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Characterization of the PSD of activated carbons by a heterogeneous surface mixed model

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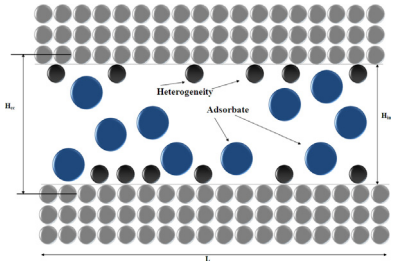
HIGHLIGHTS

- A model to calculate PSD of activated carbons taking into account surface defects is presented.
- GCMC simulations of the adsorption of probe gases (N_2 at 77 K and CO_2 at 273 K) on perfect and heterogeneous slit pores were carried out.
- Good agreement with the QSDFT method was found.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a model is proposed to calculate the Pore Size Distribution (PSD) of microporous activated carbons taking into account the defects as heterogeneity particles in the inner surface of each graphitic slit pore. We particularly examined the effects of surface heterogeneity in the determination of the PSD for a controlled series of microporous carbons prepared from peach stones as the precursor material. In order to obtain the PSDs of the samples, the Heterogeneous Surface Mixed Model (HSMM) on the basis of Grand Canonical Monte Carlo (GCMC) was used to generate simulated isotherms for the adsorption of N_2 at 77 K and CO_2 at 273 K. These results are compared with different models, like the Quenched Solid Density Functional Theory (QSDFT) and the Non Local Density Functional Theory (NLDFT) in order to check the self-consistency and robustness of the proposed model. It was found that our model is very flexible, allowing for the possibility of changing both the kind of heterogeneity particle and its coverage on the surface.

1. Introduction

Porous carbons have long been used for gas and liquid-phase adsorptive separations as well as the storage of volatile compounds because of their high surface area and strong adsorption force field. It is well recognized that the microstructure of porous carbons governs adsorption equilibrium and dynamic behavior [1]. One key carbon property used to correlate adsorption equilibrium is its pore size distribution (PSD). Any method for the determination of the PSD is based on the proposition of a model to represent the relevant geometric and structural characteristics of the porous material. It is important to stress the fact that such a model is not intended to mimic the real porous structure, but it is rather an idealized picture intended to reproduce, with a maximum degree of accuracy, the adsorptive properties of the material [2].

Most of the studies on adsorption in the literature are limited to well-defined surfaces, such as crystalline surfaces of thermally graphitized carbon black (GTCB). Unfortunately, real surfaces are far from that ideal situation and assuming a perfect surface to study adsorption in pores could lead to serious errors in the determination of adsorption isotherms [3]. Several authors have been trying to account for defects in an explicit way in their simulations by introducing edge sites [4], pore wall heterogeneity with variable number of layers [5] randomly oriented crystallites [6],

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rumpled graphite surfaces [7], pores of finite length [8–10], rough amorphous carbon surfaces [11] and reverse Monte Carlo carbon reconstruction [12]. More recent work has also included heterogeneity in the geometric shape of the pores [2]. Lucena et al. [13] applied the Seaton model [14] to test the potential of an explicit randomly etched surface model in a Grand Canonical Monte Carlo Simulation.

We have recently studied the influence of graphene sheets heterogeneity in the determination of the pore size distribution of activated carbons [15]. A considerable improvement of the fitting between the theoretical (from the calculated PSD) and the experimental isotherms was observed. In the present study, we have further improved our own model. Particles interactions between the heterogeneity and probe gas were taken into account by means of a spherical Lennard–Jones potential. The effect of surface heterogeneity in the determination of the PSD was examined for a controlled series of microporous carbons prepared from peach stones as the precursor material. The Heterogeneous Surface Mixed Model on the basis of GCMC simulated isotherms was used to obtain the PSDs of the samples by fitting experimental adsorption isotherms of N_2 at 77 K and of CO_2 at 273 K. In order to fully understand the scope of the present work within the state of the art of surface heterogeneities in microporous activated carbons, Refs. [13], [22] and [26] are encouraged to be read concurrently or beforehand.

