

LETTER TO THE EDITOR

The Characterization of Microporous Activated Carbons Utilizing a Simple Adsorption Genetic Algorithm (SAGA)

The paper presents a new simple adsorption genetic algorithm (SAGA) which is based on the genetic theory of natural selection and rivalry. This algorithm is utilized to estimate the parameters of the Dubinin–Rhadushkevich equation. The obtained results are compared with these achieved from classical optimization methods. The analysis of the error of fitting of the DR model to experimental data is discussed. It is shown that the proposed SAGA, contrary to the other methods, makes it possible to calculate the parameters of the DR equation not only very precisely but also very quickly.

© 2001 Academic Press

INTRODUCTION

Microporous activated carbons are widely used as adsorbents, catalysts, and supports. Generally, the use of such materials in various fields of science and technology requires their versatile characterization, which comprises determination of their chemical composition, their structural and energetic heterogeneity, and also, in a wider sense, their mechanical properties. Up till now, several methods of determination of heterogeneity, based on classical measurements of adsorption and desorption on solids, have been proposed (1). All those methods possess advantages and disadvantages; thus none of them can be treated as general.

Among the proposed methods of characterization of microporous solids on the ground of adsorption and desorption measurements, the theory of volume filling of micropores (proposed by Dubinin and co-workers many years ago) has become the most frequently used (2). For the description of an adsorption process in a homogeneous micropore system the classical Dubinin and Radushkevich (DR) equation is widely applied (3). Additionally, the DR equation is often used as a kernel in the global adsorption integral equation (4, 5). Although the DR equation is thermodynamically inconsistent (6–8), it still remains the most frequently used for the characterization of the microporosity of activated carbons.

In the current paper a new simple adsorption genetic algorithm (SAGA) which is based on the genetic theory of natural selection and rivalry is used to estimate the parameters of the DR equation. The results are compared with these obtained on the grounds of the classical optimization methods (for example, a gradient method (9)). Moreover, the analysis of the error of fitting of the DR model to experimental data is discussed. It is shown that the proposed SAGA, in contrast to the other methods, makes it possible to calculate the parameters of the DR equation in a very precise manner and quickly as well.

THE CONSTRUCTION OF SAGA AND THE COMPUTATION

The numerical problem of the fitting of the DR equation parameters to the experimental points of adsorption isotherm is reduced to finding the total minimum

of the sum of squared deviations expressed by (10),

$$\Omega(W_0, E_0) = \sum_i \left\{ W_i - W_0 \exp \left[- \left(\frac{A_i}{\beta E_0} \right)^2 \right] \right\}^2, \quad [1]$$

where

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

where W_i is the current and W_0 the limiting adsorption of vapor per unit volume in micropores, β is the similarity coefficient that characterizes an adsorbate, E_0 is the characteristic adsorption energy, R is the universal gas constant, T is the temperature, p_0 is the saturation vapor pressure of adsorbate, and p_i is the equilibrium pressure.

Since the proposed SAGA (as a classical simple genetic algorithm) prefers the most adopted individual, the problem of minimization of the function defined by Eq. [1] was replaced by maximization of this function by means of transformations,

$$\min \Omega(W_0, E_0) = \max \{ -\Omega(W_0, E_0) \} = \max \{ -\Omega(W_0, E_0) + \alpha \}, \quad [3]$$

where α is the arbitrarily chosen positive constant (11).

The presented SAGA is composed of procedures based on a natural selection mechanism and heredity (12). In every generation a new team of artificial organisms (of bit courses) was formed from the connections of fragments of the best-adapted representatives. In the introduced algorithm three classical genetic operations were applied: reproduction (by means of roulette), simple crossover, and mutation. Two last operations were passed peaceably with a given probability (following De Jong (12), 0.6 and 0.0333, respectively). In the presented SAGA variables were coded in a binary system. According to a suggestion of Goldberg, the size of the population was assumed to be 30, the length of the chromosomes was found to be 30, and the number of generations was assumed to equal 30 (12).

