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Characterization of PSD of activated carbons by using slit and triangular pore geometries

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ABSTRACT

A mixed geometry model for activated carbons, representing the porous space as a collection of an undetermined proportion of slit and triangular pores, is developed, evaluated theoretically and applied to the characterization of a controlled series of samples of activated carbon obtained from the same precursor material. A method is proposed for the determination of the Pore Size Distribution (PSD) for such a mixed geometry model, leading to the unique determination of the proportion of pores of the two geometries fitting adsorption data. By using the Grand Canonical Monte Carlo (GCMC) simulation method in the continuum space, families of N2 adsorption isotherms are generated both for slit and triangular geometry corresponding to different pore sizes. The problem of the uniqueness in the determination of the PSD by fitting an adsorption isotherm using the mixed geometry model is then discussed and the effects of the addition of triangular pores on the PSD are analyzed by performing a test where the adsorption isotherm corresponding to the known PSD is generated and used as the "experimental" isotherm. It is found that a pure slit geometry model would widen the PSD and shift it to smaller sizes, whereas a pure triangular geometry model would produce the opposite effect. The slit and triangular geometry families of isotherms are finally used to the fit experimental N_2 adsorption data corresponding to a family of activated carbons obtained from coconut shells through a one-step chemical activation process with phosphoric acid in air, allowing for the determination of the micropore volume, the proportion of slit and triangular pores and the PSD corresponding to the mixed geometry. The same experimental data were fit using both the conventional slit pore model and the mixed geometry model. From the analysis of the effect of different preparation procedures on the resulting PSDs, it is concluded that the proposed mixed geometry model may probably better capture the morphology and energetics of activated carbons prepared by chemical activation under mild temperatures.

1. Introduction

A central problem in the characterization of activated carbons is the accurate determination of the Pore Size Distribution (PSD) from adsorption isotherms of a probe molecule, usually N_2 at 77 K. Any method for the determination of the PSD begins with 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 idealization intended to reproduce with a maximum degree of accuracy the adsorptive properties of the material.

The slit model [1], which represents the material as a collection of slit geometry pores of different sizes, is usually assumed for the characterization of activated carbons and has been extensively used in determining their PSD [2–7]. However, the observed high values of the heat of adsorption in activated carbons, in the range between 4 and 6 kcal/mol at very low pressure [8–11], cannot be explained solely by slit micropores, even for ultra-small sizes, suggesting that an adsorbate molecule may be under the influence of more than 2 graphitic plates at low pressure. On the other hand, it is reasonable to assume that, at least in part of the material, carbon plates may accommodate in such a way as to form pores with other geometries. Bojan and Steele [12] and Davies and Seaton [13] have investigated, for example, the use of rectangular micropores. This geometry showed interesting behaviours of the adsorbate at the corners, but it was concluded that the consideration of this geometry did not introduce new features in the determination of the PSD and that a rectangular pore could always

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be replaced by a suitable combination of slit pores [13], since in rectangular pores interactions with only 2 carbon plates are present. It is not usual to find in literature clear evidence, for example from the high resolution TEM images, about the morphology of the porous space, therefore structures proposed in several models are only idealization of such space and should not be taken as real representations of the material but rather as "effective" representations to obtain a better PSD.

We have recently suggested the use of micropores with a triangular section [14]. This kind of geometry would provide adsorption regions of higher heats of adsorption, since adsorption in the center of a triangular pore is affected by 3 graphitic plates instead of 2.

On the other hand, we have found in literature very interesting morphological studies of activated carbons [27,28] based on the high resolution TEM images where, in addition to a quite disordered slit geometry structure, many places where an adsorbed molecule would interact with 3 graphitic walls can be clearly identified.

In the present work, pores with slit and triangular geometry are assumed to co-exist in undetermined proportions in activated carbons, a mixed geometry model, and a method is proposed to obtain the corresponding PSD of such a material. By using the Grand Canonical Monte Carlo (GCMC) simulation method in the continuum space, families of N2 adsorption isotherms are generated both for slit and triangular geometry corresponding to different pore sizes. The problem of the uniqueness in the determination of the PSD by fitting an adsorption isotherm using the mixed geometry model is then discussed and the effects on the PSD due to the addition of triangular pores are determined by performing a test in which the adsorption isotherm corresponding to the known PSD is generated and used as the "experimental" isotherm. The slit and triangular geometry families of isotherms are finally used to fit the experimental adsorption data corresponding to a controlled set of samples of activated carbons, allowing for the determination of the micropore volume, the proportion of slit and triangular pores and the mixed geometry PSD. Experimental N2 isotherms for a series of activated carbon samples prepared from coconut shells are used in the fitting procedure. The same experimental data are fit using both the conventional slit pore model and the mixed geometry model so that conclusions are drawn about the convenience of using the latter by analyzing the effect of different preparation procedures on the resulting PSDs.

