



The new correlation between microporosity of strictly microporous activated carbons and fractal dimension on the basis of the Polanyi–Dubinin theory of adsorption

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Abstract

Adsorption on microporous fractal carbons is investigated in terms of their microporous structure. The structure is characterised by the micropore-size distribution (MSD) proposed by Pfeifer and Avnir, and the considerations are limited only to the range of micropores, following the IUPAC classification. Beginning with numerical studies performed for model solids with different microporosity, a new relationship between the parameters of the Dubinin–Astakhov equation (adsorption energy, E_0 , and parameter, n_{DA}) and the fractal dimension (D) is derived. The obtained results are compared with those published by Jaroniec et al. and Ehrburger-Dolle. The general conclusion is that if adsorption proceeds by a micropore filling mechanism and the pore size distribution function is assumed to be the Pfeifer and Avnir one, the relationship between D and parameters of the Dubinin–Astakhov equation is more complicated than has been presumed up to the present. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Activated carbon is a very complex system from a structural point of view. The graphite-like aromatic microcrystallites create slit-shaped micropores [1] and their presence changes considerably the sorption properties, comparing to non-porous solids. Very fine pores of various sizes, that substantially affect sorption properties contribute significantly to the geometrical nonuniformity of the microporous solid. The micropore size distribution function (MSD) can be calculated from the adsorption measurements carried out at low concentrations of adsorbates (i.e. nitrogen [2–5], carbon dioxide [6] and/or benzene [7,8]).

Adsorption on microporous adsorbents can be described by the theory of volume filling of micropores (TVFM) —

developed by Dubinin and co-workers [9–12] — which occupies an important position in the theory of physical adsorption. TVFM has been developed in different ways. For example, Stoeckli [13] postulated that the original DR equation should be applied to homogeneous micropore systems and heterogeneous micropore structures should be described by a certain distribution of the characteristic energy. Some authors [7,14] have continued investigations on this subject. However, in spite of the successful application of derived equations, a detailed description of the surface and structural heterogeneity of active carbons is still far from complete [15–17].

Fractal geometry, which characterises structural heterogeneity using fractal dimension D , offers a new possibility of description of microporous solids [18–21].

Thus, the evaluation of microporosity is still a key problem. Therefore, the aim of the current paper is to provide a correlation between the fractal dimension and the parameters characterising the structural heterogeneity of micropores. This type of investigation can enrich the knowledge about the nature of porous solids and adsorption processes proceeding on them.

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2. Theoretical part

The starting point of our derivation is a general, integral adsorption isotherm equation of the form [22,23]:

$$\Theta(A) = \int_{\Delta_x} \theta_1(x, A) f_1(x) dx \quad (1)$$

where $\Theta(A)$, $\theta_1(x, A)$ are the overall and local adsorption isotherm, respectively; $f_1(x)$ is the micropore-size distribution function and Δ_x is the pore size integration range (in the case of slit-like micropores, x is their half-width). A is defined as $-\Delta G$, the negative change of the Gibbs' free energy:

$$A = RT \ln(p_s/p) \quad (2)$$

where T is temperature, R is the universal gas constant, p_s and p are the saturation vapour pressure and the equilibrium pressure of the adsorbate, respectively.

Assuming the existence of the relationship connecting characteristic adsorption energy E_0 and x , we can rewrite Eq. (1) in the following form [24]:

$$\Theta(A) = \int_{\Delta_z} \theta_1(z, A) F_1(z) dz \quad (3)$$

where $z = 1/E_0$. The micropore size distribution $F_1(z)$ is a distribution of the adsorption energy.

Several functions (for example: fractal, gamma, Gaussian, exponential, Rayleigh and others) [7,24–26] have been considered for representation of the pore size distribution (this distribution can be the function of the width and/or the energy of adsorption, the inverted energy of adsorption etc.). In this paper we are limiting our consideration to the first function mentioned above, derived by Pfeifer and Avnir [25,26]:

$$f_1(x) = \chi_x x^{2-D} \quad (4)$$

where D is the fractal pore dimension (a number between 2 and 3) and to the second one, proposed by Sircar [27] and the next used by Jaroniec and Choma [28]:

$$F_1(z) = \chi_z z^{\nu-1} \exp[-(\rho z)^n] \quad (5)$$

where ν , ρ and n are parameters of a gamma-type distribution function.

The pore-size distribution function given by Eqs. (4) and (5) should be normalised to unity and the normalisation factor (χ) should be greater than zero. One can make the assumption that the mathematical description of adsorption on microporous solids can be represented by the integral equation (Eqs. (1) and (3)) in the integration limit from zero to infinity. However, due to boundary conditions of the adsorbate–adsorbent system (x or z), it has been widely accepted to set a limit to a finite integration range. Thus the gamma function can be normalised in two different ranges of integration:

- in the range proposed by Jaroniec et al. [23,24]:

$$\chi_{z(\text{JCh})} = \frac{n_{\text{JCh}} \rho^\nu}{\Gamma\left(\frac{\nu}{n_{\text{JCh}}}\right)} \quad (0 < z < \infty) \quad (6)$$

- and in micropore region:

$$\chi_{z(\text{Ov})} = \frac{n_{\text{Ov}} \rho^\nu}{\left[\gamma\left(\frac{\nu}{n_{\text{Ov}}}, z_{\text{max}}^n \rho^n\right) - \gamma\left(\frac{\nu}{n_{\text{Ov}}}, z_{\text{min}}^n \rho^n\right) \right]} \times (z_{\text{min}} < z < z_{\text{max}}) \quad (7)$$

where z_{min} and z_{max} are the lower and upper cut-off limits; Γ and γ are gamma function and incomplete gamma function, respectively; n_{JCh} and n_{Ov} are the parameters.

In our opinion, taking into account the slit-like model of an active carbon micropore, the general integral adsorption isotherm equation should be normalised in the finite limit of the half-width of micropores, $(x_{\text{min}}, x_{\text{max}})$, where the lower limit (x_{min}) is the minimum slit-like pore size in which adsorption occurs by a micropore filling mechanism and x_{max} is the maximal slit half-width, which is equal to 1 nm (the upper limit of micropore diameters ($2x_{\text{max}}$), according to the IUPAC classification [29]). It is certain that the limits ($0 < x < \infty$ and/or $0 < z < \infty$) do not make any sense for the real solids (for example, activated carbons).

Contrary to the gamma-type distribution function, the Pfeifer–Avnir one (Eq. (4)) can be normalised only from x_{min} to x_{max} [30]:

$$\chi_x = \frac{3-D}{x_{\text{max}}^{3-D} - x_{\text{min}}^{3-D}} \quad (x_{\text{min}} < x < x_{\text{max}}). \quad (8)$$

To apply Eq. (1) to microporous solids we choose arbitrarily the local adsorption isotherm that can be represented by the DA equation [12]:

$$\theta_1 = \exp\left[-\left(\frac{A}{\beta E_0}\right)^{n_{\text{DA}}}\right] = \exp[-\mu A^{n_{\text{DA}}}] \quad (9)$$

where β is the similarity coefficient, E_0 is the characteristic energy of adsorption and $\mu = (\beta E_0)^{-n_{\text{DA}}}$ depends on an adsorbate and a kind of a microporous structure.

