Effect of the pore geometry in the characterization of the pore size distribution of activated carbons

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Abstract In this work, the characterization of Activated Carbons (AC) by using the independent pore models is discussed, with special emphasis on the issue of how the assumed pore geometry can affect the resulting Pore Size Distribution (rPSD) and on the problem of the unicity of the PSD when different probe molecules are used in adsorption experiments. A theoretical test was performed using virtual solids based in the so-called Mixed Geometry Model (MGM) (Azevedo et al. 2010). The MGM uses a kernel of adsorption isotherms generated by GCMC for different pore sizes and two pore geometries: slit and triangular. The adsorption isotherms of a virtual MGM solid were fitted with both the traditional Slit Geometry Model (SGM) and the Mixed Geometry Model (MGM). It is demonstrated that, by assuming a different pore geometry model from that of the real sample, different PSDs may be obtained by fitting adsorption isotherms of different probe gases. Finally, experimental results are shown which both point toward the MGM as an acceptable extension of the SGM and confirm that the MGM is a closer representation of the actual porous structure of most activated carbons.

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1 Introduction

Activated carbons (AC) are considered as convenient materials for a number of separation and storage processes due to their versatility in textural and surface properties as well as their low cost (Marsch and Rodríguez-Reinoso 2006; Rouquerol et al. 1999). The development of a suitable AC for a given specific application has long been the subject of an important amount of research (Lee et al. 2006; Prauchner and Rodríguez-Reinoso 2008; Rios et al. 2009; Santos et al. 2010). A central problem in these developments is the determination of the Pore Size Distribution (PSD) of the material in the most accurate way. This problem has attracted the attention of researchers for several decades, from the early developments of Dubinin et al. (1975), who used the Polanyi's adsorption potential concept to describe the adsorbed volume, up to the modern DFT (Lastoskie et al. 1993; Ravikovitch et al. 2000; Neimark et al. 2009) and Monte Carlo simulation methods (Gusev et al. 1997; Ravikovitch et al. 2000; Do and Do 2005), which have the advantage of not assuming any particular adsorption process a priori, but rather rely on realistic gas–solid and gas–gas interactions.

A common limitation in all the afore-mentioned developments has always been the assumption that the material is represented by a collection of independent pores, all of which having a determined geometric shape, usually infinite parallel plates or slits of different sizes (widths). The structure of an AC is still at the present a matter of discussion, given the complexity arising from a disordered arrangement of not well defined building blocks.

Nevertheless, a quite simple model has been extensively used for decades to represent such a structure, which we shall call the Slit Geometry Model (SGM). It considers the porous material as a collection of independent slit shaped pores formed by parallel graphitic plates separated by different widths H between plates, which stands for the pore size (Marsch and Rodríguez-Reinoso 2006). This model has being providing satisfactory interpretation of experimental adsorption data of pure gases on AC. However, when this model is applied to analyze and predict adsorption data for gas mixtures, which is a crucial problem gas in separation and storage process, difficulties arise due to the fact that the PSDs of a given AC sample obtained from adsorption data of different probe molecules turn out to be different in some cases. Within this context, there have been some attempts to propose alternative geometries to represent pore geometry of activated carbons, for instance, which show the role of mixtures of slit-like and cylindrical pores and gaps between spherical particles (Gun'ko and Mikhalovsky 2004) and that of various adsorbates for the cases when the porosity of the carbonaceous is well known (Furmaniak et al. 2009). The question of whether the PSDs obtained with different probe molecules could be equal or different is a relevant research topic in the literature (Ravikovitch et al. 2000; Scaife et al. 2000; Sweatman and Quirke 2001; Gauden et al. 2004) and cases of equal (Ravikovitch et al. 2000; Jagiello and Thommes 2004) and different (Quirke and Tennison 1996; Scaife et al. 2000; Soares Maia et al. 2011) PSDs have been reported. In our opinion, a discussion of why it should be one way or the other is still an open issue.

In the present work, we discuss how the pore geometry can affect the unicity of the PSD of a given AC for different probe molecules, providing experimental and theoretical evidence of the reasons why they may eventually be different, based on the analysis of the adsorption process via Grand Canonical Monte Carlo (GCMC) simulations.

2 Factors affecting the unicity of the PSD

Two effects are usually described in the literature, which could lead to different results on the determination of the PSD from adsorption data with different probe molecules.

