Avnir and Jaroniec [137–139] based on the Dubinin–Radushkevich adsorption isotherm equation. However, the way these authors had derived Equation (7) (and the corresponding thermodynamic equations) was controversial as suggested by Venkatraman and co-workers [111] as well as by results of our recent studies [100–105, 121–126, 140].

Since the FHH method is very simple, it has been widely used for determining the surface fractal dimension of solids, particularly in the case of activated carbons [141, 142], aerogels [128, 143–146], metal films, oxides, and related compounds [147–149], aluminophosphates [150], and thermally treated peat soils [151, 152].

From the numerical point of view, the fitting of the parameters of the fractal FHH equation to experimental data is simple. As an example, Figure 4 shows the applicability of the modification of the Nedler and Mead simplex algorithm [133, 153] for this purpose.

To escape from local minima, a multi-start technique was adopted. Again, the nitrogen adsorption data on TN330 carbon black and A200 silica are analyzed. The fractal FHH analysis (Figure 4) leads to larger values of D for the both tested materials than those obtained from the fn-BET equation. In case of A200 silica, the f-FHH equation predicts a D value around 2.6. We should like to point out that this D value is practically independent of the chosen relative pressure range (see Table 1 and Figure 4). On the contrary, for TN330 carbon black the value of D is larger and it does depend on the assumed relative pressure range (it changes between 2.38–2.62 (see Table 1 and Figure 4)).

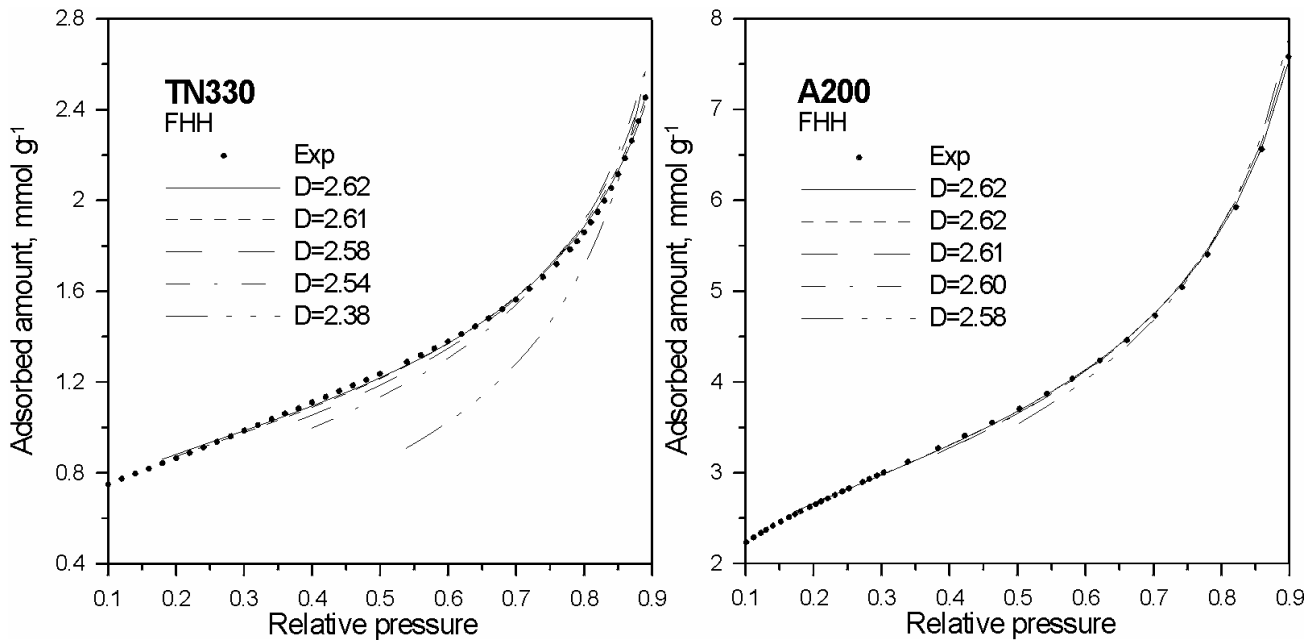


Figure 4. Application of the fractal FHH (Equation (7)) equation for the analysis of the experimental data of nitrogen adsorption on TN330 carbon black and A200 silica. The computations were performed for different pressure ranges (Table 1).

2.3. Neimark’s Thermodynamic Method

In Neimark’s method [90, 154, 155] it is assumed that the surface area (S) of a fractal solid (proportional by the fundamental relation to the D value) can be calculated by an equation developed by Kiselev [90, 154, 155]:

$$S = \frac{RT}{\sigma} \int_{N_1}^{N_h} (-\ln(p/p_0)) dN \tag{8}$$

where N is the adsorbed amount, N_h is the adsorption when (p/p_0) tends to 1, and N_1 is the adsorption at the beginning of the hysteresis loop. Therefore, the surface fractal dimension can be, in this method, calculated by applying [141]:

$$\ln S = (D - 2) \ln(\ln(p_0/p)) + \text{const.} \tag{9}$$

Thus, this method can be applied in the range of an adsorption isotherm where capillary condensation occurs. In fact, the agreement between D values calculated by this method and from the fractal FHH equation is achieved in cases where an adsorption process is dominated by capillary condensation forces [141]. The modifications of Neimark’s method applied for D calculation from porosimetry data was suggested by Kozak and co-workers [156]. Wang and Li [157] proposed a

modified Neimark's method that accounts for the effect of the volume encompassed by the liquid-gas interface in the process of capillary condensation. This modified method has been recently applied by Kukovec and co-workers for the description of surface fractal properties of silicates [158].

2.4. Generalized Fractal n-BET Equation (GFnBET)

Recently developed by Rudziński and co-workers [106, 107], the generalized fractal n-BET equation (GFnBET) seems to be a powerful tool for studying both energetic and geometric heterogeneity of porous solids. According to the above-mentioned authors, real solid surfaces are never perfectly regular and never totally irregular (the real surface is mixed between regular and fractal surface). Such surfaces are called "partially correlated" and represent an intermediate state between two extreme models of surfaces. The fractal pore size distribution is defined as:

$$\frac{\partial N}{\partial r} = \frac{C(3-D)r^{2-D}}{[1+r^{3-D}]^2} \quad (10)$$

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

$$\lim_{r \rightarrow 0} \left(\frac{\partial N}{\partial r} \right) = C(3-D)r^{2-D} \quad (11)$$

a new fractal pore size distribution is transformed to the classical Pfeiffer and Avnir fractal pore size distribution [91]. On the other hand, in the limit $r \rightarrow \infty$:

$$\lim_{r \rightarrow \infty} \left(\frac{\partial N}{\partial r} \right) = C(3-D)r^{D-4}. \quad (12)$$

Taking into account both energetic and geometric heterogeneities of a solid surface, Rudziński and co-workers [106, 107] developed two new fractal equations (GFnBET) defined as follows:

$$\ln \left[\frac{N_t/(M\phi)}{1-N_t/(M\phi)} \right] = A_0 - A_1 kT \ln X - A_2 (kT)^2 [\ln X]^2 \quad (13)$$

$$\ln \left[\frac{N_t}{M\phi} \right] = A_0 - A_1 kT \ln X - A_2 (kT)^2 [\ln X]^2 \quad (14)$$

where the unknown polynomial coefficients are defined by the formulae:

$$A_0 = \varepsilon_0 (\alpha - \beta \varepsilon_0) \quad (15)$$

$$A_1 = 2\beta \varepsilon_0 - \alpha \quad (16)$$

$$A_2 = \beta. \quad (17)$$

In Equations (13 and 14) $\phi(x)$ is a function describing multilayer formation on the fractal surfaces proposed by Fripiat [94, 95]:

$$\phi(x) = \frac{1}{X} \sum_{i=1}^n i^{2-D} \sum_{j=i}^n x^j \quad (18)$$

where $X = \sum_{i=1}^n x^i$; k is Boltzmann constant; T temperature; M is monolayer capacity; N_t a value of adsorption; and

α , β , ε_0 are parameters characterizing the energetic heterogeneity of an investigated porous material. The adsorption energy (ε) distributions on fractal surfaces corresponding to Equations (13) and (14), respectively, are defined by:

$$\chi(\varepsilon) = (3-D) \left[\left(\frac{\partial F}{\partial \varepsilon} \right)_{\varepsilon_0} + \left(\frac{\partial^2 F}{\partial \varepsilon^2} \right)_{\varepsilon_0} (\varepsilon - \varepsilon_0) + \dots \right] \times \frac{\left(\frac{1}{r_0} \right)^{3-D} \exp \left\{ (3-D) \left(\frac{\partial F}{\partial \varepsilon} \right)_{\varepsilon_0} (\varepsilon - \varepsilon_0) + \frac{3-D}{2} \left(\frac{\partial^2 F}{\partial \varepsilon^2} \right)_{\varepsilon_0} (\varepsilon - \varepsilon_0)^2 + \dots \right\}}{\left[1 + \left(\frac{1}{r_0} \right)^{3-D} \exp \left\{ (3-D) \left(\frac{\partial F}{\partial \varepsilon} \right)_{\varepsilon_0} (\varepsilon - \varepsilon_0) + \frac{3-D}{2} \left(\frac{\partial^2 F}{\partial \varepsilon^2} \right)_{\varepsilon_0} (\varepsilon - \varepsilon_0)^2 + \dots \right\} \right]^2} \quad (19)$$

$$\chi(\varepsilon) = (3-D)r_0^{3-D} \left[\left(\frac{\partial F}{\partial \varepsilon} \right)_{\varepsilon_0} + \left(\frac{\partial^2 F}{\partial \varepsilon^2} \right)_{\varepsilon_0} (\varepsilon - \varepsilon_0) + \dots \right] \times \exp \left\{ -(3-D) \left(\frac{\partial F}{\partial \varepsilon} \right)_{\varepsilon_0} (\varepsilon - \varepsilon_0) - \frac{3-D}{2} \left(\frac{\partial^2 F}{\partial \varepsilon^2} \right)_{\varepsilon_0} (\varepsilon - \varepsilon_0)^2 + \dots \right\} \quad (20)$$

where

$$\alpha = (3-D) \left(\frac{\partial F}{\partial \varepsilon} \right)_{\varepsilon_0} \quad \beta = \frac{3-D}{2} \left(\frac{\partial^2 F}{\partial \varepsilon^2} \right)_{\varepsilon_0} \quad r_0 = \exp(-\varepsilon_0), \quad (21)$$

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

Obviously, the fractal pore size distribution can be obtained on the basis of Equation (10) or by the simple relations:

$$\frac{\partial V}{\partial r} = -\chi(\varepsilon) \frac{d\varepsilon}{dr} \quad (22)$$

$$r = \exp \left\{ -F(\varepsilon_0) - \left(\frac{\partial F}{\partial \varepsilon} \right)_{\varepsilon_0} (\varepsilon - \varepsilon_0) - \frac{1}{2} \left(\frac{\partial^2 F}{\partial \varepsilon^2} \right)_{\varepsilon_0} (\varepsilon - \varepsilon_0)^2 - \dots \right\}. \quad (23)$$

Figure 5 shows the effect of changing the D values on the adsorption isotherm (plotted in the coordinates of Equation (14)) and the energy distribution (Equation (20)).