Substituting Eqs. (5) and (6) to Eq. (3), Jaroniec and Choma [28] obtained the overall adsorption isotherm (the JCh equation), which can be expressed as follows:

$$\Theta_{\text{JCh}} = \left[1 + \left(\frac{A}{\beta \rho}\right)^{n_{\text{JCh}}} \right]^{-\nu/n_{\text{JCh}}} \quad (0 < z < \infty). \quad (10)$$

For the micropore region of x ($E_0 = E_0(x)$ and $z = 1/E_0$)

from Eqs. (3), (5), and (7), we obtain the following equation:

$$\theta_{Ov} = \left[1 + \left(\frac{A}{\beta\rho} \right)^{n_{Ov}} \right]^{-\nu/n_{Ov}} \times \left[\frac{\gamma \left(\frac{\nu}{n_{Ov}}, z_{max}^{n_{Ov}} \left(\frac{A^{n_{Ov}}}{\beta^{n_{Ov}}} + \rho^{n_{Ov}} \right) \right) - \gamma \left(\frac{\nu}{n_{Ov}}, z_{min}^{n_{Ov}} \left(\frac{A^{n_{Ov}}}{\beta^{n_{Ov}}} + \rho^{n_{Ov}} \right) \right)}{\left[\gamma \left(\frac{\nu}{n_{Ov}}, z_{max}^{n_{Ov}} \rho^{n_{Ov}} \right) - \gamma \left(\frac{\nu}{n_{Ov}}, z_{min}^{n_{Ov}} \rho^{n_{Ov}} \right) \right]} \right] \quad (11)$$

$(z_{min} < z < z_{max})$.

Many authors have investigated the dependence of the adsorption energy E_0 on the pore size, x (for slit-like micropores), both experimentally [31–35] and theoretically [4,5,36]. Dubinin and others derived a very simple expression [37]:

$$x = \kappa/E_0 = \kappa z \quad (12)$$

where κ is a constant in the micropore region and its value, for the reference system (benzene vapour on activated carbon), is about 12 kJ×nm/mol. We have previously shown, using the relation given by Eq. (12) and substituting Eqs. (4), (8), and (9) to Eq. (1), that the integral adsorption isotherm equation can be solved analytically and as a result the fractal analog of the Dubinin–Astakhov equation (FRDA) is obtained [30,38–40]:

$$\theta_{FRDA} = \frac{\chi_x}{n} (\mu A^n)^{D-3/n} \left[\gamma \left(\frac{D-3}{n}, x_{max}^n \mu A^n \right) - \gamma \left(\frac{D-3}{n}, x_{min}^n \mu A^n \right) \right] \quad (13)$$

Experimental and theoretical studies have shown that the relation $x = f(E_0)$ is more complex [4,5,31–35] than it was suggested by Dubinin [37]. Therefore, in the presented paper we focus our attention on the empirical relation proposed recently by Stoeckli et al. [41]:

$$x = 2852.5z^3 + 15z + 0.014z^{-1} - 0.75. \quad (14)$$

Although Eq. (14) predicts, in our opinion, too high values of micropore widths, and does not take into account the parameter n_{DA} of the DA equation [4,5], this equation is chosen because we want to compare the final results of our calculations with those published by Jaroniec et al. [24] who widely propagate the validity of this relationship.

If the relation between z and the micropore half-width x is known, the distribution function $F_1(z)$ can be converted to the micropore-size distribution [24]:

$$f_1(x) = F_1(z)(dx/dz)^{-1} \quad (15)$$

where $x(z)$ must be a monotonic increasing function.

From Eqs. (5)–(7), (14), and (15), the following equations are derived:

$$F_{JCh}(x) = \frac{n_{JCh} \rho^\nu z^{\nu-1} \exp[-(\rho z)^{n_{JCh}}] (15 + 8557.5z^2 - 0.014z^{-2})^{-1}}{\Gamma \left(\frac{\nu}{n_{JCh}} \right)} \quad (16)$$

$$F_{Ov}(x) = \frac{n_{Ov} \rho^\nu z^{\nu-1} \exp[-(\rho z)^{n_{Ov}}] (15 + 8557.5z^2 - 0.014z^{-2})^{-1}}{\left[\gamma \left(\frac{\nu}{n_{Ov}}, z_{max}^{n_{Ov}} \rho^{n_{Ov}} \right) - \gamma \left(\frac{\nu}{n_{Ov}}, z_{min}^{n_{Ov}} \rho^{n_{Ov}} \right) \right]} \quad (17)$$

3. Results of calculation and discussion

3.1. The theoretical background of the generation of the starting isotherms

In the current study computer experiments are used, based on the considerations and principles outlined above, to investigate the physical adsorption on activated carbons containing slit-like micropores. Eqs. (18a and b), in the form obtained from substituting Eqs. (4), (8), (9) and (14), to Eq. (1), are the starting point for our investigation:

$$\Theta(A) = \frac{3 - D_{start}}{x_{max}^{3-D_{start}} - x_{min}^{3-D_{start}}} \times \int_{x_{min}}^{x_{max}} \exp \left[- \left(\frac{A}{\beta E_0(x)} \right)^{n_{start}} \right] x^{2-D_{start}} dx \quad (18a)$$

and

$$x(E_0) = \frac{15}{E_0} + \frac{2852.5}{E_0^3} + 0.014E_0 - 0.75. \quad (18b)$$

Eq. (18a) is integrated numerically (this cannot be solved analytically contrary to Eq. (13) because of the complexity of the relation between E_0 and x). The properties of Eqs. (18) are investigated assuming the following conditions.

- The adsorbate is benzene ($\beta=1$) according to Dubinin’s recommendation [10], who recommended this adsorbate for characterising the microporosity of activated carbons.
- The temperature is taken as 293 K.
- The adsorbent is an activated carbon. It is modelled to be microporous and characterised by the pore fractal dimension D_{start} . It is assumed that the fractality prevails in the limited range (only in micropores). Therefore, the maximal slit half-width (x_{max}) is equal to 1 nm (the upper limit of micropore diameters recommended by IUPAC [29]). The adsorbate has a

molecular size and it is connected with the minimal slit half-width (x_{\min}) (for benzene $x_{\min} = 0.2295$ nm [42]).

- The adsorption isotherms are generated at the relative pressure range from 10^{-7} to 10^{-1} p/p_s (the range where the DA equation is usually applied [7]).

The typical values of the parameters that are (the most frequently) reported in the literature are considered in the current paper. The aim of our procedure is to generate adsorption isotherms according to Eqs. (18) for the different n_{start} values (from 2.0 to 3.0 with the step equal to 0.1) and D_{start} values (from 2.0 to 2.9 with the same step as above; 2.95 and 2.99). A total of 151 points on the adsorption isotherm are generated for each case. Adsorption data obtained in this way are fitted numerically using Eqs. (9)–(11) (the values of z_{\min} and z_{\max} are obtained from x_{\min} and x_{\max} based on Eq. (14)). The non-linear fitting procedure, used in this work, was described by Nash [43] (see also Ref. [7]). The goodness of the fit is expressed by the determination coefficient (DC). The resulting values of DC are summarised in Table 1. In all cases the DC values are close to unity (the Dubinin–Astakhov equation (Eq. (9))) or are equal to 1 (Eq. (11)). Two cases of the Jaroniec–Choma equation (Eq. (10)) are considered. In the first case the parameter n_{JCh} is optimised during the fitting (the function given by Eq. (16) is denoted as $F_{\text{JCh}}(x)$ in this case). In the second case this parameter is assumed to be constant ($n_{\text{JCh}} = n_{\text{DA}} = 3.0$) as was suggested by Stoekli et al. [44] (in this case the function given by Eq. (16) is denoted as $F_{\text{JChn3}}(x)$). The determination coefficient values are equal to unity if three parameters are optimised (ρ , ν , and n_{JCh}) and they are slightly smaller than unity when two (ρ , ν) are optimised.

