

LETTER TO THE EDITOR

A Simple Method of the Determination of the Structural Heterogeneity of Microporous Solids

A new procedure for determining the structural heterogeneity of microporous solids is presented. Applying the concept of a general adsorption isotherm equation, a method for solving this equation for adsorption in micropores is developed, and the applicability of a new simple algorithm for determining the parameters of microporous structure of two commercial carbons is shown. © 2001 Academic Press

1. INTRODUCTION AND THE DESCRIPTION OF THE METHOD

The determination of the structural heterogeneity of microporous solids (for example, active carbons) remains the most important and difficult problem in the field of the theoretical description of adsorption. Numerous advanced techniques have been adopted to study the structure and energetic heterogeneity of these materials. Among them, adsorption thermal analysis and inverse gas chromatography are the most popular due, probably, to relatively low cost.

Dubinin and Stoeckli (1) were the first to propose the concept of the distribution of the characteristic energy of adsorption. Applying this concept, the general form of the adsorption integral equation (with the Dubinin–Radushkevich (2) isotherm as a kernel) can be written as

$$a_{mic}(p) = a_{mic}^0 \int_{\Omega(E_0)} \exp\left[-\left(\frac{A(p)}{\beta E_0}\right)^2\right] f\left(\frac{1}{E_0^2}\right) d\left(\frac{1}{E_0^2}\right), \quad [1]$$

where

$$A = RT \ln\left(\frac{p_0}{p}\right), \quad [2]$$

a_{mic}^0 is the maximum amount adsorbed in micropores, $a_{mic}(p)$ is the amount adsorbed in micropores at the equilibrium pressure p and the absolute temperature T , β is a similarity coefficient, R is the universal gas constant, E_0 is the characteristic energy of adsorption, and p_0 is the saturation pressure of an adsorbate.

Jaroniec and Piotrowska (3) proposed to apply the shifted Gamma distribution function, defined by

$$f\left(\frac{1}{E_0^2}\right) = \frac{q^{n+1}}{\Gamma(n+1)} \left(\frac{1}{E_0^2} - \frac{1}{E_{0,max}^2}\right)^n \exp\left[-q\left(\frac{1}{E_0^2} - \frac{1}{E_{0,max}^2}\right)\right]. \quad [3]$$

When Eq. [3] is substituted into [1] and the integration range $\Omega(E_0) = (1/E_{0,max}^2, \infty)$ is assumed, where $E_{0,max}$ is the maximum characteristic energy of adsorption that the solid possesses, it leads to the equation

$$a_{mic} = a_{mic}^0 \exp\left[-\frac{1}{E_{0,max}^2} y\right] \left[\frac{q}{q+y}\right]^{n+1}, \quad [4]$$

where

$$y = \left(\frac{A}{\beta}\right)^2. \quad [5]$$

Equation [4] can be simplified, assuming that the maximum characteristic energy of adsorption is equal to infinity (4):

$$a_{mic} = a_{mic}^0 \left[\frac{q}{q+y}\right]^{n+1}. \quad [6]$$

Under this assumption Eq. [3] reduces to the form

$$f\left(\frac{1}{E_0^2}\right) = \frac{q^{n+1}}{\Gamma(n+1)} \left(\frac{1}{E_0^2}\right)^n \exp\left(-q \frac{1}{E_0^2}\right). \quad [7]$$

It should be noted that the range of integration, $\Omega(E_0)$, must reflect the boundary conditions of a microporous system, and the correct range should be between E_{min} and E_{max} (5–16). The lower limit (E_{min}) is the characteristic energy of adsorption associated with the largest pores in the system, while the upper limit (E_{max}) associates with the smallest accessible micropores. It is obvious, and was discussed recently (15, 16), that the application of the integration range in Eq. [4] as equal to $\Omega(E_0) = (1/E_{0,max}^2, \infty)$ and in Eq. [6] as equal to $\Omega(E_0) = (0, \infty)$ is questionable and should be treated as an approximation (15, 16). In spite of this Eq. [6] is widely used for the description of an adsorption process (4, 17); thus, we do not want to consider in detail the correctness of the above-mentioned assumption.