2. Heterogeneous surface mixed model (HSMM)

In order to simulate the effects of a realistic partially crystalline surface structure, we used a variant of the Randomly Etched Graphite (REG) model [14]. In order to account for surface heterogeneity on the adsorbent, we roughened the fluid-solid energy landscape by placing additional carbon molecules randomly distributed over the surface. In our model (Fig. 1), surface heterogeneity was introduced by means of random and irreversible adsorption of spherical particles on the surface of the pores at different coverages θ. These particles interact with the adsorbate by way of a spherical Lennard–Jones potential with carbon parameters. In order to calculate the solid–fluid potential with these particles (heterogeneity source), we use the summation of pairwise potentials between the adsorbate (N_2 or CO_2) and all carbon atoms randomly distributed over the outermost layers of both pore walls. The pairwise potential is assumed to follow the LJ 12–6 equation as in Eq. (1) with the collision diameter and the well depth of interaction energy being those for solid–fluid interaction (Table 1). In this work, the influence of heterogeneity coverage has been set at 5%, 15% and 25% in the characterization study of activated carbon series using the Heterogeneous Surface Mixed Model. The HSMM is a combination of pure slit pores and pores at which the heterogeneity was introduced. As the degree of defect increases, it has already been observed that the surface loses its crystallite structure and becomes amorphous when the percentage of heterogeneity is greater than 30% [3].

Table 1
Parameters used in the GCMC for the LJ.

Parameter	N_2	CO_2	Carbon
ε_{gs}/k_B	53.22 K	81.49 K	–
σ_{gs}	3.49 Å	3.43 Å	–
ε_{gg}/k_B	101.5 K	246.15 K	–
σ_{gg}	3.62 Å	3.65 Å	3.4

3. Grand canonical Monte Carlo simulation

The adsorption of N_2 and CO_2 in the activated carbon micropores has been investigated by Grand Canonical Monte Carlo simulation because it allows the direct calculation of the phase equilibrium between a gas phase and an adsorbed phase. The implementation of this simulation method is both well established and well documented [16]. The interaction between adsorbate molecules is modeled by using the truncated Lennard–Jones potential.

$$U_{gg}(r) = -4\epsilon_{gg}[(\frac{\sigma_{gg}}{r})^6 - (\frac{\sigma_{gg}}{r})^{12}] \quad (1)$$

where ε_{gg} and σ_{gg} are the energetic and geometrical parameters of the LJ potential and r is the molecular separation. Each wall of the model graphitic slit pore was represented by a series of stacked planes of LJ atoms. The interaction energy between a fluid particle and a single pore wall at a distance z (measured between the centers of the fluid atom and of the atoms in the outer layer of the solid)

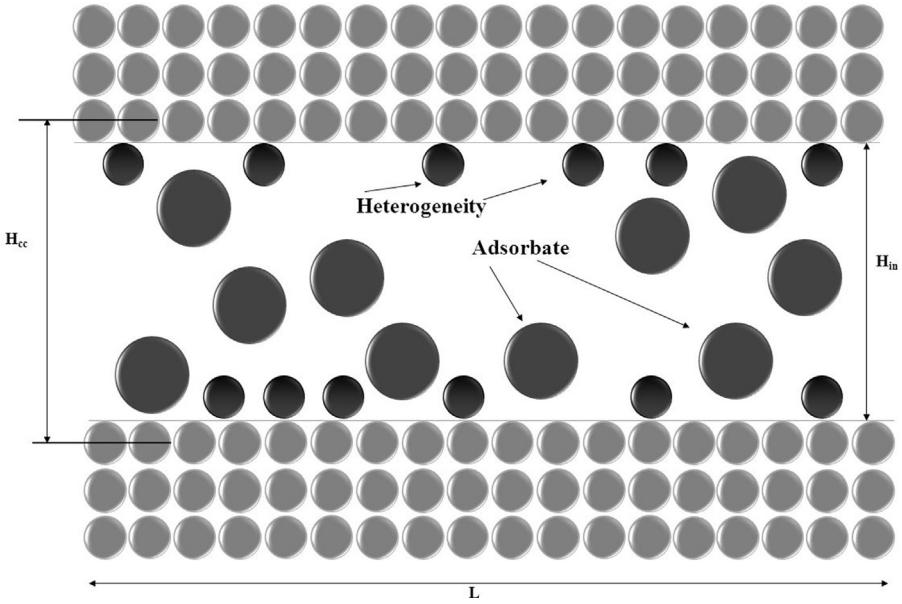

Fig. 1. Schematic diagram of a slit pore with heterogeneous particles pictured in black

was described by the Steele's 10-4-3 potential [17].