3.2. The properties of the MSD plots presented in the double logarithmic co-ordinates

It has been shown [25,26] that from log–log plots of the fractal pore-size distribution function (Eq. (4)) one can obtain D_{calc} by:

$$\log f_1(x) = \log \chi_x - (D_{\text{calc}} - 2)\log x. \quad (19)$$

Jaroniec et al. [24] proposed the calculation of D_{calc} in the following way.

- The evaluation of the parameters (ρ and ν) of the Jaroniec–Choma equation (Eq. (10)), assuming $n_{\text{JCh}} = 3.0$ and using the fitting procedure.
- The generation of the micropore-size distribution $F_{\text{JCh}}(x)$ (Eq. (16)) from the parameters obtained above (the relation between x and z is given by Eq. (14); the distribution function $F_1(z)$, (Eq. (5)) can be simply converted to the MSD).
- The plotting of the micropore-size distribution (Eq. (16)) in the log–log scale.
- The evaluation of the fractal dimension D_{calc} from the slope of the linear region of the obtained log–log plot.

In order to use Eqs. (16) and (17) to calculate MSDs for the model active carbons, the parameters of ρ , ν , and n_{JCh} or n_{Ov} are required; and they are evaluated by fitting Eqs. (10) and (11) to the generated benzene adsorption isotherms (Eq. (18)). In Fig. 1 the micropore-size distribution plotted in a log–log scale for the parameters summarised in Table 2 for the studied system ($n_{\text{start}} = 2.5$ and $D_{\text{start}} = 2.5$) are presented. It is seen that each curve has a different shape. The linear regions are observed for MSD function given by Eq. (16) (for $n_{\text{JCh}} = 3.0$) and Eq. (17). It is obvious (see Eq. (19)) that for the Pfeifer–Avnir distribution function only the straight line is obtained in the whole range of x ($x_{\min} < x < x_{\max}$). It is seen that the deviations from linearity of the log–log plots occur at the low and high values of x , respectively. It is caused by the properties of Stoekli’s relationship (Eq. (14)). This result is the same as published by Jaroniec et al. [24], who studied the adsorption of benzene on 11 active carbons. For all the cases they found that the log–log plots of micropore-size distribution are linear over the same ranges of the half-width of the pores.

Each cut-off value is determined explicitly from the double logarithmic plot. These values are taken as the limits of the fractal linear region (upper and lower cut-off values: $x_{\min(\text{cut-off})}$ and $x_{\max(\text{cut-off})}$) [45] and they are chosen in such a way that the value of the determination coefficient of the log–log plot (DC_{crit}) is equal to 0.9990 (it should be pointed out that it is chosen arbitrarily, because in this type of plot it is difficult to define the number of points belonging to the straight line). For example for n_{JCh} equal to 3.0, the following cut-off values

Table 1

The values of the determination coefficients (DCs) obtained by fitting Eqs. (9)–(11) to the adsorption isotherms generated for fractal microporous solids using the typical values of n_{start} and D_{start}

Starting parameters of Eq. (18)	Eq. (9)	Eq. (10) ($n_{\text{JCh}} = 3.0$)	Eq. (10) (n_{JCh} is optimised)	Eq. (11)
$n_{\text{start}} = 2.0$, $D_{\text{start}} = 2.0$	0.9998	0.9901	1.0000	1.0000
$n_{\text{start}} = 2.5$, $D_{\text{start}} = 2.5$	0.9995	0.9980	1.0000	1.0000
$n_{\text{start}} = 3.0$, $D_{\text{start}} = 2.99$	0.9991	1.0000	1.0000	1.0000

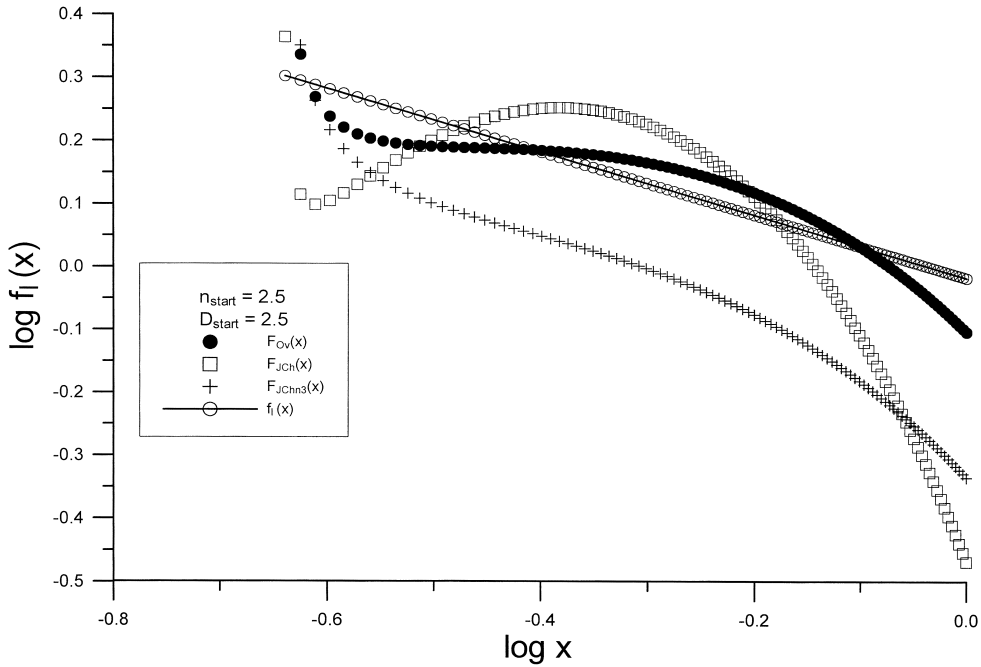


Fig. 1. The comparison of the log–log plots of the micropore-size distributions generated by Eqs. (16) and (17) for parameters presented in Table 2. Initial values of Eq. (18) are $x_{\min}=0.2295$ nm, $x_{\max}=1$ nm, $n_{\text{start}}=2.5$ and $D_{\text{start}}=2.5$. Solid line represents the Pfeifer–Avnir distribution (Eq. (4)).

are chosen: 0.2896 nm and 0.5385 nm ($D_{\text{calc}}=2.8543$ for this case).

It is seen that for Eq. (17) the cut-offs at the points 0.2911 nm and 0.4221 nm are obtained. The value of the fractal dimension (D_{calc}) calculated from the slope of the linear region is equal to 2.0672 and the highest possible DC value that we could obtain ($DC < DC_{\text{crit}}$) was equal to 0.9866. If the parameter n_{JCh} is optimised, the linear region cannot be achieved.

To illustrate how the values of n_{start} (at a fixed value of the fractal dimension D) influence the shape of the log–log plots of MSDs, the micropore-size distributions generated using optimised parameters (listed in Table 2) are com-

pared with the Pfeifer–Avnir one. The results are presented in Figs. 2–4. To illustrate this $D=2.5$ is chosen as above; however, it should be pointed out that the cases of other D values will be discussed below.

