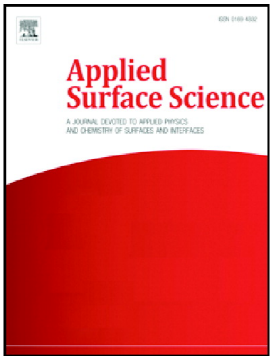

Effects of potential models on nitrogen adsorption on triangular pore: An improved mixed model for energetic characterization of activated carbon

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Effects of potential models on nitrogen adsorption on triangular pore: An improved mixed model for energetic characterization of activated carbon.

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ABSTRACT

Studies of the importance of shape considering both adsorption molecule and pore geometry were performed by Monte Carlo simulation in grand canonical ensemble (GCMC) for activated carbons (AC). The effects on adsorption capacity and isosteric heat were investigated in different pore sizes using a pseudo-sphere model and a multi-site potential (elongated shape) on triangular-shaped pore. The triangular geometry was considered as a need to allow for the simultaneous interaction of an adsorbed molecule with three graphite walls to account for the high values observed in the isosteric heat of adsorption at low pressures. Kernels of adsorption isotherms were generated by GCMC for different pore sizes considering two potential models for the determination of pore size distribution that allows for the characterization of various micro and mesoporous solids. We propose using a mixed geometry model (slit-triangular) and an elongated molecule potential to characterize activated carbons. The model is used to characterize a family of AC samples both texturally and energetically. The isosteric heat of adsorption was determined from the experimental isotherm by Monte Carlo simulation and the results were contrasted with experimental data obtaining a good agreement. In

addition, the work reports the interesting result on the need to use multi-atom potential (together with the mixed model) to predict heat of adsorption values of the order of those reported experimentally.

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1. Introduction

There is an increasing interest in developing better microporous materials due to multiple industrial applications like gas separation, purification and reaction processes. Hence, an appropriate characterization of porous carbons for their structural properties, such as pore size distribution (PSD) is an important issue. Measures of nitrogen adsorption are commonly used for the determination of the PSD of porous carbons. The calculation of these textural properties and, in particular of the PSD, depend largely upon the model used to represent the geometrical and physical characteristics of the porous space [1–7].

In addition, calorimetric data provide another source of potential information to characterizing on the surface properties of adsorbents, the isosteric heat of adsorption is one of the most important quantities characterizing energetic heterogeneity of the adsorbent, Cimino and collaborators recently have been studied the importance of taking into account heterogeneity to determination of the isosteric heat of adsorption [8].

Although there is experimental evidence suggesting that the carbon pores have a slitlike geometry, several works [9–13] suggest that the use of triangular-shaped pores introduces an energetic heterogeneity due to the pore shape, which might produce better agreement to experimental measurements of the isosteric heat of adsorption obtained using slit pores as a model. The mixed model is not better than existing models that consider heterogeneity, such as QSDFT or the Two-Dimensional NLDFT model[14,15]. Each correctly interpreted model allows us to obtain valuable complementary information and in this way advance in the understanding of the phenomena that occur in the real material, of course, the model has to reproduce the experimental data.

The importance of the shape of adsorbate on surfaces and in confined spaces has been previously studied considering slit geometry by Do and other researchers [16]. In this study the roles of molecular shape in adsorption of common probes used in the characterization of porous media were analyzed. Differences in the capacity of adsorption, isosteric heat of adsorption and PSD were found when contrasting the results obtained for the potential pseudo-sphere and the multi-site model, especially in small pores. On the same lines, we studied the importance of the shape of adsorbate considering triangular-shaped pores.

Simulations provide an appealing way to predict heats of adsorption because they can be obtained directly at any pressure and temperature. The obtaining of the heat of adsorption using simulation is well established for a single simulation and the combination of isosteric heats of single pores to predict the isosteric heat of a solid[17–19]. It is well understood too by the characterization community but to the best of our knowledge, is the first time that it is predicted the isosteric heat of an AC using a mixed model with multi-atom potential.

Our interest is twofold, on the one hand, we investigated the influence of both the shape of the adsorbate molecule (using a pseudo-sphere and a multi-site model potential) and the geometry of the adsorbent (triangular) in the processes of nitrogen adsorption. On the other hand, we also studied the best way to characterize energetically and texturally porous carbons using mixed geometry models incorporating multi-site potentials to model the interaction of nitrogen.

2. Molecular model and simulation details

Two geometries are present in this study that allow for the representation of the idealized porous space, the slit and triangular geometry pores. The gas-solid potential for the slit geometry is given, as usual, by the superposition of two Steele potentials [20], one per each infinite plate:

$$U_{gs-STEELE}(z) = 2\pi\ \varepsilon_{fs}\rho_C\,\sigma^2{}_{fs}\Delta\left\{\frac{2}{5}\left(\frac{\sigma_{fs}}{z}\right)^{10}+\left(\frac{\sigma_{fs}}{z}\right)^4-\frac{\sigma^4{}_{fs}}{3\Delta(z+0.61\Delta)^3}\right\} \quad (1)$$

where Δ is the separation between layers in graphite (0.335 nm), ρ_c is the number density of carbon atoms per unit volume of graphite (114nm^{-3}), and ε_{fs} and σ_{fs} are the fluid-solid Lennard-Jones parameters.

For the triangular geometry, only equilateral triangles are considered in order to keep the number of parameters to a minimum. The pore size (H) is given by the diameter of the circle inscribed in the triangular section of the pore. The fluid-solid potential is obtained by summing the contributions of three semi-infinite plates. The potential of each semi-infinite plate is given by [21]:

$$U_{fs}(z,y_e) = 4\varepsilon_{fs}\rho_c\{-\sigma_{fs}^6 I_3(z,y_e) + \sigma_{fs}^{12} I_6(z,y_e)\} \quad (2)$$

$$I_n(z,y_e) = \int_{-\infty}^{+\infty}dx\int_{ye}^{\infty}dy\,\frac{1}{(x^2+y^2+z^2)^n} \quad (3)$$

where y_e is the distance from the truncated edge. The fluid-fluid nitrogen interaction was considered by means of two different models. The pseudo-spherical potential via Lennard-Jones functions commonly used in the literature:

$$U_{ff}(r_{ij}) = -4\varepsilon_{ff}\left[\left(\frac{\sigma_{ff}}{r_{ij}}\right)^6-\left(\frac{\sigma_{ff}}{r_{ij}}\right)^{12}\right] \quad (4)$$

and a model based on two sites per molecule interacting via Lennard-Jones potential and electrostatic quadrupolar energies that accounts for the correct molecular shape [22]

$$U_{ff}(r_{ij}) = -4\varepsilon_{ff}\left[\left(\frac{\sigma_{ff}}{r_{ij}}\right)^{6} - \left(\frac{\sigma_{ff}}{r_{ij}}\right)^{12}\right] + \left\{\frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}\right\} \qquad (5)$$

where the first term is the Lennard-Jones (LJ) 12-6 potential and the second term is the Coulomb interaction potential between point charges q_i and q_j of sites i and j separated by distance r_{ij}. The parameters of the potential models are summarized in Table 1. The parameters for unlike-pair interactions are calculated using the Lorentz-Berthelot combining rules commonly used in molecular simulations [23].

