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A Simple Method to Determine Cumulative Surface-Area Distributions of Porous Solids

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By means of simple equations, which essentially are modified forms of the BET equation, the specific surface area of a porous solid and its cumulative surface-area distribution can be determined simultaneously from the gas adsorption isotherm. The method proposed, which is rather accurate and very straightforward, may be useful for technological purposes.

1. INTRODUCTION

Some properties of porous solids, such as the specific surface area and the cumulative surface-area distribution can be calculated from gas adsorption or desorption isotherms. The determination of the specific area is usually based on the multilayer adsorption theory proposed by Brunauer, Emmett, and Teller (*1*). The cumulative surface-area distribution or the pore-size distribution is usually determined with the aid of the Kelvin equation, but the necessary calculations are rather lengthy and tedious.

It turns out to be possible, however, to determine the specific surface area as well as the cumulative surface-area distribution by a simple method using rather naive equations for the adsorption isotherms. As this method (which is not intended to be a substitute for other, more refined, methods used in more fundamental research) may be of some practical value for those who are interested in a quick first approximation for technological purposes, we will give a short outline of it in this paper without going into any theoretical detail.

2. EQUATIONS

The equations used are special cases of a general formula for the description of adsorption phenomena proposed earlier by us (*2*). The basis of this formula is the BET theory (*1*), but with the generalization that the heat of adsorption as well as the accessible surface area for adsorption depend on the layer number. Special cases occur by postulating special functions for those dependencies.

The special case that we use here is the following: As in the BET model the heats of adsorption of the second and higher layers are taken equal to the heat of condensation such that we are left only with the BET C constant. The accessible surface areas, however, are taken to be equal only for the first n layers, while from layer n on they are taken to decrease with a constant factor $s \leqslant 1$:

$$V_i = \begin{cases} V_1 & \text{for } i \leqslant n \\ V_1 s^{i-n} & \text{for } i > n \end{cases} \tag{1}$$

Here, V_i is the capacity of layer i, i.e., the amount of gas that can be adsorbed in layer i. Putting assumption (1) in the general formula referred to above, the following isotherm equation is obtained:

$$v = \frac{V_1 C\, x\,(1 - sx - x^n + sx^n)}{(1 - x)(1 - sx)[1 + (C - 1)x]}, \tag{2}$$

where v is the amount adsorbed at the relative pressure x.

This equation is still rather general. For $s = 1$ or $n \rightarrow \infty$ it reduces to the BET equation, while for $s = 0$ the equation proposed by Pickett (*3*) results. For $n = 1$ we get one of the equations proposed by Anderson (*4*).

Practical values of the parameters n and s are $n = 1, 2, 3$ and $0.1 < s < 0.8$. With those values, Eq. (2) describes the adsorption that takes place in narrow pores, because then after adsorption of the very first layers the capacity V_i decreases very rapidly to zero for increasing i. Equation (2) thus neglects the eventual existence of wider pores. An approximate way of correcting for this neglect is to put

$$V_i = \begin{cases} V_{\text{in}} + V_{\text{ex}} & \text{for } i \leqslant n, \\ V_{\text{in}} s^{i-n} + V_{\text{ex}} & \text{for } i > n, \end{cases} \tag{3}$$

where V_{in} represents the capacity of the first layer adsorbed on the "internal" surface offered by the narrower pores and V_{ex} the capacity of the layers adsorbed on the "external" surface offered by the wider pores. Instead of Eq. (2) one then finds

$$v = \frac{Cx}{(1-x)[1+(C-1)x]} \times \left[\frac{V_{\text{in}}(1 - sx - x^n + sx^n)}{(1-sx)} + V_{\text{ex}}\right]. \tag{4}$$

Equations (2) and (4) take into account that the accessible surface area for adsorption decreases, due to the filling of the pores, when the number of adsorbed layers increases. A pore is completely filled when r/d layers are adsorbed, d being the thickness of an adsorbed layer and r half the pore width. (In principle it would be possible to take into account pore distributions which show more structure, but this would increase the number of parameters and thus decrease the practical value of the method proposed.)