Therefore, Eq. [6] can be written as

$$\ln(a_{mic}) = X + (n+1) \ln\left[\frac{q}{q+y}\right], \quad [8]$$

where

$$X = \ln(a_{mic}^0). \quad [9]$$

This adsorption isotherm Eq. [8] has three parameters, a_{mic}^0 , q , and n , the last two being the structural ones. The parameter a_{mic}^0 can be easily determined using independent methods (for instance, measurements of apparent and true densities, α_s -method and/or others), and, to simplify the procedure, we assume that a_{mic}^0 is known.

The aim of the current study is to propose a simple and new method of solving Eq. [8].

According to the well-known least-squares method, we can define the functional in the following form:

$$\Psi(q, n) = \sum_i \left\{ \ln(a_{mic,i}) - X - (n+1) \left[\frac{q}{q+y_i}\right] \right\}^2. \quad [10]$$

Applying the condition for the minimum of Eq. [10], one can define the formula which can be used for the estimation of the parameter q :

$$\frac{\sum_i \ln(a_{mic,i}) \ln\left(\frac{q}{q+y_i}\right) - X \sum_i \ln\left(\frac{q}{q+y_i}\right)}{\sum_i \left[\ln\left(\frac{q}{q+y_i}\right)\right]^2} + \frac{X \sum_i \frac{y_i}{q+y_i} - \sum_i \ln(a_{mic,i}) \frac{y_i}{q+y_i}}{\sum_i \ln\left(\frac{q}{q+y_i}\right) \left(\frac{y_i}{q+y_i}\right)} = 0. \quad [11]$$

Equation [11] can be solved using, for example, the iterative, bisection, or falsi method (18). Knowing the value of parameter q , parameter n can be found using

$$n = \frac{\sum_i \ln(a_{mic,i}) \ln\left(\frac{q}{q+y_i}\right) - X \sum_i \ln\left(\frac{q}{q+y_i}\right)}{\sum_i \left[\ln\left(\frac{q}{q+y_i}\right)\right]^2} - 1. \quad [12]$$

The micropore-size distribution (assuming a slit-like model) can be easily determined applying Dubinin's transform (1, 19, 20),

$$\frac{1}{E_0^2} = \left(\frac{x}{c}\right)^2 = c^* x^2, \quad c^* = \left(\frac{1}{c}\right)^2, \quad [13]$$

$$J(x) = 2 * c^* x F\left(\frac{1}{E_0^2}\right), \quad [14]$$

$$J(x) = \frac{2(qc^*)^{n+1}}{\Gamma(n+1)} x^{2n+1} \exp(-qc^* x^2), \quad [15]$$

where c , according to Dubinin, is assumed to equal 12 (kJ nm/mole) for benzene adsorption on an activated carbon (1).

The distribution (Eq. [15]) can be characterized by the following quantities:

—the value of the micropore size at which the function $J(x)$ has a maximum,

$$x_{\max} = \left(\frac{2n+1}{2qc}\right)^{1/2}, \quad [16]$$

—the average micropore size,

$$\bar{x} = \gamma \left(\frac{n+1}{qc}\right)^{1/2}, \quad [17]$$

—and the dispersion,

$$\delta_x = \left[(1-\gamma^2) \frac{n+1}{qc}\right]^{1/2}, \quad [18]$$

where

$$\gamma = \frac{\Gamma(n+3/2)}{(n+1)^{1/2} \Gamma(n+1)}. \quad [19]$$

The applicability of this simple algorithm for the determination of the structural heterogeneity of active carbons is presented below for two commercial adsorbents.

