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Comments on “An Isotherm Equation for Adsorption on Fractal Surfaces of Heterogeneous Porous Materials”

Some years ago Avnir and Jaroniec¹ attempted to solve the “global” adsorption isotherm (GAI) equation using Dubinin and Radushkevich (DR) isotherm² and the fractal pore size distribution proposed by Pfeifer and Avnir.^{3,4}

In our opinion, it is hard to agree with some statements¹, and the procedure applied by Avnir and Jaroniec leads to an adsorption equation that neither can be treated as an approximate solution of the GAI nor can be called a fractal analogue of the FHH equation. It is important to point out that the aim of this Comment is not to discuss the applicability of DR or DA equations for the description of the adsorption in homogeneous microporous system; i.e., we do not want to discuss the validity of the application of DR or DA equations as local adsorption isotherms in the GAI.

The form of the GAI applied by Avnir and Jaroniec can be written as

$$\Theta = \int_{x_{\min}}^{x_{\max}} \theta_1 f_1(x) dx \quad (1)$$

where $f_1(x)$ is, in this case, the fractal pore size distribution proposed by Pfeifer and Avnir^{3,4}

$$f_1(x) = \rho x^{2-D} \quad (x_{\min} < x < x_{\max}) \quad (2)$$

This distribution should be normalized (it is important to emphasize that the normalization takes place in the range $x_{\min} < x < x_{\max}$) giving the normalization factor

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

where x_{\min} and x_{\max} are the resolution at which fractality prevails (i.e., the lower and upper limit of “pore fractality” of an investigated object), D is the pore fractal dimension (when $D = 2$ a homogeneous pore size distribution is obtained, when D is close to 3, the pores are nearly the same diameter, i.e., a homogeneous pore system occurs). Using the DR equation as the local isotherm (θ_1) in eq 1 they obtained

$$\Theta = \int_{x_{\min}}^{x_{\max}} \exp(-\mu A^n x^n) \rho x^{2-D} dx \left(\equiv \int_{x_{\min}}^{x_{\max}} B dx \right) \quad (4)$$

where A is the adsorption potential. Avnir and Jaroniec split up the GAI into three integrals

$$\Theta \equiv \int_{x_{\min}}^{x_{\max}} B dx = \int_0^\infty B dx - \int_0^{x_{\min}} B dx - \int_{x_{\max}}^\infty B dx \quad (5)$$

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- (1) Avnir, D.; Jaroniec, M. *Langmuir* **1989**, *5*, 1431.
- (2) Dubinin, M. M. *Progress in Membrane and Surface Science*; Cadenhead, D. A., Ed.; Academic Press: New York, 1970; Vol. 9, p 1.
- (3) Pfeifer, P.; Avnir, D. *J. Chem. Phys.* **1983**, *79*, 3558.
- (4) Pfeifer, P.; Avnir, D. *J. Chem. Phys.* **1984**, *80*, 4573.

Then they have claimed that “numerical analysis of eq 5 (in their paper¹ eq 10) shows that for microporous solids in the region of moderate values of adsorption potential A (from 0.05 to the micropore-filling pressures) eq 5 may be approximated by the first integral term” leading to

$$\Theta_{AJ} \left(\equiv \int_0^\infty B dx \right) = \int_0^\infty \exp(-\mu A^n x^n) \rho x^{2-D} dx = \frac{\rho}{n} (\mu A^n)^{(D-3)/n} \Gamma\left(\frac{3-D}{n}\right) \quad (6)$$

where Γ denotes the gamma function, and $\mu = (\kappa\beta)^{-n}$. Equation 6 is developed by us as the solution of the integral for the DA equation, and if $n = 2$, the equation proposed by Avnir and Jaroniec (AJ) is obtained.

Two alternative forms of eq 6 were used by those authors; each of them has a different form of constant $K_{(j)}$ ^{1,5} (the superscripts are given following the journals where they were published)

$$K_{\text{Lan}} = \frac{\rho}{n} \mu^{(D-3)/n} (RT)^{D-3} \Gamma\left(\frac{3-D}{n}\right) = K_{\text{JChP}} (RT)^{D-3} \quad (7)$$

On the other hand, we have developed^{6,7} the analytical solution of eq 4 (for the both DR and/or DA equations), and it can be written as

$$\Theta_{\text{FRDA}} \left(\equiv \int_{x_{\min}}^{x_{\max}} B dx \right) = \frac{\rho}{n} (\mu A^n)^{(D-3)/n} \left[\gamma\left(\frac{3-D}{n}, x_{\max}^n \mu A^n\right) - \gamma\left(\frac{3-D}{n}, x_{\min}^n \mu A^n\right) \right] \quad (8)$$

where γ is an incomplete gamma function. If $n = 2$, the fractal analogue of the Dubinin and Radushkevich isotherm is obtained (FRDR equation^{8–11}).