$$U_{gs\text{-}STEELE}(z) = 2\pi\,\epsilon_{gs}\rho_C\,\sigma^2{}_{gs}\Delta\left\{\frac{2}{5}\left(\frac{\sigma_{gs}}{z}\right)^{10} + \left(\frac{\sigma_{gs}}{z}\right)^{4} - \frac{\sigma^4}{3\Delta z + 0.61\Delta^3}\right\} \quad (2)$$

where Δ is the separation between layers in graphite (0.335 nm), ρ_C is the density of carbon atoms per unit volume of graphite ($114\,nm^{-3}$), z is the distance from the site of a fluid molecule to the nuclei of the carbon atoms on the surface of the graphitic plane, ε_{gs} and σ_{gs} are the LJ parameters for the interaction between an adsorbate molecule (gas) and a graphite carbon atom (solid). The cross LJ parameters are determined using the standard Lorentz–Berthelot combining rules (arithmetic mean for collision diameter and geometric mean for well depth). The values of the parameters included in the interaction potentials ((1) and (2)) are summarized in Table 1 [18,19]. Three types of attempts with equal probability are performed at random in each GCMC simulation step [20,21]: displacement, adsorption and desorption. Transition probabilities for each Monte Carlo attempt are given by the usual Metropolis rules. The lateral dimensions of the cell for the slit geometry were taken as $L = 10.3$ nm and periodic boundary conditions were used in these directions. The cutoff distance, beyond which the potential is negligible, is assumed to be $5\sigma_{gg}$. Equilibrium was generally achieved after 2×10^7 MC attempts, after which mean values were taken over the following 2×10^7 MC attempts for configurations spaced by 10^3 MC attempts, in order to ensure statistical independence. The volume of the simulation cell is given by $L \times L \times H$, where L is the length and H is the width. The accessible pore volume for a perfect slit pore is defined as the space available to the center of an adsorbate molecule where the solid–fluid potential is negative [22]. The volume available to the fluid molecule is

$$V = (H_{cc}\text{-}2z_0\text{-}\sigma_{gg})A\text{-}V_h \quad (3)$$

where $A = L \times L$, z_0 is the distance at which the solid–fluid potential is zero, H_{cc} is the physical width of the pore (which is defined as the distance from the plane passing through the centers of all carbon atoms of the outermost layer of one wall to the corresponding plane of the opposite wall). V_h is the volume due to pore heterogeneity and for the perfect slit pore V_h is equal to zero [15].

Seven kernels were calculated for each gas. Kernel 1 is a collection of simulated isotherms calculated with only perfect slit pores. Kernel 2 is calculated with only the heterogeneous slit pore for three different coverages, 5%, 15% and 25%. Kernel 3 corresponds to our HSMM that was obtained by combination of Kernel 1 and 2 as follows. First, n columns of the design matrix are obtained from the Kernel 1 and the columns $n+1$ to $2n$ are obtained from Kernel 2. In this way, the number of variables that can describe two components of the "total" PSD as a function of pore size are doubled. For example, HSMM-5% is the combination of Kernel 1 and Kernel 2–5%.

4. Pore size distributions

Pore size distributions for perfect and heterogeneous model pores have been calculated with kernels containing pore sizes between 4 and 52 Å for N_2 (39 isotherms) and 4 to 15 Å for CO_2 (11 isotherms). The theoretical adsorption isotherm, θ_{theor}, can be expressed as a superposition of isotherms corresponding to each pore size (H_j), which we took to be equal to the internal pore width $H_{in} = H_{cc} - \sigma_{cc}$, using $\sigma_{cc} = 3.4$ Å for the effective diameter of the carbon atom. Those theoretical adsorption isotherms are called "local isotherms", θ^L, each one with a contribution corresponding to the pore size distribution,

$$\theta_i^{theor} = \int_{j=1}^{m} \theta_i^L(H_j, P_i, T) f(H_j) dH_j \quad (4)$$

Solution of Eq. (4) is represented as a matrix equation, which is solved using the discrete Tikhonov regularization method combined with the non-negative least square algorithm. An adaptable procedure has been developed which chooses an optimal regularization parameter close to the corner of the so-called L-curve [23], which gives a fair balance between the quality of fit of the experimental isotherm and the size of the solution vector.