2. The model

The two geometries proposed in this model to represent the idealized porous structure of an activated carbon are the slit and triangular geometry pores represented in Fig. 1; only equilateral triangles are considered for the latter in order to keep the number of parameters to a minimum. The gas–solid potential for the slit geometry is given, as usual, by the superposition of two Steele potentials, one per each infinite plate:

$$U_{\mathrm{gs-Steele}}(z) = 2\pi\varepsilon_{\mathrm{gs}}\,\rho_{\mathrm{C}}\,\sigma_{\mathrm{gs}}^2\,\Delta\left\{\frac{2}{5}\left(\frac{\sigma_{\mathrm{gs}}}{z}\right)^{10} + \left(\frac{\sigma_{\mathrm{gs}}}{z}\right)^{4} - \frac{\sigma_{\mathrm{gs}}^4}{3\Delta(z+0.61\Delta)^3}\right\}$$

For the triangular geometry, the gas–solid potential is obtained by summing the contributions of three semi-infinite plates. The potential of each semi-infinite plate is given by [12]:

$$U_{\mathrm{gs}}(z, y_{\mathrm{e}}) = 4\varepsilon_{\mathrm{gs}}\rho_{\mathrm{C}}\{-\sigma^6 I_3(z, y_{\mathrm{e}}) + \sigma^{12} I_6(z, y_{\mathrm{e}})\}$$

$$I_{\mathrm{n}}(z, y_{\mathrm{e}}) = \int_{-\infty}^{+\infty} \mathrm{d}x \int_{y_{\mathrm{e}}}^{\infty} \mathrm{d}y \frac{1}{(x^2+y^2+z^2)^n}$$

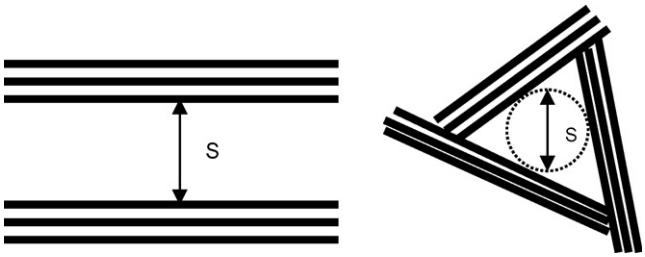

Fig. 1. Slit (left) and triangular (right) geometry pore showing how the size S is defined.

where y_{e} is the distance from the truncated edge. The gas–gas potential is taken as the usual Lennard–Jones potential:

$$U_{\mathrm{gg}}(r) = -4\varepsilon_{\mathrm{gg}}\left[\left(\frac{\sigma_{\mathrm{gg}}}{r}\right)^6 - \left(\frac{\sigma_{\mathrm{gg}}}{r}\right)^{12}\right]$$

The values of all parameters included in the interaction potentials for N_2 adsorption at 77 K are given in Table 1. For nitrogen, the minimum value of the gas–solid potential (corresponding to the maximum differential heat of adsorption at very low adsorbed quantity) is represented in Fig. 2 as a function of the pore size S. From the figure, it can be seen that only the triangular geometry can provide a high value between 4 and 6 kcal/mol for the differential heat of adsorption, as observed experimentally [8–11].

A collection of adsorption isotherms (the local isotherms, θ_{L}) was obtained through the GCMC method, following the algorithm outlined in Ref. [16], both for the slit and the triangular geometries with the values used for the interaction potential parameters as given in Table 1. Transition probabilities for each Monte Carlo attempt, displacement, adsorption and desorption of molecules, are given by the usual Metropolis rules. The lateral dimensions of the cell for the slit geometry and the longitudinal dimension for triangular geometry were taken as 10.3 nm and the periodic boundary conditions were used in those directions. Equilibrium was generally achieved after 10^7 MC attempts, after which mean values were taken over the following 10^6 MC attempts for configurations spaced by 10^3 MC attempts, in order to ensure statistical independence. This collection of isotherms can be used in three ways to fit a given experimental isotherm: (a) pure slit pores; (b) pure triangular pores; (c) a mixture of slit and triangular pores, with an undetermined fraction x of slit pores.

A minimization method for the mean square error, with a regularization term, as described in Ref. [2], was proposed to fit an experimental isotherm with the theoretical isotherm given by:

$$\theta_i^{\mathrm{theor}} = \sum_{j=1}^{m} \theta_{\mathrm{L}}(S_j^*, P_i, T)\;\; f(S_j^*)\delta S_j$$

In the above equation, $\theta_i^{\mathrm{theor}}$ stands for the theoretical value of adsorbed amount at pressure P_i and S_j^* for the value of the pore size in the middle of the jth size interval.