The results obtained using SAGA were compared with the results obtained applying the algorithm utilizing the least-squares and iterative procedure (LS). In that case the system of nonlinear equalizations of the following form was led out:

$$\begin{cases} W_0 = \frac{\sum_i W \exp \left[- \left(\frac{A_i}{\beta E_0} \right)^2 \right]}{\sum_i \left\{ \exp \left[- \left(\frac{A_i}{\beta E_0} \right)^2 \right] \right\}^2} \\ \frac{\partial \Omega(W_0, E_0)}{\partial E_0} = 0. \end{cases} \quad [4]$$

Additionally, the calculations were executed using two optimization methods: a simple gradient (SGM) one (9) and the so-called Hook–Jeeves (HJ) (13) method. In the case of the simple gradient method, the gradients were defined

applying the statements

$$\frac{\partial \Omega(W_0, E_0)}{\partial W_0} = 2 \left\{ W_0 \sum_i \left\{ \exp \left[- \left(\frac{A_i}{\beta E_0} \right)^2 \right] \right\}^2 - \sum_i W_i \exp \left[- \left(\frac{A_i}{\beta E_0} \right)^2 \right] \right\} \quad [5]$$

$$\frac{\partial \Omega(W_0, E_0)}{\partial E_0} = \frac{4W_0}{\beta^2 E_0^3} \left\{ W_0 \sum_i \left\{ \exp \left[- \left(\frac{A_i}{\beta E_0} \right)^2 \right] \right\}^2 A_i^2 - \sum_i W_i \exp \left[- \left(\frac{A_i}{\beta E_0} \right)^2 \right] A_i^2 \right\}. \quad [6]$$

The transformation of the classical DR equation to a linear form leads to the well known, and widely used in standard calculations, statement defined by the following formula (LR):

$$\Omega(W_0, E_0)_{LR} = \sum_i \left\{ \ln(W_i) - \ln(W_0) + \left(\frac{A_i}{\beta E_0} \right)^2 \right\}^2. \quad [7]$$

The equation [7] can be easily solved applying the standard least squares procedure called regression (14).

RESULTS AND DISCUSSION

The data of three adsorption isotherms of benzene ($\beta = 1$) on activated carbons, published by Dubinin (15), were used as an example for the estimation of DR equation parameters on the basis of the methods presented above.

From the data in Table 1 it can be seen that the obtained results differ slightly in the case of nonlinear methods. A linear procedure gives the values of parameters that are hard to reproduce, comparing them with the value of the global minimum defined by Eq. [1]. As can be seen, the differences strongly depend on the quality

TABLE 1

DR Equation Parameters Obtained Applying Different Optimization Methods: (LR) Linear Regression, (LS) Least Squares Procedure, (HJ) Hook-Jeeves Method, (SGM) Simple Gradient Method, (SAGA) Simple Adsorption Genetic Algorithm

Method	Parameter	Activated carbon		
		ACS	ACZ	ACT-K
LR	$W_0, \text{cm}^3/\text{g}$	0.4329	0.5457	1.0797
	$E_0, \text{kJ/mol}$	31.6228	19.2450	12.9099
	$\Omega(W_0, E_0)_{LR}$	0.00077	0.03623	0.33552
LS	$W_0, \text{cm}^3/\text{g}$	0.4322	0.5972	1.3418
	$E_0, \text{kJ/mol}$	31.2050	16.7590	10.0560
	$\Omega(W_0, E_0)$	0.00062	0.01808	0.08312
HJ	$W_0, \text{cm}^3/\text{g}$	0.4322	0.5972	1.3418
	$E_0, \text{kJ/mol}$	31.2045	16.7592	10.0561
	$\Omega(W_0, E_0)$	0.00062	0.01808	0.08312
SGM	$W_0, \text{cm}^3/\text{g}$	0.4322	0.5972	1.3418
	$E_0, \text{kJ/mol}$	31.2039	16.7594	10.0561
	$\Omega(W_0, E_0)$	0.00062	0.01808	0.08312
SAGA	$W_0, \text{cm}^3/\text{g}$	0.4353	0.5960	1.3424
	$E_0, \text{kJ/mol}$	30.9889	16.8499	10.0599
	$\Omega(W_0, E_0)$	0.00067	0.01811	0.0809