Now, in Eqs. (1) and (3) V_i represents the capacity for adsorption in the pores that have a width equal to or larger than $2\,id$. The capacity and the surface area of a layer differ only by a constant depending on, e.g., the density, which is supposed to be constant, and the effective surface area occupied by one molecule. In fact, V_i can be compared with the cumulative surface area defined by Barrett, Joyner, and Halenda (*5*). The two concepts are not completely equivalent, however. The difference is that Barrett *et al.* (*5*) start from the Kelvin equation, which is a macroscopical equation and consequently leads to a cumulative surface-area distribution that is a continuous function of r, while we start from a BET-like equation [i.e., Eq. (2) or (4)], which is essentially a microscopic equation, therefore giving rise to a discrete cumulative surface-area distribution (V_i decreases stepwise as a function of i). Both approaches are, of course, in principle incorrect. On the one hand, a macroscopic point of view is only allowed when the adsorbate molecules can be considered to be very small in comparison with the principal pore size of the adsorbent, and this is usually not the case. On the other hand, due to the capricious shape of the pores and the liquidlike behavior of the adsorbed molecules, one cannot expect that a strictly layerwise adsorption takes place. It should be noted, also, that the calculation of distributions by means of the Kelvin equation depends on the exact shape of the pores that one assumes; this dependence is rather weak, however, as was pointed out, e.g., by Innes (*6*).

Neglecting these difficulties, we will simply compare cumulative capacity distributions determined by application of Eqs. (1) and (2) or Eqs. (3) and (4) to experimental data with the distributions obtained by application of the Kelvin equation. The main justification of this approach is that the results of the two methods will be found to agree.

3. Method of Computation

The experimental data and the cumulative surface-area distributions derived from them by means of the Kelvin equation, which both are necessary for the comparison, were taken from the literature. Fitting Eq. (2) or Eq. (4) to the experimental isotherms we find the appropriate values of the parameters. That is, we rewrite Eq. (2) as

$$\frac{A_{sn}(x)}{v} = \frac{1}{V_1 C} + \frac{C-1}{V_1 C}\,x \tag{5}$$

where $A_{sn}(x)$ is defined by

$$A_{sn}(x) = \frac{x(1 - sx - x^n + sx^n)}{(1 - x)(1 - sx)} \quad (6)$$

This latter expression assumes a simple form for the low n values ($n = 1, 2, 3$) that are of practical importance. For these n values, and for $s, x = 0.1, 0.2, \ldots, 0.9$ the quantity $A_{sn}(x)$ can be easily tabulated. (A copy of this table may be obtained from the authors.) By means of that table and the values of v at $x = 0.1, 0.2, \ldots, 0.9$ taken from a plot of the experimental isotherm it is easy to find values of s and n for which a graph of $A_{sn}(x)/v$ versus x gives approximately a straight line. From the intercept at $x = 0$ and the slope of the resulting straight line for $A_{sn}(x)/v$ one can then evaluate V_1 and C, similar to the usual BET treatment. When the form of the experimental isotherm suggests the occurrence of an "external" surface (wide pores), such that use should be made of Eq. (4) rather than of Eq. (2), the treatment is somewhat more elaborate and involves more guesswork. One may still proceed first in the manner outlined above, fixing the m value and finding approximate values for s, C, and V_1. The value found for V_1 may be taken to be approximately equal to $V_{\text{in}} + V_{\text{ex}}$. Choosing a suitable value for V_{ex} one can calculate the volume adsorbed on the external surface as a function of the relative pressure. After subtraction from the experimental isotherm, the remaining part can be treated in the way outlined above for Eq. (2), which gives values for V_{in} and s. By iterating this procedure one or two times, the definite values of V_{ex}, V_{in}, and s are found. In the process, two different C values may be tolerated, C_{in} and C_{ex}, which anyhow have little meaning when the low-pressure part of the isotherm is not determined accurately.

To perform the calculations we need a value for the effective layer thickness for the case of N_2 as adsorbate, which is the only case considered here. By assuming the correctness of the BET specific surface area Schüll (*7*) calculated a value of 4.3 Å for the thickness of one adsorbed layer of N_2. This value was adopted by Barrett *et al.* (*5*), whereas Lippens and de Boer (*8*) assign to this thickness a value of 3.6 Å. In the literature some other evaluations of this thickness may be found, but in view of the uncertainties involved in these assignments and the crudeness of the comparison that we want to make we feel justified in assuming an average value of 4 Å for the layer thickness.