2.1 Pore size accessibility

(Marsch and Rodríguez-Reinoso 2006; Scaife et al. 2000; Jagiello and Thommes 2004; Jagiello et al. 2007). Probe molecules may have different Van der Waals diameters and diffusive behavior, in such a way that smaller pores can be accessed by one species and not by another. This effect would, however, produce only limited variations in the

region of ultramicropores between PSDs corresponding to different gases. Moreover, it could be minimized by waiting for enough time in experiments to ensure that each point of the isotherm has reached equilibrium conditions (Marsch and Rodríguez-Reinoso 2006).

2.2 Reliability window

(Gusev et al. 1997; Davies et al. 1999; Davies and Seaton 2000). As the pore size increases, the adsorbate gas has a critical size above which adsorption isotherms for different sizes begin to be linearly dependent. This critical size, which is different for different adsorbates under different conditions, determines a "reliability window" delimiting the range of pore sizes at which the PSD, obtained by fitting the experimental adsorption isotherm using a kernel of simulated isotherms, is meaningful. The reliability window for a given probe adsorbing gas usually depends on its thermodynamic state in the conditions of the adsorption experiment (temperature and pressure range). If a given probe molecule is closer to the critical point than another probe molecule in the conditions of the experiment, then the former will fill larger pores at larger pressures than the latter, leading to a smaller reliability window. Therefore, it is to be expected that PSDs obtained by fitting experimental isotherms for different adsorbates, in conditions where the reliability windows of these adsorbates differ considerably, will be different. However, again, we could argue that this difference is "non-essential", that is to say, the PSD corresponding to the adsorbate with the largest reliability window is complementary to that corresponding to the adsorbate with the smallest reliability windows, extending the size range of the latter. Moreover, this effect could be minimized by expanding the pressure range in the isotherm measurement and in the simulation of monopore isotherms for the gas with the lowest reliability window, so that its reliability window becomes of the same size as that of the stronger adsorbing gas.

Hence, the two effects just mentioned are circumstantial and could be conveniently avoided, or minimized, as explained. Having said that, we propose a third and more fundamental reason to account for the non unicity of the PSDs obtained from the adsorption isotherms of different adsorbates: the pore geometry assumed in the calculations.

2.3 Pore geometry

As already pointed out, any characterization method relies on the assumption of a given pore geometry, which must be regarded as an idealization of the real structure of the microporous material. In the case of an AC, the most widely accepted pore geometry has been the slit geometry (SGM).

High resolution TEM images of AC improved by means of digital image processing tools (Marsch and Rodríguez-Reinoso 2006; Rouzaud and Clinard 2002; Huang et al. 2002), like the one represented in Fig. 1, adapted from Huang et al. (2002), clearly show regions where the pore geometry could only be poorly represented by two parallel graphitic plates. One can easily find smaller regions where an adsorbed molecule would be interacting with three graphitic plates simultaneously (regions indicated by arrows in the figure). This is a much closer representation of the "real" porous structure of an AC than the "idealized" picture assumed in the SGM. Denoyel et al. (1993) have reported differential adsorption enthalpies at low coverage close to the maximum attainable value with two graphitic plates, which is approximately 4 kcal/mol. In particular, Prasad et al. 1999 show experimental differential adsorption enthalpies values of the order of 6 kcal/mol for a very "pure" AC (phosphorous and sulfur contents less than 0.005 %) obtained by physical activation, providing evidence of interactions of adsorbate molecules with more than two graphitic walls. These facts support the Mixed Geometry Model (MGM), proposed and tested in the last few years (Azevedo et al. 2010; Soares Maia et al. 2010; Toso et al. 2011), which assumes that the AC porous network is better represented by a mixture of infinitely long slit geometry pores and triangular geometry pores of different sizes. The model isotherm of MGM is given by the following expression.

$$N_{MGM}(P_i, T) = \sum_{j=1}^{m} \left[\rho_S(H_j, P_i, T) f_S(H_j) \delta H_j + \rho_T(H_j, P_i, T) f_T(H_j) \delta H_j \right] \quad (1)$$

where $N_{MGM}(P_i, T)$ is the amount of gas in the model solid at pressure P_i ($i = 1,...,n$) and temperature T, $\rho_S(H_j, P_i, T)$ ($\rho_T(H_j, P_i, T)$) is the slit (triangular) adsorption gas density in a model pore of characteristic size H_j, δH_j is the j-th quadrature interval, $f_S(H_j)$ and $f_T(H_j)$ ($j = 1,...,m$) are, respectively, the slit and triangular PSDs of the model solid. Notice in the Eq. (1) that the m "S" terms within the summation are the SGM adsorption isotherms, i.e., the MGM is an extension of the SGM.