Table 1: Parameters used in the LJ potentials for the GCMC simulations.[16]

Molecule	Potential Model	σ(nm)	ε/kB (K)	q(e)	Distance atom-c.o.m. (nm)
N_2	Pseudo-spherical LJ (1C)	0.3615	101.5		
$N_{(N2)}$	Multi-sites (3C)	0.331	36.0	−0.482 +0.964	0.055
Carbon		0.340	28.0		

2.1 Grand canonical Monte Carlo simulation

Using Monte Carlo simulation it is possible to obtain a collection of adsorption isotherms (the local isotherms, θ_L) considering different pore sizes both for the slit and triangular geometries and two adsorbate models, which we term the independent pore model. The general procedure is as follows: Transition probabilities for each Monte Carlo attempt, adsorption, desorption, translations and rotations rigid molecules are given by the usual Metropolis rules. In general, the box length is 10 times the collision diameter for the slit geometry; the longitudinal dimension for triangular geometry was taken as 50 nm; periodic boundary conditions were used in those directions, and the cut-off radius was considered half of the box length. Equilibrium was generally achieved after 10^8 MC attempts, after which mean values were taken over the following 10^7 MC attempts for configurations spaced by 10^3 MC attempts, in order to ensure statistical independence.

This collection of local isotherms can be combined in different ways to fit a given experimental isotherm:

(i) *Model PSGM-1C:* Pure slit pore geometry kernel using a pseudo-sphere model potential.

(ii) *Model PSGM-3C:* Pure slit pore geometry kernel using a multi-site model potential (elongated shape).

(iii) *Model MGM-1C:* a kernel of a mixture of the slit and triangular pores geometry modeling the interaction of the adsorbate by a pseudo-sphere potential model.

(iv) *Model MGM-3C:* a kernel of a mixture of the slit and triangular pores geometry modeling the interaction of the adsorbate by a multi-site potential model.

A minimization method for the mean square error, with a regularization term, as described in[1,24,25] was proposed to fit an experimental isotherm with the theoretical isotherm given by:

$$\theta_i^{theor} = \sum_{j=1}^{m} \theta_L\left(H_j^*, P_i, T\right) f\left(H_j^*\right) \delta H_j \quad . \text{(6)}$$

In the above equation, θ_i^{theor} stands for the theoretical value of adsorbed amount at pressure P_i and H_j^* for the value of the pore size in the middle of the jth size interval. Here, $f(H_j^*)$ is called a PSD and it is optimised to minimise the difference, usually measured in terms of the root-mean-square (rms) deviation between the experimental isotherm and the isotherm calculated from equation (6).

The accessible pore volume is defined as the volume accessible to the center of a particle at zero loading. This is determined by the Monte Carlo method of integration as reported in Do et al. [16].

2.1.1Methods for the determination of isosteric heat of adsorption

A thermodynamic quantity of interest that can be readily obtained from the GCMC is the “heat of adsorption” [26]. The use of the term isosteric enthalpy of adsorption is recommended by the IUPAC [27]. Using the fluctuation theory, the isosteric heat is calculated during a GCMC simulation from the energy and the amount adsorbed in each single pore [28]:

$$q_{st} = \frac{\langle U\rangle\langle N\rangle - \langle UN\rangle}{\langle N\rangle\langle N\rangle - \langle NN\rangle} + Tk_B \qquad (7)$$

where $\langle\rangle$ is the ensemble average, N is the number of particles and U is the configuration energy of the system.

It is important to be able to contrast the results obtained by the simulation with the experimental data. The calculations for a pore (or arbitrary structure) can be combined to determine the heat of adsorption of the solid of interest, such as activated carbon. In this study, we determine the isosteric heat of adsorption of a porous carbon based on equation[19]:

$$q_{st,T}(P) = -\left(\frac{\partial U_T(P)}{\partial N_T(P)}\right)_{T,V_T} + k_B T \qquad (8)$$

where $q_{st,T}$ is the total contribution of the adsorbed phase in the solid to the isosteric heat, V_T a is the total volume of the adsorption system, and U_T is the total energy of the adsorbed phase. The use of equation (8) requires the determination of the pore size distribution for the different proposed models, both in the case of pure geometries and when considering mixed geometry models.

2.1.2 Adsorption histograms

Our intention was to explore the influence of the molecular shape of the adsorbate in the adsorption process considering triangular geometry pores. To that purpose we analyzed both the molecular position (pseudo-spherical potential model and multi-site) and molecular orientation (in the case of the multi-site potential model) for different pore sizes. For the latter, we consider the angular position (ϕ) and the orientation (θ) with respect to the central axis of the pore (see Figure 1).

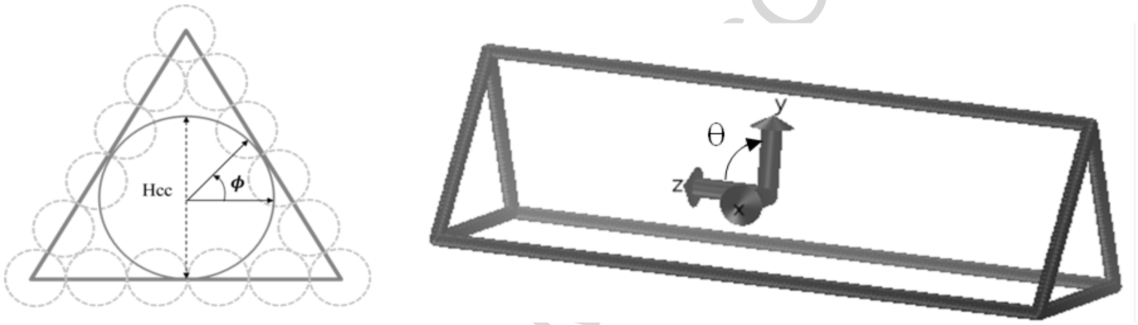


Figure 1: Angular position and molecular orientation in triangular pore geometry.