4. RESULTS

The parameter values for 19 nitrogen adsorption isotherms measured on various samples are given in Table 1. In the second column the type of adsorbent is given together with the indication used in the references quoted. The fourth and fifth columns contain the parameters obtained by fitting the BET equation. The remaining columns give the parameters obtained by fitting Eq. (2). The lower part of the table refers to Eq. (4) (see below).

For all samples, the BET equation (as usual) fits the isotherm only for relative pressures $x \lesssim 0.3$. In contrast, Eq. (2) fits the isotherms in almost all cases in the range $x \lesssim 0.7$. The only exceptions are sample P, where Eq. (2) could be fitted up to $x \lesssim 0.5$ (still better than the BET equation), and samples E and F, where Eq. (2) could be fitted only up to $x \approx 0.3$ [in fact, the fit obtained by means of Eq. (2) becomes for these last two cases identical with the BET fit]. As examples, Figs. 1–3 give the fits obtained by means of the BET equation and by means of Eq. (2) to several experimental isotherms.

By means of Eq. (4) one may obtain still better fits. As the calculations are somewhat more tedious than those necessary when using Eq. (2), whereas the improvement is rather marginal, we have done this only in two cases, namely samples H and J. The parameter values obtained are given in the second part of Table 1. The fits obtained for these cases by means of Eq. (4) are compared with the experimental results and the fits of the BET equation and Eq. (2) in Fig. 3. It should be noted that, for computational convenience, we used two different C values, C_{in} and C_{ex},

TABLE 1
PARAMETERS OBTAINED BY FITTING THE BET EQUATION, EQ. (2), AND EQ. (4) TO SEVERAL EXPERIMENTAL NITROGEN ADSORPTION ISOTHERMS

Sample	Type	Ref.	BET equation		Eq. (2)			
			V_1	C	V_1	C	s	n
A	Al_2O_3 (By 200)	*8*	6.06	85	7.1	37	0.5	1
B	Al_2O_3 (By 250)	*8*	111.8	80	133.2	65	0.1	1
C	Al_2O_3 (By 270)	*8*	105.7	95	134.4	34	0.1	1
D	Al_2O_3 (By 450)	*8*	94.3	47	132.6	18	0.1	1
E	Al_2O_3 (By 580)	*8*	56.1	200	56.1	200	1	—
F	Al_2O_3 (By 750)	*8*	30.7	100	30.7	100	1	—
G	Al_2O_3 (BOG 450)	*8*	3.9	150	4.2	120	0.47	1
H	Al_2O_3 (BOG 580)	*8*	15.0	120	20.3	25.3	0.33	1
J	Al_2O_3 (BOG 750)	*8*	4.4	115	4.66	59.7	0.65	2
K	Al_2O_3 (A 120)	*8*	139.4	67	144.0	53	0.93	3
L	Al_2O_3 (A 450)	*8*	94.7	350	95.4	200	0.90	4
M	Al_2O_3 (A 750)	*8*	59.2	400	60.6	200	0.70	3
N	Al_2O_3 (MiBo 5)	*8*	58.4	90	59.2	82	0.90	3
P	Al_2O_3 (BoW 120)	*8*	14.6	170	15.4	90	0.90	1
Q	Al_2O_3 (BoW 450)	*8*	21.1	150	24.5	48	0.70	1
R	Clay Crack Cat.	*5*	64.9	70	68.6	49.2	0.3	2
S	Silica	*5*	185.2	95	188.7	73	0.40	3
T	Act. carbon	*5*	238.0	500	277.4	79	0.2	1
U	Silica I	*9*	164	840	226	36	0.1	1

Sample	Type	Ref.	Eq. (4)					
			V_{in}	C_{in}	s	n	V_{ex}	C_{ex}
H	Al_2O_3 (BOG 580)	*8*	20.2	21.6	0.20	1	0.92	100
J	Al_2O_3 (BOG 750)	*8*	3.93	80.5	0.57	2	0.69	100