For all the cases ($F_{\text{JChn3}}(x)$, $F_{\text{JCh}}(x)$ and $F_{\text{Ov}}(x)$) the plots of MSDs in the log–log scale are different from the reference Pfeifer–Avnir distribution. Moreover, the Pfeifer–Avnir micropore-size distribution function does not depend on the parameter n_{start} . The plots of $F_{\text{JChn3}}(x)$ strongly change shape with decreasing n_{start} values (Fig. 2) in contrast to the cases of Eqs. (16) ($F_{\text{JCh}}(x)$) and (17) ($F_{\text{Ov}}(x)$) — Figs. 3 and 4. The increase in the non-linear region for higher values of the starting parameter n_{start} (see

Table 2

The result of the fitting procedure of Eq. (9) (DA), Eq. (10) ($n_{\text{JCh}}=3.0$, $F_{\text{JChn3}}(x)$ and n_{JCh} is optimising parameter, $F_{\text{JCh}}(x)$) and Eq. (11) ($F_{\text{Ov}}(x)$) to Eq. (18) ($x_{\min}=0.2295$ nm, $x_{\max}=1.0$ nm, $D_{\text{start}}=2.5$ and different n_{start} values)

n_{start}	Eq. (9)		Eq. (10) ($n_{\text{JCh}}=3.0$)		Eq. (10) (n_{JCh} is optimised)			Eq. (11)		
	E_0 (kJ/mol)	n_{DA}	ρ (kJ/mol)	ν	ρ (kJ/mol)	ν	n_{JCh}	ρ (kJ/mol)	ν	n_{Ov}
2.0	22.1056	1.9151	13.7816	1.9439	31.3737	6.1581	1.9975	53.7578	13.0398	2.0072
2.3	22.1312	2.1728	17.8267	2.9712	27.2460	5.8577	2.2944	42.0278	11.4388	2.3112
2.5	22.1479	2.3375	20.8660	4.0121	25.5348	5.7255	2.4908	37.1485	10.6023	2.5144
2.7	22.1642	2.4961	24.2802	5.5205	24.3140	5.6328	2.6856	33.6242	9.9163	2.7179
2.9	22.1802	2.6481	28.3173	7.8613	23.4205	5.5695	2.8784	30.9799	9.3391	2.9215
3.0	22.1881	2.7215	30.7226	9.5882	23.0634	5.5466	2.9740	29.9033	9.0885	3.0234

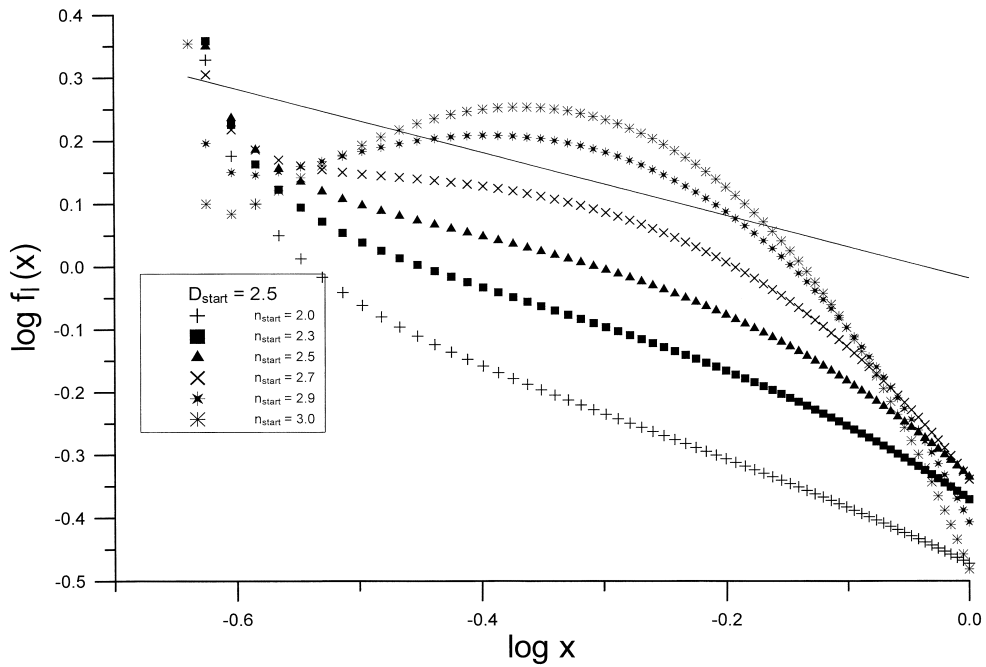


Fig. 2. The influence of the increase in n_{start} (Eq. (18), $D_{\text{start}} = 2.5$) on the log–log plots of the pore-size distribution given by Eq. (16) ($n_{\text{JCh}} = 3.0$). Solid line represents the Pfeifer–Avnr distribution (Eq. (4)).

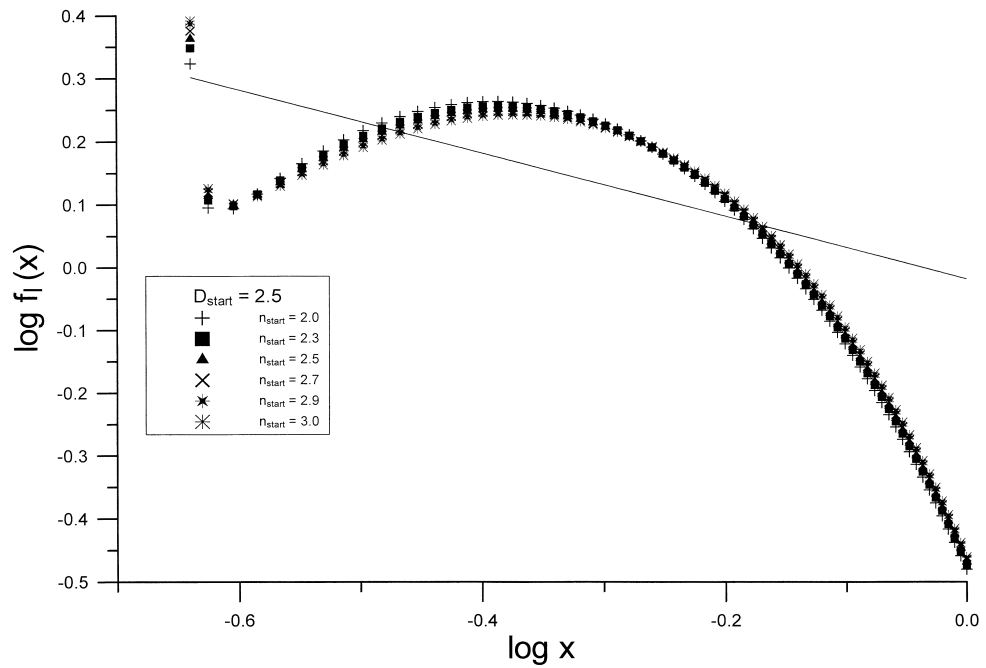


Fig. 3. The influence of the increase in n_{start} (Eq. (18), $D_{\text{start}} = 2.5$) on the log–log plots of the pore-size distribution given by Eq. (16) (n_{JCh} is optimised). Solid line represents the Pfeifer–Avnr distribution (Eq. (4)).

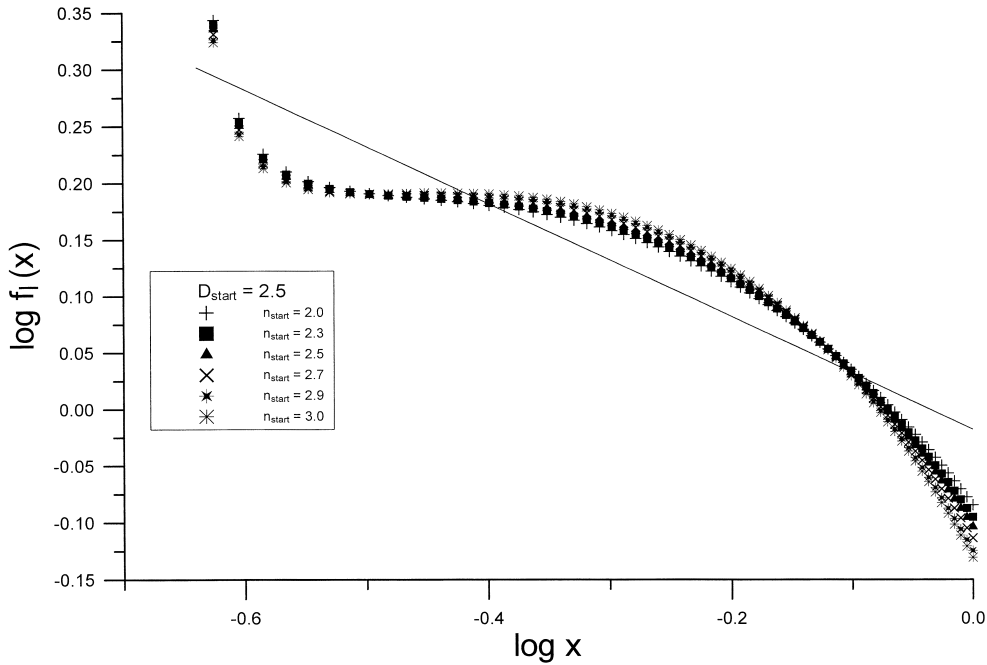


Fig. 4. The influence of the increase in n_{start} (Eq. (18), $D_{start} = 2.5$) on the log–log plots of the pore-size distribution given by Eq. (17). Solid line represents the Pfeifer–Avnir distribution (Eq. (4)).