The pore size (Hcc) is defined as the diameter of the circle inscribed in the triangular section formed by the planes of C-atom centers in the outermost layer.

3. Results and discussion

In the first part we will study the effect of molecular shape on capacity and enthalpy of adsorption of N_2 when pores of triangular geometry are considered. Different pores size are analyzed; the smallest pore size that can adsorb a single row of molecules correspond to Hcc= 6.5Å.

The adsorption isotherms and the isosteric heats of the two potential models are shown in Figure 2, and we can observe that these differ notably. A similar behavior was found in previous studies for slit pore geometry [16], indicating again that the pseudo-sphere does not properly describe adsorption in small pores.

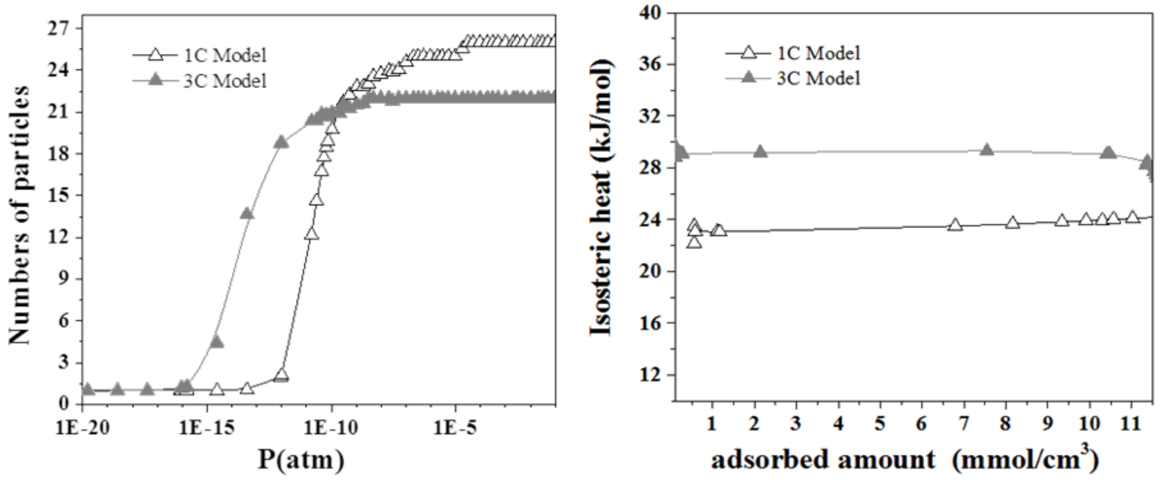


Figure 2: Adsorption isotherm and isosteric heat of nitrogen adsorption in Hcc= 6.5Å triangular pore at 77K. The pseudo-spherical model is shown with unfilled triangular symbols, while the multi-site model is indicated with grey symbols.

This pore size allows adsorption only at the center of the pore for both the 1-site model and the multi-site potential (Figure 3). In the case of the elongated shape model, we can study the orientation of molecules adsorbed in the pore. In Figure 4 it is observed that nitrogen molecules reside preferentially parallel to the pore axis with an angle of zero degrees.

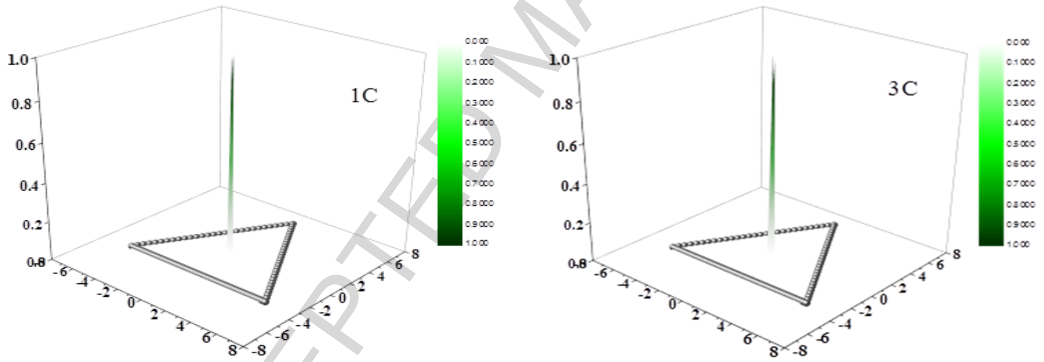


Figure 3: Histogram of nitrogen adsorption in Hcc=6.5Å triangular pore at P_0 to both potential model.

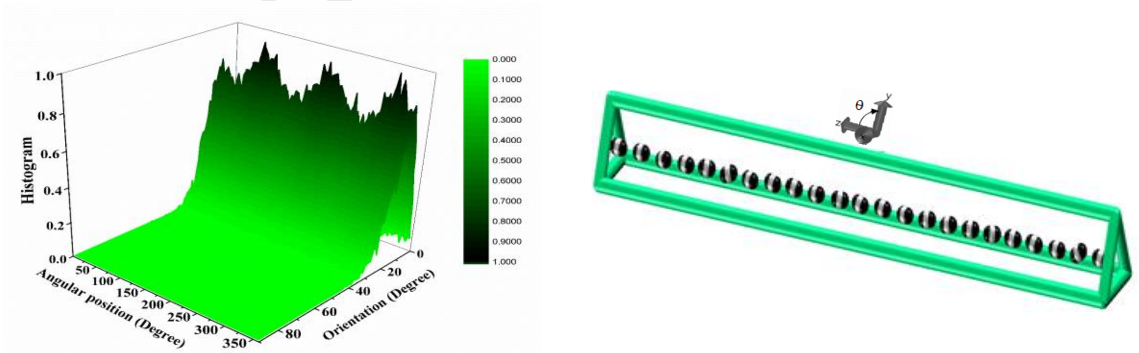


Figure 4: Orientation distribution of nitrogen adsorption in Hcc=6.5Å triangular pore at P_0 to multi-site model and snapshots from nitrogen adsorption simulations.