The system studied is aerosil A200 silica. It is noticed, that D practically does not influence the obtained energy distributions. This is in accordance with the model numerical studies of Sokołowska and co-workers [159, 160].

In the present study, a special hybrid algorithm was constructed to fit the GFnBET equation to the experimental data. Such a two-step algorithm consists of classical Monte Carlo (*i.e.* a pure random search method) and evolutionary searching procedures. The first method was used for a global exploration of the search space. The second method starts from the best solution obtained by Monte Carlo and sequentially approaches the global minima of the defined functional (*i.e.* objective function, fitness function, and so on). In contrast to fractal n-BET and FHH equations, the generalized fractal n-BET equation (GFnBET) proposed by Rudziński and co-workers [106, 107] leads to larger differences in D values for the investigated samples. For TN330 carbon black, the isotherm shape suggests a very smooth surface. However, for A200 silica, Rudziński's method predicts D approaching 3.0 (*i.e.* a strong surface irregularity). The obtained results are similar to those published by Rudziński and co-workers (see Table 2) since we used the same pressure range for fitting the generalized fractal n-BET equation (see Table 1).

Table 2. Energetic Parameters Found by Solving the Equation System (Equations (18)–(20)). The Values are Shown in Parenthesis.

Adsorbent	α kJ mol ⁻¹	β (kJ mol ⁻¹) ²	ε_0 kJ mol ⁻¹	ε_1 kJ mol ⁻¹	SSD
TN330	0.594 (0.505)	0.061 (0.069)	3.728 (3.41)	-1.139 (-0.025)	0.014 (0.014)
A200	0.32 (0.199)	0.037 (0.038)	2.803 (1.145)	-1.524 (-1.49)	0.0098 (0.011)

The differences for the A200 sample are caused by the different forms of the functionals minimized (*i.e.* we optimize one parameter (N_i) more than Rudziński's group). As seen from Figures 6 and 7, our proposed new algorithm for fitting the GFnBET equation to experimental data leads to very stable results especially in case of TN330 carbon black.

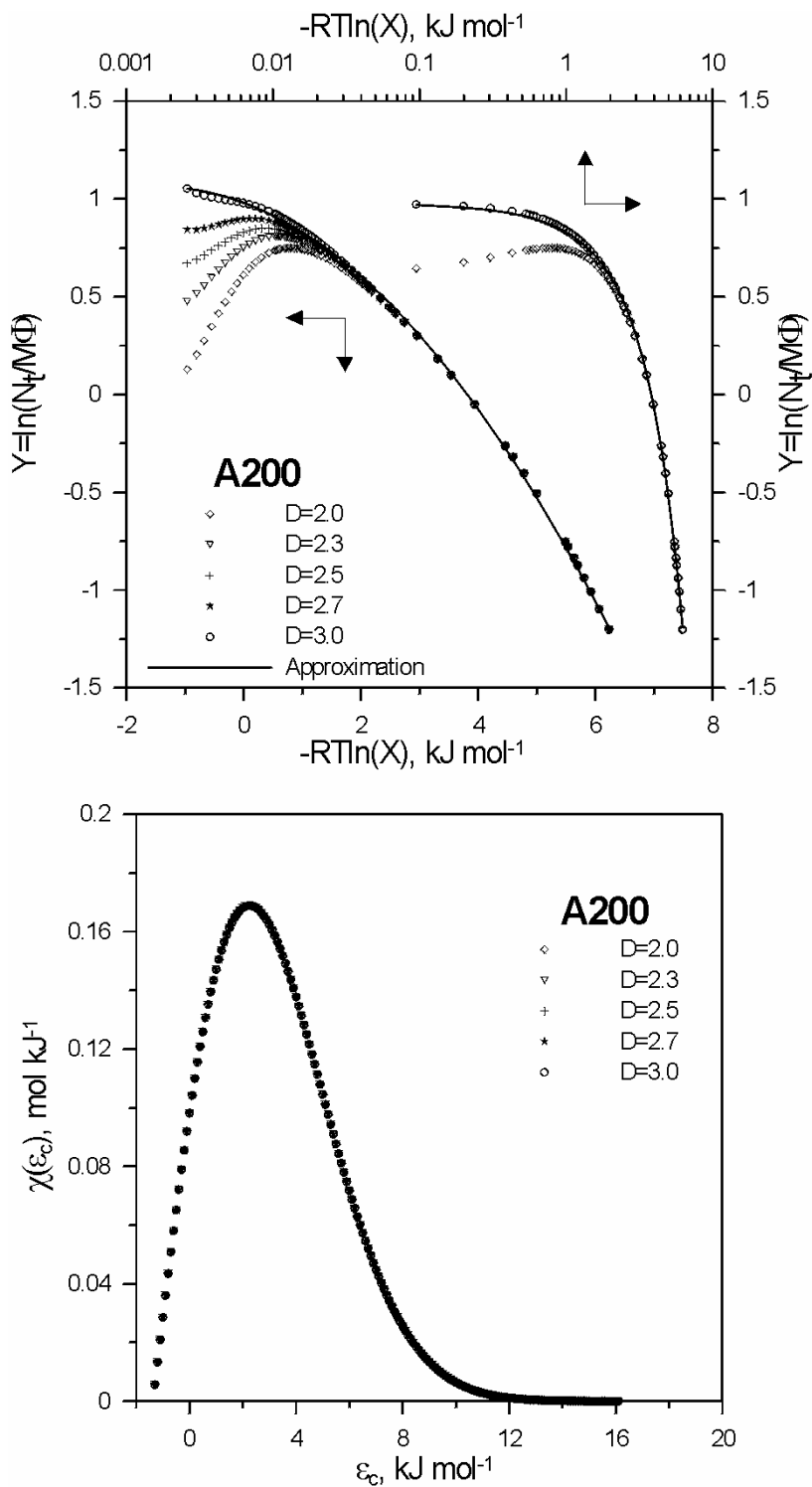


Figure 5. Influence of D on the adsorption isotherm (plotted in the coordinates of Equation (14)) and the energy distribution (Equation (20)) for arbitrarily chosen D values (studied adsorbent - A200 silica).

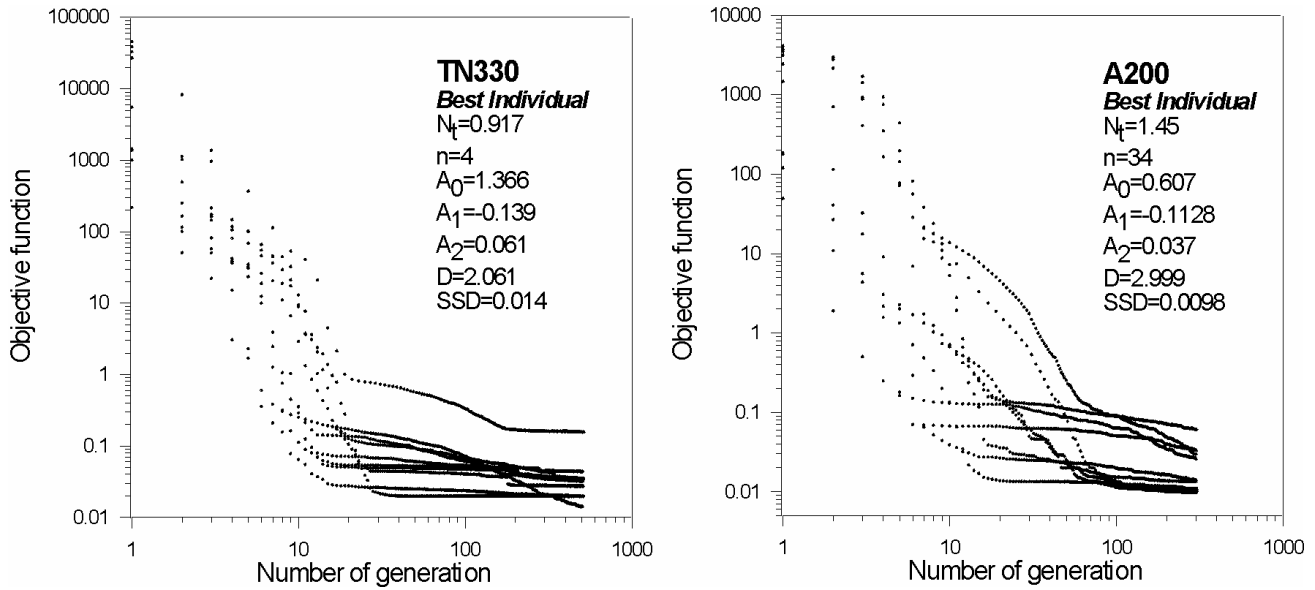


Figure 6. The changes of objective function during the minimization process (GFnBET equations - Equations (13) and (14), and the new algorithm described in the text) for TN330 carbon black and A200 silica. The computations were repeated ten times.