5. Experimental

5.1. Samples

The activated carbons (AC) samples used in this study have been prepared in our laboratory by chemical activation with phosphoric acid using peach stones as a precursor, following the experimental procedure described elsewhere [24], which we briefly review here. The precursor was pre-treated in two different ways, which gave rise to two sample groups: in the A samples, the precursor was washed with water only before impregnation; and in the B samples, it was washed with a diluted (10 wt%) H_2SO_4 solution and further washed with water until neutral pH. Both of them were impregnated with phosphoric acid at low concentration (26%, phosphorous/precursor mass ratio = 0.16), for two hours at 85 °C. After the impregnation, the samples were heated at 450 °C during 2 h under two different atmospheres: air and nitrogen. After carbonization, the samples were washed with distilled water up to pH 6 in order to thoroughly remove the remaining phosphoric acid. Finally, the samples were dried at 100 °C for 2 h.

5.2. Isotherms

Porous texture analysis of all samples was carried out at sub atmospheric nitrogen and carbon dioxide adsorption at 77 K and 273 K, respectively, using an Autosorb-1 MP apparatus (Quantachrome, U.S.A.). Specific surface areas were determined according to the BET method and the micropore volumes were estimated using the Dubinin–Radushkevich (DR) equation [25].

6. Results and discussion

The nomenclature identifying the samples describes the particular activation procedure applied to each one of them. For example, B10n corresponds to a sample subject to precursor pre-washing with sulfuric acid followed by water and a heating rate of 10 °C/min to reach carbonization temperature (450 °C) under a nitrogen flow (100 ml/min).

In Fig. 2, GCMC simulated adsorption isotherms for N_2 are shown for some selected sizes for perfect and heterogeneous slit pores. The adsorption isotherm has a stepped behavior when the pore is perfect (0% heterogeneity) and takes a smoother behavior when the amount of defects is increased. This is simply due to the irregular packing in the case of heterogeneous pores as compared to a much more ordered layering in the case of perfect slit pores [15]. As expected, the maximum adsorption capacity is higher in the perfect pore. An analogous behavior is observed for CO_2.

The PSDs calculated from the application of Kernel 1 (39 perfect slit pores) for the activated carbon samples are shown in the Fig. 3. It is observed that the GCMC is compared to the NLDFT [26] as a preliminary characterization of the samples for N_2 at 77 K. The PSDs

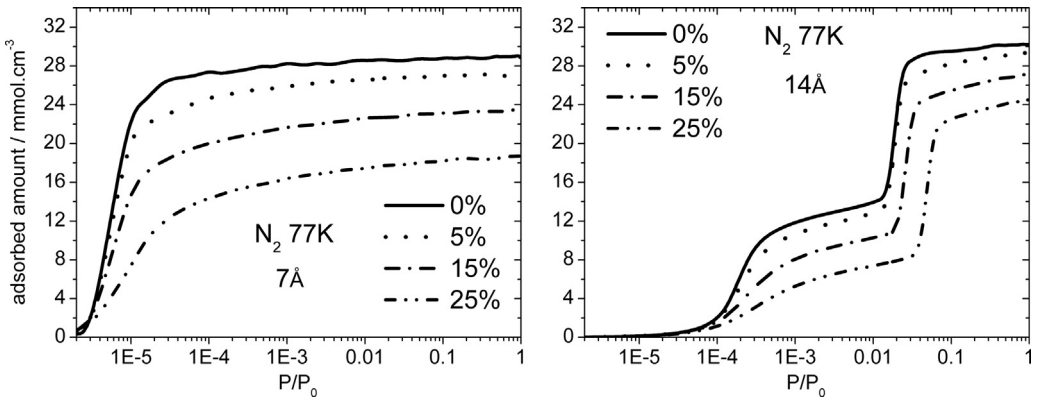

Fig. 2. The adsorption isotherms in a 7 and 14 Å pore with the top layers of each wall having various percentages of defects. Pore sizes are internal (H_{in}).