This molecular arrangement in the center of the pore was also observed for the pore sizes of 7 and 7.5Å. However, this larger size allows the molecules to be oriented preferably perpendicular to the pore axis, thus maximizing the energy of interaction and accommodating more molecules inside the pore (see Figure 5).

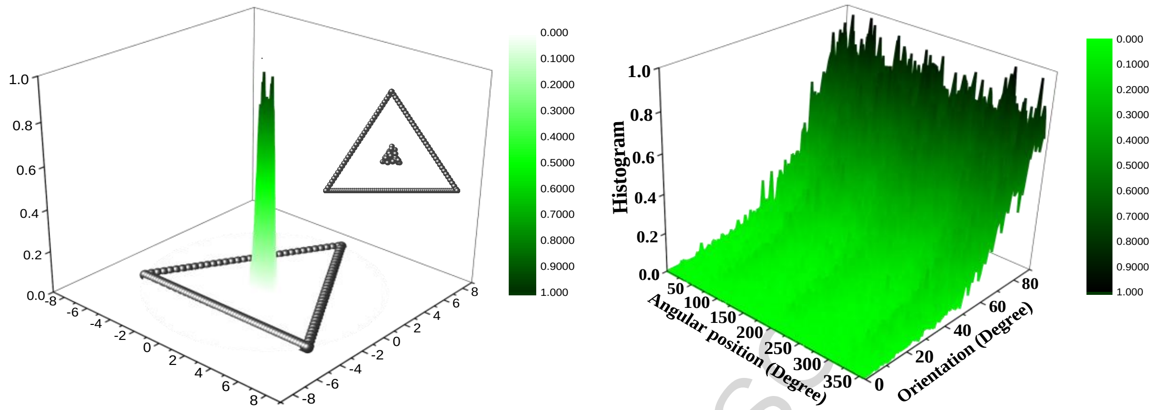


Figure 5: Histogram and Orientation distribution of nitrogen adsorption in Hcc=7.5Å triangular pore at P_0 to multi-site model.

An interesting behavior occurs when considering a pore too large for one row, as in the case of 8Å pore, where the pseudo-spherical and multi-site model exhibits remarkable differences. A similar adsorption capacity at low pressures can be observed from the isotherms. Nevertheless, the 3C model start to adsorb at a lower pressure in accordance with the higher isosteric heats obtained (Figure 6).

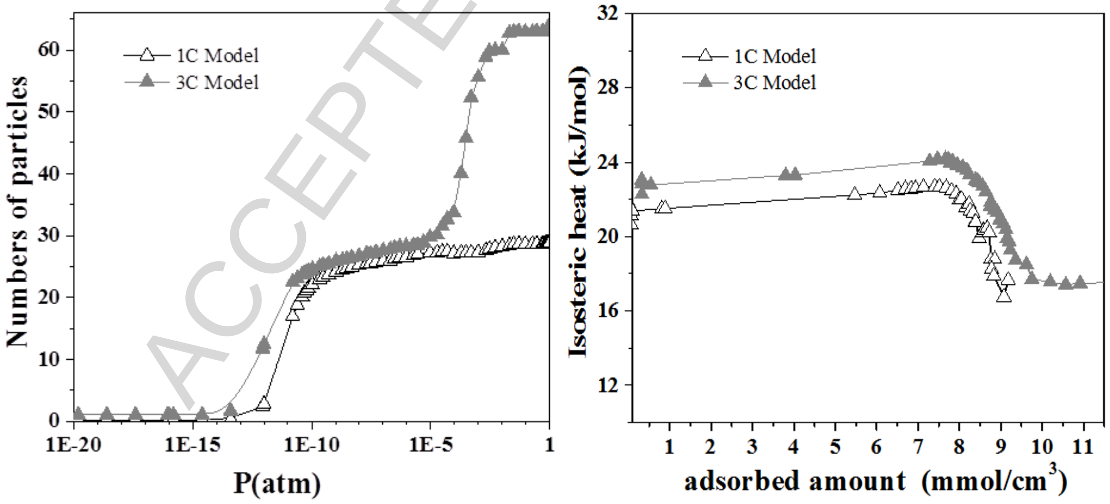


Figure 6: Adsorption isotherm and isosteric heat of nitrogen adsorption in Hcc=8Å triangular pore at 77K.

For higher pressures the 1C model reaches saturation, but the multi-site model continues to increase and accommodates a remarkably larger number of molecules. The molecular shape affects the packing, resulting in different capacity at saturation.

The adsorption histograms and the snapshots shown in Figures 7 and 8 for a fractional loading of 10% and 100% help us understand how the adsorption process depends on molecular shape. At lower adsorption, the molecules are adsorbed preferentially at the center of the pore without preferential orientation, i.e. they behave essentially as pseudo-spheres; therefore, both potential molecular models present similar behaviors. However, at maximum adsorption (100%), while the 1C model accommodates a single row of molecules in the center, for the 3C model the molecules are preferentially arranged parallel to the longitudinal axis of the pore near the wedges (maximizing their interaction energy) in a three-row arrangement and, thus increasing the number of molecules adsorbed (Figure 9).

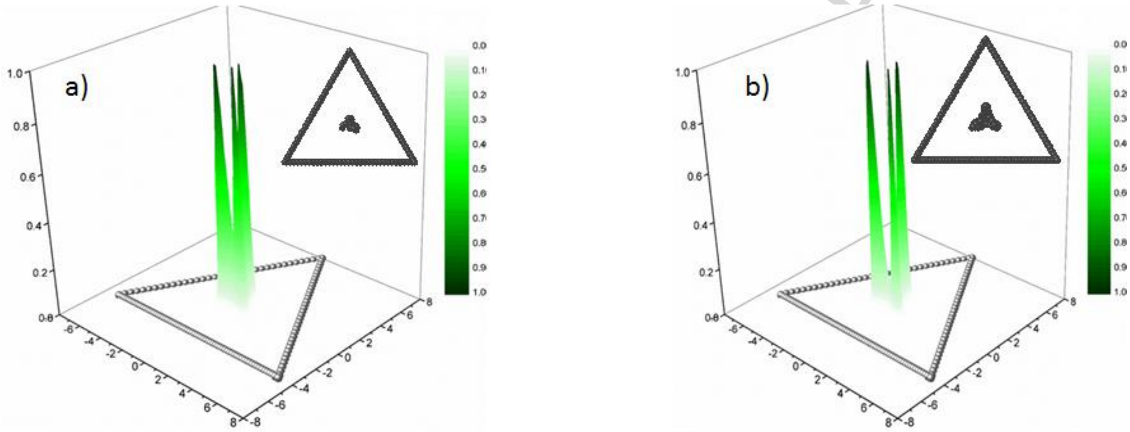


Figure 7: Histogram of nitrogen adsorption in Hcc=8Å triangular pore at a) 10% and b) 100% fractional loading to pseudo-spherical potential model (1C).