2. EXPERIMENTAL

The granulated activated carbon Filtrasorb F 400 (Calgon Carbon Corporation, U.S.A.) (fraction with the diameter 0.35–0.3 mm) was applied as an initial adsorbent (denoted as F 400 (F)). The same carbon was deashed using the method of Korver and the procedure described previously (21) (the obtained carbon is denoted as F 400 (S)). Benzene adsorption–desorption isotherms

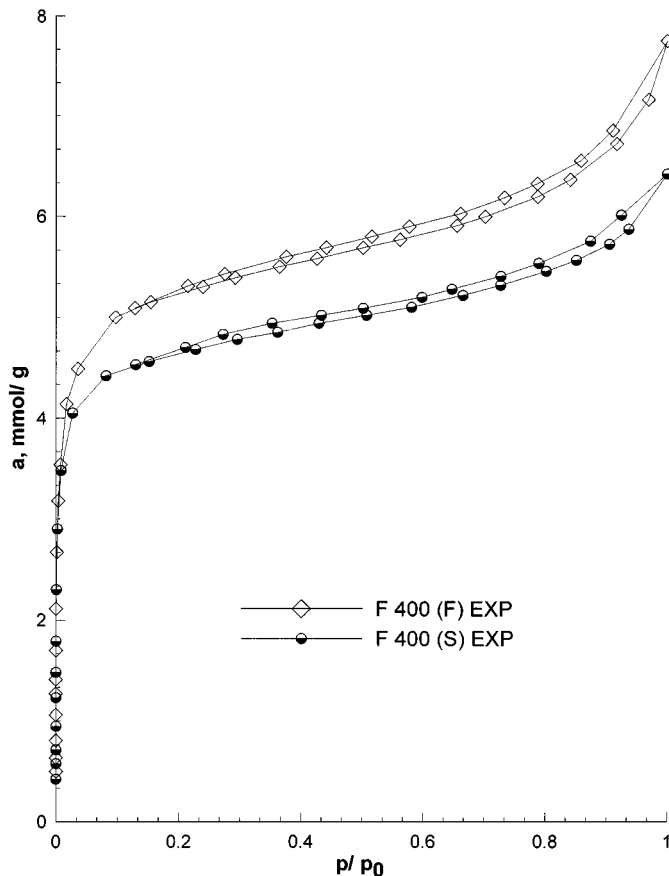


FIG. 1. Experimental adsorption–desorption isotherms of benzene (293.15 K) on studied carbons.

(Fig. 1) were measured at 293.15 K using the McBain–Bakr balance (22). Before the measurement, the samples were desorbed in vacuum at 393 K for 8 h. Adsorption isotherms were measured in the range of relative pressure from 10^{-5} up to 1.

3. RESULTS AND DISCUSSION

It is well known that the total amount adsorbed (a) is the sum of the amount adsorbed in micropores and the amount adsorbed in mesopores (a_{mes}):

$$a = a_{mic} + a_{mes}. \quad [20]$$

The Γ adsorbed in micropores was calculated applying the well-known Dubinin equations (23–25),

$$a_{mic} = a - \gamma S_{mes} \quad [21]$$

$$\gamma = 9.16 \times 10^{-3} \exp\left(\frac{A}{6.35}\right) \quad [22]$$

$$S_{mes} = \frac{1}{\sigma_a} \int_{a_1}^{a_s} A da, \quad [23]$$

where σ_a is the free surface energy of an adsorption film, a_1 is the adsorption value at the starting point of the sorption hysteresis, and a_s is the adsorption value at the equilibrium relative pressure equal to unity.

TABLE 1
Adsorption Parameters Obtained on the Basis of the Dubinin–Astakhov Equation and Value of ε Defined by Formula [20]

Carbon	a_{mic}^0 , mmol/g	E^0 , kJ/mol	n	ε , %
F 400 (F)	5.192	19.603	1.77	1.207
F 400 (S)	4.795	20.348	1.78	1.262

The data for adsorption of benzene in micropores were described by applying DA adsorption isotherm equation and Eq. [8] using the procedure presented in the current paper. The average relative error (ε), the sum of squared deviations (SSD), and the determination coefficient (DC) have been adopted to describing the goodness of fit of Eq. [8] to the experimental data (18),

$$\varepsilon = \frac{\sum_i \left(\left| \frac{a_{exp} - a_{cal}}{a_{exp}} \right| \right)_i}{N} \times 100 \quad [24]$$

$$SSD = \sum_i (a_{exp} - a_{cal})_i^2 \quad [25]$$

$$DC = 1 - \frac{\sum_i (a_{exp} - a_{cal})_i^2}{\sum_i (a_{exp} - \bar{a}_{exp})_i^2} \quad [26]$$