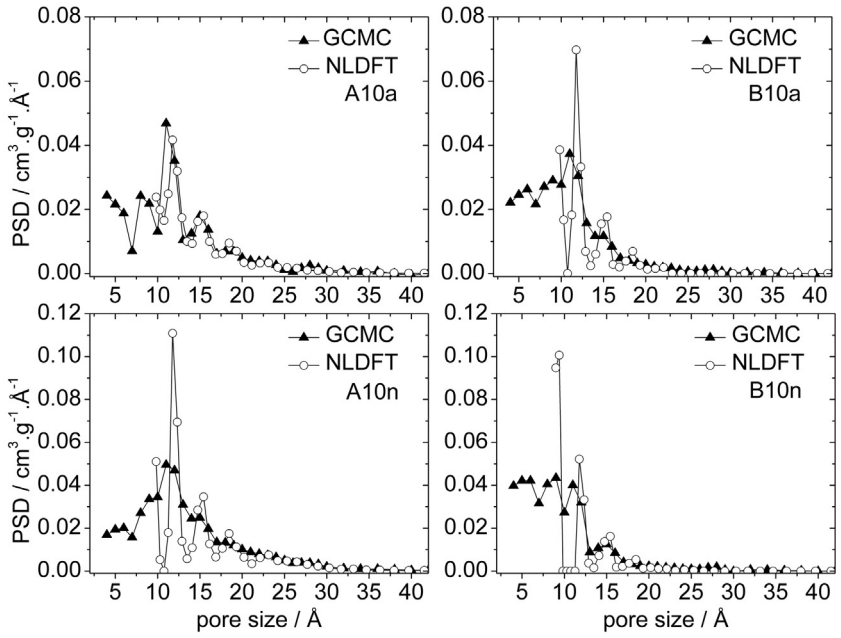

Fig. 3. PSDs of activated carbon series calculated from N_2 isotherms at 77 K, using NLDFT implemented into Quantachrome's data reduction software (slit kernel) and GCMC slit pore models.

calculated by the HSMM (Kernel 3) contrasted to those calculated with the QSDFT [27] are shown in the Fig. 4. For the Heterogeneous Surface Mixed Model, three different coverages, or degrees of heterogeneity were examined, which shows the flexibility of this model. It also enables us to calculate more realistic PSDs by reducing the spikiness in some of samples. For example, for the A10a sample, the effect of the heterogeneity coverage is clearly observed in the smoothness of the PSDs. The analysis of the calculated error of the fit from N_2 adsorption isotherms using the different models are summarized in Table 2 and it provides some insight into the usefulness of the proposed characterization model. In general, our model has lower error values than the QSDFT and both models are an improvement of the models compared in the Fig. 3 (perfect slits and NLDFT). Even though the NLDFT does not take into account any chemical and geometrical heterogeneity on the pore walls, the fits for the samples A10n and B10a have the lowest error values.

The specific surface areas and the pore volumes calculated for the activated carbon samples for N_2 at 77 K are summarized in Table 3. As reported previously [28], these values evidence the effect of the chemical impregnation of the precursor at low phosphoric acid concentration on the characteristics of the resulting materials.

In Fig. 5, the PSD obtained by applying the HSMM to fit CO_2 experimental isotherms at 273 K were compared to one of the PSD predictors implemented Quantachrome's data reduction software. The latter consists in a GCMC slit kernel which considers the three-center model for CO_2 [19]. The same qualitative behavior is observed for the PSDs of all samples regardless the model choice. It is interesting to note that in these heterogeneous pores the spherical molecules do not form a dense packing like in

Table 2
Error of the fit from N_2 adsorption isotherms using the different models.

N_2 77 K	$E = \left(\sum_i^n (y_i^{exp} - y_i^{mod})^2 \right)^{1/2}$			
Model	A10a	A10n	B10a	B10n
NLDFT	1.1404	0.5764	0.4380	0.6555
QSDFT	0.9482	1.1341	0.7754	0.7274
SLIT PORE	0.2393	0.9356	0.5514	0.1884
HSMM 5%	0.1942	0.8841	0.5291	0.1464
HSMM 15%	0.2090	0.7442	0.4750	0.0849
HSMM. 25%	0.1855	0.7392	0.5158	0.4050