Table 3) can be observed. From the double logarithmic plots of x and $f_1(x)$ the fractal parameters D_{calc} , $x_{min(cut-off)}$, and $x_{max(cut-off)}$ are received. The average micropore size \bar{x} [24] connected with Eq. (19) is calculated, which is defined in the region $x_{min(cut-off)}$ and $x_{max(cut-off)}$ (Table 3):

$$\bar{x} = \int_{x_{min(cut-off)}}^{x_{max(cut-off)}} x f_1(x) dx$$

$$= x_{min(cut-off)} \left(\frac{3 - D_{calc}}{4 - D_{calc}} \right) \left(\frac{r^{4-D_{calc}} - 1}{r^{3-D_{calc}} - 1} \right) \quad (20)$$

Table 3

The fractal parameters D_{calc} , $x_{min(cut-off)}$ and $x_{max(cut-off)}$ calculated by Eq. (19) from pore-size distribution given by Eq. (16) for a fixed value of n_{JCh} equal to 3.0 and critical value of determination coefficient DC_{crit} (=0.9990). Starting parameters are $x_{min} = 0.2295$ nm, $x_{max} = 1.0$ nm, $D_{start} = 2.5$ and different n_{start} values

n_{start}	$F_{JChn3}(x)$ (Eq. (16))			Eq. (21)
	D_{calc}	$x_{min(cut-off)}$ (nm)	$x_{max(cut-off)}$ (nm)	\bar{x} (nm)
2.0	2.7884	0.2996	1.0000	0.5957
2.3	2.6903	0.2958	0.7211	0.4869
2.5	2.8543	0.2896	0.5385	0.4074
2.7	2.8588	0.3065	0.3890	0.3474
2.9	–	–	–	–
3.0	–	–	–	–

where

$$r = \frac{x_{max(cut-off)}}{x_{min(cut-off)}} \quad (21)$$

A general tendency observed in Fig. 2 is that for a fixed starting value of the fractal dimension, log–log plots of micropore-size distributions become linear at the narrower range of half-width of pores ($x_{max(cut-off)}$ and \bar{x} values decrease and converge to $x_{min(cut-off)}$), and D_{calc} values increase with n_{start} .

In cases where we could not find the linear regions of MSDs in the logarithmic co-ordinates (Fig. 2), the cut-off values are assumed to be equal to the starting values of the half-width of micropores: $x_{max(cut-off)} = x_{max} = 1.0$ nm and $x_{min(cut-off)} = x_{min} = 0.2295$ nm, and the whole curve is fitted (closed symbols; $n_{start} = 2.5, 2.7, 3.0$ for $F_{JChn3}(x)$). This procedure is applied in order to compare the properties of MSD plots based on the gamma-type distribution function with the Pfeifer–Avnir one.

For the same reason an analogous procedure is used for Eq. (16) ($F_{JCh}(x)$) and Eq. (17) ($F_{Ov}(x)$) and D_{calc} is calculated only for the whole region of micropore sizes. This region is applied because D_{calc} close to 2.0 is always obtained from the linear part (Fig. 4, Eq. (17)). Only in one of the investigated cases (Eq. (17)) a very good agreement between the calculated and starting values of D is observed. It is not surprising because Eqs. (17) and (18) are connected with the micropore-size distribution function

and are normalised in the same micropore region (Eqs. (7) and (8)). We did not change the pore diameters of the micropore region during all calculations that are described in this part of the article.

The values of the fractal dimensions are also calculated for other values of D_{start} . Figs. 5–7 show the relation between the evaluated values of the fractal dimension D_{calc} and the values of fractal dimension taken to the generation of the starting isotherms (based on Eqs. (18)). The solid line represents the ideal condition, $D_{start} = D_{calc}$. For Eq. (16) ($F_{JChn3}(x)$) the values of fractal dimension D_{calc} are calculated from the linear part of curves only for n_{start} equal to 2.0, 2.3, 2.5 and 2.7 (open symbols in Fig. 5).

The small deviation from linearity for higher values of D_{start} (Fig. 7) can probably be caused by some details of the applied procedure of calculation. The opposite situation is observed in Fig. 5 ($F_{JChn3}(x)$), where the correlation between the two described fractal dimensions cannot be found, and D_{calc} is sometimes greater than 3.0 (unphysical values). Also, in the case of $F_{JCh}(x)$ (Fig. 6) one can observe that the evaluated D_{calc} values belong to the region of $D_{calc} > 3$ (for higher $D_{start} (\geq 2.7)$). Moreover, all the values of the fractal dimension are shifted to the higher values of D_{calc} and they are grouped above the reference line. The lack of the correlation between D_{calc} and D_{start} for the two cases presented in Figs. 5 and 6 (Eq. (16)) is due to inequality of the values of micropore widths used in calculations. We should limit the linear part of the plots at certain points ($x_{max(cut-off)}$ and $x_{min(cut-off)}$) to evaluate the

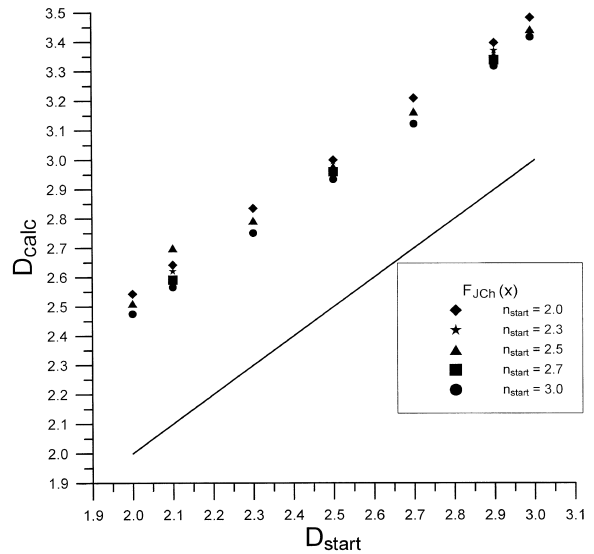


Fig. 6. The comparison of starting values of fractal dimensions (D_{start}) and values of fractal dimensions calculated (D_{calc}) within initial region of micropore half-widths (x_{min} , x_{max} are cut-off) of the log plots of micropore-size distribution based on Eq. (16) (n_{JCh} is optimised) and Eq. (19). Solid line represents the condition, $D_{start} = D_{calc}$.

values of D by means of the procedure described above and proposed by Jaroniec and co-workers. The upper and lower cut-off values are not equal to infinity and zero,