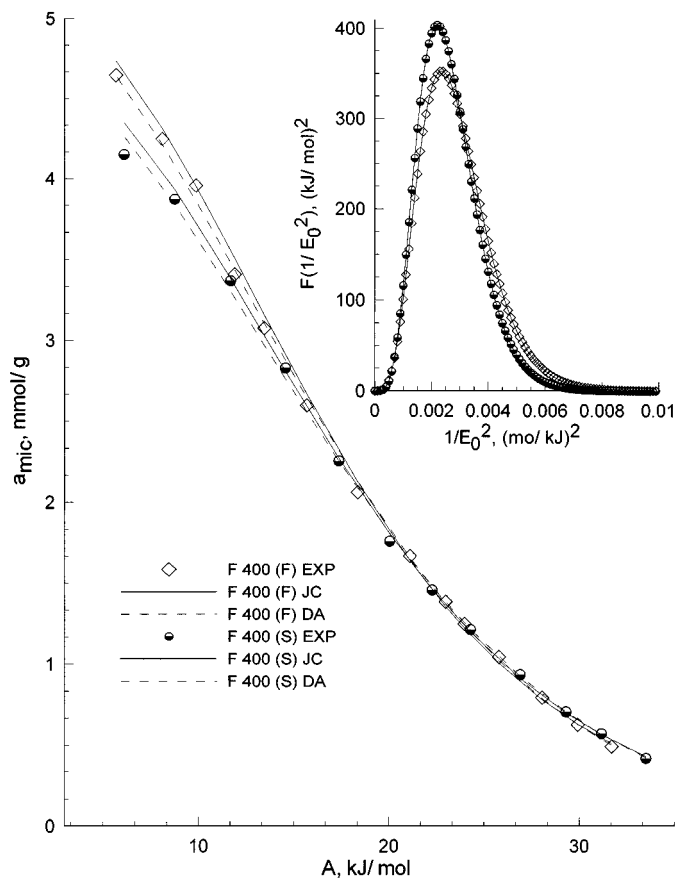


FIG. 2. Characteristic curves of adsorption: EXP—experimental points, JC—Eq. [6], DA—Dubinin–Astakhov equation. Inset: distribution of the function $f(1/E_0^2)$ obtained on the basis of Eq. [7].

TABLE 2
Adsorption and Structural Parameters Obtained on the Basis of Equations [16]–[18] and Value of the SSD, ε , and DC

Carbon	q	n	ε , %	SSD	DC	x_{max} , nm	x_{ave} , nm	δ
F 400 (F)	1905.558	4.477	2.187	0.043	0.998	0.613	0.629	0.136
F 400 (S)	2329.961	5.132	1.646	0.048	0.997	0.590	0.603	0.123