Furthermore, different adsorbates differ essentially in their interaction energy parameters, gas–gas (gg) and gas–solid (gs). This necessarily leads to a different "sensitivity" for different adsorbates with respect to a given geometry of the pores, i.e., an adsorbate with weaker $\varepsilon_{gg}/k_B T$ and $\varepsilon_{gs}/k_B T$ interaction energy factors will be less sensitive to the geometrical shape of the pores than an adsorbate with stronger gas–gas and gas–solid interactions. Therefore it is reasonable to think that a highly disordered material like an AC, whose micropore structure encompasses a mixture of pore geometries, will be "seen" by different adsorbates (and/or working temperature) as having different PSDs when the structure is modeled by a single pore geometry, like in the SGM. In the next section, some experimental
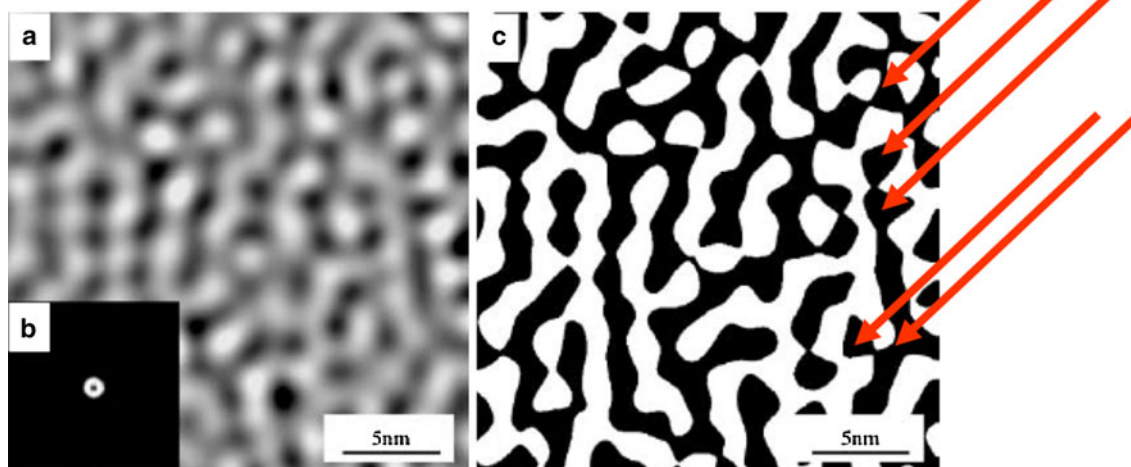

Fig. 1 High resolution TEM image of an activated carbon revealing a disordered micropore structure where many regions can be identified where an adsorbate molecule would feel a simultaneous interaction with three graphitic walls (some of them are indicated by *arrows*). Adapted from Huang et al. 2002

measurements and a theoretical test will be provided to better support this hypothesis with the aid of the MGM.

3 Results and discussion

In this section we discuss the issue of whether PSDs obtained with different probe molecules may be different. The discussion will be focused on the issue of pore geometry, as discussed in item (c) of the previous section.

In Fig. 2 we present cumulative N_2 (T = 77 K) and CO_2 (T = 273 K) PSDs for a family of ACs obtained from peach stones by chemical activation with phosphoric acid. The details of the experimental procedure may be found elsewhere [34]. Briefly speaking, prior to chemical activation, the precursor was pre-treated by rinsing it with either only water (A samples) or a dilute (10 % wt) H2SO4

solution and further washing with water until neutral pH (B samples). Both sample groups (A and B) were impregnated with phosphoric acid at varying concentration for two hours at 85 °C. After impregnation, the samples were heated at 450 °C during 2 h under two different atmospheres: air and nitrogen. Therefore, all samples mentioned in the following figure follow this key: the first character (A or B) indicates the kind of pre-treatment, the second character (a number) indicates the H_3PO_4 concentration of the impregnating solution and the third character (a or n) indicates the atmosphere at which carbonization took place (air or nitrogen, respectively).