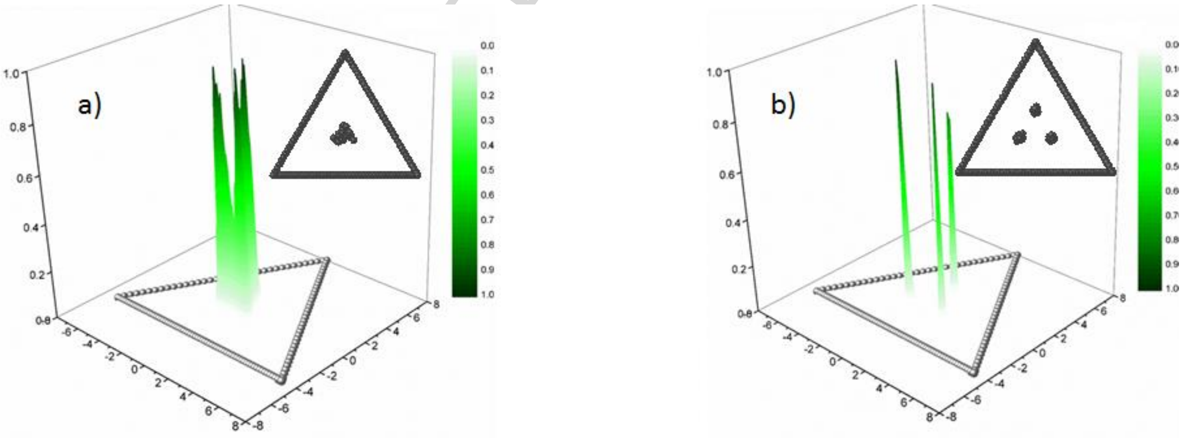


Figure 8: Histogram of nitrogen adsorption in Hcc=8 Å triangular pore at a) 10% and b) 100% fractional loading to multi-site potential model (3C).

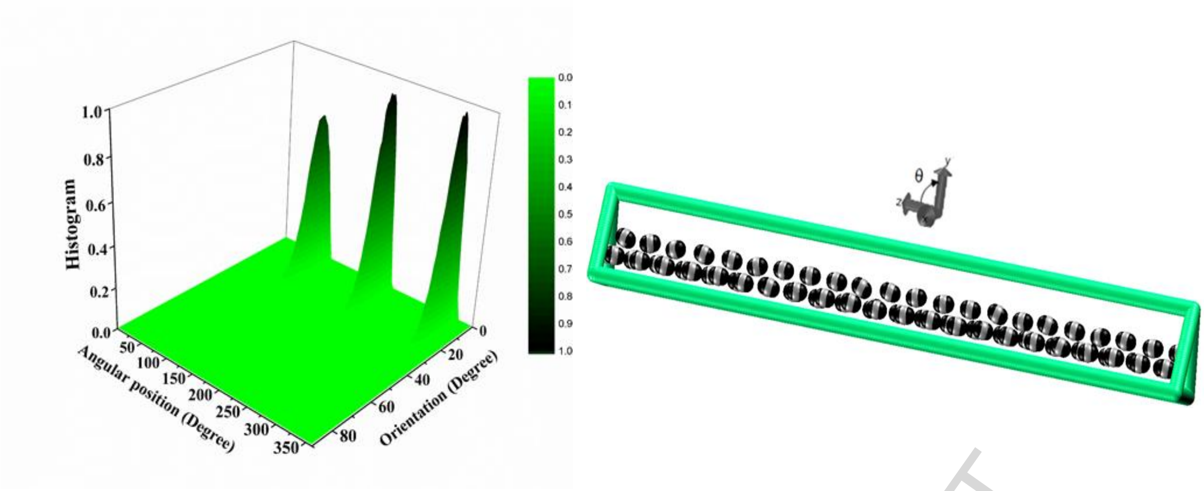


Figure 9: Orientation distribution of nitrogen adsorption in Hcc=8Å triangular pore at P_0 to multi-site model and snapshots from nitrogen adsorption simulations.

When large pores are analyzed, it can be observed that the behavior of both adsorption and isosteric heat for the different molecular potentials is quite similar (Figure 10). It is, however, interesting to examine the orientation of adsorbed molecules in the larger pores.

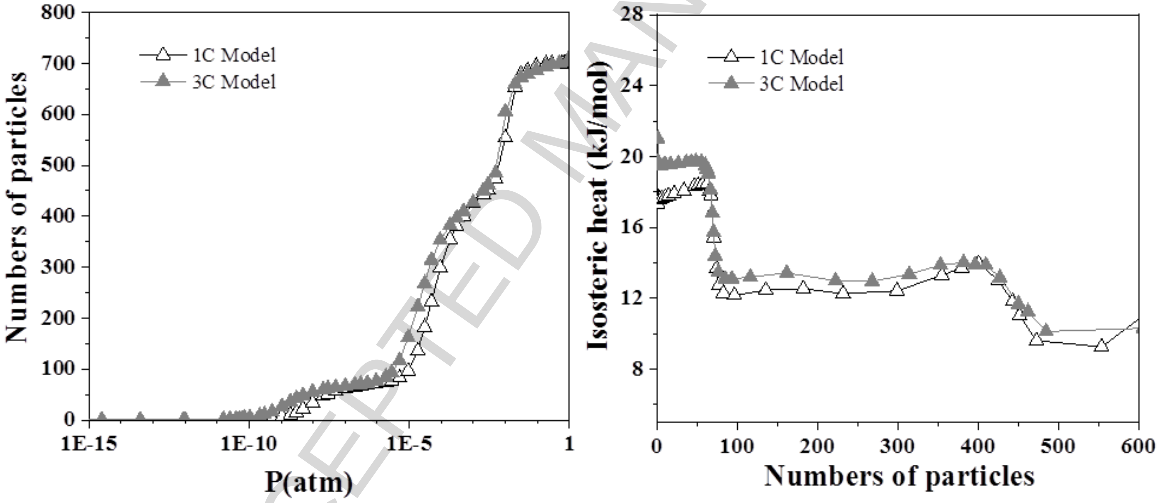


Figure 10: Adsorption isotherm and isosteric heat of nitrogen adsorption in Hcc=20Å triangular pore at 77K. The pseudo-spherical model is shown with unfilled triangular symbols, while the multi-site model is indicated with grey symbols.