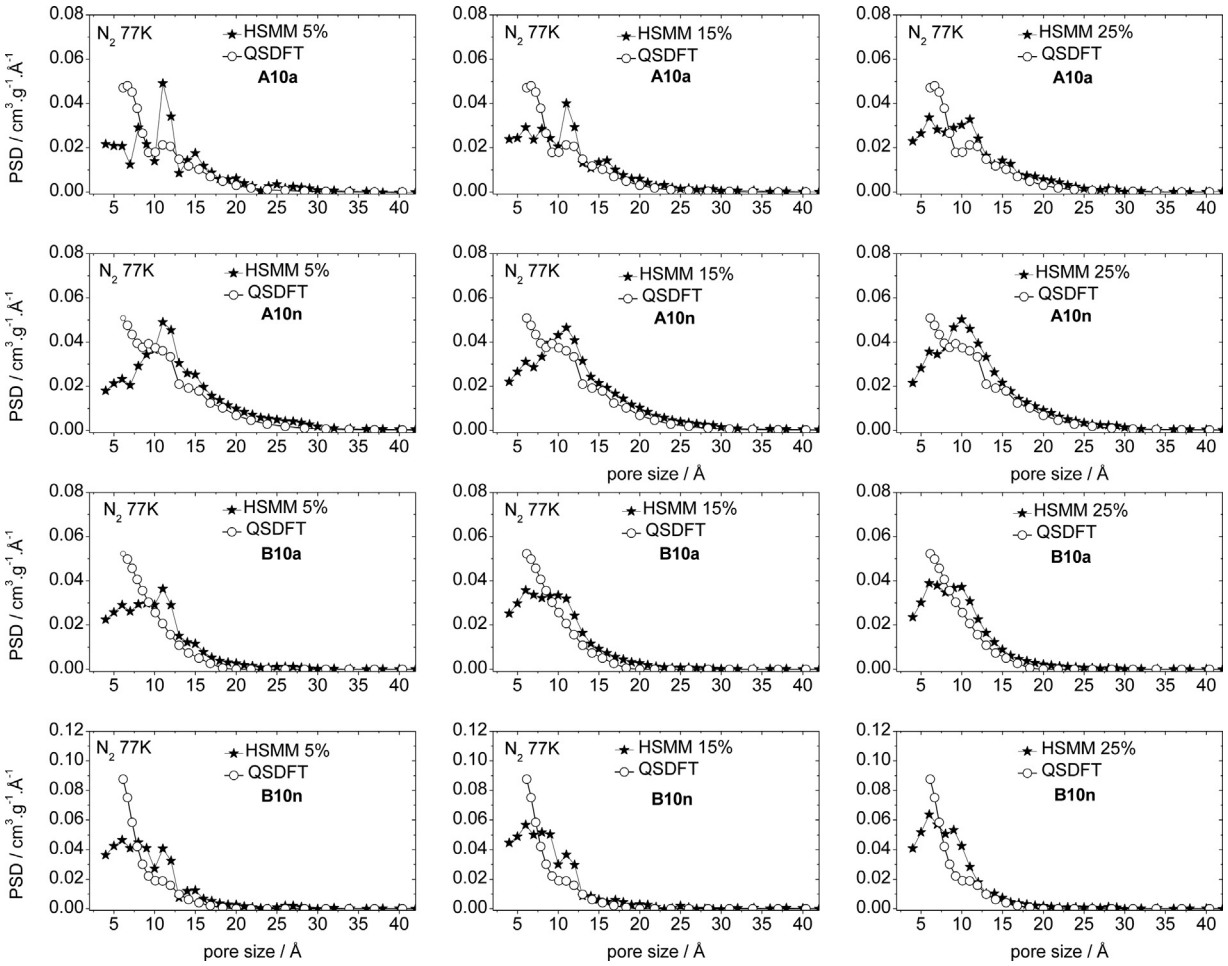

Fig. 4. PSDs of activated carbon series calculated from N_2 isotherms at 77 K, using QSDFT implemented into Quantachrome's data reduction software and HSMM models with different coverage.

Table 3
Specific surface areas and pore volume calculated for N_2 adsorption isotherms at 77 K.

N_2 77 K	Specific surface area (m^2/g)				Total pore volume (cm^3/g)			
Model	A10a	A10n	B10a	B10n	A10a	A10n	B10a	B10n
GCMC	727	882	762	1059	0.33	0.48	0.33	0.42
BET	772	1054	775	1019	–	–	–	–
DR	–	–	– –	–	0.32	0.47	0.32	0.40
HSMM 5%	762	931	801	1104	0.34	0.50	0.34	0.43
HSMM 15%	829	1037	878	1232	0.36	0.52	0.36	0.46
HSMM 25%	870	1093	896	1261	0.37	0.54	0.37	0.47

the three-center CO_2 model, which forms a less dense structure determined by an interplay between the tendency to lie flat to the wall and the tendency to form T-like configurations due to the quadrupole moment [18]. In the Table 4, it is presented the calculated error of the fit from CO_2 adsorption isotherms using the different models. In general, our model has again lower error values than the three-center CO_2 model. However, these error values are too similar and we need another characterization tool to get a better

Table 4
Error of the fit from CO_2 adsorption isotherms using the different models.