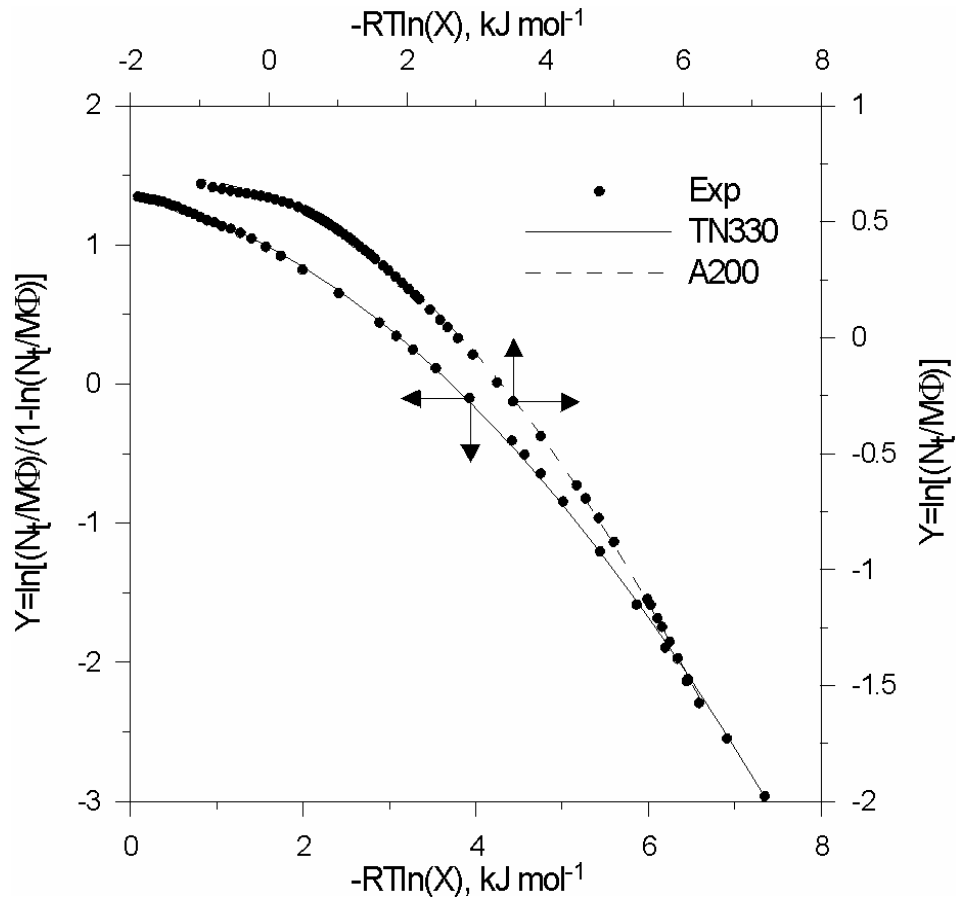


Figure 7. Application of GFnBET equations (i.e. Equations (13) and (14)) to correlate the experimental data on the TN330 carbon black and A200 silica.

Rudziński and coworkers proposed a classical exhaustive search for the estimation of the GFnBET equation parameters. On the other hand, our procedure combines the exhaustive search method with a parabolic approximation. The obtained results are shown as contour plots in Figure 8.

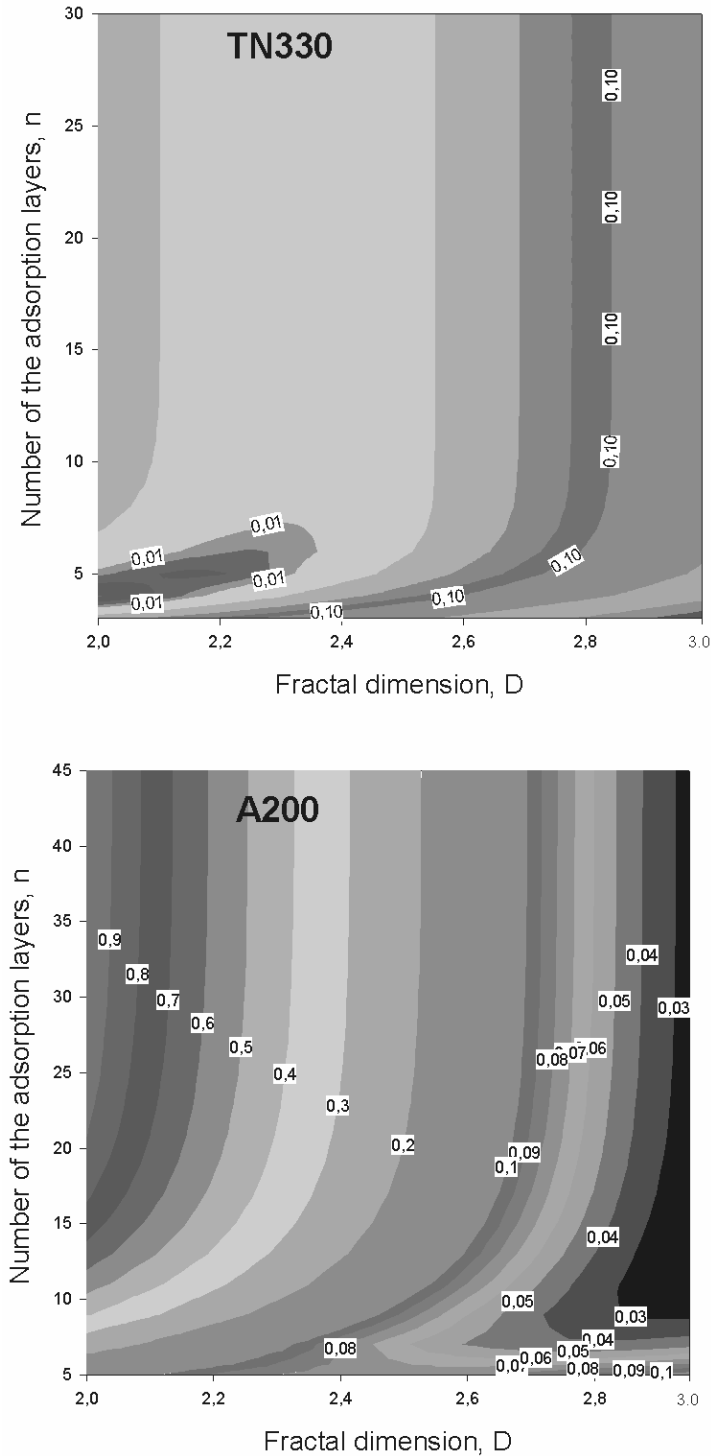


Figure 8. Searching of the minima of GFnBET equations (Equations (13) and (14)) for both systems considered by the proposed novel algorithm (exhaustive search method combined with parabolic approximation).

One can also see that the TN330 carbon black is characterized by a well-developed single global minimum. That minimum is characterized by a very low value of fractal dimension ($D \rightarrow 2.0$) and a small number of adsorption layers ($n \cong 4$). In case of A200 silica, the contour plot has completely different features. The minimum is broader and not so clearly visible, but it is placed at a larger value of the fractal dimension ($D \rightarrow 3.0$) and a larger number of adsorption layers ($n \cong 20$). Table 2 shows the energy distribution parameters calculated using Equation (19), and Figure 5 the plot for A200. Since the results are almost the same as published by Rudziński and coworkers, the graphical representation for TN330 can be omitted.

Finally, we emphasize that the main advantage of the method of Rudziński *et al.* [106, 107] is that their 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 other methods will be the subject of a forthcoming study.

2.5. Fractal Analogue of the Dubinin–Astakhov Adsorption Isotherm Equation (FRDA)

The fractal analogues of the Dubinin–Astakhov (FRDA) and Dubinin–Radushkevich (FRDR) adsorption isotherm equations were developed [100–105, 121–126, 140] based on the concept of the global adsorption isotherm equation (GAI) (Equation (1)), the Pfeiffer–Avnir function (see Equation (35) below) [91] and the DR or DA isotherm equations [161–164]. Wojsz and Terzyk [104, 140] were first to assume in their theoretical fractal adsorption model that the fractal properties of a microporous solid occur within a finite limit of pore sizes [37, 165]. The integration of GAI in the finite limit of microporosity (the real system is finite: $\Omega_x \in \langle x_{\min}, x_{\max} \rangle$) leads to the equation [100–105, 121–126, 140]:

$$\theta = \frac{\rho}{n} (\mu A^n)^{\frac{D-3}{n}} \left[\gamma \left(\frac{3-D}{n}, x_{\max}^n \mu A^n \right) - \gamma \left(\frac{3-D}{n}, x_{\min}^n \mu A^n \right) \right] \quad (24)$$

where θ is the degree of micropore filling, $A = -\Delta G = RT \ln(p_0/p)$ R the universal gas constant, T temperature, p_0 and p are the saturation vapor pressure and the equilibrium pressure of the adsorbate, respectively, γ is the incomplete gamma function, and n is the parameter. Moreover:

$$\rho = \frac{3-D}{x_{\max}^{3-D} - x_{\min}^{3-D}} \quad (25)$$

and

$$\mu = (\beta \kappa)^{-n} \quad (26)$$

where D is the pore fractal dimension for pores with minimal and maximal slit half-widths between x_{\min} and x_{\max} , β is the affinity coefficient and κ is a constant [8, 166, 168].

As was shown previously, if $n = 2$, the fractal DR equation is obtained. The main properties of both fractal analogues (FRDR and FRDA) together with an application for the description of experimental adsorption data and related thermodynamic formulas were shown elsewhere [100–105, 121–126, 140]. As an example, Figure 9 shows numerically generated (by Equation (24)) benzene adsorption isotherms ($T = 293$ K, $\beta = 1$) for different D values, the corresponding distributions of the adsorption potentials, and changes of adsorption enthalpy and entropy. They are similar in shape to the experimental ones.

Figure 10 shows an application of the FRDA isotherm equation for the description of cyclohexane adsorption data determined by Dubinin and Polstyanov [100, 103, 124, 169–171]. The experimental details as well as the procedure of minimization were given in [100, 103, 104, 124, 140]. The FRDA Equation (24) describes experimental adsorption, enthalpy, and entropy data reasonably well, especially in the low pressure area, where the theory of volume filling of micropores is accepted to be valid. Table 3 shows the parameters of Equation (24) obtained from the fit of the adsorption isotherm and the corresponding enthalpy data (Figure 10) for systems studied by Dubinin and Polstyanov [100, 103, 124, 169–171].

Table 3. Parameters of FRDA Equation Applied for the Simultaneous Description of Adsorption Isotherm and Enthalpy for the Systems Studied by Dubinin and Polstyanov [169–171].