To illustrate, here we take three different fractional loadings, 5%, 35% and 100% . In Figure 11, we show the orientation distributions for the 20Å pore. At low loading (5%), adsorbed molecules are mostly accommodated in a parallel orientation to maximize energy interaction with the wedge pore wall. At 35% pore filling, the molecules were adsorbed by the pore walls due to the potential of the fluid-fluid interaction produced by the molecules initially adsorbed on the wedges completing the monolayer. It is interesting to analyze the orientation of the molecules in this situation, given that a percentage of these molecules are adsorbed adopting a vertical orientation so that the energy interaction is maximized both with the molecules already adsorbed and with the pore walls. Finally, at saturation we can observe a randomization of the orientation of molecules, so that they do not adopt a preferential orientation.

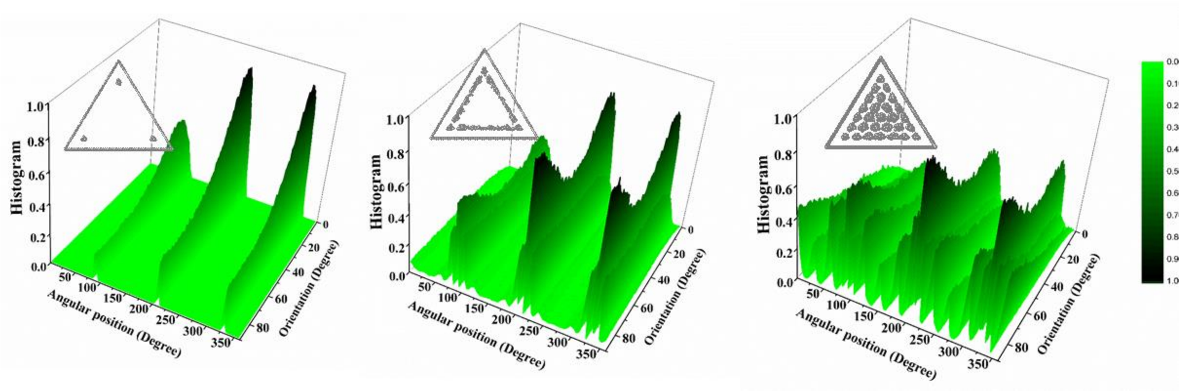


Figure 11: Orientation distribution of nitrogen adsorption in 20A triangular pore at 5%, 35% and 100% fractional loading and snapshots from nitrogen adsorption simulations respectively.

3.1 *Characterization of activated carbon*

To evaluate the goodness of fit of the models to characterize activated carbons, we analyzed the experimental N_2 adsorption isotherms of four samples of AC: A2n, A2a, B10a and 53w2N. The three first samples were obtained from peach stones as the precursor organic material reported by Soares Maia and collaborators [9] and the last sample was obtained from coconut shells[9]. In the present study, the samples were characterized using the following models: i) the PSGM-1C and PSGM-3C models based on kernels of the usual slit pore geometry with 1C and 3C potential adsorbate models respectively; ii) the MGM-1C and MGM-3C models based on a mixed kernel of the slit and triangular pore geometry with 1C and 3C potential adsorbate models respectively.