The PSDs were obtained from the Grand Canonical Monte Carlo Simulation following the procedure explained in former publications (Azevedo et al. 2010; Soares Maia et al. 2010), using Lennard-Jones gas–gas and gas–solid parameters given in references (Vishniakov et al. 1999; Ravikovitch et al. 2000), and using both the SGM and the
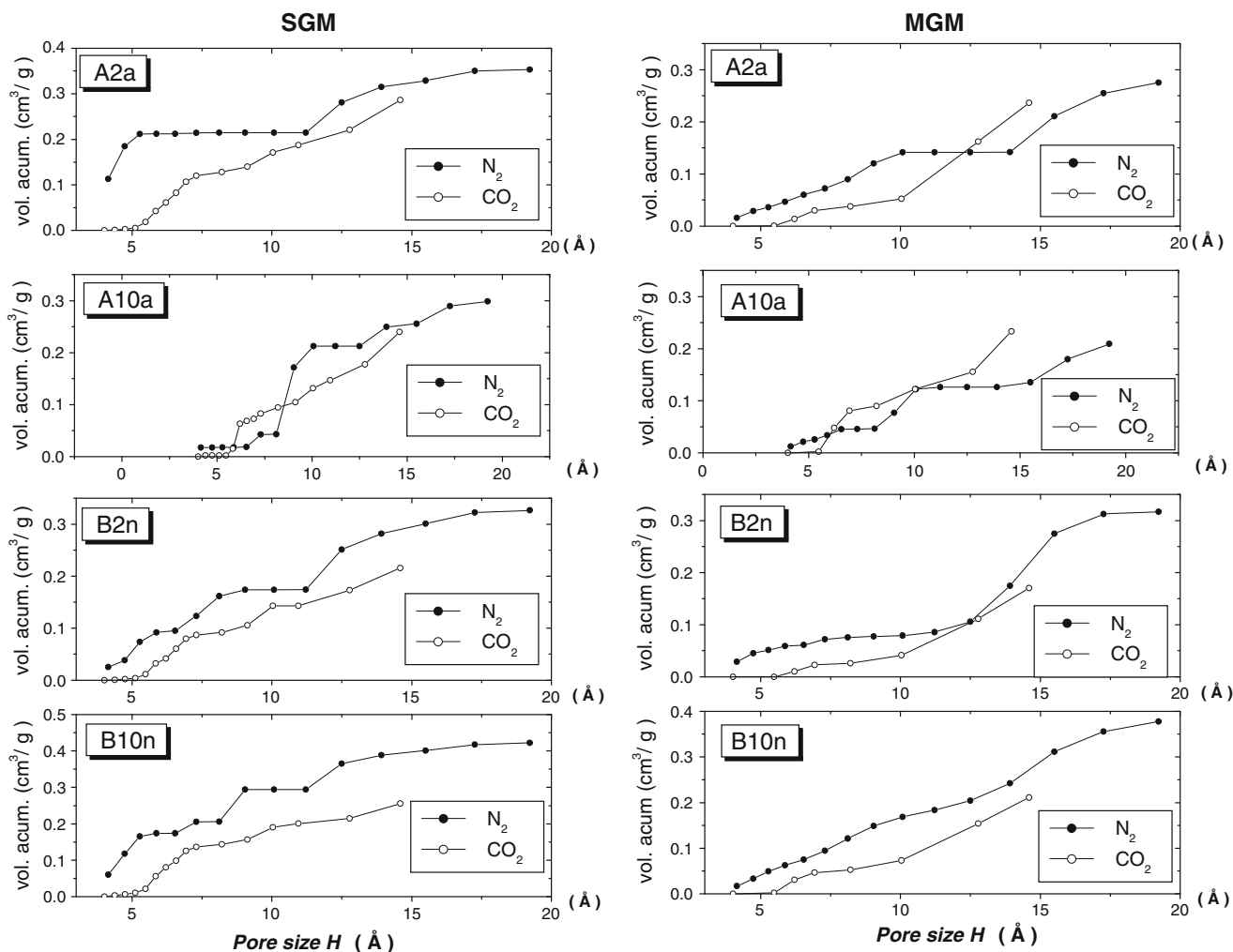

Fig. 2 Comparison of N_2 77 K and CO_2 273 K cumulative PSDs of samples obtained from peach stone (Soares Maia et al. 2011) through the SGM (*left* column) and the MGM (*right* column)

MGM. Appreciable differences between N_2 and CO_2 PSDs may be appreciated in Fig. 2. The above experimental data seems to corroborate our hypothesis on the role of the geometric effect on the unicity of the PSD. The following theoretical test will provide the necessary robustness to support that.