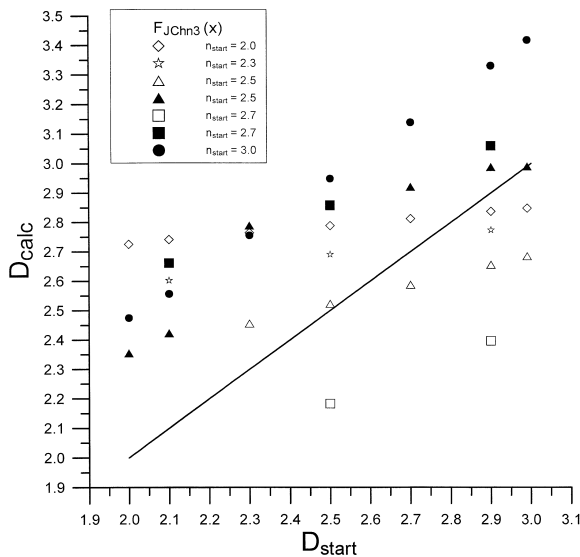


Fig. 5. The comparison of starting values of fractal dimensions (D_{start}) and values of fractal dimensions calculated (D_{calc}) from the linear regions of the log plots of MSDs (open symbols) and for cut-off values equal to x_{min} and x_{max} , respectively (closed symbols) based on Eq. (16) ($n_{JCh} = 3.0$) and Eq. (19). Solid line represents the condition, $D_{start} = D_{calc}$.

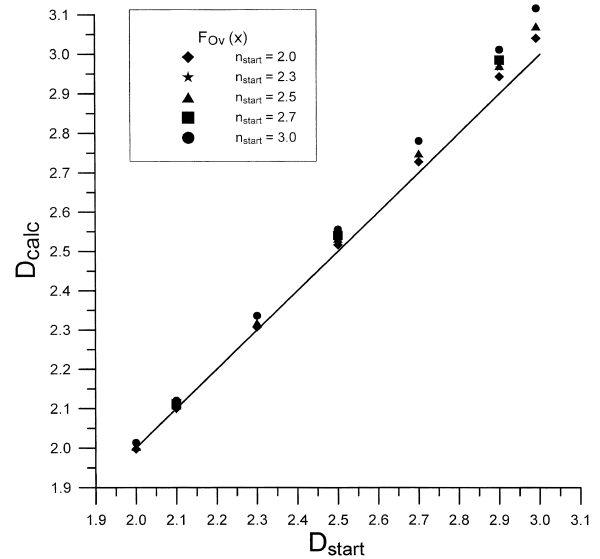


Fig. 7. The comparison of starting values of fractal dimensions (D_{start}) and values of fractal dimensions calculated (D_{calc}) within initial region of micropore half-widths (x_{min} , x_{max} are cut-off) of the log plots of micropore-size distribution based on Eq. (17) and Eq. (19). Solid line represents the condition, $D_{start} = D_{calc}$.

respectively. One must remember that Jaroniec and Choma [24] used the gamma distribution function (Eq. (5)) that was normalised in the following region ($0 < z < \infty$) [23]. In our opinion, this inconsistency is the reason for this difference.

3.3. The existing relationships between D and the parameters of the potential theory, and the development of the new equation

Jaroniec et al. [24] proposed (based on the adsorption data measured for 11 active carbons) the linear relationship between D and \bar{x} using the procedure for evaluating D described above (Section 3.2):

$$D = 6.44 - 6.17\bar{x} \quad (22)$$

Ehrburger-Dolle [46] proposed a relation similar to that derived by Jaroniec and co-workers:

$$D = 3 - \frac{24}{E_{\text{OFR}}} \left(1 - \frac{E_{\text{OFR}}}{E_{\text{ODR}}} \right) \quad (23)$$

where E_{OFR} and E_{ODR} are the characteristic energy obtained from Eq. (9) assuming $n = 1$ and $n = 2$, respectively. For $E_{\text{OFR}} < 18$ kJ/mol and/or $E_{\text{ODR}} < 12$ kJ/mol Eq. (23) becomes [46]:

$$D = 3 - \frac{8}{E_{\text{OFR}}}. \quad (23a)$$

The formulas (23) and (23a) were proposed based on the consideration of a modified Freundlich equation and the analysis of derivatives of the experimental isotherms of adsorption.

In the current paper, 132 adsorption isotherms (151 points each) are generated, using the method described above, and then they are numerically fitted to Eq. (9) (two best fit parameters: E_0 and n_{DA} were calculated). The typical results are listed in Tables 1 and 2. The achieved n_{DA} values ($1.9099 < n_{\text{DA}} < 2.7542$) are not equal to the initial n_{start} values ($2.0 \leq n_{\text{start}} \leq 3.0$) (Table 2). We obtained a slightly different range of E_0 values ($21.2436 < E_0 < 23.1579$ for $2.00 \leq D < 2.99$) than proposed by other authors. The ranges of E_0 values from Eqs. (22) and (23) — assuming $2 \leq D < 3$ — are as follows:

- ($16.6757 < E_0 < 21.5233$) for Eq. (22) since \bar{x} is deduced from E_0 by means of Eq. (12) [24,47,48],
- ($17.1133 < E_0 < 18.3268$) for Eq. (22) since \bar{x} is deduced from E_0 by means of Eq. (14) [41],
- for Eqs. (23) and (23a) [46] the values of D depend on the ratio of $E_{\text{OFR}}/E_{\text{ODR}}$.

The relation between D and \bar{x} (and E_0 , respectively), Eq. (22), was derived by Jaroniec et al. based on experimental

data. The typical log–log plots of the pore-size distributions, calculated according to Eq. (16), contained the linear segments in a wide pore region (see Fig. 3 and Fig. 4, Ref. [24]). It has been shown that for the different carbons different cut-off values were evaluated. The calculated $x_{\text{max(cut-off)}}$ values were close to 1 nm but some of them exceeded this value. Moreover, the evaluated $x_{\text{min(cut-off)}}$ values, for the carbons studied by those authors, belong to the region considered in our calculations. Therefore the similarity in micropore ranges calculated by Jaroniec et al. and obtained in this paper should give comparable limits of the characteristic energy values for Eq. (22) and proposed below, Eq. (24).

This equation is derived as follows. We try to correlate the fractal dimension D values with both parameters of the DA equation (i.e. not only with E_0 but with n_{DA} as well). Eqs. (22) and (23) neglect the parameter n_{DA} ; however, as we showed previously [4,5], this parameter is strictly related to the pore width. The numerical procedure of a simultaneous optimisation of those parameters is analogous to the one described previously [4,5]. The average determination coefficient value is minimised. The following relation is obtained:

$$D = \frac{E_0(15.3897 - 3.6083 \times 10^{-4} n_{\text{DA}}) - 283.3356 + 6.3019 \times 10^{-3} n_{\text{DA}}}{E_0(0.9396 + 0.1054 n_{\text{DA}}) + 1.0557 - 1.8407 n_{\text{DA}}}. \quad (24)$$

The average determination coefficient between the data obtained from the fitting procedure and those calculated using Eq. (24) is equal to 0.999977. In Fig. 8 the plots of Eq. (22) (assuming the relationships (12) and (14)) and of Eq. (24) are shown in the region of the characteristic energy applied for derivation of Eq. (24). It is assumed that the n_{DA} value is equal to 3.0 (this value is chosen because, as was mentioned above, some authors presume the equality between n_{JCh} and n_{DA} [24,48]). In Fig. 9 the comparison of the D values predicted by Eqs. (23) and (24) is shown. Twelve adsorption isotherms are generated using Eq. (9) and assuming $n = 2$. Then they are described using the same equation and assuming $n = 1$, to evaluate the values of E_{OFR} .