Carbon	Adsorbate	W_0 [cm ³ /g]	n	x_{\min} [nm]	x_{\max} [nm]	D
AG	benzene	0.394	2.165	0.520	1.100	2.505
	cyclohexane	0.348	2.104	0.590	1.051	2.451
SA	benzene	0.475	2.070	0.505	0.523	2.890
	cyclohexane	0.437	1.988	0.461	0.500	2.915
SK	benzene	0.806	2.167	0.450	1.200	2.300
	cyclohexane	0.702	2.002	0.456	1.100	2.297

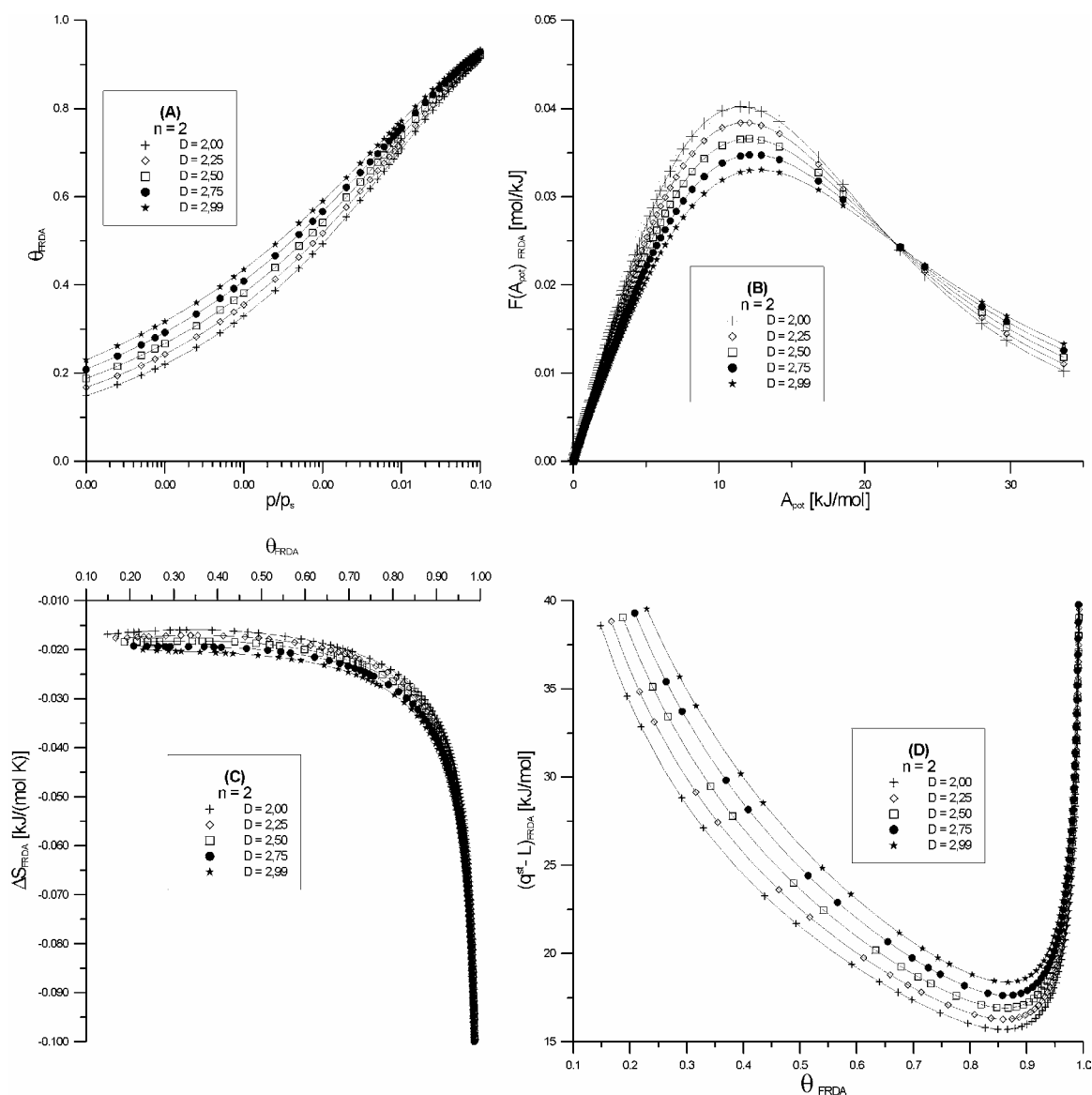


Figure 9. Adsorption isotherms (A), differential adsorption potential distributions (B), differential entropies of adsorption (C), and 'pure' enthalpies of adsorption (D) of benzene generated using the FRDA equation.

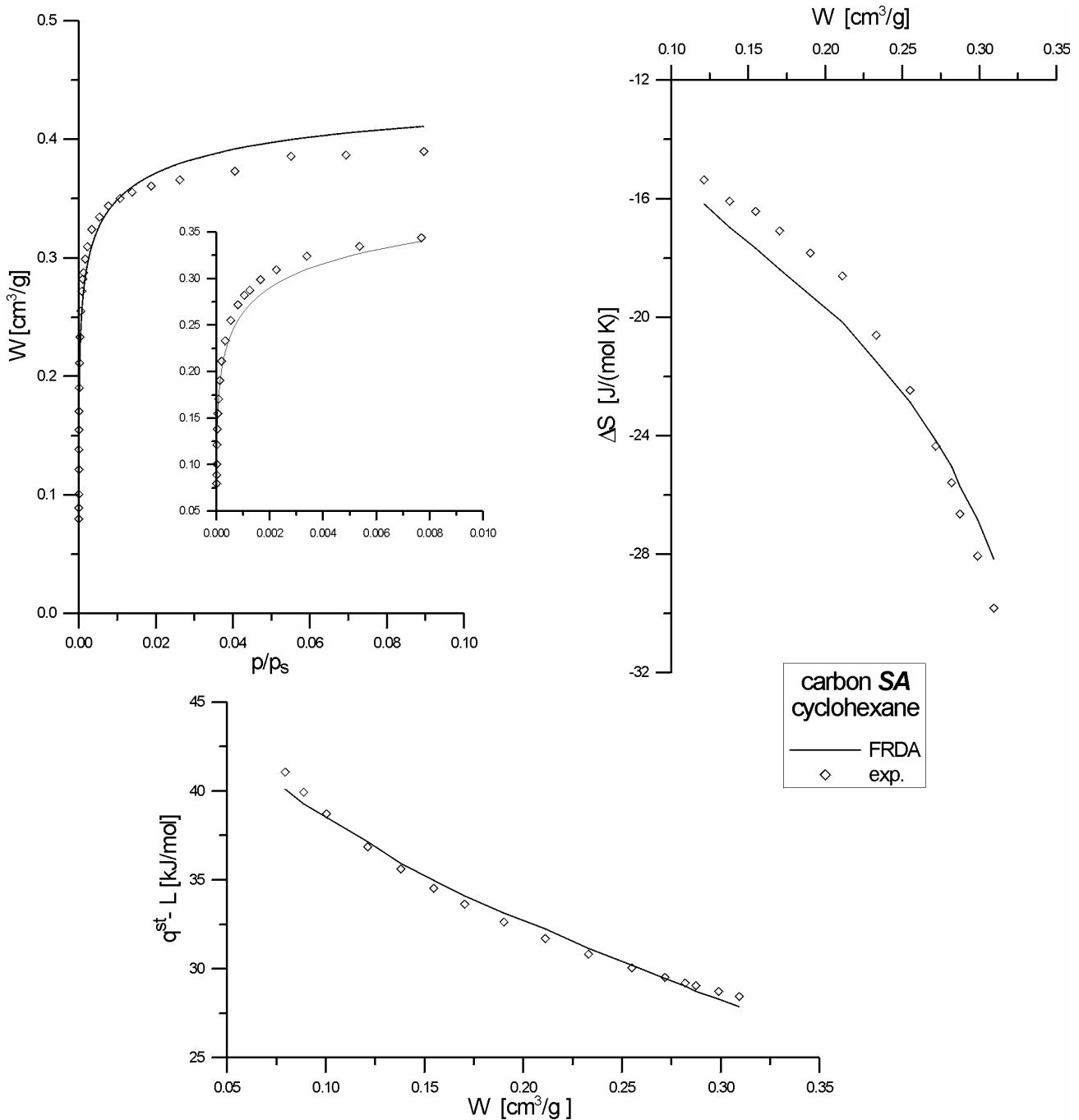


Figure 10. Comparison of experimental data (points - 'exp.') with theoretical adsorption isotherms ('FRDA') for the system: cyclohexane-carbon SA at 353.15 K.

Based on Equation (24) it was possible to postulate the relation between the parameters of the DA adsorption isotherm equation and the value of the fractal dimension. Different relations of this type have been proposed [82, 139, 172–174] and applied by other authors [175–177]. It was shown [102, 103] that for strictly microporous carbons ($x_{\min}=0.2295$ nm; $x_{\max}=1.0000$ nm) the description of the nitrogen adsorption isotherm data ($T=77.5$ K) by the typical DA isotherm can lead to the evaluation of the pore fractal dimension of micropores by means of the following relation:

$$D = \frac{E_0(15.3897 - 3.6083 \times 10^{-4} n_{DA}) - 283.3356 + 6.3019 \times 10^{-3} n_{DA}}{E_0(0.9396 + 0.1054 n_{DA}) + 1.0557 - 1.8407 n_{DA}} \quad (27)$$

where E_0 and n_{DA} are parameters obtained from fitting the experimental nitrogen adsorption data by the typical DA equation. Relationships of this type have been also proposed in [82, 139, 172–173], however Equation (27) seems to be the most advanced one. Figure 11 graphically compares Equation (27) with the relations proposed by other authors.

Application of Equation (27) for experimental data can be found in [102, 103]. Equation (27) gives reasonable fractal dimension values for strictly microporous carbons, *i.e.* for the E_0 values $21.2436 < E_0 < 23.1579$ and for $1.9099 < n_{DA} < 2.7542$ ($2.00 \leq D < 2.99$). For the other relations some unrealistic D values can be observed (see the captions of Figure 11 in this paper and Table 4 in [102]).

Table 4. The Fit of JCh Adsorption Isotherm Equation (Equation (33)) to FRDA (Equation (24)) Data for Two Values of n . DC is the Determination Coefficient.