The main remarks and questions arising from the detailed analysis of the derivation of the AJ equation, as well as from the general comparative analysis (the detailed analysis will be published in the future) of the AJ and FRDA equations are as follows. First of all, while splitting up eq 5 into three integrals and making the assumption that the mathematical description of the process can be represented by the first integral, a change in the integration limit without any change in the normalization factor occurs. It can be easily shown that the Pfeifer–Avnir pore size distribution (eq 2) cannot be normalized from zero to infinity. Moreover, this can be done assuming that the minimal pore diameter is larger than zero; however, in this case, a negative normalization factor is obtained.

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(6) Wojsz, R.; Terzyk, A. P. *Comput. Chem.* **1996**, *20*, 427.

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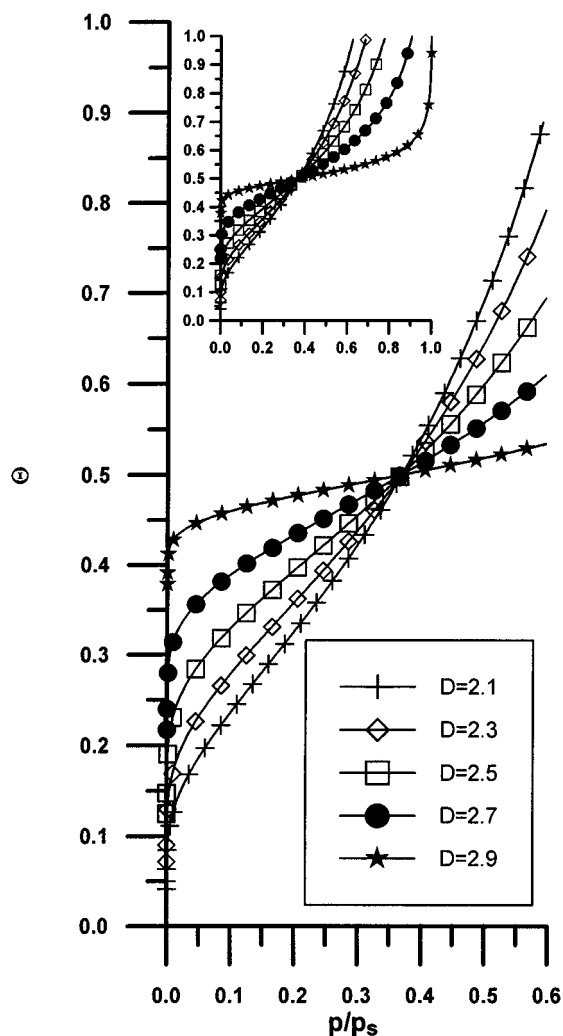


Figure 1. Recalculated adsorption isotherms using the AJ equation (eq 6) for two relative pressure ranges ($K_{\text{Lan}} = 0.5$).

Thus, it is hard to agree with the statement that eq 6 can be called as the fractal analogue of the FHH equation.

It is also hard to agree with the conclusion that presented by Avnir and Jaroniec¹ (Figure 1), the adsorption isotherm type changes with change in D . Figure 1 shows the adsorption isotherms recalculated using eq 6 for the same pressure range¹ and for the whole relative pressure range (using the same parameters¹). Following IUPAC definition (i.e., "the adsorption isotherm curve can be assigned as the I type of BET classification when adsorption approaches a limiting value as $p/p_s \rightarrow 1$ "),¹² their shape remains unchanged. This can be also confirmed by the analysis of the derivative ($-d\Theta/dA = F(A)$ (differential adsorption potential distribution)) which is the asymmetrical bell-shaped function for the I type adsorption isotherm (for example, for the curves generated by FRDA eq 8) and decreases to zero with increase in the relative pressure. For the AJ equation, it increases to infinity, and it is in practice the hyperbolic function. It is obvious that the approximate solution of eq 4 generates only the II type BET adsorption isotherm shapes, and it is not in agreement with the conclusions given by the above-mentioned authors.