From Figs. 8 and 9 it can be concluded that, for this region of the characteristic energy values, all the relationships generate different plots.

3.4. The experimental verification of the relationships

In Table 4 the results of the calculation of the fractal dimension values, based on Eqs. (22)–(24) are presented, for some experimental data. The characteristic energy values ($n_{\text{DA}} = 2.0$) used in the calculation were published by Domingo-Garcia et al. [49]. Following the results presented in Section 3.3 we chose the data describing the adsorption on strictly microporous carbons (i.e. the charac-

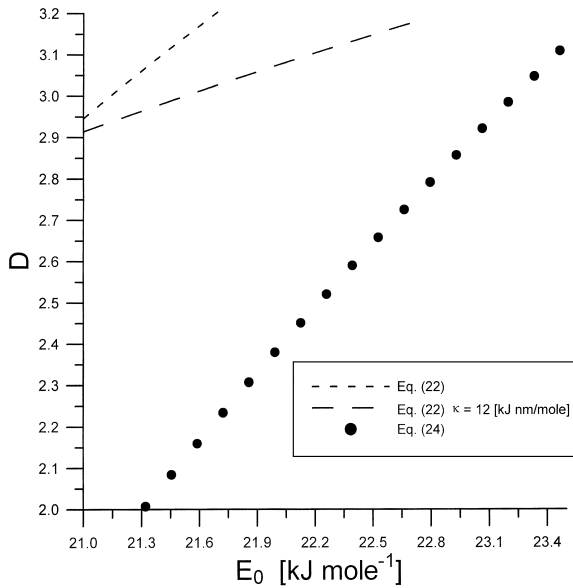


Fig. 8. The comparison of the predicted fractal dimension values (using relations given by Eq. (22) since \bar{x} is deduced from E_0 by means of Eq. (12) and/or (14)) with calculated D values from Eq. (24) ($n_{\text{DA}} = n_{\text{JCh}} = 3.0$) for the region of the characteristic energy used to obtain Eq. (24).

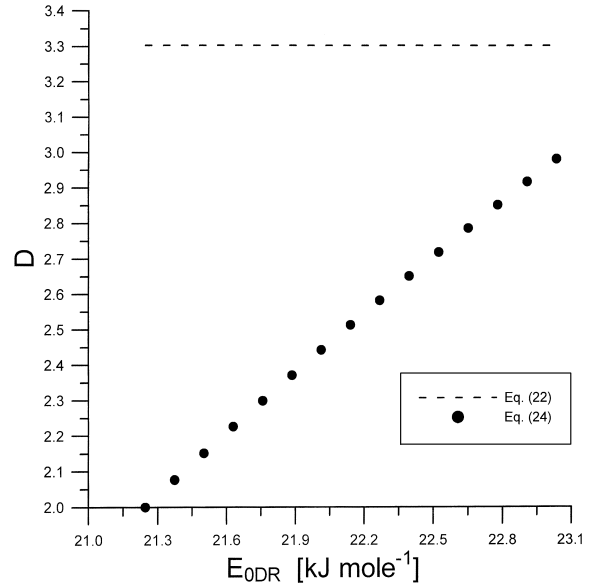


Fig. 9. The comparison of the predicted fractal dimension values (using relations given by Eq. (23)) with calculated D values from Eq. (24) ($n_{\text{DA}} = 2.0$) for the region of the characteristic energy used to obtain Eq. (24).

teristic energy ranges are close to those considered in this paper for the derivation of Eq. (24)). The values of E_{OFR} are calculated fitting the experimental isotherms, generated using the values of the parameters of Eq. (9) tabulated by those authors.

The evaluated D values belong to the region of $D > 3$ for Eq. (23). A similar situation is observed for Eq. (22) because all fractal dimensions are greater than 3.0. Only for the case of Eq. (24) the obtained D values cover the range between 2 and 3.

4. Conclusions

The method of calculation of the fractal dimension proposed by Jaroniec et al. [24] is very simple because D

can be calculated from the linear part of the log–log plot of the micropore-size distribution, based on Eq. (19). However, one can obtain this region of the plots only if two (ρ and ν) of three parameters of the Jaroniec–Choma equation (Eq. (3)) are optimised and it is necessary to fix the n_{JCh} value as equal to 3.0. Following the procedure of the determination of D proposed by these authors, one should also evaluate (from the linear part of the MSD curve) the certain low and high cut-off values of the half widths of micropores. Unfortunately, the inconsistency arises because these cut-off values do not cover the pore size integration range ($0 < z < \infty$ and/or $0 < x < \infty$) of the general integral adsorption isotherm equation (Eq. (3)) and the pore-size distribution function (Eq. (5)) that led Jaroniec et al. to the JCh equation [28] (Eq. (9)). This fact makes it impossible to find the equality between the initial

Table 4

The fractal dimension (D) values obtained from Eqs. (22)–(24) based on the characteristic energy E_0 ($n_{\text{DA}} = 2.0$) published by Domingo-Garcia et al. [49]

E_{ODR} (kJ/mol)	E_{OFR} (kJ/mol)	Eq. (22) and Eq. (14)	Eq. (22) and Eq. (12)	Eq. (23)	Eq. (24) ($n_{\text{DA}} = 2.0$)
21.40	29.33	4.762	2.980	3.303	2.092
21.71	29.92	4.897	3.030	3.303	2.272
22.44	31.33	5.192	3.141	3.304	2.674
21.68	29.86	4.884	3.025	3.303	2.255
22.06	30.59	5.042	3.084	3.304	2.468
22.80	32.05	5.326	3.193	3.304	2.862

and calculated fractal dimension values. On the other hand one can obtain this equality (i.e. $D_{\text{start}} = D_{\text{calc}}$) by the application of the same micropore region of x in calculations; i.e. the overall adsorption isotherm should be integrated, the pore-size distribution function should be normalised and the fractal dimension values should be evaluated, in the same micropore range. All these observations lead to the conclusion that the relationship between D and the parameters of the Dubinin–Astakhov equation (E_0 and n_{DA}) is more complicated than it has been presumed up to the present [24,46]. Taking all these results into account leads to the new Eq. (24), which seems to be attractive for determining the fractal dimension values for strictly microporous carbons.