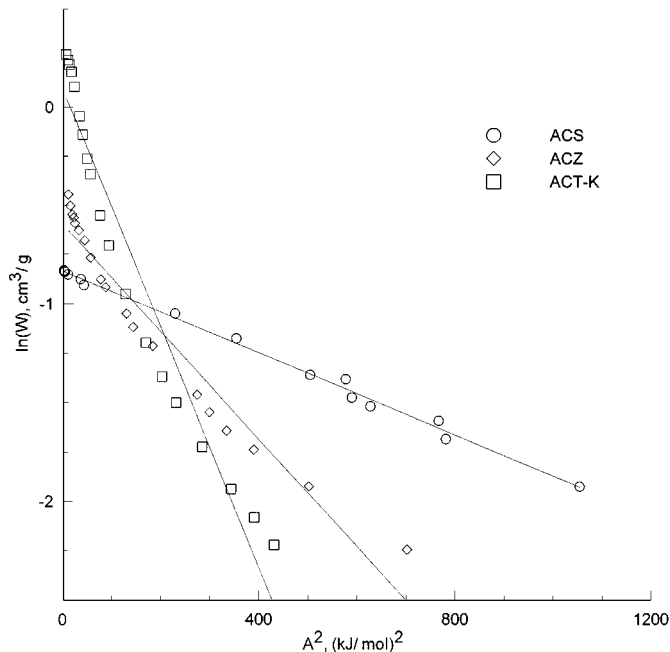


FIG. 1. The experimental adsorption data plotted in the linear co-ordinates of the DR equation (points) and the fits obtained using Eq. [7] for all investigated activated carbons.

of the fit of the straight line to the experimental data in the linear coordinates of the DR equation (see Fig. 1). In the case of ACS activated carbon, for all the presented methods, the results of parameters and sums of squared deviations are very close. In contrast to ACS activated carbon, the values of DR parameters as well as those of the error (defined by the sum of squared deviations) differ simultaneously for the two remaining samples (ACZ and ACT-K).

The sum of squared deviation valleys obtained on the basis of the HJ method for ACS activated carbon is presented in Fig. 2. From Table 1 it is clearly seen that this method is characterized by the highest accuracy. However, we want to emphasize that the calculations made by this method were time-consuming and, what is more important, obtain results strongly dependent on the value of the starting point of the optimization process. The changes of the sum of squared deviations for all tested activated carbons (SGM method) versus characteristic

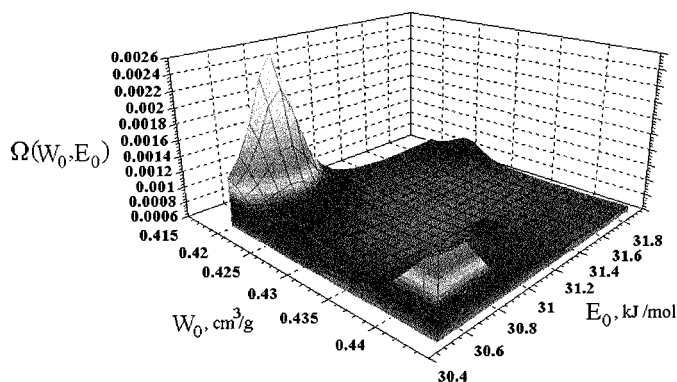


FIG. 2. The changes of the function defined by Eq. [1] for ACS activated carbon.

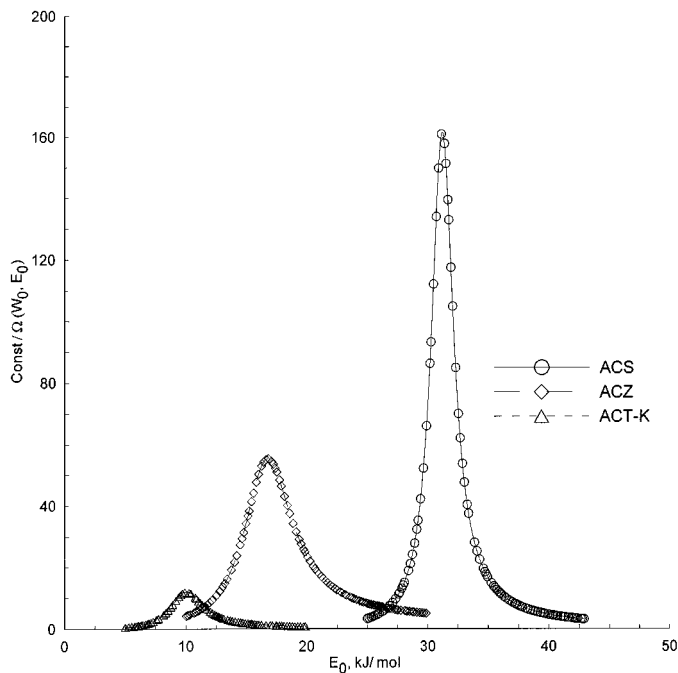


FIG. 3. The behavior of $\text{Const}/\Omega(W_0, E_0)$ with the change of E_0 for all analyzed adsorption isotherms (SGM method). (Const is equal to 0.1 for ACS and to unity for ACZ and ACT-K activated carbons.)