FRDA (Equation (24))		JCh (Equation (33))				
D	n_{FRDA}	n_{JCh}	q	v	D	DC
2	3	3.012	2632.398	-0.3618	1.078	0.9999
2.2	3	3.005	2632.398	-0.4128	1.235	0.9999
2.4	3	2.991	2632.397	-0.4562	1.373	0.9999
2.6	3	2.970	2632.398	-0.4924	1.493	0.9999
2.8	3	2.939	2632.398	-0.5215	1.594	0.9999
2.99	3	2.901	2632.398	-0.5424	1.672	0.9999
2	2	2.064	369.1407	0.10854	0.712	1
2.2	2	2.061	369.1410	0.03184	0.874	1
2.4	2	2.050	369.1411	-0.02855	1.009	1
2.6	2	2.029	369.1413	-0.07138	1.116	1
2.8	2	2.000	369.1418	-0.09933	1.198	1
2.99	2	1.968	369.1418	-0.11682	1.262	1

The FRDA adsorption isotherm Equation (Equation (24)) has been successfully applied for the characterization of the heterogeneity of different carbonaceous materials [87, 88, 180–183]. More recently Rozwadowski and co-workers applied this equation for determining the fractal dimension of different micro-mesoporous zeolites [184]. Unfortunately, for benzene adsorption data this equation led to some strange results (see for example Tables 4 and 5 in [184] where the values of D were as high as 1500 or sometimes even negative). They concluded that the studied adsorbents cannot be considered as fractals. On the other hand, Pfeifer [185] pointed out that “zeolites and expandable clays, on length scales above the respective pore width, have $D_{pore} = 3$ and thus are equally pore, mass, and surface fractals”. Also the application of the molecular probe method [119] led others to the statement that zeolites are fractals possessing D in the range 2.37–2.92. Rozwadowski and co-workers did not specify the range of relative pressures they applied for the fitting of Equation (24) to experimental data. What is also important, since the adsorbents studied possess a large amount of mesopores in their structure, the experimental isotherms should be corrected [186, 187] to obtain the values of adsorption in micropores as Equation (24) is only applicable for micropores. This was not done in [184] and they also did not

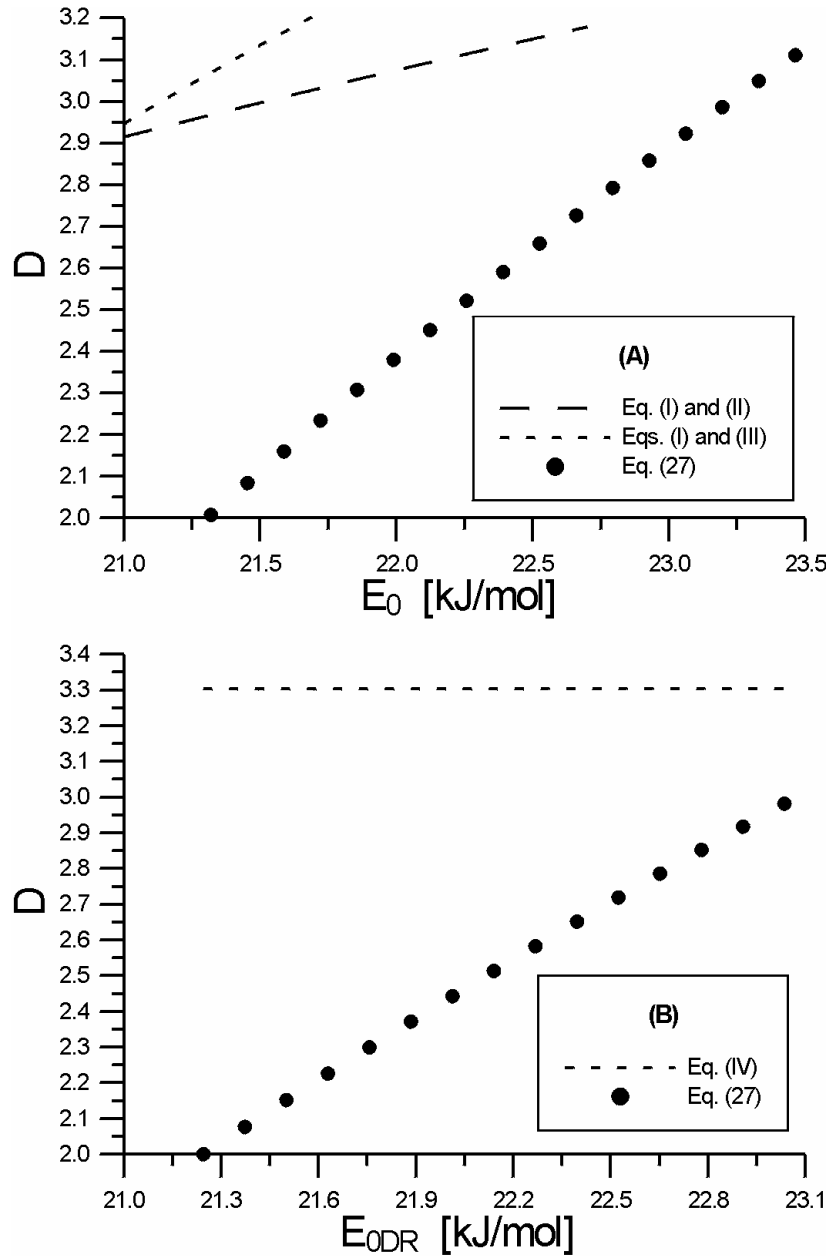


Figure 11. Comparison of the predicted fractal dimension values ((A) - using relations given by Equation (I) [139, 172] where the average half-width ($x_{\#}$) is deduced from E_0 by means of Equations (II) [167] and/or (III) [178, 179]; (B) - using relations given by Equation (IV) [82, 173]) with D values calculated from Equation (27) [102, 103].

$$D = 6.44 - 6.17x_{\#} \quad (I)$$

$$x_{\#} = \frac{\kappa}{E_0} \quad (II)$$

$$x_{\#} = \frac{15}{E_0} + \frac{2852.5}{E_0^3} + 0.014E_0 + 0.75 \quad (III)$$

$$D = 3 - \frac{24}{E_{0FR}} \left(1 - \frac{E_{0FR}}{E_{0DR}} \right) \quad (IV)$$

specify the type of algorithm used for fitting the experimental data by Equation (24). It is also important that these authors did not say anything about the range of minimal and maximal slit half-widths (x_{\min} and x_{\max}) applied in the calculations. It is obvious, and was pointed out in almost all review papers dealing with fractals [27–35], that in real systems self-similarity is always restricted to a finite range of length scales, namely $x_{\min} < x < x_{\max}$ [185]. Lately Wojsz and Terzyk applied Equation (24) for describing fractality of some zeolites [140] and showed that this range can be very narrow (for example for *A*-type zeolite 0.33–0.5 nm, $D = 2.71$, respectively; similar D values *i.e.* 2.57 and 2.88 were obtained for zeolite 5 *A* by Sze and Lee [119]). It should be also mentioned, that the effective pore diameter of *A*-type zeolites varies in the range 0.29–0.5 nm, and depends on the cationic form. Therefore it is obvious that in theoretical models dealing with adsorption on fractals the range (cut-offs) of fractality should also be treated as adjustable parameters.

3. THE PFEIFER–AVNIR FRACTAL PORE SIZE DISTRIBUTION AS A SPECIAL CASE OF THE GAMMA TYPE ONE, AND THE NEW DERIVATION OF THE FRACTAL FHH EQUATION

For real solids different types of pore-size distributions can be observed [1–5, 14, 103, 125, 188–190]. Therefore it can be presumed that the fractal pore-size distribution is a special case of some general function. We can assume that the micropore-size distribution function $y(t)$ (where the variable t denotes the slit-pore half-width, x , or the structural parameter, B) can be written as two equivalent general forms [125]:

$$y(t) = a_{(i)}(t - t_0)^b \exp[d(t - t_0)^e] \quad (28a)$$

and/or

$$y(t) = a_{(i)}t^b \exp[dt^e] \quad (28b)$$

where the parameter $a_{(i)}$ is a factor that takes care of the normalization condition [101, 125, 191]; b , d , and e are the parameters of the pore size distribution function, and t_0 is the characteristic value of the variable t for this distribution function. Equations (28) can be reduced under some assumptions to simpler expressions [101, 125, 192], for example, to the Rayleigh-type ($b = 1$, $d < 0$, and $e = 2$), to the Maxwell–Boltzmann ($b = 0.5$, $d < 0$, and $e = 1$), to the Gaussian ($b = 0$, $d < 0$, and $e = 2$), to the gamma-type ($e = 1$) and others.

The gamma-type micropore-size distribution function (for an arbitrary value of the parameter n) proposed by Jaroniec and co-workers [138] and generalized by us can be written as:

$$J(x)_{\text{GTMon}} = \chi_{\text{GTMon}} x^{n-1} (x^n - x_0^n)^\nu \exp[-qc(x^n - x_0^n)] \quad (29)$$

where q and ν are parameters, x_0 is the characteristic value of variable x , Γ denotes the gamma function and χ_{GTMon} is a normalization factor (in Jaroniec and co-workers' case [138] it is obtained from the integration of the gamma-type MSD function (Equation (29)) from zero to infinity — $\chi_{\text{GTMon}}(0, \infty)$). The MSD function, expressed by Equation (29), can be compared with the starting and general form Equation (28a) and are derived:

$$a_{(i)} = a_{(0, \infty)} = \chi_{\text{GT}(0, \infty)} = n \frac{(qc)^{\nu+1}}{\Gamma(\nu+1)} \quad (30a)$$

$$t = x^n \quad (30b)$$

$$t_0 = x_0^n \quad (30c)$$

$$b = \nu \quad (30d)$$

$$e = 1 \quad (30e)$$

$$d = -cq. \quad (30f)$$

The parameters x and x_0 can be calculated based on the dependence of the pore-size x (for slit-like micropores) on the structural parameters [8, 125, 166], for example the characteristic energy of adsorption:

$$x = \kappa / E_0 . \tag{31}$$

The problem of normalization of the gamma-type MSD function (Equation (29) for $x_0 = 0$) was presented previously by Gauden and Terzyk [125]. A general conclusion of [125] was that if adsorption proceeds by a micropore filling mechanism and the structural heterogeneity is described in the finite region (val_{min}, val_{max}), then for all possible values of the MSD functions parameters the generated isotherms (the gamma-type adsorption isotherm (GTAI)) belong to the first class of the IUPAC classification — *i.e.* Langmuir-type behavior is observed:

$$\Theta_{GT(x_{min}, x_{max})} = \frac{\left(\frac{A_n}{\beta^n q} + 1\right)^{-(v+1)} \left[\gamma\left(v+1, \left(\frac{A_n}{\beta^n} + q\right) \zeta x_{max}^n\right) - \gamma\left(v+1, \left(\frac{A_n}{\beta^n} + q\right) \zeta x_{min}^n\right) \right]}{[\gamma(v+1, \zeta \rho x_{max}^n) - \gamma(v+1, \zeta \rho x_{min}^n)]} . \tag{32}$$