CO_2 273 K $\quad E = \left(\sum_i^n (y_i^{exp} - y_i^{mod})^2 \right)^{1/2}$

Model	A10a	A10n	B10a	B10n
NLDFT	0.01617	0.05651	0.1847	0.2413
SLIT PORE (CO_2 three-centers)	0.02714	0.02790	0.06297	0.08789
SLIT PORE (CO_2 one-center)	0.04902	0.02003	0.03605	0.05694
HSMM 5%	0.04685	0.01921	0.03516	0.05664
HSMM 15%	0.04911	0.01877	0.03676	0.05846
HSMM 25%	0.04898	0.01973	0.03591	0.05674

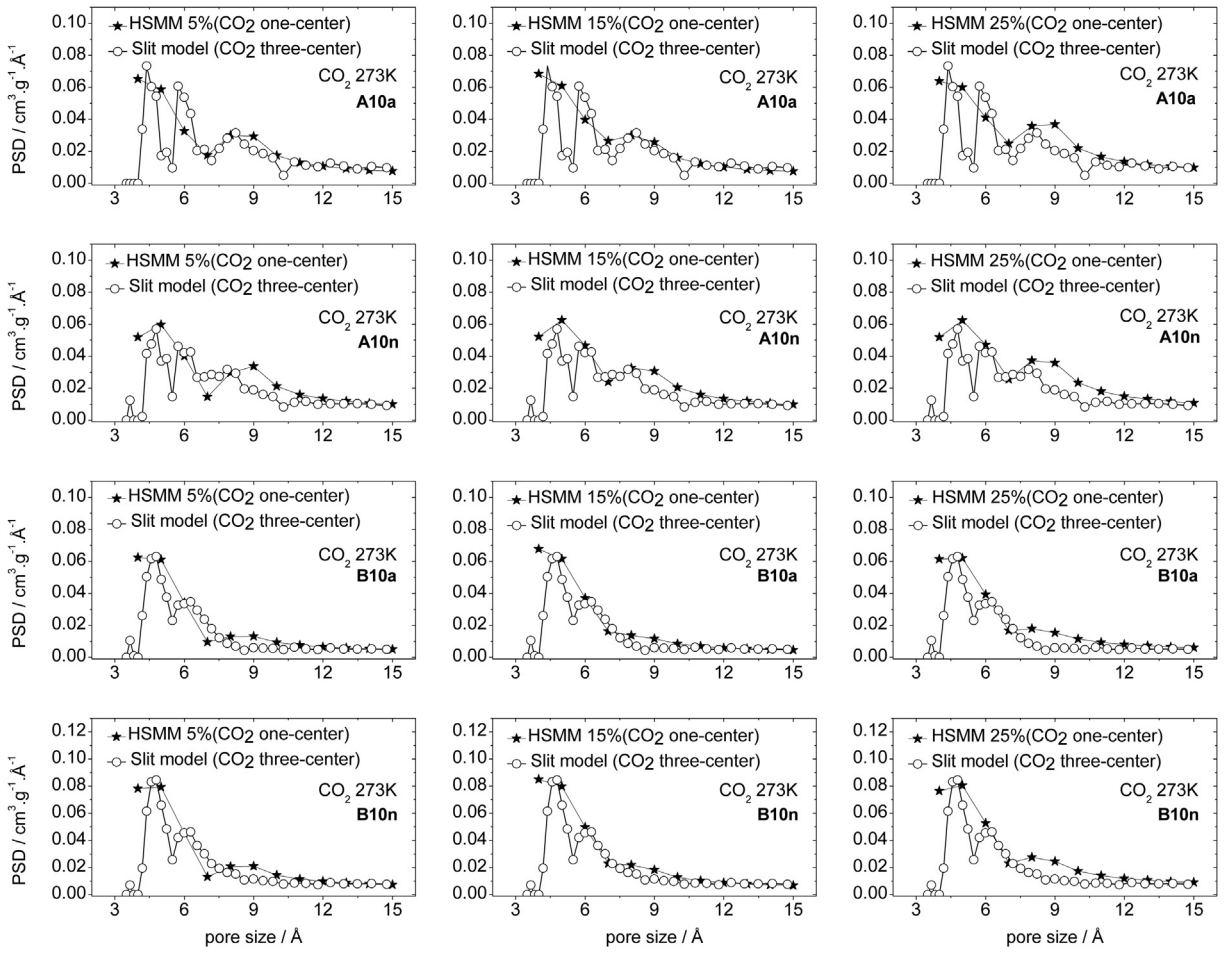

Fig. 5. PSDs of activated carbon series calculated from CO_2 isotherms at 273 K, using GCMC three-center CO_2 implemented into Quantachrome's data reduction software (slit kernel) model and HSMM with different coverage.