The theoretical tests using virtual solids are a useful tool to check models and to explore some properties of porous solids (Lueking et al. 2009; Jagiello et al. 2011; Terzyk et al. 2012). The idea of the test is to generate a MGM solid (virtual AC sample) from a unique (and arbitrary) source PSD (sPSD) with different proportions of slit and triangular pore volumes. Then, by using Eq. (1) with N_2 @ 77 K and the CO_2 @ 273 K GCMC kernels, one obtains the corresponding N_2 and the CO_2 pseudo-experimental adsorption isotherms (Soares Maia et al. 2010). Finally these pseudo-experimental isotherms are fitted by using the SGM (the

m "S" terms within the brackets in Eq.(1)) for N_2 and CO_2, thus obtaining the resulting PSDs (rPSDs). These rPSDs are the PSDs of the same ideal sample "sensed" by different adsorbates. In Fig. 3 this procedure is illustrated for the special case of a virtual 100 % triangular pore solid. It is clear (Fig. 3c, d) that not only the "slit" rPSDs is different from "triangular" sPSD for a given probe gas, but also CO_2 and N_2 rPSDs are different from one another. A known and expected trend is also clearly observed: both N_2 and CO_2 rPSDs show an important increase in the smaller pores population at low pore sizes. This is due to the fact that the SGM will try to compensate for the stronger adsorption in small triangular pores (present in the ideal AC sample) by increasing the fraction of the smallest slit pores, which do not actually exist in the sPSD (Azevedo et al. 2010).

Following the procedure above, in Fig. 4, results using four other sPSDs (with the same range of the sPSD of Fig. 3a) with different slit/triangular proportions are shown. It is clear that as the "slit" proportion increases, the agreement between N_2 and CO_2 rPSDs improves, as well as
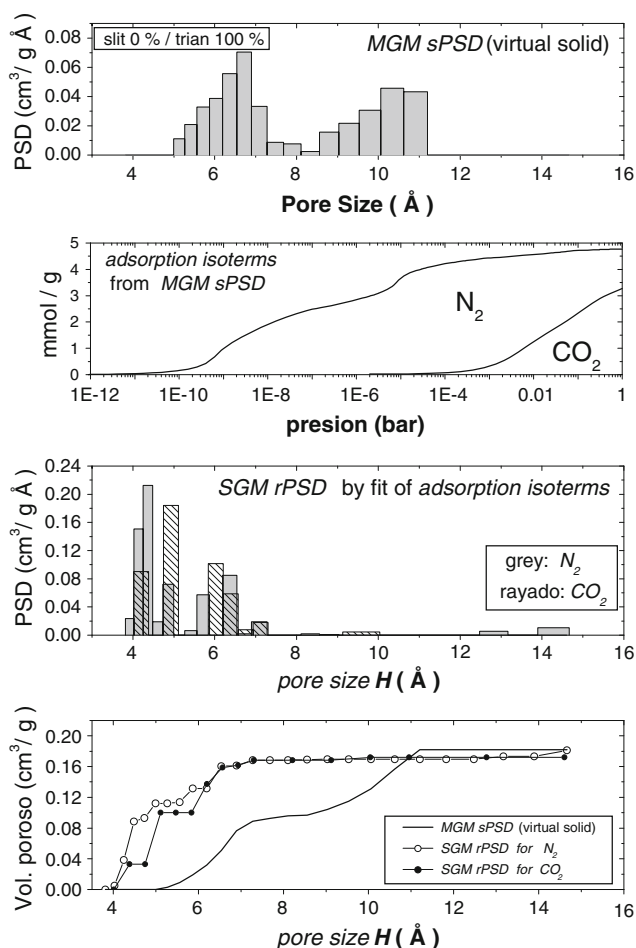