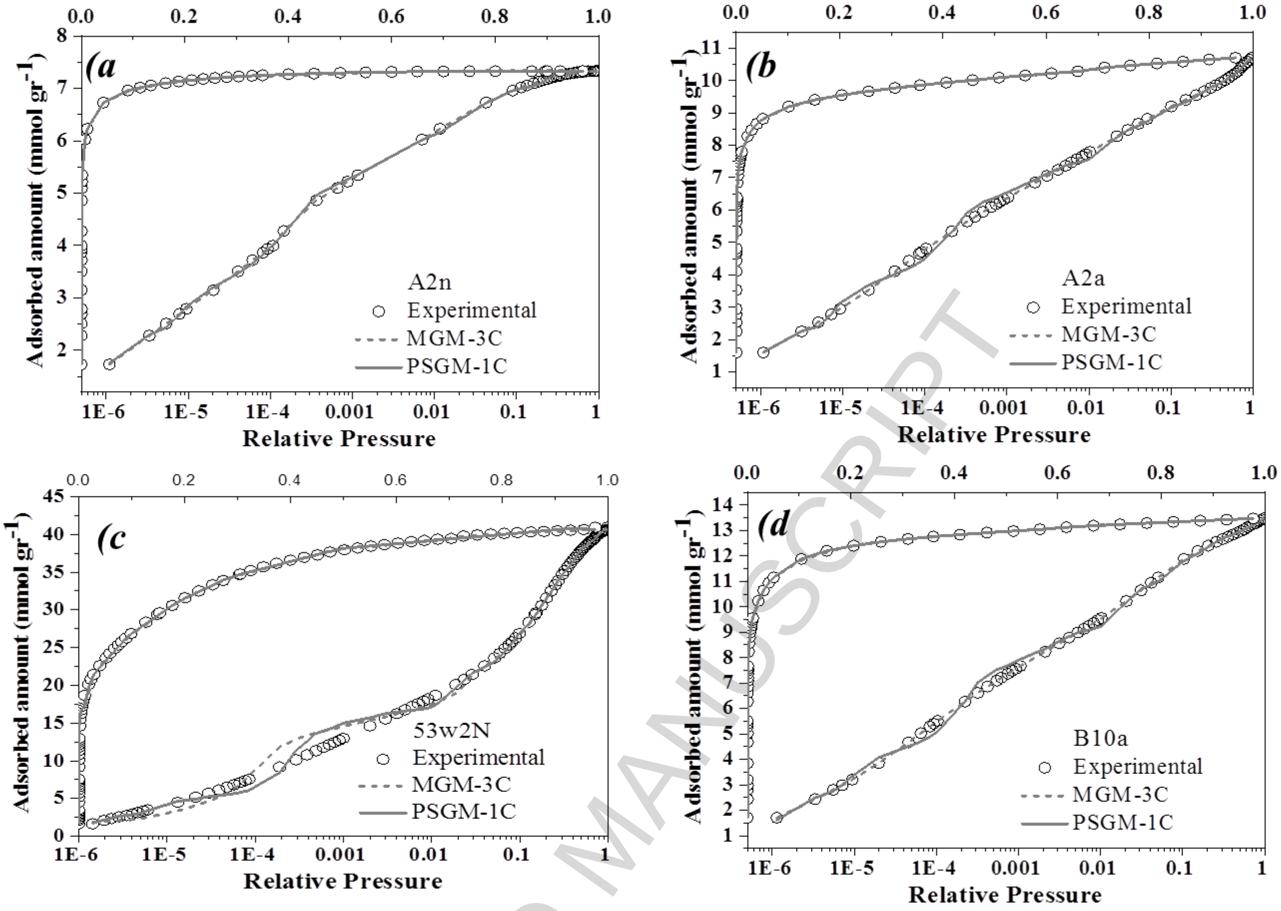


Figure 12: Experimental isotherm fits obtained from the PSGM-1C and MGM-3C models for different AC samples.

The experimental adsorption isotherms for each sample were fitted with the different models and their respective PSDs were obtained. In Figure 12, only the theoretical fittings for the PSGM-1C (full line) and for the MGM-3C (broken line) for the different experimental isotherms (circles) are shown for the sake of clarity. As a first observation, it may be said that both models fit the experimental isotherms satisfactorily, and a similar behavior was found for the other models.

However, when the fitting errors are analyzed (see Table 2), it is clearly observed that the mixed models present smaller fit errors, suggesting that they produce a more reliable representation of the carbon material. The best fittings (for all samples studied) corresponded to those values obtained from the MGM-3C model.

Table 2: Fit errors of the experimental isotherms obtained by the different models.

$$Error = \sqrt{\sum_{i}^{n} \left(\theta_i^{exp} - \theta_i^{Theo}\right)^2}$$

Sample Model	A2n	A2a	53w2N	B10a
PSGM-1C	0.2468	0.9545	7.139	1.4798
PSGM-3C	0.5333	0.8574	8.743	1.2605
MGM-1C	0.1434	0.3734	6.713	0.6041
MGM- 3C	0.1906	0.3486	7.768	0.4096

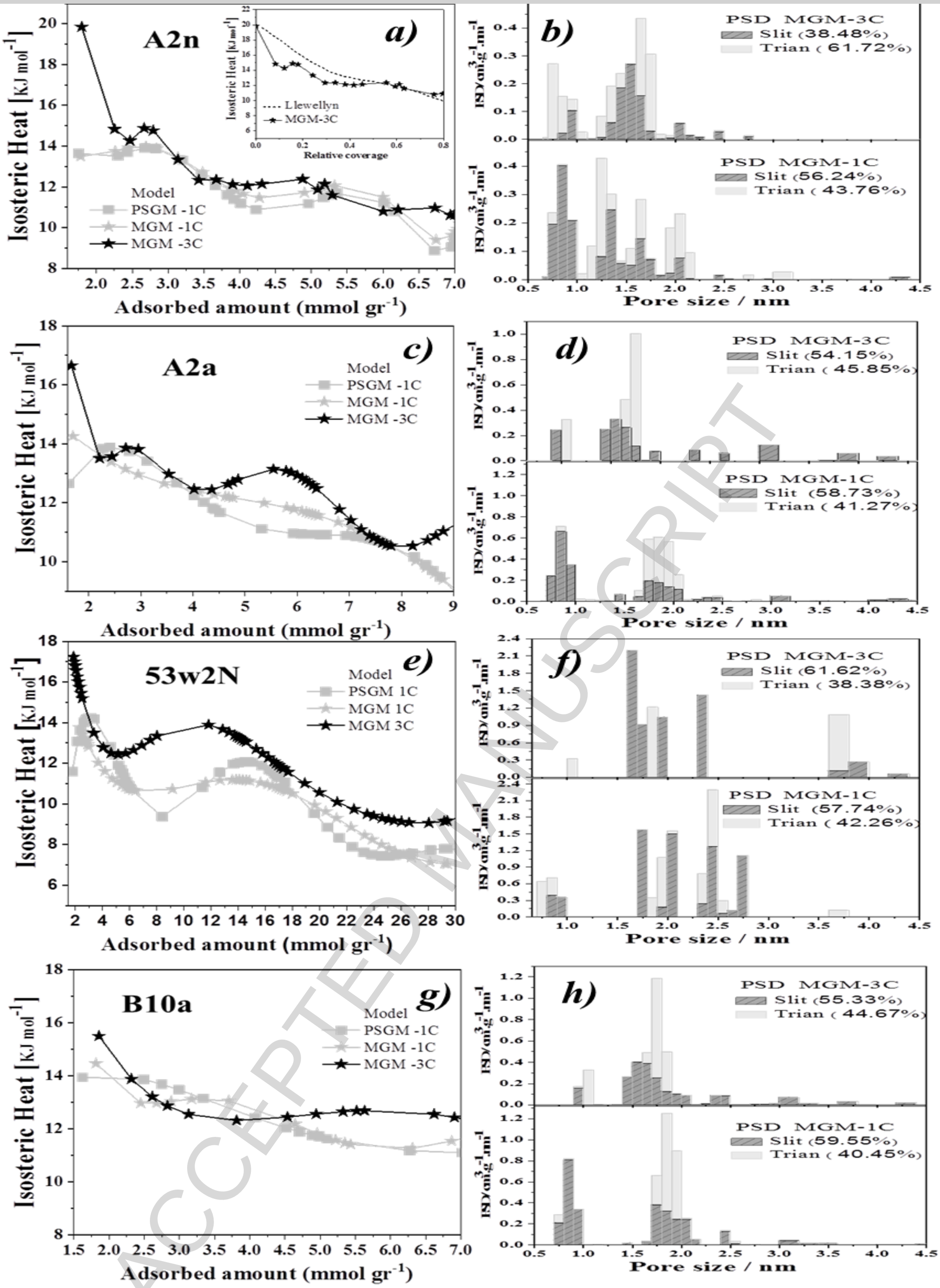
As mentioned above, the principal interest to study the adsorption in triangular-shaped pores resulted from the fact that this geometry introduces an energetic heterogeneity since an adsorbate molecule may interact simultaneously with three graphitic plates. We determine the isosteric heat of adsorption from experimental isotherms by the methods proposed in [19] from equation (8).