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References

- Everett DH, Powl JC. Adsorption in slit-like cylindrical micropores in the Henry's law region. *J Chem Soc Faraday Trans* 1976;72:619–36.
- Horvath G, Kawazoe K. Method for the calculation of effective pore size distribution in molecular sieve carbon. *J Chem Eng Jpn* 1983;16(6):470–5.
- Cheng LS, Yang RT. Improved Horvath–Kawazoe equations including spherical pore models for calculating micropore size distribution. *Chem Eng Sci* 1994;49(16):2599–609.
- Terzyk AP, Gauden PA, Rychlicki G, Wojsz R. New relationships between the characteristic energy of nitrogen adsorption (at 77.5 K) and the average effective diameter of carbon slit-like micropores. *Carbon* 1998;36(11):1703–5.
- Terzyk AP, Gauden PA, Rychlicki G, Wojsz R. *Carbon* 1999;37(3):539–40.
- Moreno-Castilla C, Ferro-Garcia MA, Joly JP, Bautista-Toledo I, Carrasco-Martin F, Rivera-Utrilla J. Activated carbon surface modifications by nitric acid, hydrogen peroxide, and ammonium peroxydisulfate treatments. *Langmuir* 1995;11:4386–92.
- Wojsz R. Characteristics of the structural and energetic heterogeneity of microporous carbon adsorbents regarding the adsorption of polar substances, Toruń: UMK, 1989, In Polish.
- Moreno-Castilla C, Rivera-Utrilla J, Carrasco-Martin F, Lopez-Ramon MV. On the carbon dioxide and benzene adsorption on activated carbons to study their micropore structure. *Langmuir* 1997;13:5208–10.
- Dubinin MM. In: Walker PL, editor, *Chemistry and physics of carbon*, vol. 2, New York: Marcel Dekker, 1966, pp. 51–120.
- Dubinin MM. In: Cadenhead A, editor, *Progress in surface and membrane science*, vol. 9, New York: Academic Press, 1975, pp. 1–70.
- Dubinin MM. Adsorption and porosity, Warszawa: WAT, 1975, In Polish.
- Dubinin MM, Astakhov AV. Development of the theory of the volume filling on microporous solids. *Izv AN SSSR Ser Khim* 1971;1:5–28, In Russian.
- Stoeckli HF. A generalisation of the Dubinin–Radushkevich equation for the filling of heterogeneous micropore systems. *J Colloid Interface Sci* 1977;59(1):184–5.
- McEnaney B, Mays TJ, Causton PD. Heterogeneous adsorption on microporous carbons. *Langmuir* 1987;3:695–9.
- Rychlicki G, Terzyk AP. Indispensability of the use of calorimetric measurements for the description of adsorption process in microporous systems. *J Thermal Anal* 1995;45:961–5.
- Rychlicki G, Garbacz JK, Terzyk AP. The comparison of isosteric and calorimetric heats of carbon tetrachloride adsorption on two types of microporous activated carbon. *Polish J Chem* 1994;68:1659–62.
- Rychlicki G, Terzyk AP. The thermodynamic verification of the theory of volume filling of micropores for adsorption on activated carbons. *Adsorption Sci Technol* 1998;16:8–18.
- Avnir D, editor, *The fractal approach to heterogeneous chemistry: surfaces, colloids, polymers*, Chichester: Wiley, 1989.
- Cerofolini GF, Rudzinski W. Equilibria and dynamics of gas adsorption on heterogeneous solids surfaces. In: Rudzinski W, Steele WA, Zgrablich G, editors, *Studies in surface science and catalysis*, vol. 104, Elsevier Science, 1997, chapter 1.
- Sato M, Sukegawa T, Suzuki T, Kaneko K. Surface fractal dimension of less-crystalline carbon micropore walls. *J Phys Chem* 1997;101(10):1845–50.
- Diduszko R, Świątkowski A, Trznadel BJ. On surface of micropores and fractal dimension of activated carbon determined on the basis of adsorption and SAXS investigation. *Carbon* 2000;38(8):1153–62.
- Dubinin MM. Generalisation of the theory of volume filling of micropores to nonhomogeneous microporous structures. *Carbon* 1985;23(4):373–80.
- Jaroniec M, Lu X, Madey R. Correlation between the fractal dimension and the microporous structure of a solid. *Monatsh Chem* 1991;122:577–84.
- Jaroniec M, Gilpin RK, Choma J. Correlation between microporosity and fractal dimension of active carbons. *Carbon* 1993;31(2):325–31.
- Pfeifer P, Avnir D. Chemistry in noninteger dimensions between two and three. I. Fractal theory of heterogeneous surfaces. *J Chem Phys* 1983;79(7):3558–65.
- Pfeifer P, Avnir D. Chemistry in noninteger dimensions between two and three. I. Fractal theory of heterogeneous surfaces. *J Chem Phys* 1983;79(9):4573.
- Sircar S. New adsorption isotherm for energetically heterogeneous adsorbents. *J Colloid Interface Sci* 1984;98(2):306–18.
- Jaroniec M, Choma J. In: Thrower PA, editor, *Chemistry and physics of carbon*, vol. 22, New York: Marcel Dekker, 1987, pp. 197–243.
- Sing KSW, Everett DH, Haul RAW, Moscou L, Pierotti RA, Rouquerol J, Siemieniewska T. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure Appl Chem* 1985;57:603–19.
- Terzyk AP, Gauden PA, Rychlicki G, Wojsz R. Comments on

- 'An isotherm equation for adsorption on fractal surfaces of heterogeneous porous materials'. *Langmuir* 1999;15:285–9.
- [31] Stoeckli HF. Microporous carbons and their characterisation: the present state of the art. *Carbon* 1990;28(1):1–10.
- [32] Centeno TA, Stoeckli F. On the activation of asturian anthracite following various pretreatments. *Carbon* 1994;32(8):1463–7.
- [33] McEnaney B. Estimation of the dimensions of micropores in active carbons using the Dubinin–Radushkevich equation. *Carbon* 1987;25(1):69–75.
- [34] McEnaney B, Mays TJ. In: Proceedings of the COPS II conference, Alicante, 1990, pp. 477–90.
- [35] Choma J, Jaroniec M. An attempt of the determination of the relationship between the characteristic energy of adsorption and the micropore sizes based on the simulated adsorption isotherms. *Karbo-Energochemia-Ekologia* 1997;11:368–72, In Polish.
- [36] Chen SG, Yang RT. Theoretical investigation of relationships between characteristic energy and pore size for adsorption in micropores. *J Colloid Interface Sci* 1996;177:298–306.
- [37] Dubinin MM, Stoeckli HF. Homogeneous and heterogeneous structures in carbonaceous adsorbents. *J Colloid Interface Sci* 1980;75(1):34–42.
- [38] Wojsz R, Terzyk AP. Fractal dimension of microporous carbon on the basis of first solution of a Laplace transform using an incomplete gamma function. *Computers Chem* 1996;20(4):427–30.
- [39] Wojsz R, Terzyk AP. The structural parameters of microporous solid, including fractal dimension, on the basis of the potential theory of adsorption — the general solution. *Computers Chem* 1996;21(2):83–7.
- [40] Terzyk AP, Wojsz R, Rychlicki G, Gauden PA. Fractal dimension of microporous carbon on the basis of the Polanyi–Dubinin theory of adsorption. 2. Dubinin–Astakhov adsorption isotherm equation. *Colloid Surf A* 1997;126:67–73.
- [41] Stoeckli HF, Ballerini L, De Bernardini A. On the evolution of micropore widths and areas in the course of activation. *Carbon* 1989;27(3):501–2.
- [42] Clifton B, Cosgrove T. Simulation of liquid benzene between two graphite surfaces: a molecular dynamic study. *Mol Phys* 1998;93(5):767–76.
- [43] Nash JC. Compact numerical methods for computers: linear algebra and function minimization, Halsted Press, 1979.
- [44] Stoeckli HF, Rebstein P, Ballerini L. On the assessment of microporosity in active carbons, a comparison of theoretical and experimental data. *Carbon* 1990;28(6):907–16.
- [45] Pfeifer P, Obert M. In: Avnir D, editor, The fractal approach to heterogeneous chemistry: surfaces, colloids, polymers, Chichester: Wiley, 1989, Chapter 1.2.
- [46] Ehrburger-Dolle F. Some new correlations between Dubinin–Radushkevich and Freundlich equations and fractal dimension of microporous solids. *Langmuir* 1994;10:2052–5.
- [47] Schieferstein E, Heinrich P. Diffusion coefficients calculated for microporous solids from structural parameters evaluated by fractal geometry. *Langmuir* 1997;13:1723–8.
- [48] Rudziński W, Nieszporek K, Cases JM, Michot LI, Vilieras F. A new molecular probe method to study surface topography of carbonaceous solid surfaces. *Langmuir* 1996;12:170–82.
- [49] Domingo-Garcia M, Fernandez-Morales I, Lopez-Garzon FJ, Moreno-Castilla C. Use of activated carbons obtained from agricultural byproducts for the adsorption of some hydrocarbons. *Langmuir* 1991;7:339–43.