Fig. 3 Theoretical test based on a virtual sample prepared with a MGM sPSD with 100 % of triangular pores (*top* row). The resulting adsorption isotherms for N_2 77 K and CO_2 273 K (*second* row) are then fitted through the SGM giving the N_2 77 K and CO_2 273 K SGM rPSDs (*third* rows). Cumulative MGM sPSD and SGM rPSDs are compared in the bottom row
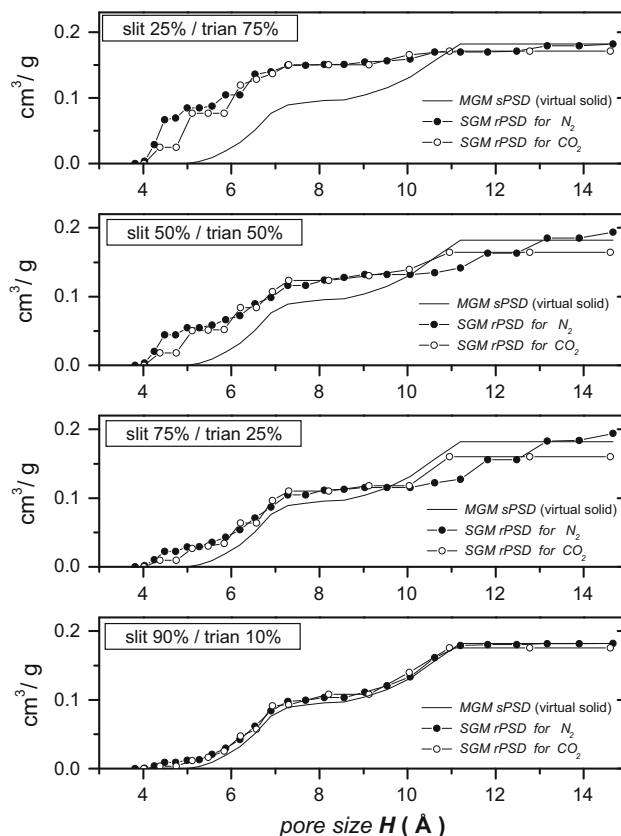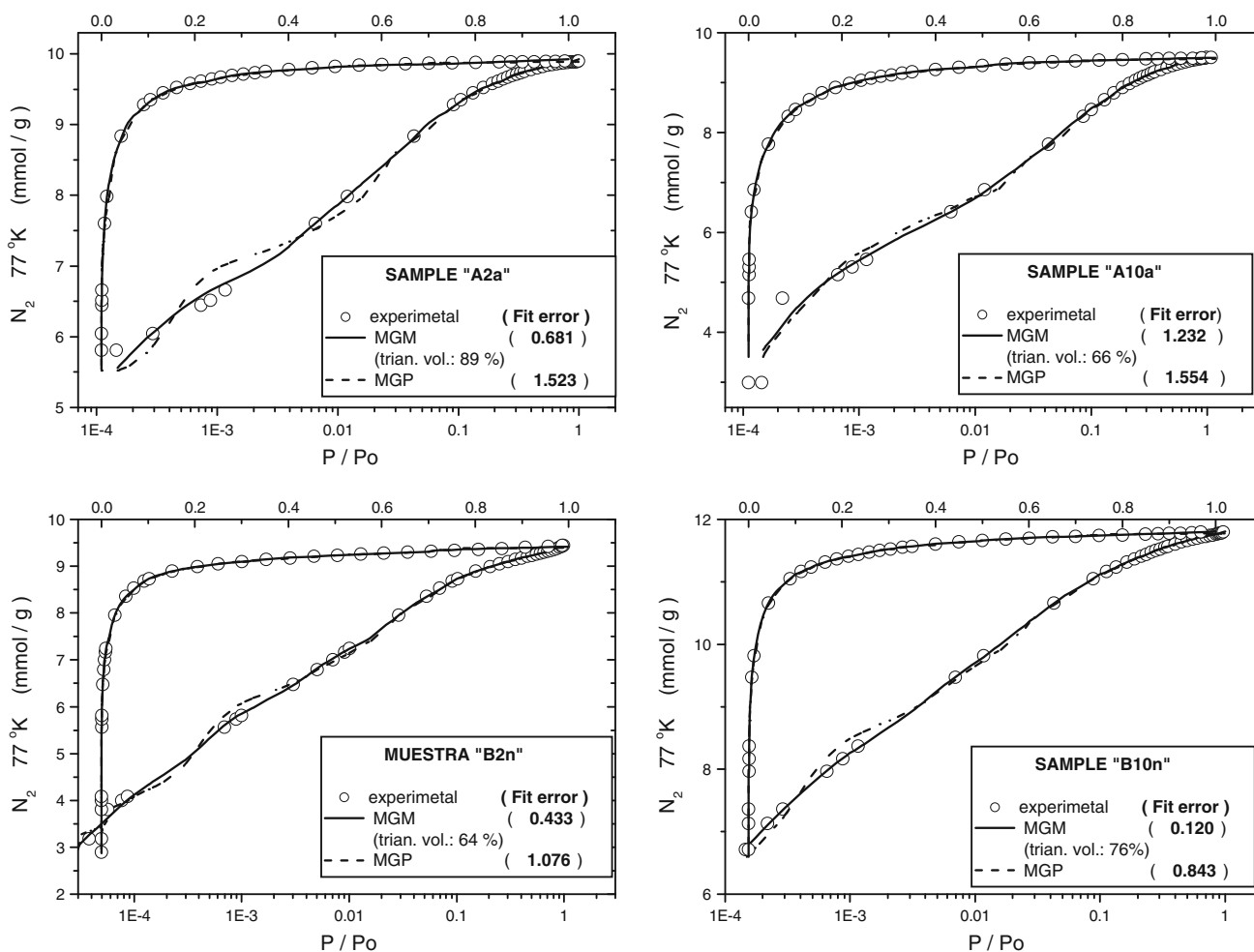