Figure 13 shows the isosteric heats and PSDs obtained from experimental isotherms of nitrogen adsorption on B10n, A2n, A2a and B2a samples for MGM-1C and MGM-3C models; we also compared the isosteric heat determined with the standard PSGM model as a reference. Although the models of mixed geometries yielded similar fits in the experimental isotherms (Table 2), it can be observed that modeling the interaction of the adsorbate with the multi-site potential produces higher values of isosteric heats.

When the pore size distributions are analyzed, we can observe that for each of the samples studied, the PSDs obtained from the mixed geometry models (MGM-1C and MGM-3C) report the same pore size range and a similar behavior. However, the presence of triangular pores in ultramicropores range (< 0.7nm) reported in the PSDs by the MGM-3C model is associated with the highest values of heat obtained. This behavior is expected since, as we have seen, the molecular shape has significant effects on isosteric heat of adsorption, especially in small pores.

In the cases in which PSDs report more contribution of triangular micropores, the MGM-3C model presents higher isosteric heat of adsorption at low loading with values around 18KJ/mol in good agreement with reported calorimetric measurements on porous carbon (see inset in Figure 13*a*), while the PSGM-1C model, typically used for the characterization of these materials, predicts a lower isosteric heat with a value of 6 KJ/mol below the experimental data.

Figure 13: Isosteric heats and PSDs on B10n, A2n, A2a and B2a samples. Inset a) Comparison of isosteric heats on B10n determined by GCMC (MGM-3C) and calorimetric measurements by Llewelyn on AC[29].



In particular, although the mixed models presented significantly improve the fitting of experimental isotherms, the MGM-3C model is the only one that predicts the high isosteric heats observed experimentally [29,30]. On the other hand, our analysis suggests the fact that only the fit of the experimental adsorption isotherm is not enough for a reliable characterization of AC. It validates the PSDs obtained by the MGM-3C since only the isosteric heats of adsorption determined from these mixed PSDs, considering the multi-site model, are of the order of those reported experimentally. Note that a very good fit of experimental isotherms (MGM-1C) does not produce high isosteric heats.

It is important to note that the isosteric heat of adsorption is determined from experiments either directly by calorimetric measurements or indirectly by the thermodynamic isosteric method (based on the application of the Clausius-Clapeyron equation for the adsorption isotherms measured at different temperatures), significantly greater expense methods than the GCMC simulations. In this context, these results confirm the need to incorporate the MGM-3C model for the characterization of activated carbons.

4. Conclusions

This work studied the influence of molecular shape in nitrogen adsorption on triangular-shaped pores in order to propose a mixed geometry model (slit and triangular geometry) that allows for an adequate textural and energetic characterization of activated carbons. We found that the elongated shape model (multi-site) presents energetic and packaging differences with the pseudo-spherical model, especially in small pores.

Of the models studied in this work, the mixed geometry MGM-3C model, which incorporates the multi-site potential to describe the interaction of $N_{2,}$ provides the best fit for the experimental isotherm. The analysis of the adsorption isotherms and obtained PSD produces a more consistent picture of the sample of adsorbents.

The MGM-3C model can be used to determine the isosteric heat by simulation to characterize microporous material energetically. The very good agreement with the experimental measurements clearly demonstrates the applicability of the MGM-3C method for reliable pore size distribution and isosteric heat analyses of porous carbon materials.

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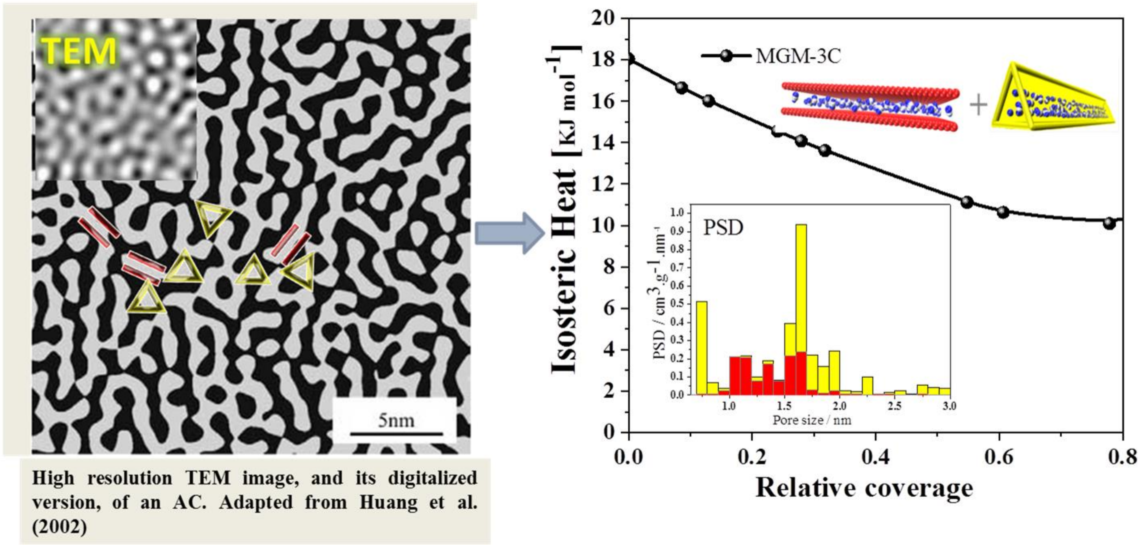

High resolution TEM image, and its digitalized version, of an AC. Adapted from Huang et al. (2002)

Graphical abstract

Highlights

- The importance of the shape of adsorbate in confined spaces considering triangular-shaped pores was studied. Both the capacity of adsorption and isosteric heat were analyzed.

- A mixed geometry model, incorporating multi-site potentials to model the interaction of nitrogen, was propose for the textural and energetic characterization of activated carbons.

- The isosteric heat of adsorption was determined from the experimental isotherm by Monte Carlo simulation considering mixed geometry model.

- The work reports the interesting result on the need to use multi-atom potential (together with the mixed model) to predict heat of adsorption values of the order of those reported experimentally.