A more general problem, however, is that for the approximate solution of GAI, another approximation was

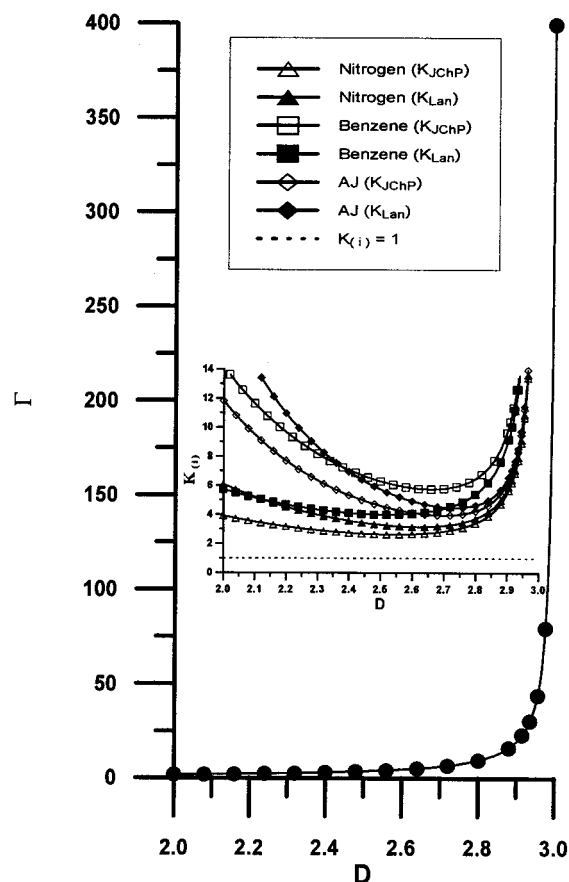


Figure 2. Behavior of $K_{(i)}$ and gamma function (Γ) with the change of D . Dashed horizontal line represents $K_{(i)} = 1$ ($R = 0.008\,134\,41$ [kJ K⁻¹ mol⁻¹], $\kappa = 12$ [kJ nm mol⁻¹]) (the parameters of adsorbates: benzene ($x_{\text{min}} = 0.25$ nm, $x_{\text{max}} = 1$ nm, $\beta = 1$, $T = 298.15$ K); nitrogen ($x_{\text{min}} = 0.1$ nm, $x_{\text{max}} = 1$ nm, $\beta = 0.33$, $T = 77.3$ K); parameters used by Jaroniec and co-workers⁵ ($x_{\text{min}} = 0.1$ nm, $x_{\text{max}} = 1$ nm, $\beta = 1$, $T = 77.3$ K)).

applied (the statement that $K_{(i)}$ in eq 7 can be treated as constant¹) by the authors and it is rather impossible to agree with its correctness. It can be concluded from the analysis of the Figure 2 that $K_{(i)}$ strongly depends on the fractal dimension D . Due to different forms of the constant $K_{(i)}$, we have calculated it assuming that the $(RT)^{D-3}$ factor is included in this constant¹ and/or is not.⁵ We used the same values of parameters;⁵ moreover, those constants were calculated for two adsorbates. It is obvious that either assuming that the term $(RT)^{D-3}$ contributes to the $K_{(i)}$ value or not, the parameter $K_{(i)}$ cannot be treated as a constant one. Besides, if D tends to 3, $K_{(i)}$ tends to infinity. This effect is mainly caused by the dependence of the Γ function on D . The term $(RT)^{D-3}$ can either increase (for example, at the temperature of 298.15 K) or decrease (for example, at the temperature of 77.3 K) with D , but the Γ function always increases with D . The subsequent interesting remark is that in practice the $K_{(i)}$ value is always larger than unity.

On the other hand, if $K_{(i)}$ is constant, the results obtained by two sets of calculations (i.e., assuming the constant and real $K_{(i)}$ values) should be similar. To check it, we calculated Θ values using eq 6 for the relative pressure range 10^{-7} –1, assuming benzene as the adsorbate (the same parameters as in⁵) for different values of D and $n = 2$ (Figure 3) but for real $K_{(i)}$ values.