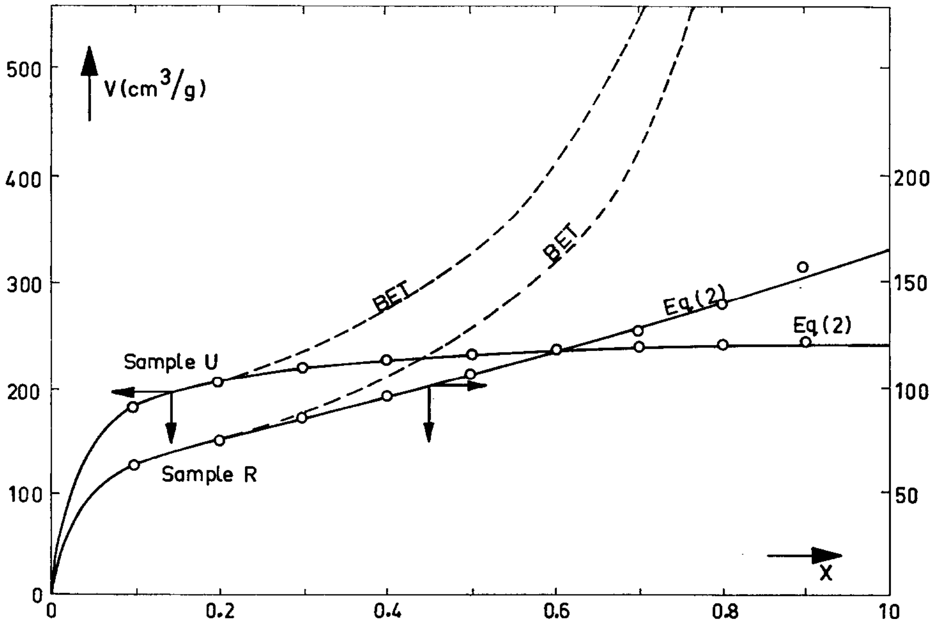

FIG. 1. Nitrogen adsorption isotherms of a silica and a clay cracking catalyst. The circles denote experimental points taken from the literature quoted. The curves are best fits of the equations indicated.

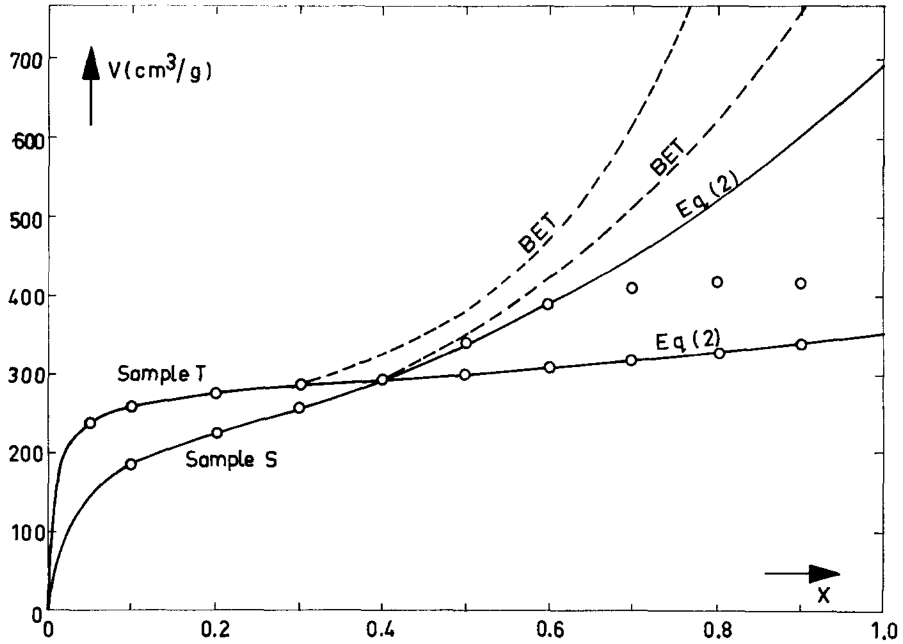

FIG. 2. The same as Fig. 1 but for a silica and an activated carbon.

for, respectively, the "internal" and the "external" contribution, i.e., for, respectively, the first and the second term in square brackets of Eq. (4). This is allowed because the theoretical isotherms depend only very weakly on the precise value of the C constants, which have little quantitative meaning (as is well known for the BET C constant).