At this point, it is important to discuss the problem of the uniqueness of the solution of the fitting procedure when a mixed slit–triangular geometry is used. In fact, it could be argued that if

Table 1
Values of potential parameters.

Parameter	Value	Ref.
ρ_{C}	0.114 Å^{-3}	[17]
Δ	3.35 Å	[17]
$\varepsilon_{\mathrm{gs}}/k\mathrm{B}$	53.22 K	[18]
σ_{gs}	3.494 Å	[18]
$\varepsilon_{\mathrm{gg}}/k\mathrm{B}$	101.5 K	[18]
σ_{gg}	3.615 Å	[18]

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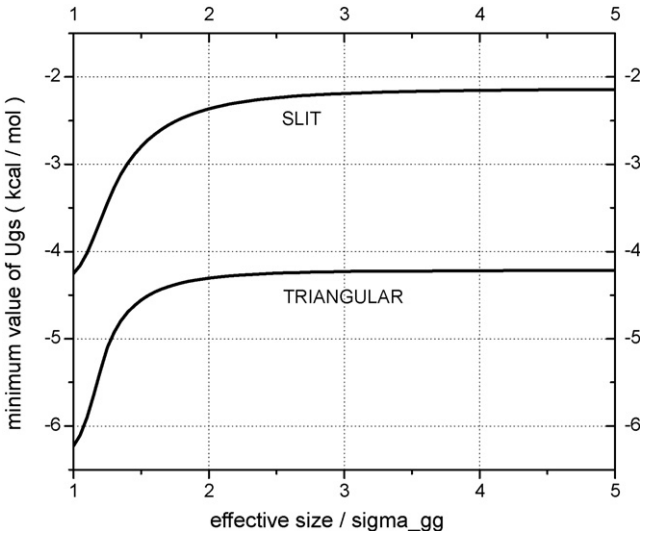

Fig. 2. Gas–solid potential minima.

the adsorption isotherm of a slit pore of size S_i is similar to that of a triangular pore of size S_j, then any fraction x of one and $1 - x$ of the other will give the same fit for all $0 \leq x \leq 1$. To this end, we have calculated a matrix $D(i,j)$, for all slit geometry sizes S_i and all triangular geometry sizes S_j, where each element represents the percent relative error between the isotherms corresponding to the two geometries. The smallest matrix element found was 23%, the second smallest value found was 30%. Fig. 3 shows the comparison between the adsorption isotherms for the two geometries in both cases. The mean matrix element value turned out to be 71%, while the maximum value found was 87%. We therefore conclude that the solution for the slit–triangular mixed geometry is unique, in contrast to what happens in the case of the slit–rectangular mixture [13].

The uniqueness of the solution can be reinforced by the following test: a random mixed geometry PSD is generated, the one shown in Fig. 4a, and, by using the simulated collection of adsorption isotherms, a total adsorption isotherm is generated, which is now taken as the "experimental" isotherm to test the model. This isotherm is then fitted by using the mixed geometry model and a "predicted" PSD is obtained, which is exactly equal to the original PSD in Fig. 4a, including the proportions of slit and triangular pores, and therefore this is not shown in a separate figure. When the "experimental" isotherm is fitted by using a pure slit geometry model the PSD in Fig. 4b is obtained, which clearly