From Figure 3 it can be noticed that for each obtained isotherm (they all still are the II type of BET classification) the region can be found for which Θ possesses unphysical values. Moreover, the increase in D values results in a

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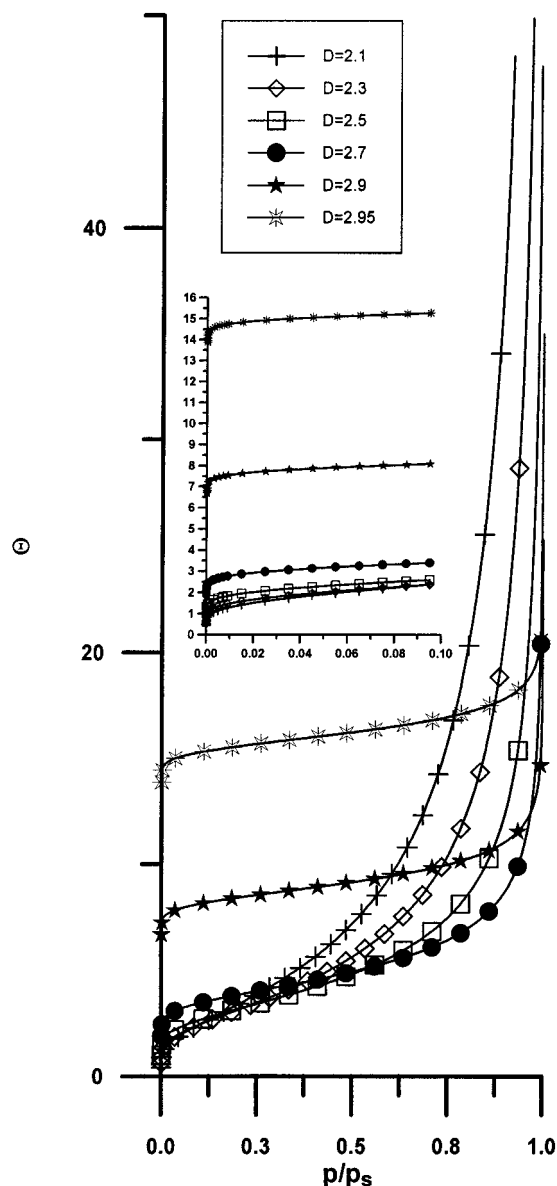


Figure 3. Benzene adsorption isotherms generated from the AJ equation (eq 6) for the same parameters as in Figure 2.

fake decrease of relative pressure for which $\Theta < 1$ can be obtained (for example, for $D = 2.5$ the p/p_s value should be as small as 2×10^{-28} to obtain $\Theta = 0.5$). In the range up to 0.1 the increase in D brings about the same effect, i.e., unphysical values of Θ . There is some strange behavior of the obtained adsorption isotherms with the change in D value.

We presented previously⁸ the results of the same analysis but for the analytical solution (eq 8, $n = 2$). It was shown that for the FRDR equation the increase in D leads to the growth in Θ value (Θ values are lower than unity in the whole relative pressure range); the change of the shapes of generated curves with D does not occur, and the obtained isotherms are all of the I type of BET classification. It is certain because the adsorbent containing only micropores cannot generate the II type BET isotherms for benzene and/or, for example, nitrogen. This is the most important difference between both equations (i.e., eq 6 and FRDA).

From the properties of the FRDA equation⁹ it can be noticed that generally the effect of structural heterogeneity on an adsorption isotherm is rather small (exactly a contrary conclusion was given on the basis of the analysis

Table 1. Comparison of Fractal Dimensions Calculated from Different Relative Pressure Ranges Using the AJ Isotherm Linearization Procedure with Real Ones (i.e., Assumed in the Analytical Solution)

range of relative pressure	benzene			nitrogen		
	$D = 2.2$	$D = 2.5$	$D = 2.8$	$D = 2.2$	$D = 2.5$	$D = 2.8$
0.1–0.075	2.7968	2.8118	2.8065	2.8975	2.9121	2.9264
0.1–0.05	2.7668	2.7840	2.8010	2.8822	2.8991	2.9155
0.1–0.025	2.7181	2.7391	2.7596	2.8574	2.8778	2.8978
0.1–0.01	2.6609	2.6863	2.7110	2.8279	2.8528	2.8777
0.1–0.0075	2.6016	2.6316	2.6607	2.7972	2.8268	2.8553
0.1–0.005	2.5706	2.6030	2.6344	2.7812	2.8132	2.8440
0.1–0.0025	2.5328	2.5681	2.6024	2.7614	2.7964	2.8301
0.1–0.0001	2.4937	2.5321	2.5691	2.7407	2.7790	2.8157

of the AJ equation¹). This is in agreement with the findings reported previously and based on the applications of fractal geometry for the description of solids heterogeneity.^{13–16}