The fits obtained by means of Eq. (2) or Eq. (4) are a considerable improvement over the fits obtained by means of the BET

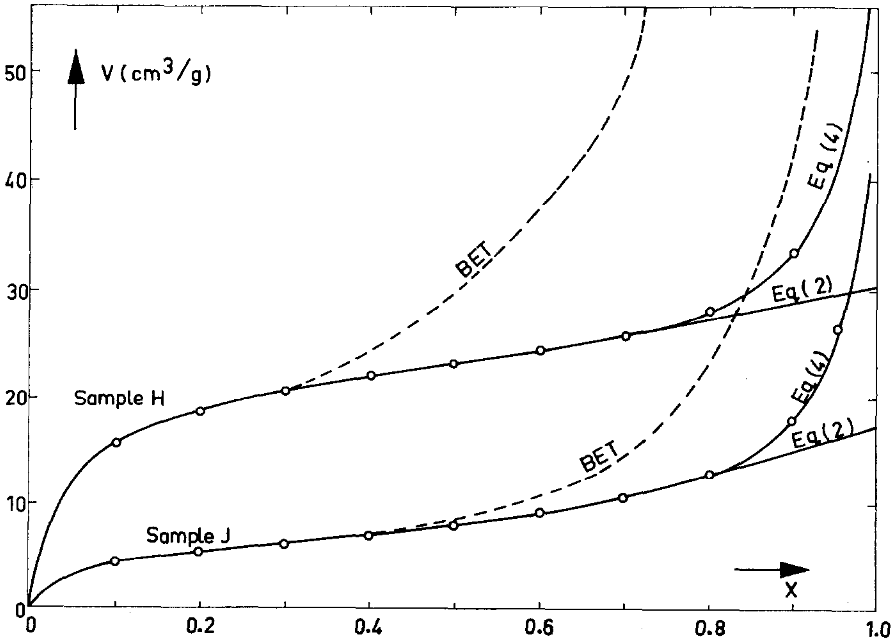

FIG. 3. The same as Fig. 1 but for two alumina samples.

equation. However, this has been achieved by tolerating in the theory a larger number of adjustable parameters, a procedure which is justified only if the additional parameters have physical meaning. To show that this is indeed the case we make the following comparison. On the one hand the parameters obtained by fitting Eq. (2) or Eq. (4) together with the value of 4 Å for the nitrogen layer thickness determine an accessible surface distribution according to Eq. (1) or Eq. (3). On the other hand, this distribution can also be found in a completely independent manner, i.e., by means of an application of the Kelvin equation to the experimental isotherms (*5*). Now, the articles quoted in Table 1, from which the experimental isotherms were taken, were selected just because their authors also give the surface-area or pore-size distributions for the various adsorbents calculated by means of the Kelvin equation. Therefore a comparison between these surface-area distributions and those found by our method is possible without necessitating us to go through all the computational detail brought about by an application of the Kelvin equation. The comparison is made in Fig. 4, in which only an unbiased sample of all cases studied is