Fig. 4 Comparison between cumulative rPSDs (N_2 77 K and CO_2 273 K) and cumulative sPSDs for virtual samples with different proportions of slit and triangular pores. The distributions tend to overlap as the proportion of slit (*triangular*) pores volume increase(*decreases*)

Table 1 Theoretical test using virtual MGM solids whit different proportions of slit and triangular pore volume and N_2 77 K isotherms fit using SGM

Virtual MGM solid [vol. slit (%); vol. tria.(%)]	SGM fit error (*LSQ "R"*) (N_2 77 K) $R = \sum_{i=1}^{n} \left[N_{exp} - N_{SGM} \right]^2$	Pore volume ($cm^3\ g^{-1}$)		Surface area ($m^2\ g^{-1}$)		
		Virtual solid (MGM)	Model solid (SGM)	Virtual solid (MGM)	Model solid (SGM)	Relative difference (%)
(0; 100)	0.31	0.182	0.181	944	716	−24
(25; 75)	0.21	0.182	0.182	826	656	−21
(50; 50)	0.14	0.182	0.182	708	593	−16
(75; 25)	0.07	0.182	0.182	590	533	−9.7
(90; 10)	0.03	0.182	0.182	519	496	−4.4
(100; 0)	0.00	0.182	0.182	472	472	0

Fig. 5 N_2 77 K adsorption isotherms of samples shows in Fig. 2 and the model fit (Soares Maia et al. 2010). It is reported the percentage of "triangular" pore volume in the MGM fit (100 % level is completed by "slit" volume)

the agreement between these rPSDs and the sPSD (solid line). Another interesting aspect is to analyze the test result focusing on one gas. We here discuss the case of N_2 @ 77 K, because for the working pressures up to 1 atm, N_2 @ 77 K (and not CO_2 @ 273 K) saturates the whole range

range of micropores so, N_2 @ 77 K characterization is more robust than CO_2 @ 273 K characterization. Thus N_2 adsorption analysis is shown in Table 1. The second column of Table 1 shows the *LSQ Residual* between the pseudo-experimental MGM isotherm (sPSD) and model

SGM isotherm, for different slit-triangular pore volume proportions (first column). It is noteworthy that, as the "slit" proportion increases, the agreement between "experimental" and simulated isotherms improves. That is to say, as the model solid is closer to the actual solid, the experiment-model isotherm fit improves. As for the solid characterization (third and fourth columns), it is observed that whereas the surface area is affected by the model, the pore volume is not.

Figure 5 shows N_2 @ 77 K experimental adsorption isotherms of real AC samples (Soares Maia et al. 2010) that can be related to what was discussed in Table 1. These isotherms correspond to the same AC samples shown in Fig. 2 and were fitted both with SGM and MGM by using the same number of fit parameters, that is: half pore size intervals for MGM and SGM. In all the samples, the MGM fitted experimental data with smaller errors than the SGM. Another observation is that the MGM isotherms do not present the characteristic "S" shape of the SGM. Adding to the better fit of MGM, the corresponding rPSDs (not shown

here) yields high proportion of triangular pore volume (these values are reported in Fig. 5). Following the same reasoning of the preceding paragraph (Table 1), the results shown in Fig. 5 allow us to say that the MGM is a closer representation of the porous structure of most ACs than the SGM.