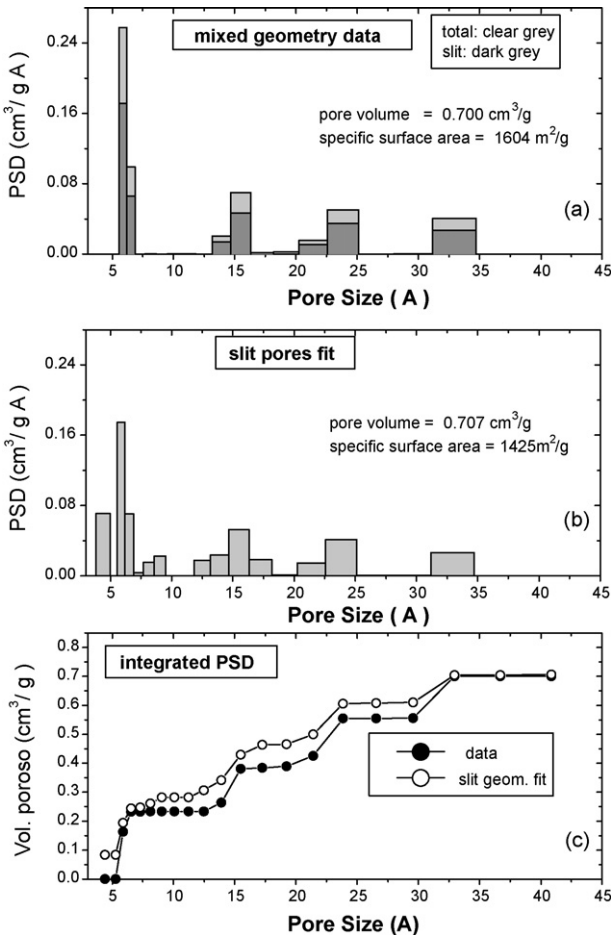

Fig. 4. Results of the theoretical test: (a) mixed geometry PSD used in obtaining the data isotherm; (b) PSD obtained by fitting the data isotherm with a pure slit geometry model; (c) comparison of the two integrated PSDs.

differs from the original PSD. Fig. 4c shows the two integrated PSDs for a better comparison. This test also shows, as it may be observed in Fig. 4, that the effects of neglecting triangular pores are more notable at smaller sizes and below the limit of micropores. These effects consist in spreading of the peaks of the PSD and a shift toward smaller sizes. Both effects can be easily understood: (a) in the small micropores region slit pores need to be smaller than triangular pores to account for the same adsorption energy; (b) the pure slit geometry needs a wider collection of sizes to account for

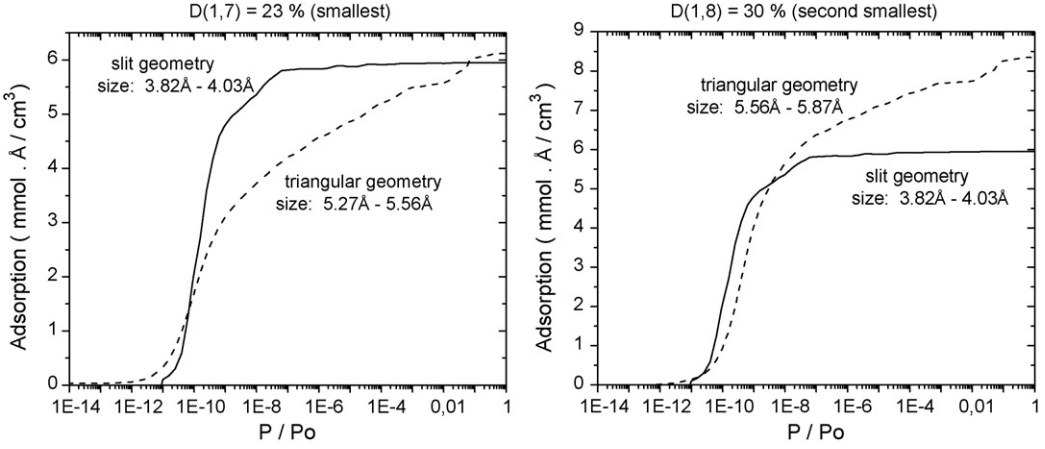

Fig. 3. Comparison between the adsorption isotherms for the two geometries for $D(1,7) = 23\%$ and $D(1,8) = 30\%$.

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the adsorption capacity of a sharper peak generated with a mixed geometry. It is worth highlighting the results of these effects on the porous volume and the specific surface of the sample: while the change in porous volume is relatively small, the specific surface area predicted by the pure slit geometry model is noticeably lower than the "true" value corresponding to the proposed sample. This can also be easily understood, since the surface area contributed by a triangular pore is appreciably higher than that corresponding to a slit pore of the same size.

To complement the information obtained from the above test, the opposite check was also performed, by generating an "experimental" isotherm with a given pure slit pores distribution and fitting it with a pure triangular geometry model. The results, not given here, show that the PSD distribution obtained with the triangular pores is shifted toward the larger sizes, as it would be expected.

We therefore conclude that, if the activated carbon to be characterized presents a differential heat of adsorption larger than ~4 kcal/mol at low pressures, as usually happens, indicating the influence of more than 2 graphitic plates in the energetics of adsorption, then the use of the mixed geometry model would result in a PSD representing more precisely the adsorption properties of the material.

It is therefore of great importance to design characterization experiments where both the adsorption isotherm and the differential heat of adsorption may be measured for the same sample. In addition, it has been shown that the fitting of adsorption heat data is more sensitive and provides more reliable results than the fitting of adsorption isotherms [19]. Unfortunately, it is still unusual to find such combined data (adsorption isotherms and heats) for a controlled family of carbons in the literature, therefore we are planning to obtain such data in our laboratory in the future.