energy of adsorption are presented in Fig. 3. The main disadvantage of this method is the need to define a gradient of function [1]. It is very interesting that the form of the peaks changes regularly in comparison to the quality of fitting of the DR model to experimental data. In other words, the sharpness of the peak

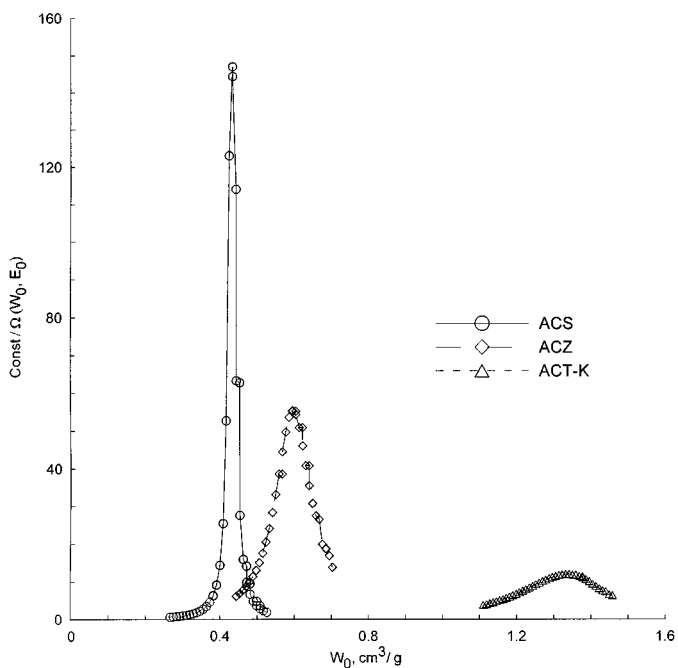


FIG. 4. The sum of squared deviations calculated using Eq. [1] and applying SAGA for all analyzed activated carbons. (Const is equal to 0.1 for ACS and to unity for ACZ and ACT-K activated carbons.)

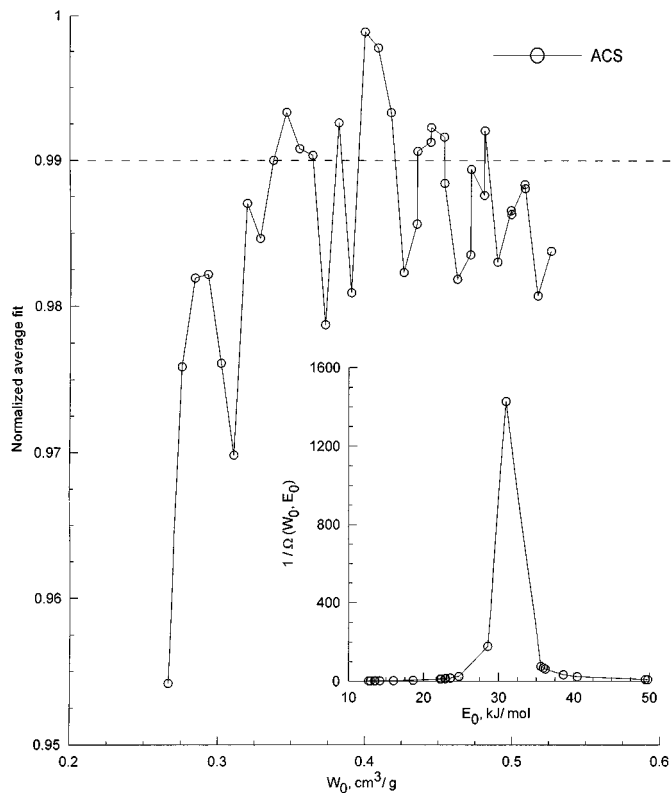


FIG. 5. Normalized average fit obtained using SAGA versus pore capacity for ACS activated carbon. Internal part of the picture shows the changes of the sum of squared deviations for the best population.

is strongly connected with the homogeneity of a micropore system; i.e., when the sharpness of the peak increases, so does the homogeneity of the micropore system.