Finally, there is an interesting finding for N_2 @ 77 K adsorption using the MGM. Figure 6 shows differential and cumulative PSDs for AC samples obtained from coconut shells by chemical activation (Toso et al. 2011). The MGM and SGM N_2 isotherm fits, not shown here, are very similar. It is remarkable that the PSDs given by the MGM has only slit pore volume contribution together with the fact that the MGM PSD and the SGM PSDs are in excellent agreement. Therefore, when the MGM triangular kernel does not contribute significantly to the isotherm fit, the MGM PSD agrees with the PGM PSD, which is an evidence of the consistency of the model and allows us to conclude that the MGM as an acceptable extension of the SGM.
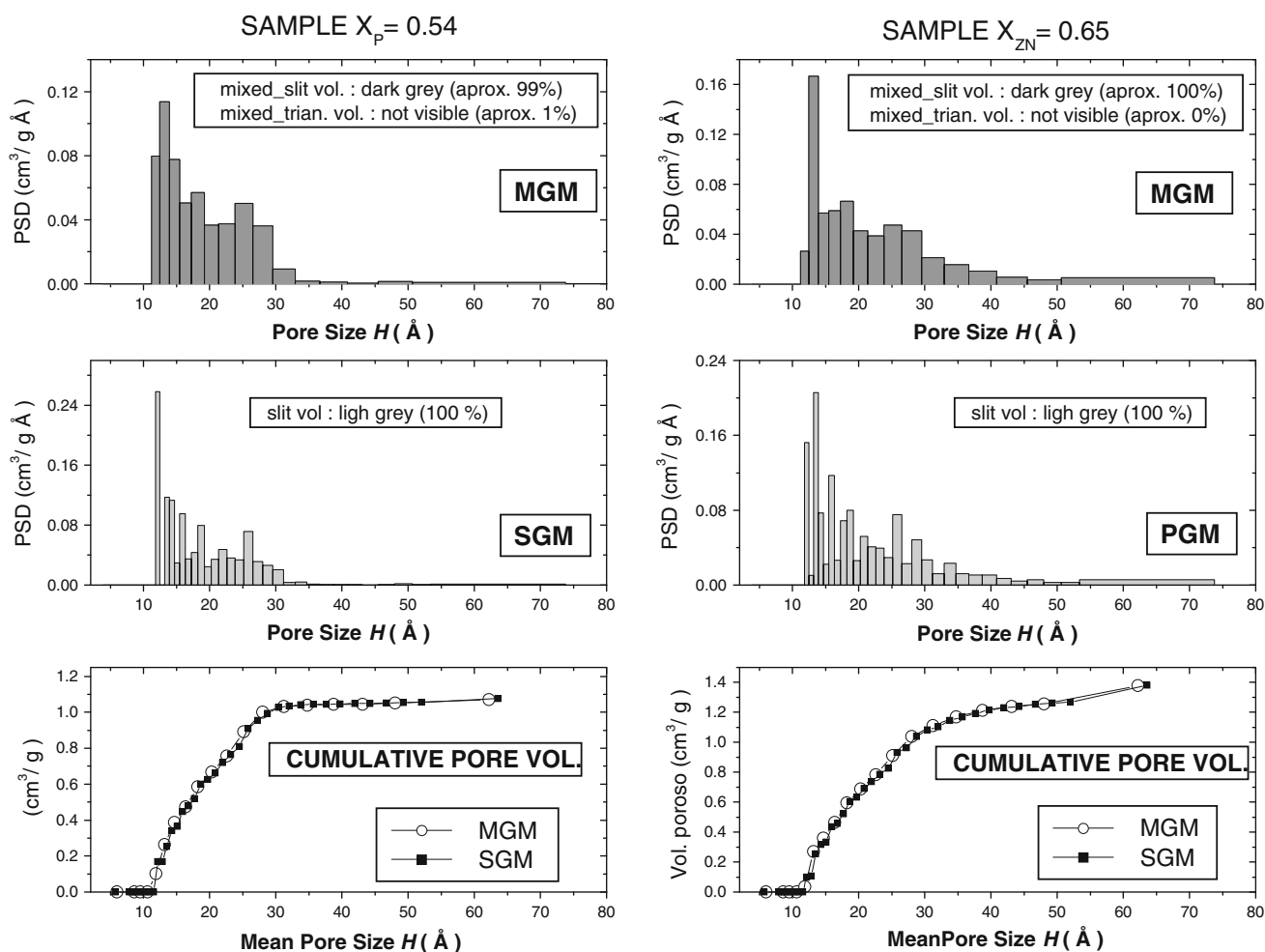

Fig. 6 PSD from N_2 77 K adsorption isotherms of samples obtained from peach coconut shells (Toso et al. 2011) through the SGM and the MGM

4 Conclusions

The problem of the unicity of the PSD of an AC as determined by using different probe gas molecules has been discussed. From a simple theoretical test using virtual solids and pseudo-experimental adsorption data, we have shown that assuming a pore geometry model different from the real geometry of the sample may lead to different PSDs sensed by different probe gases, even if the effects of accessibility and reliability window are properly ruled out. We have also shown that the surface area could be significantly affected (but not pore volume) by different model geometry chosen to represent the real solid.

We presented here experimental results that support the assumption that the recent MGM is an acceptable extension of the traditional SGM: for the same number of parameters, the MGM can improve or at least have equally accurate fits as compared to the SGM. The MGM is a very simple extension of the SGM, but of course other simple geometries can be tested, such as square and rectangular (Davies and Seaton 1998), or mixed geometries (Jagiello et al. 2011), or even a specific geometry for a given carbon sample. It remains for future research studies to compare the relative accuracy of these different approaches to describe pore geometry.

In conclusion, the pure slit geometry hypothesis applied to AC independent pore models should be revised and the recent MGM, or other alternative mixed geometry models, may be an acceptable extension of the traditional SGM.

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