It was also shown by us^{8,9} that the only possible way to obtain the II type of BET adsorption isotherm from the FRDA (and/or FRDR) equation is the increase of x_{\max} (the maximal value of x) beyond the micropore diameter, and this should be treated as an illustrative example only (we have not postulated that the theory of volume filling of micropores is valid for larger pores, and it is well-known that it is accepted only for micropores).

For both, approximate and analytical isotherms, the formalism of thermodynamics of adsorption in microporous systems can be applied.^{5,10,17,18} The obtained discrepancies between the approximated (eq 6) and analytical (eq 8) adsorption isotherm formulas, however, lead to some enormous differences in the thermodynamical description of the micropore filling process.

The applicability of the FRDA isotherm as well as of corresponding adsorption enthalpy equation for the simultaneous description of experimental adsorption isotherms and of corresponding adsorption heat data on microporous solids^{6,7,10,11} was demonstrated by us previously.

A more general question arises about the error connected with the application of the AJ equation to experimental data. This can be analyzed as follows: we assumed benzene and nitrogen as adsorbates and we modeled, using the analytical solution, the adsorption isotherms for three fractal dimension values $D = 2.2$, 2.5, and 2.8. Then we plotted the obtained isotherms in the coordinates of the AJ equation ($\ln \Theta$ vs $\ln(\ln(p_s/p))$). We linearized the obtained plots for different relative pressure ranges and then D was calculated (Table 1). The first pressure range (i.e., 0.1–0.05) was proposed¹ from the analysis of the range of applicability of the approximate equation. For this pressure range the comparison of fractal dimension values obtained analytically (FRDR) and those approximated by eq 6 shows that the approximate solution leads practically to the constant D value, whereas in practice the fractal dimension changes by about 30%. The general observation is as follows: the wider the range of the relative pressure applied, the lower the fractal dimension

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Table 2. Relative Pressure Ranges That Should Be Applied for Linearization of Adsorption Data in the AJ Equation Coordinates To Obtain the Same D Values as Real

adsorbate	D_{FRDA}	D_{AJ}	range of relative pressure
benzene	2.2	2.2018	0.1 to 2×10^{-6}
	2.5	2.4989	0.1 to 3×10^{-4}
	2.8	2.8010	0.1 to 5×10^{-2}
nitrogen	2.2	2.5076 ^a	0.1 to 2×10^{-4}
	2.5	2.5827 ^a	
	2.8	2.7892	

^a Lowest possible D value for the assumed pressure range (0.1 to 1×10^{-7}).