The presented thesis is confirmed by the results obtained on the basis of SAGA and shown in Fig. 4. In this case, the broadest peak, with very low intensity, was obtained for activated carbon ACT-K (this reflects the poor fit of the DR adsorption model to experimental data). As an example, the changes of the normalized average fit versus the total micropore capacity for ACS activated carbon (obtained applying the proposed SAGA) are presented in Fig. 5 (larger figure). The shape of the curve is typical of optimization processes applying the genetic algorithm technique (stochastic character of the method). One can observe the significant increase of the goodness of the fit for pore volumes varying in the range 0.35–0.45 cm^3/g .

Finally, the obtained results lead to the statement that the proposed SAGA is a very accurate, convenient, and quick procedure. The most important is that, in contrast to other presented methods, the results obtained on the basis of SAGA do not depend on the starting point of the optimization process; this is obvious, taking into account the mechanism of natural selection and rivalry. From individuals only the best-adapted (possessing very high fitness) can survive.

ACKNOWLEDGMENTS

P. K. gratefully acknowledges Professor Lech Solarz for his help in solving the problems of the theory of numerical optimization. A.P.T. gratefully acknowledges financial support from KBN Grant 3T09A 005 18. P.A.G. gratefully acknowledges financial support from the Foundation for Polish Science.

REFERENCES

1. Rudziński, W., and Everett, D. H., "Adsorption of Gases on Heterogeneous Surfaces." Academic Press, New York, 1992.
2. Wojsz, R., "Characteristics of the Structural and Energetic Heterogeneity of Microporous Carbon Adsorbents Regarding the Adsorption of Polar Substances." UMK, Toruń, 1989. [In Polish]
3. Dubinin, M. M., *Prog. Surf. Membr. Sci.* **9**, 1 (1975).
4. Wojsz, R., and Terzyk, A. P., *Comput. Chem.* **20**, 427 (1996).
5. Jaroniec, M., and Piotrowska, J., *Monatsh. Chem.* **117**, 7 (1986).
6. Toth, J., *Adv. Colloid Interface Sci.* **55**, 54 (1995).
7. Toth, J., *J. Colloid Interface Sci.* **163**, 299 (1994).
8. Cerofolini, G. F., and Re, N., *Riv. Nuovo Cimento* **16**, 7 (1993).
9. Press, W. H., Teukolsky, S. A., Vetterling, W. T., and Flannery, B. P., "Numerical Recipes in Fortran," 2nd ed. Cambridge Univ. Press, Cambridge, UK, 1992.
10. Fortuna, Z., Macukow, B., and Wąsowski, J., "Numerical Methods," 4th ed. WNT, Warsaw, 1998. [In Polish]
11. Michalewicz, Z., "Genetic Algorithms + Data Structures = Evolution Programs," 2nd ed. WNT, Warsaw, 1999. [In Polish]
12. Goldberg, D. E., "Genetic Algorithms in Search, Optimization, and Machine Learning," 2nd ed. WNT, Warsaw, 1998. [In Polish]
13. Hook, R., and Jeeves, T. A., *J. Assoc. Comput. Mach.* **8**, 212 (1961).
14. Gerald, C. F., "Applied Numerical Analysis," 2nd ed. Addison-Wesley, California (1977).
15. Dubinin, M. M., *Carbon* **27**(3), 457 (1989).

P. Kowalczyk*
 A. P. Terzyk†¹
 P. A. Gauden†
 R. Leboda‡

**Department of Respiratory Protection
 Military Institute of Chemistry and Radiometry
 Chruściel Avenue 105
 00-910 Warsaw, Poland*
 †*Physicochemistry of Carbon Materials Group
 Department of Chemistry
 N. Copernicus University
 Gagarin St. 7
 87-100 Toruń, Poland*
 ‡*Department of Chemical Physics
 Faculty of Chemistry
 Maria Curie-Skłodowska University
 M. C. Skłodowska Sq. 3
 20-031 Lublin, Poland*

Received February 13, 2001; accepted May 4, 2001

¹ To whom correspondence should be addressed.