3. Analysis of experimental data using the mixed geometry model

In order to illustrate the use of the mixed geometry model as applied to a controlled family of materials, activated carbon samples were prepared by a standard chemical activation with phosphoric acid as an activating agent [15,20–26]. The precursor for the present family of activated carbons was coconut shells and the preparation procedure is described in detail in Ref. [26]. The prepared samples were labelled as PAC – W1/W2 – N, where: PAC = Phosphoric Acid Concentration (% w/w); W1 = washing of the precursor only with distilled water; W2 = washing of the precursor with sulfuric acid (2 h) and distilled water; N = carbonization under nitrogen atmosphere

Nitrogen adsorption isotherms at 77 K were measured for the prepared AC samples using an Autosorb-1 MP apparatus (Quantachrome, U.S.A.). Each isotherm was fitted with both pure slit geometry model and mixed geometry model, by using the same number of parameters in both cases.

The N_2 isotherms for the samples of series W1 and the respective curve fittings for both slit pore and mixed pore geometry are shown in Fig. 5. The isotherms show that – within the range under study – there is no significant improvement in nitrogen uptake as the H_3PO_4/precursor ratio increases, except for the highest ratio, 53. This reflects on the calculated textural

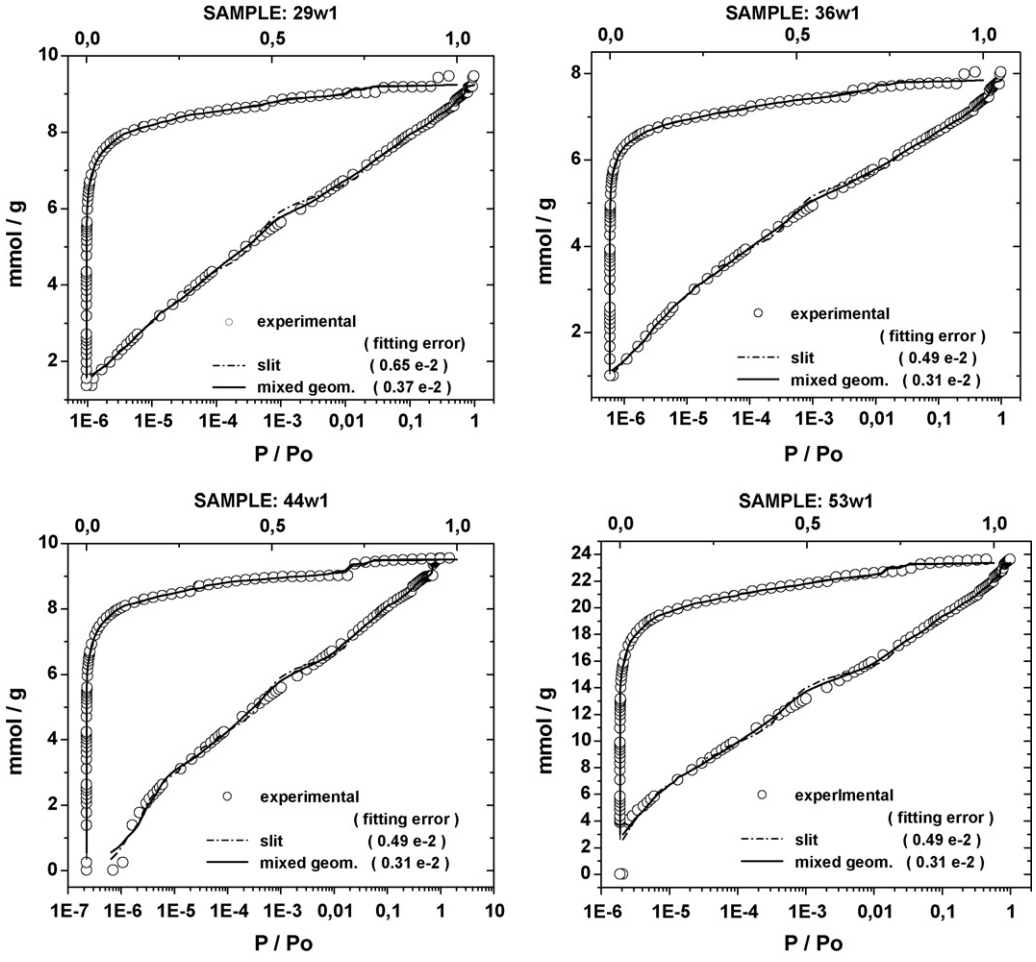

Fig. 5. Experimental N_2 isotherms at 77 K (symbols) and theoretical fits (lines) for the samples with the increasing H_3PO_4/precursor ratio.

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Table 2
Surface areas (m^2/g) and total pore volumes (cm^3/g) of samples as estimated from the slit pore and mixed geometry models (Monte Carlo simulations) together with the values reported by the equipment software, in the case of surface area.