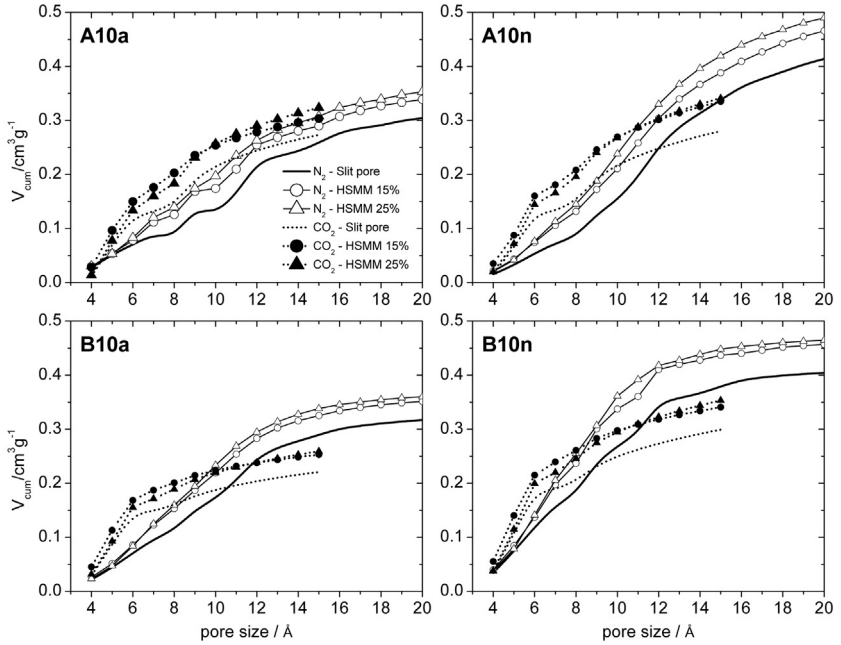

Fig. 6. Cumulative pore volume distribution of activated carbon series for CO_2 273 K and N_2 77 K. It was calculated using Slit Pore Geometry and the HSMM (coverage of 15% and 25%). The caption for the sample A10a is the same for all samples.

Table 5
Micropore volume calculated for CO_2 adsorption isotherms at 273 K.

CO_2 273 K	Total pore volume (cm^3/g)			
Model	A10a	A10n	B10a	B10n
SLIT PORE (CO_2 one-center)	0.27	0.28	0.22	0.30
DR	0.21	0.22	0.20	0.26
HSMM 5%	0.28	0.30	0.23	0.32
HSMM 15%	0.30	0.34	0.25	0.34
HSMM 25%	0.32	0.34	0.26	0.35

conclusion about which PSD is the most representative of the solid surface.

The greater consistency in the characterization of the AC series obtained through the HSMM can also be observed by comparing the behavior of micropore volumes for both adsorbates. The micropore volumes calculated for the activated carbon samples for CO_2 at 273 K are summarized in Table 5.

In the Fig. 6 it was calculated the cumulative pore volume distribution of the activated carbon series for CO_2 273 K and N_2 77 K. It can be observed that the curves for both gases are complementary. The CO_2 at this experimental temperature clearlyadsorbs in the narrow micropores, not accessible to N_2. It is due to restricted diffusion of N_2 in such small pores at 77 K. This behavior is observed for all samples independently of the chosen model. This is more evidence that only N_2 adsorption isotherms are not enough to have a good characterization of micropores materials [29,30].

7. Conclusions

It was used the Heterogeneous Surface Mixed Model (HSMM) to improve the characterization of an activated carbon series obtained from peach stones. The PSDs calculated by the HSMM and compared with the QSDFT are very similar, which prove the consistency of our model. Besides that, it shows the flexibility of this model, which has the possibility of change the kind of heterogeneity particle and also change the coverage. It also enables us to calculate more realistic PSDs by reducing the spikiness of the result in some of samples.

This HSMM provided a realistic estimate of the internal structure of the activated carbon series under study. The agreement between the simulated and experimental data is a positive step for further application of this model to study the adsorption in microporous solids.

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