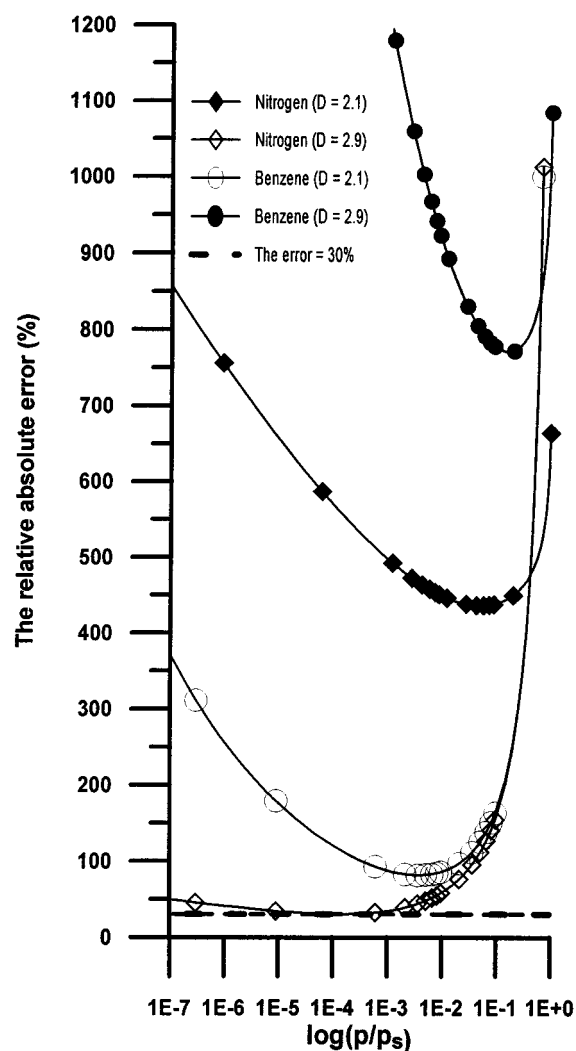


Figure 4. Relative absolute error calculated using eq 13 for the two adsorbates described in Figure 2. The horizontal dashed line represents the error equal to 30%.

value. In Table 2 we also show what pressure ranges should be applied for the linearization of adsorption data in coordinates of approximate equation to obtain the same fractal dimensions from the both equations. However, not for all cases is such a procedure possible. For example, in the case of nitrogen for D values equal to 2.2 and 2.5, respectively, it is impossible to find the pressure ranges that lead to the same fractal dimensions as from the analytical solution. For those cases the lowest possible D_{AJ} values are included in Table 2 and they were calculated for the widest possible relative pressure ranges ($0.1-10^{-7}$

p/p_s) (0.1 is generally accepted as the highest possible limit of the validity of volume filling mechanism¹⁹).

The next problem arising from the analysis of eq 6 is that $K_{(i)}$ is the function of minimum and maximum slit half-widths and D . The assumption of $K_{(i)}$ as constant is incorrect; moreover, this assumption is very dangerous from the point of view of the evaluation of characteristics of an adsorbent. The reason is that it can lead to such a combination of all parameters that two adsorption isotherms can be practically identical in the pressure range proposed for the application of an approximate isotherm, however, they can be described by different parameters characterizing a solid (especially D).

Summing up, we are presenting the detailed analysis of eq 5. Using simple mathematics all the integrals can be solved analytically and we obtain

$$\int_0^{x_{\min}} B dx = \frac{\rho}{n} (\mu A^n)^{(D-3)/n} \gamma \left(\frac{3-D}{n}, x_{\min}^n \mu A^n \right) \quad (9)$$

$$\int_{x_{\max}}^{\infty} B dx = \frac{\rho}{n} (\mu A^n)^{(D-3)/n} \left[\Gamma \left(\frac{3-D}{n} \right) - \gamma \left(\frac{3-D}{n}, x_{\max}^n \mu A^n \right) \right] \quad (10)$$

We can rewrite eq 5 as follows

$$\int_0^{\infty} B dx - \int_{x_{\min}}^{x_{\max}} B dx = \int_0^{x_{\min}} B dx + \int_{x_{\max}}^{\infty} B dx \quad (11)$$

$$\Theta_{\text{AJ}} - \Theta_{\text{FRDA}} = \frac{\rho}{n} (\mu A^n)^{(D-3)/n} \left[\Gamma \left(\frac{3-D}{n} \right) + \gamma \left(\frac{3-D}{n}, x_{\min}^n \mu A^n \right) - \gamma \left(\frac{3-D}{n}, x_{\max}^n \mu A^n \right) \right] \quad (12)$$

On the basis of this equation we can calculate the relative absolute error using

$$\frac{|\Theta_{\text{AJ}} - \Theta_{\text{FRDA}}|}{\Theta_{\text{FRDA}}} \times 100\% \quad (13)$$

Figure 4 shows the errors calculated for the two adsorbates described above. It is seen that the lowest possible error is close to 30% and the higher the D value the higher the absolute error. This analysis indicates with no doubt that the neglectance of the last two integrals in eq 5 cannot be treated as an approximation, and in the region of moderate values of adsorption potential eq 5 cannot be approximated by the first integral term.

The FRDR and AJ adsorption equations lead to absolutely different descriptions of adsorption and related adsorption thermodynamics in micropores of fractal solids. Moreover, eq 6 cannot be treated even as a rough approximation of the FRDA equation. This leads to the general conclusion that the approximate AJ isotherm, though attractive because simple in calculation, cannot be applied for the description of adsorption process proceeding according to the volume filling of micropores in solids possessing the structural heterogeneity described by the Pfeifer and Avnir pore size distribution.

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A response by Avnir and Jaroniec will appear in a later issue.