Sample	Specific surface area (m^2/g)				Total pore volume (cm^3/g)		
	Slit pore geometry	Mixed pore geometry	Reported by BET-type equipment		Slit pore geometry	Mixed pore geometry	
			BET	Langmuir		Total	Slit pore only
29W1	861	874	520	897	0.3478	0.3267	0.1543 (47%)
29W2	1405	1411	1072	1889	0.7471	0.7319	0.4482 (61%)
36W1	767	784	434	758	0.3008	0.2855	0.1392 (49%)
36W2	1281	1283	844	1462	0.5647	0.5464	0.3591 (66%)
44W1	859	861	536	916	0.3629	0.3521	0.2411 (68%)
44W2	1471	1476	1065	1810	0.6875	0.6593	0.4161 (63%)
53W1	1989	1991	1283	2264	0.8757	0.8478	0.5937 (70%)
53W2	1296	1309	1103	1797	0.6708	0.6450	0.3815 (59%)
53W2N	2112	2518	2290	3962	1.4195	1.7094	0.4521 (26%)

properties of the samples, such as porosity and surface area, as may be seen in Table 2. The values calculated by considering slit and mixed geometry do not vary significantly, except for the samples carbonized under N_2. However, they do differ from the values calculated by the equipment software in some cases, especially for the estimation of surface area by BET, which tends to be underestimated as compared to the values obtained by molecular simulations. Except for concentration 53%, no marked trend is observed in textural properties as the H_3PO_4/precursor ratio increases, which is apparently contradictory to other authors' observations [21,22,23], who have reported the BET areas directly proportional to the H_3PO_4/precursor ratio. However, the increase in surface area observed for the increasing H_3PO_4/precursor ratio occurs as a consequence of micropores formation, some authors suggest there may be a considerable amount of ultramicropores, which cannot be detected by N_2 adsorption isotherms due to restricted diffusion in such small pores at 77 K [25].

The acid wash step prior to impregnation, as proposed in Ref. [21], has a significant effect on the sample textural properties. The sulfuric acid degrades and redistributes the biopolymers of raw material, triggering further development of meso- and macropores. In this new structure, the phosphoric acid may act more efficiently to form micropores during the chemical activation and hence raise surface area and micropore volume. Moreover, the formation of supermicropores and mesopores signalled by the shoulders in the obtained isotherms (see Fig. 5) is confirmed by Laine et al. [23] for the same precursor and activation agent carbonized in air. They report the occurrence of large micropores (8–18 Å) and mesopores (>18 Å) increase for higher acid concentrations. This is clearly observed in the pore size distributions represented by the histograms of Fig. 6, for the W2 series. The upper rows show the Pore Size Distribution obtained with the slit pore geometry, whereas the lower rows show the PSDs for the mixed geometry model; dark gray bars denote the contribution of the slit pores, whereas light gray ones stand for the total PSD. Although both model produce similar small fitting errors, distinct PSD may be appreciated. In general, for the mixed geometry, the contribution of triangular pores appears in the range of large micropores and mesopores, becoming more perceptible as the H_3PO_4/precursor ratio increases. This is particularly notorious for the sample prepared with 53% phosphoric acid, represented in Fig. 7, which deserves a separate discussion. Laine and Yunes [20] have studied different activation methods to produce activated carbons from coconut shells and concluded that – in the case of impregnation with H_3PO_4 – a less ordered stack of aromatic sheets should be expected due to the relatively low carbonization temperature as compared to other modes of activation. The authors mention that there is an incomplete "slide stacking" of aromatic sheets, so that the assumption that some of pores may have a triangular cross-section is quite realistic in this case.