For the other cases ($val \in \langle 0, \infty \rangle$):

$$\Theta_{GT(0, \infty)} = \left(\frac{A_n}{\beta^n q} + 1\right)^{-(v+1)} , \tag{33}$$

and for $val \in \langle val_{min}, \infty \rangle$:

$$\Theta_{GT(x_{min}, \infty)} = \frac{\left(\frac{A_n}{\beta^n q} + 1\right)^{-(v+1)} \left[\Gamma(v+1) - \gamma\left(v+1, \left(\frac{A_n}{\beta^n} + q\right) \zeta x_{min}^n\right) \right]}{[\Gamma(v+1) - \gamma(v+1, \zeta q x_{min}^n)]} , \tag{34}$$

erroneous and ambiguous results might be obtained [125].

On the other hand, assuming in Equation (29) that $q = 0 = x_0$ it can be shown that under some specific conditions Equation (29) reduces to the Pfeiffer–Avnir pore size distribution [91, 125]:

$$J(x)_{PA} = \chi_{PA} x^{2-D} = \frac{3-D}{x_{max}^{3-D} - x_{min}^{3-D}} x^{2-D} . \tag{35}$$

Thus, the pore fractal dimension can be written in the form:

$$D = 3 - n(v+1) . \tag{36}$$

As the acceptable values of D are $2 \leq D < 3$ (28–32, 45–51) by Equation (36) the limit values of the parameter v of the gamma-type function are [101]:

$$\begin{aligned} D = 2 &\Rightarrow v = \frac{1-n}{n} \\ D \rightarrow 3 &\Rightarrow v \rightarrow -1 . \end{aligned} \tag{37}$$

The above two relationships are true for $n > 0$ due to the assumption of the identity of the parameter n of the MSD functions and of the Dubinin–Astakhov isotherm. Due to the fact that Equations (36) and (37) have been developed from comparison of the PSD functions, they are general and do not depend on the mechanism of adsorption, *i.e.* on the type of local adsorption isotherm equation applied in GAI. Therefore, the analytical solution of the GAI with Equation (35) as the PSD given by Equation (35) leads to the FRDA adsorption isotherm Equation (Equation (24)), which is a special case of Equation (32). On the other hand, as was shown elsewhere [103, 105, 121–124], the Avnir–Jaroniec adsorption isotherm equation, equivalent to the fractal FHH one (Equation (7)), is only an approximate form of Equation (24). Avnir

and Jaroniec postulated that the fractal analogue of the FHH isotherm equation (called sometimes the AJ equation) can be derived from GAI (Equation (1)) applying the DR isotherm as a kernel and Equation (35) as the PSD function [105, 124, 137, 138]. However, since the AJ equation is only an approximation, the plots of generated adsorption isotherms in the low relative pressure range change their shapes with the change in D value, *i.e.* the I type was observed for $D \rightarrow 3$, and the II type for $D \rightarrow 2$. Therefore, the derivation of the FHH from the DR isotherm was possible because the mentioned authors assumed incorrect range of integration. In fact, the fractal analogue of the FHH equation can also be developed for example from Equation (33) (so called Jaroniec–Choma (JCh) adsorption isotherm equation [193]). As shown above, Equation (33) was also obtained assuming an unphysical range of the parameters ($val(\equiv B, E_0, \text{ and/or } x)$)

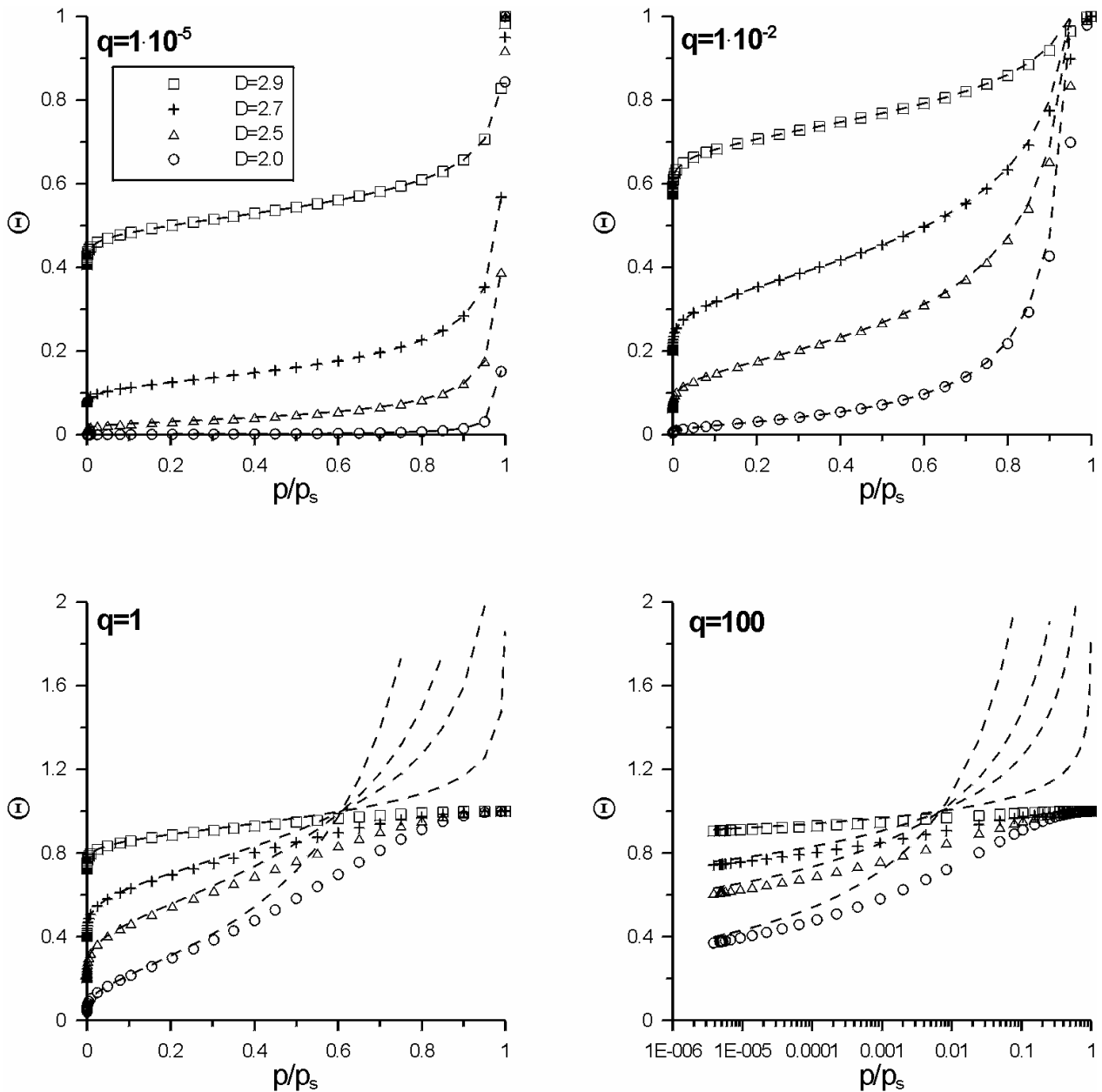


Figure 12. The comparison of low-temperature nitrogen adsorption isotherms generated numerically with Equation (38) (points) and Equation (40) (dashed lines) for different values of q and/or D .

characterizing the geometric heterogeneity of a solid (*i.e.* from zero to infinity [125]). Under some specific assumptions, this equation really reduces to the fractal FHH. One can re-write this in the following form:

$$\Theta_{GT(0,\infty)} = \left(\frac{A^n}{\beta^n q} + 1 \right)^{-(v+1)} = (\beta^n q)^{v+1} (A^n + \beta^n q)^{-(v+1)} \quad (38)$$

for small values of q the second term in bracket can be neglected (especially, for $p/p_0 \rightarrow 0$ and/or $A \rightarrow 1$) and:

$$\Theta_{GT(0,\infty)} = (\beta^n q)^{v+1} (A)^{-n(v+1)}. \quad (39)$$

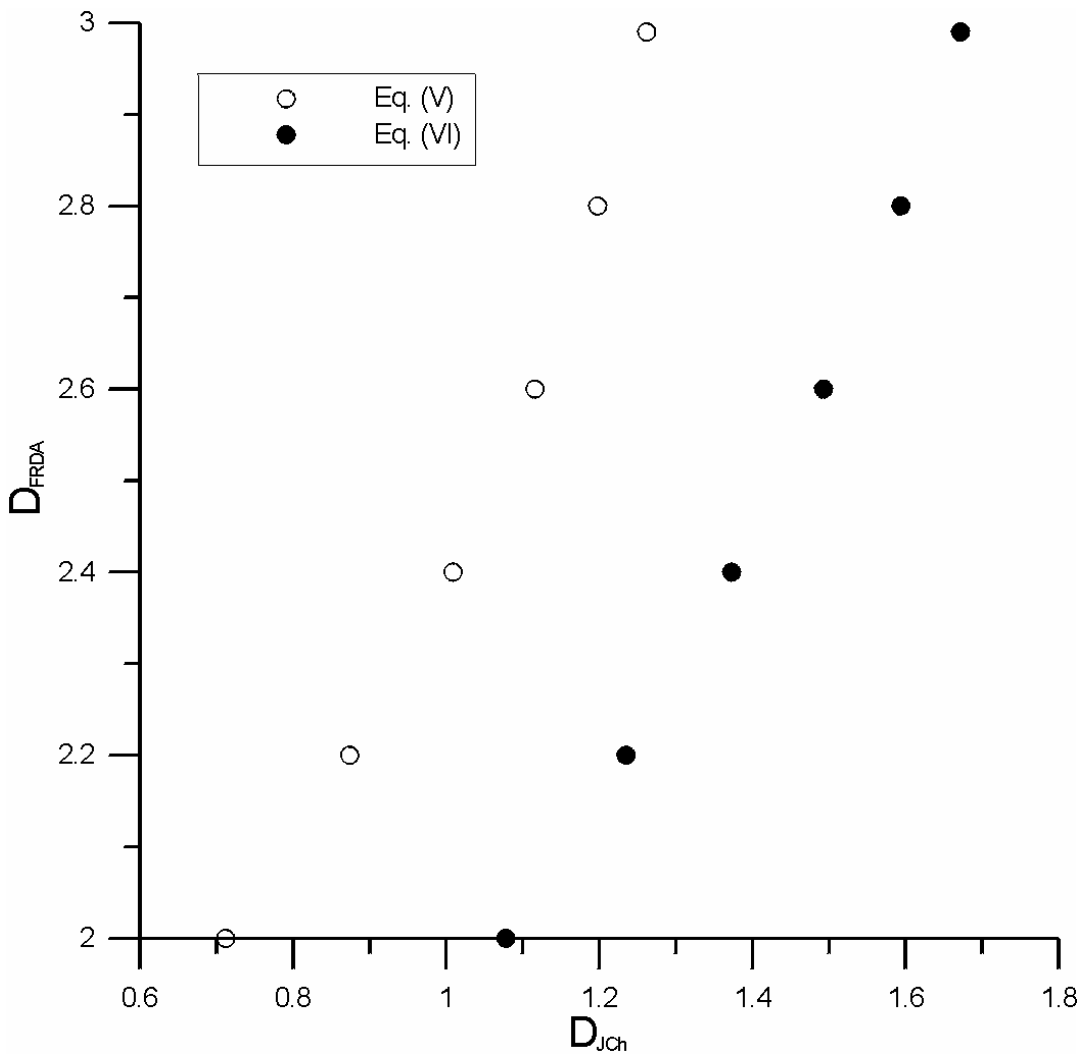


Figure 13. Results of fitting the JCh adsorption isotherm equation (Equation (33)) to FRDA (Equation (24)) data for two values of n .

$$D_{FRDA} = 0.1817 + 1.6459D_{JCh} \quad \text{for } n = 3 \quad (V)$$

$$D_{FRDA} = 0.6806 + 1.7673D_{JCh} \quad \text{for } n = 2 \quad (VI)$$

Taking into account Equation (36), and denoting $((RT)^n/(\beta^n q))^{-(v+1)} = \kappa$ one can write:

$$\Theta_{GT(0,\infty)} \approx \kappa (\ln p_0/p)^{-(3-D)}. \quad (40)$$

Equation (40) is equivalent to the above-described fractal analogue of the FHH adsorption isotherm equation described above (Equation (7)). Figure 12 shows the graphical comparison of the equations (JCh (Equation (33)) and f-FHH (Equation (7) or (40))).

Nitrogen ($\beta = 0.32$) adsorption isotherms at 77.5 K were generated numerically applying Equation (33) (or Equation (38)) in the range of relative pressure $4 \cdot 10^{-6} - 1$ ($n = 2$) for different values of q (from $1 \cdot 10^{-5}$ up to 100) and D (from 2 up to 2.9). In Figure 12 they are compared with the plots of FHH adsorption isotherms (Equation (40)). It is noticed that an increase in the value of D (at constant q) leads to the gradual increase in adsorption, however, a change in the shape of the isotherm into the I type occurs at very high values of q . On the other hand, according to Equation (24), the changes in D between 2 and 3 lead to the increase in adsorption, however, the isotherm is still of the I class. The general conclusion of this part is that the JCh equation can be simplified to fractal FHH ones for low values of the q parameter. However, this simplification is only possible since the JCh isotherm is derived for unphysical range of pore sizes. The fitting of FHH to JCh decreases with the increase in q , thus, if a change in adsorption isotherm from II to I type is observed, the FHH equation does not describe the data adequately, as observed in our previous studies [103, 124].

Finally, we tried to answer the question how far the assumptions, made during the derivation of Equation (33), influence the description of exact data, *i.e.* the data generated by analytically solved GAI equation. Assuming the fractal nature of an activated carbon, 12 adsorption isotherms were generated from the FRDA Equation (Equation (24)). As above, nitrogen at 77.5 K was assumed as the adsorbate. The range of relative pressure was $1 \cdot 10^{-7} - 0.999$. Minimal and maximal slit half-widths (x_{\min} and x_{\max}) were assumed as equal to 0.15 and 1 nm, respectively (the range of microporosity following IUPAC classification [194]). Then, the obtained isotherms were fitted by JCh Equation (Equation (33)). The values of D were calculated from Equation (36). The results are collected in Table 4.

For both cases, *i.e.* for FRDR and FRDA, a very good correlation between the two equations exists. However, the assumptions made during the derivation of the JCh Equation (Equation (33)) lead to lower D values than those assumed in the analytical solution. It can be shown that both groups of D are correlated (Figure 13).

4. THE COMPARISON OF D VALUES DETERMINED BY DIFFERENT METHODS

Different authors performed the comparative analyses of D values obtained by various methods. Sokołowska *et al.* [195] compared the D values calculated from adsorption data applying the f-FHH isotherm equation and porosimetry data. The value of D determined from mercury porosimetry was higher than that obtained from adsorption data. They concluded that micro- and mesopores belong to different fractality regions. The same authors found a more complicated situation for kaolin [196]. Different regions of fractality of porous silicas were also studied by Fadeev *et al.* [197]. They compared D values from mercury porosimetry, gas adsorption (nitrogen and benzene), and chemisorption of chlorosilanes. They concluded that the term “fractality” depends on the range of the studied pore diameters. For example, the silicas studied by them have fractal surfaces in the range of cross-sectional areas of the investigated adsorbates; while in the range of larger pores they can hardly be considered as a porous fractal. Sahouli and coworkers [198] compared D obtained from SAXS and from the f-FHH equation, for different carbon blacks. They found differences, and concluded that the length scales over which the fractal dimension is calculated by the two methods is different. For the SAXS measurements it extends from 5 to 38 nm, the f-FHH equation corresponds to the range from 0.35 nm (nitrogen monolayer) to several nm. In other words, a similar conclusion to that given by Sokołowska and coworkers [195] was obtained, *i.e.* the differences are caused by the different scales of the surface texture analyzed by the two methods. On the other hand, Weidler and coworkers [199] observed a reasonable agreement between D values from SAXS and adsorption data for two synthetic goethites. Esquena *et al.* [200] compared D values of silica calculated from the f-FHH equation, from Neimark’s method, and from the modified Neimark’s method [157]. They concluded that f-FHH and modified thermodynamic methods always lead to physical values of D ($2 \leq D < 3$). In contrast, the thermodynamic method leads in some cases to non-physical D values ($D > 3$). The modified thermodynamic method

leads to significantly lower D values than the f-FHH equation and thermodynamic method. On the other hand, a good agreement was obtained between the modified Neimark's method and the f-FHH equation for adsorption on silicates [158]. Meng and coworkers [201] obtained similar D values for titania aerogels using adsorption data applying the f-FHH equation, and a molecular probe method. The same group documented similarities between D calculated from the f-FHH equation and from the thermodynamic methods for two mesoporous titania aerogels [143]. Darmstadt *et al.* [202] showed that three different models, namely the fractal BET, the fractal FHH, and the thermodynamic method lead to almost the same D . An agreement between fractal BET and FHH methods was also reported by Khalili and coworkers for different carbons [203]. Malekani and coworkers [204] compared the values of D obtained from SAXS, NMR, and the molecular probe method (D was calculated from the monolayer capacities of five molecules adsorbed on clay minerals). They observed large differences and stated that each technique measures a D value through phenomena that "see" the material from a different perspective. For example, the scattering probes the chemical heterogeneity through contrasts in electron density, the adsorption method probes the physical surface irregularity, while NMR deals with the mass fractal distribution of certain structural sites. Similar conclusions were drawn by Mathieu and coworkers [205] from the analysis of the texture of gels. They compared D calculated from the f-FHH equation and SAXS (the latter method always leads to larger D). The differences were attributed to the physical differences in the object described by the two methods, *i.e.* the overall structure scanned by scattering methods, and the structure of the voids which form the pore network identified by nitrogen adsorption-desorption. Ma and coworkers [206] also obtained lower D values from adsorption data than from SANS. They explained in detail the obtained differences and suggested that the properties of liquid are altered in small pores and, moreover, the volume occupied by the adsorbed film is not identical to that probed by SANS. Furthermore, one should remember that while SANS or SAXS "see" the total porosity of a system (including so-called closed pores), the adsorbed molecules can only penetrate the pores accessible for them, *i.e.* larger than the molecular diameter and, obviously, open.

A similar analysis was given by Blacher and *et al.* [207]. Jarzębski and co-workers [208] showed that in some cases (adsorption on silica aerogels) SAXS and f-FHH analyses lead to similar D values, and, for some, they do not. The similarity occurs as the surface roughness increases. Therefore, these authors recommended a simultaneous application of the two methods to obtain a coherent and complete picture of the pore structure.

A comparative analysis of D determined from adsorption data of different adsorbates was performed by Sokołowska and coworkers. They analyzed the similarities [209] and differences [210] in D values obtained from nitrogen and water adsorption data as well as from mercury porosimetry on soils. Sato *et al.* [211] showed that D obtained from benzene and nitrogen adsorption data strongly depend on the probe size (despite similarities in molecular diameters). They concluded that the differences in the probe molecule-pore wall interaction energy affect the observed behavior. On the other hand in our recent studies (Table 3) D values calculated from adsorption data of benzene and cyclohexane adsorbed onto two carbons are almost the same.

An interesting theoretical analysis of the methods of D determination was given by Jaroniec and co-workers [212, 213]. For the series of argon adsorption isotherms simulated by DFT method they calculated D applying different methods based on adsorption isotherm analysis. They confirmed the validity of the f-FHH and Neimark's method; however they showed that the results of the D calculation depend on the range of analyzed pore sizes.