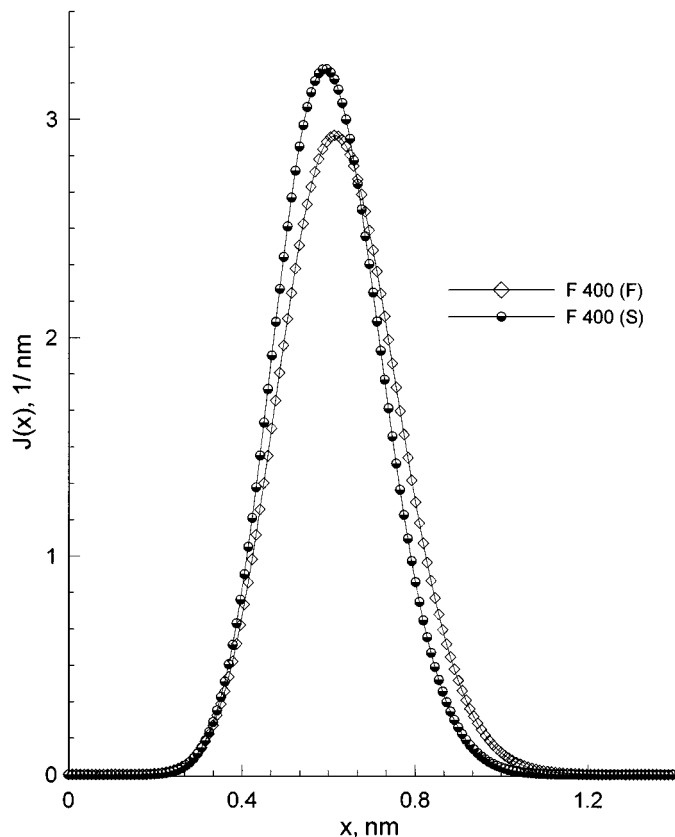


FIG. 3. Micropore-size distribution for both carbons obtained from Eq. [15].

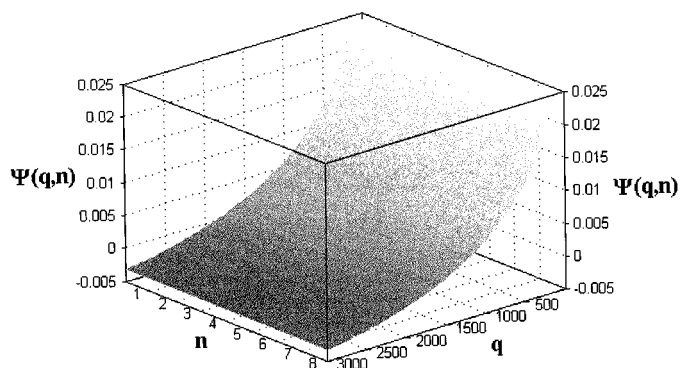


FIG. 4. The properties of the functional defined by Eq. [10] for F 400 (F) activated carbon.

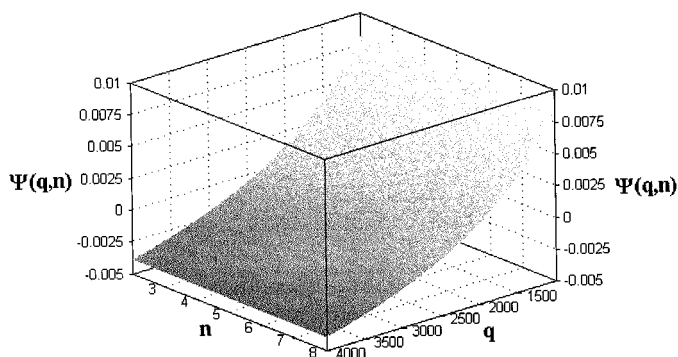


FIG. 5. The properties of the functional defined by Eq. [10] for F400 (S) activated carbon.

where

$$\bar{a}_{\text{exp}} = \frac{1}{N} \sum_i a_{\text{exp}}^i \quad [27]$$

and N is the number of experimental points.

The falsi method was applied to solve Eq. [11] and it was solved with accuracy equal to 10^{-12} .

The obtained results of the fit of the DA equation, as well as Eq. [8], to the experimental data are shown in Fig. 2 (in this figure the plot of the shifted gamma-distribution function is also shown (Eq. [7])) and in Tables 1 and 2. It can be noticed that for both carbons the parameter n of the DA equation is smaller than 2. This probably leads to the slightly higher values of ε obtained for the fit of Eq. [8] to the experimental data than obtained for DA equation (it should be remembered that the DR equation is applied as the kernel in Eq. [1]). However, based on Eq. [8], the pore-size distribution function can be easily calculated (Fig. 3), which is impossible based upon the DA isotherm.

Finally, in Figs. 4 and 5 the properties of the functional defined by Eq. [10] for both activated carbon samples are shown.

CONCLUSIONS

The obtained results show that the deashing of the investigated carbon slightly influences the micropore diameter. This is in agreement with the previous study (25) and similar behavior was observed for the series of different commercial carbons.

Finally, it can be stated that the new procedure of solving of Eq. [8], presented in this study, is simple, easy, and fast and the obtained results are of high accuracy. Thus, we recommend applying it for the determination of the heterogeneity of microporous carbonaceous materials.

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