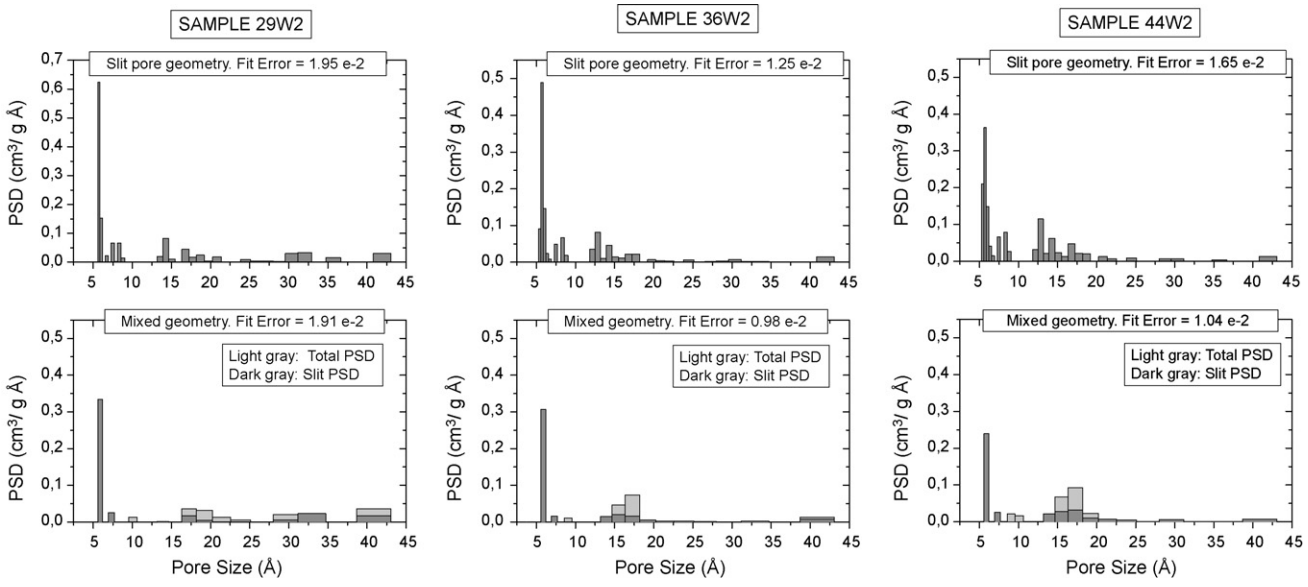

Fig. 6. PSDs of activated carbon samples considering slit pore (upper rows) and mixed (lower rows) geometry.

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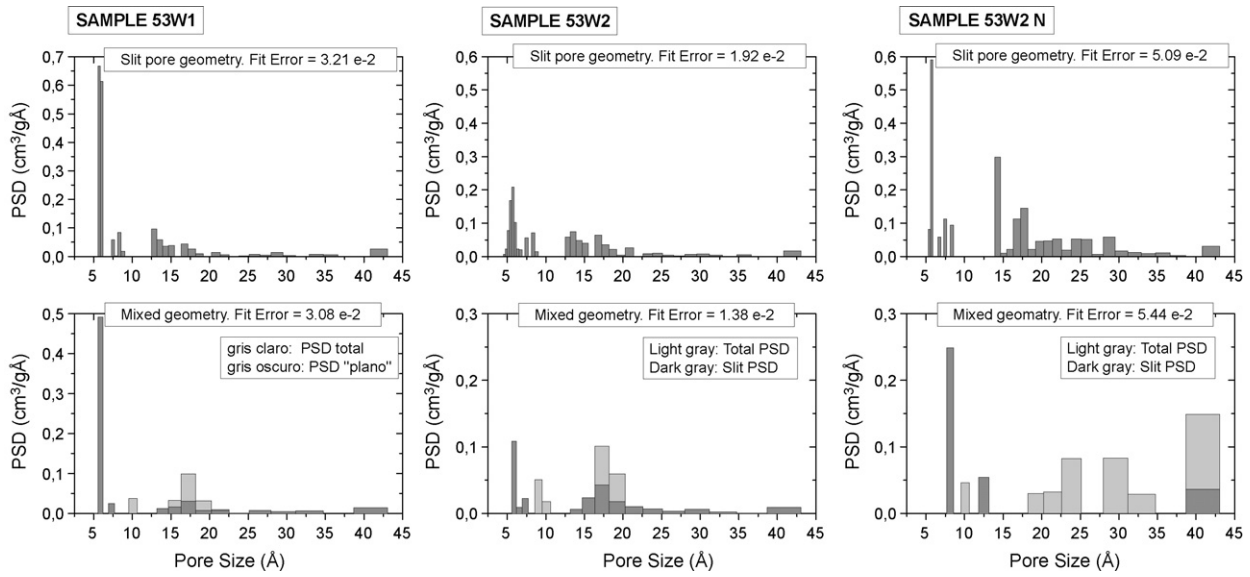

Fig. 7. PSD of the sample carbonized under air (left and center) and inert atmosphere (right) considering slit pore (top) and mixed (low) geometries.