As is shown above, for some cases, a good agreement between the D determinations from different methods can be observed. Sometimes, differences occur, and a partial explanation has been given above. However, in some cases it must be realized that different methods can lead to quite different fractal dimensions. This problem was also discussed by Lee and Lee [29]. They pointed out that D obtained, for example, from pore-size distribution analysis is not the same as the surface fractal dimension. It is obvious that different types of the fractal dimension can characterize a solid (*i.e.* mass, pore, surface, and edge [31, 185]). It is well known that SAXS method can distinguish between mass and surface fractals; however, in the light of the results presented above, questions arise about the boundary between pore and surface fractality. In our opinion, this problem needs further theoretical studies, especially since DFT [214, 215] as well as other advanced methods of porosity calculation (for example the method of Nguyen and Do [19, 216–218]) assume the homogeneity of pore walls.

5. A NEW “HYBRID” MODEL OF ADSORPTION ON FRACTALS

It can be postulated that Equation (24) adequately represents the adsorption process in micropores of fractals, due to the realistic boundaries of integration. Thus, it can be postulated that the adsorption isotherm in the porous system of a fractal solid can be written as a hybrid model:

$$a_{FR} = a_{0mic} \frac{3 - D_p}{n(x_{max}^{3-D_p} - x_{min}^{3-D_p})} (\mu A^n)^{(D_p-3)/n} \left[\gamma \left(\frac{3 - D_p}{n}, x_{max}^n \mu A^n \right) - \gamma \left(\frac{3 - D_p}{n}, x_{min}^n \mu A^n \right) \right] + a_{0ex} \kappa_{FHH} (\ln p_s/p)^{(D_s-3)}. \quad [41]$$

If a_{0mic} is small the f-FHH term dominates, and, on the contrary, for microporous systems the external surface is small and the FRDA equation is assumed to describe the adsorption process. Equation (41) offers a means to take into account the difference between pore (D_p) and surface (D_s) fractal dimensions. Figure 14 illustrates the behavior of Equation (42) for $D_s = D_p$. The applicability of this equation for actual adsorption data will be reported in future studies.

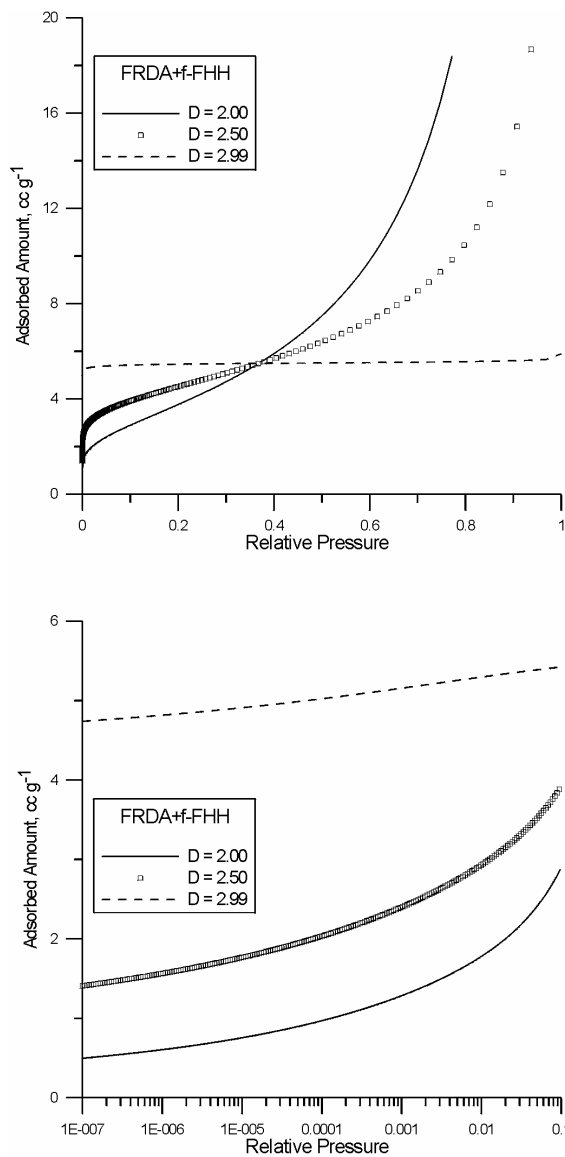


Figure 14. “Hybrid” model (Equation (42)) – the influence of the fractal dimension value (assuming $D_p = D_s$). Parameters used for the calculation (nitrogen T = 77.5 K): $x_{min} = 0.15$ nm, $x_{max} = 1.0$ nm, $n = 2$, $a_{0mic} = 1$ cc g⁻¹, $\kappa = 12$ kJ nm/mole; $\beta = 0.32$; $a_{0ex} = 0.3$ cc g⁻¹, $\kappa_{FHH} = 1.5$.

6. CONCLUSIONS

Fractal geometry offers a new interesting tool for the characterization of heterogeneous solids. The fractal dimension D can be determined by several independent (including spectroscopic) methods; however the comparison of fractal dimensions calculated from different adsorption models is problematic. Further studies in this field are necessary, especially an advanced theoretical and experimental comparative analysis of the different methods of D determination for solids possessing different types of porosity.

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LIST OF ACRONYMS AND SYMBOLS

A	The adsorption potential
$a_{(i)}$	A parameter of Equations (28a) and (28b)
A_0	The coefficient defined by Equation (15)
A_1	The coefficient defined by Equation (16)
A_2	The coefficient defined by Equation (17)
AFM	Atomic Force Microscopy
b	The parameter of the pore-size distributions (28a) and (28b)
C	A proportionality constant in Equations (10)–(12)
C	The constant of BET and fn-BET equations (5) and (3)
const.	A constant
D	The fractal dimension
d	The parameter of the pore-size distributions (28a) and (28b)
D_p	The pore fractal dimension
D_s	The surface fractal dimension
e	The parameter of the pore-size distributions (28a) and (28b)
E_0	The characteristic energy of adsorption of Dubinin–Astakhov and/or Dubinin–Radushkevich adsorption isotherm equation
F	A function describing the features of an adsorption system - Equations (19) and (20)
$f(z)$	The distribution function of the parameter z - Equation (1)
f-FHH	Fractal analog of the FHH adsorption isotherm - Equations (6) and (7)
FHH	Frenkel–Halsey–Hill adsorption isotherm equation
FRDA	Fractal Analogue of the Dubinin–Astakhov adsorption isotherm equation
FRDR	Fractal Analogue of the Dubinin–Radushkevich adsorption isotherm equation
GAI	Global adsorption isotherm equation
GFnBET	Generalized Fractal n-BET equation (3)
IUPAC	International Union of Pure and Applied Chemistry
$J(x)_{\text{GTMon}}$	The general gamma-type pore-size distribution - Equation (29)
$J(x)_{\text{PA}}$	The Pfeifer–Avnir pore-size distribution - Equation (35)

M	The monolayer capacity in Equation (13)
m	The parameter of the f-FHH equations (6) and (7)
N	Adsorption value - Equations (3), (6), (7), (10)–(12)
n	The parameter of the FRDA Equation (24)
N_1	Adsorption value at the beginning of the hysteresis loop - Equation (8)
n-BET	Brunauer–Emmett–Teller adsorption isotherm Equation (5)
n_{DA}	The parameter of the Dubinin–Astakhov adsorption isotherm equation
N_h	Adsorption value at the end of the hysteresis loop - Equation (8)
n_m	Monolayer capacity - Equation (2)
$N_{\text{mono, f-FHH, CC}}$	The monolayer capacity of the f-FHH Equation (7)
$N_{\text{mono, f-FHH, VdW}}$	The monolayer capacity of the f-FHH Equation (6)
$N_{\text{mono, fn-BET}}$	The monolayer capacity of the fn-BET Equation (3)
NMR	Nuclear Magnetic Resonance
N_t	Adsorption value - Equations (13) and (14)
p	Pressure
p_0	Saturated vapor pressure
PIXE	Proton-Induced X-ray Emission
q	The parameter of the general gamma-type pore-size distribution - Equation (29)
r	The radius of a (spherical) molecule - Equations (10)–(12)
R	The universal gas constant
S	The surface area of a fractal solid - Equation (8)
SANS	Small-Angle Neutron Scattering
SAXS	Small-Angle X-ray Scattering
SEM	Scanning Electron Microscopy
t	A slit-pore half-width or the structural parameter B
T	Temperature
t_0	The characteristic value of the variable t - Equation (28a)
VdW	Van der Waals
x	Relative pressure - Equations (3)–(5)
x	slit half-width
x_{max}	Maximal slit half-width
x_{min}	Minimal slit half-width
$y(t)$	The micropore-size distribution function defined by Equations (28a) and (28b)
z	The parameter describing the heterogeneity of an adsorbent - Equation (1)

GREEK SYMBOLS

α	The parameter characterizing the energetic heterogeneity of an adsorbent - Equation (21)
β	The parameter characterizing the energetic heterogeneity of an adsorbent - Equation (21)
β	The affinity coefficient in Equation (26)
γ	The incomplete gamma function

Γ	The gamma function
ε	The adsorption energy - Equations (19) and (20)
ε_0	The parameter characterizing the energetic heterogeneity of an adsorbent - Equation (21)
θ	The degree of micropore filling - Equation (24)
$\theta_i(p)$	Global (experimental) adsorption isotherm Equation (1)
$\theta_{\text{theor}}(z,p)$	The local adsorption isotherm in GAI Equation (1)
κ	The constant of in Equation (26)
κ_{FHH}	The constant of the f-FHH Equations (6) and (7)
μ	The parameter of the FRDA equation (24) defined by the Equation (26)
ν	The parameter the general gamma-type pore-size distribution - Equation (29)
ρ	The constant of a porous adsorbent defined by Equation (25)
σ	Molecular size, cross sectional area of an adsorbate - Equations (2) and (8)
ϕ	The function defined by Equation (18)
χ_{GTMon}	The normalization factor of the general gamma-type pore-size distribution - Equation (29)
$\chi_{\text{GT}(0,\infty)}$	The normalization factor of the general gamma-type pore-size distribution - Equation (29) integrated from zero to infinity
χ_{PA}	The normalization factor of the Pfeifer-Avnir pore-size distribution - Equation (35)

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