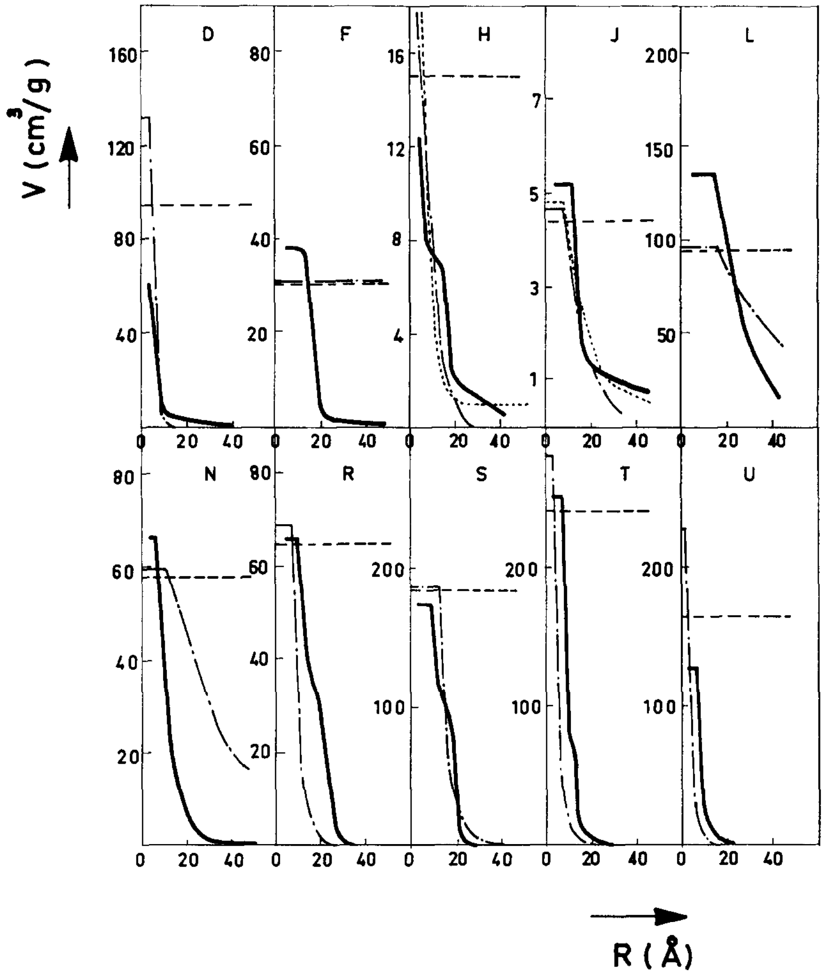

FIG. 4. Comparison of the cumulative volume adsorbed as a function of pore radius according to Eqs. (1) and (2) (dot-dash curves) or Eqs. (3) and (4) (dotted curves) with those derived by means of the Kelvin equation (full curves). The BET monolayer capacity is also indicated (broken lines).

given. In this figure the cumulative surface-area distributions found by means of the different equations are given, transferred to the same dimensions (cumulative volume adsorbed in cm^3/g against pore radius in Å). In view of the fundamental shortcomings of both our method and the Kelvin equation method the qualitative agreement between the results apparent from Fig. 4 is quite remarkable. Below a pore radius of say 5 Å the Kelvin equation is utterly unreliable (it has not been given in Fig. 4 for such pore radii). The combination of Eqs. (1) and (2) cannot be expected to give trustworthy information about pores with a radius larger than say 20 Å; that information is mainly concentrated in the last part of the isotherm, with relative pressures $x \gtrsim 0.7$, which part is not described by Eq. (2). This situation is improved by means of the combination of Eqs. (3) and (4), as is shown in Fig. 4 for the cases H and J.

Let us indicate briefly the reasons why in our opinion the method described works. The adsorption isotherm is the best information available about the pores present in the adsorbent. The fictions introduced either by capillary condensation theories or by multilayer adsorption theories merely serve to simulate in one way or the other the amount adsorbed under certain circumstances, i.e., the pore volume filled. The better one tries to take the experimental isotherm into account, the more one is forced to reckon with the pore volume actually present in the adsorbent. Of course, a varying heat of adsorption during the filling of the pores will play a disturbing role, but it determines only the rate of filling, not the absolute amount of filling; moreover, one may expect its influences to be smeared out and to partly cancel against each other. Or, by fitting the isotherm as well as possible, one tries at least to fulfill the necessary condition that the theoretically determined integral amounts adsorbed under certain circumstances agree with the then available actual pore volume. Obviously, this is only a very qualitative explanation, but the best we have in view of the utter complexity of the phenomenon. It is interesting to see that it does not seem to matter so much which concept (multilayer adsorption or capillary condensation) is used for a description of the underlying phenomenon: in either way roughly the same pore distribution is found. Of course, this remark is not meant to invalidate the use of the Kelvin equation, which at the cost of more labor may lead to more refined descriptions.

5. CONCLUSION

Application of the equations proposed in this paper, in particular of Eqs. (1) and (2), results in a fit to experimental isotherms up to relative pressures $x \approx 0.7$–0.8. The capacity of the first layer adsorbed found from this application agrees in general very well with the BET monolayer capacity. In addition, two parameters (n and s) are found which give a crude characterization of the pore-size distributions, in qualitative agreement with the results of the Kelvin equation. Application of Eqs. (1) and (2) to the experimental isotherms is, however, much simpler than the tedious procedure necessitated by the Kelvin equation. Therefore, in spite of interpretation difficulties and of the fundamental shortcomings inherent in our equations equally well as in the BET equation and in the Kelvin equation, we feel justified in concluding the following. The method outlined in this paper, while not being a substitute for more refined methods, may prove a useful tool in the description of adsorption data, when for technological purposes one wishes to be able to give a simple phenomenological characterization of an adsorbent in terms of the specific surface area and the pore-size distribution.

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