Fig. 7 shows the PSDs obtained for the sample with higher acid concentration, for which the percent volume of developed micropores is maximal, hence showing the highest surface areas. This concentration, which corresponds to a phosphorus/precursor ratio of 0.42, has been shown to produce the best textural properties (highest surface area, highest micropore volume) for gas storage applications [22] for carbonization carried out under nitrogen atmosphere. Marked differences have been found for sample 53W2N for the two representations. The mixed geometry model predicts that supermicropores and mesopores are much more abundant and mainly of triangular section for the sample carbonized in an inert atmosphere. The effect of different atmospheres (either in continuous or static modes) for carbonization of lignocellulosic materials impregnated with H_3PO_4 is controversial. While some authors have obtained better results with air, and state that oxygen has a crucial role in developing porosity [23], others claim that textural properties are practically unaltered by either an oxidative or inert environment during carbonization at low temperatures, such as 450 °C [15]. In an inert environment, it is believed that there is a dehydration and redistribution of biopolymers, possibly by partial dissolution in the acid solution, together with the cleavage of ether bonds between the lignin and the cellulose, followed by recombination reactions in which larger structural units are formed, with the end result of a rigid crosslinked solid. Jagtoyen et al. [24] state that, due to this crosslinked structure, restricted shrinkage is expected and limited volatile loss may facilitate the development or conservation of porous elements present in the starting material. Note that among all samples, this is the only one for which the slit model gives a specific surface area below that predicted by BET, therefore indicating that the slit geometry alone is not taking account of the total porosity. This again strengthens the assumption that a mixed geometry model may better capture the PSD of such activated carbons, especially those carbonized under an inert atmosphere.

All samples produced in this work are intended for gas storage and should be essentially microporous [26]. PSDs obtained through simulations clearly reflect this property, although some samples do present some mesoporosity, which is more evidenced in the mixed geometry PSD. Following the line of reasoning given in Refs. [12,13], a real activated carbon is very likely to present a mixture of pores of different geometries and the pores with the rectangular cross-section were proposed. However, as already discussed above, in order to account for the large differential heat of adsorption observed at very low adsorbed amounts [8–11], a triangular geometry seems to be mandatory. Therefore, on the basis of the observed maximum adsorption energies, we propose that the PSD should be calculated through a model where the porous space is represented by a mixture of slit and triangular pores. PSDs obtained by considering the material as formed by a unique geometry results to be biased toward either smaller or larger pores. Hence, a mixed-geometry PSD may probably better capture the energetics of the adsorption system. The fact that, in the series of activated carbons studied here, the great majority of samples can be analyzed without appreciable differences either through a slit geometry model or through a mixed geometry model, except for sample 53W2N in Fig. 7 where the interpretation of the experimental results clearly favours the mixed geometry model, gives us confidence in the use of the new proposed model.

4. Conclusions

Real activated carbons are very likely to present a mixture of pore geometries, as a result of different packing of graphitic plates. The maximum adsorption energy provided by each graphitic plate is approximately 2 kcal/mol. Therefore, in order to account for the experimentally observed values between 4 and 6 kcal/mol, the interaction of a nitrogen molecule with three graphitic plates is necessary. This interaction can only be provided by pores with a triangular section. Clear evidence that many places exist in the porous structure where interaction of the adsorbed molecule with 3 graphite walls occurs is provided by the analysis of high resolution TEM images of an activated carbon in Refs. [27,28].

A mixed geometry model, combining slit and triangular pores, was developed, evaluated theoretically and applied to the characterization of a controlled series of samples of activated carbon obtained from the same precursor material. It was shown that the proportion of slit and triangular pores can be uniquely determined by fitting an adsorption isotherm and that the use of a pure slit geometry model would produce a PSD with wider peaks and shifted toward smaller pore sizes, while the use of a pure triangular geometry model would produce the opposite effect. It is concluded that the mixed geometry model may probably better capture the energetics of the adsorption system. It is particularly interesting to notice that the mixed geometry model smoothes the

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stepwise behaviour of the pure slit geometry model, as it can be appreciated in Fig. 5. Besides, the determined proportion of slit and triangular geometry pores may be very useful to model other processes in the material, for example diffusion.

Finally, the model has been used to characterize the controlled series of activated carbon samples that were prepared by chemical activation (H_3PO_4) of coconut shells, since the carbonization step is usually carried out at relatively low temperatures (around 500 °C), leading to a much more disordered porous structure as compared to high temperature pyrolysis. PSDs were obtained by fitting the experimental N_2 isotherms at 77 K. The PSDs reflected the microporous character of the samples prepared in this way. Increasing the amount of activation agent did not seem to result in improved porosity from the N_2 adsorption isotherms, possibly due to diffusional restrictions in ultramicropores. Nevertheless, the increasing presence of supermicropores (close to 20 Å) and mesopores could be well characterized by the mixed geometry model. Previously washing the precursor with a dilute acid solution also enhances the formation of larger micropores and mesopores, a considerable part of which is represented by a triangular shape. Carbonization under inert atmosphere led to a material with highly developed porosity, having a substantial amount of triangular shaped pores in the supermicropore and mesopore regions. The results obtained in analyzing this family of AC samples indicated that the proposed model is reliable and particularly convenient for this type of chemical activation.

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