Micropore size distribution of activated carbons: a key factor for a deeper understanding of the adsorption mechanism of pharmaceuticals

Distribución de tamaño de microporos en carbones activados: un factor clave para una comprensión más profunda del mecanismo de adsorción de productos farmacéuticos

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Abstract

The elucidation of the pore structure of activated carbons requires complementary adsorption data and is of fundamental importance for the comprehension of the adsorption mechanism of organic molecules, as is the case of pharmaceutical compounds. The present work reports studies developed in the Adsorption and Adsorbent Materials Group highlighting the contribution of the micropore size distribution (MPSD), obtained from the fitting of CO_2 adsorption data, for the deeper understanding of kinetic and equilibrium adsorption data of pharmaceutical compounds with distinct dimensions and behaviours in solution.

Resumen

La elucidación de la estructura porosa de carbones activos requiere datos de adsorción complementarios y es de importancia fundamental para la comprensión del mecanismo de adsorción de moléculas orgánicas, como es el caso de compuestos farmacéuticos. El presente estudio reporta los trabajos desarrollados en el Grupo de Adsorción y Materiales Adsorbentes de la Universidad de Lisboa destacando la contribución de la distribución del tamaño de microporos, obtenida mediante lo ajuste de los datos de adsorción de CO_2, para la comprensión más profunda de los datos cinéticos y de equilibrio de la adsorción de compuestos farmacéuticos con distintas dimensiones y comportamientos en solución.

1. Introduction

The detailed characterization of activated carbons (texture, chemical composition, morphology) is quite a challenging task, given the extreme complexity regarding size and shape of pores, and variety of structures and surface functionalities.

The most effective experimental approach for obtaining information on the adsorption process is the experimental determination of an isotherm, which contains information on the adsorption process. On the other hand, knowledge of the surface chemistry of carbon materials is also of fundamental importance, since their behaviour is strongly influenced by the presence of chemical species at the surface that will allow their use in various technological fields. Regardless the unquestionably importance of the surface chemistry characterization, in this paper, we will focus on the key role of the textural characterization of the materials to allow deeper insights on the adsorption mechanism of pharmaceutical compounds (Figure 1).

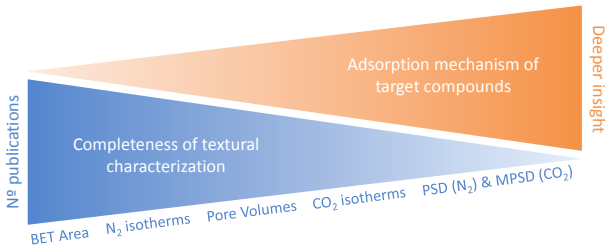

Figure 1. Relationship between the degree of completeness of activated carbons' textural characterization and the deeper comprehension of the adsorption mechanism of pharmaceutical compounds (PSD – pore size distribution; MPSD – micropore size distribution).

Figura 1. Relación entre el grado de exactitud de la caracterización textural carbones activados y la comprensión más profunda del mecanismo de adsorción de compuestos farmacéuticos (PSD - distribución del tamaño de poros; MPSD - distribución del tamaño de microporos).

The textural characterization of activated carbon consists on the determination of N_2 and CO_2 isotherms and on the use of mathematical models for the quantification of the specific surface area, pore volume and pore size distribution. However, the great majority of studies reporting the use of activated carbon materials for the removal of contaminants presents only few information regarding the porous network of the adsorbents, which consequently limits a thorough analysis of the collected data and the comparison with other literature studies.

As illustrated in Figure 1, , the most often reported textural parameter is, by far, the specific surface area (BET area), determined by the model proposed by S. Brunauer, P. H. Emmett and E. Teller, in 1938, which aimed to quantitatively describe the physical adsorption of vapor in non-porous solids [1]. Yet, there is a general awareness of the shortcomings in relation to the underlying theory of this model, and in the particular case of microporous adsorbents, such as activated carbons, there is also a lack of a real physical meaning. So, the comparison of the textural properties of different samples based only on the BET area value can therefore be misleading, and further characterization of the texture is advised.

The simple analysis of the shape of experimental isotherms according to the IUPAC classification [2] enables to gather qualitative information about the type and fraction of pores of an activated carbon. However, beyond the analysis of the shape of the curves, isotherms must also be interpreted quantitatively, so that comparisons between materials can be made. This quantitative analysis of the micro, meso and

total pore volumes can be performed by numerous analytical methods that can be applied to the N_2 adsorption data, as is the case of Gurvich rule for total pore volume or the Dubinin-Raduskevich equation, *t*-method or a_s method for the micropore volume [3-7].

Even with the information gathered from all the above mentioned methods, it is not possible to justify some results regarding adsorption processes in liquid or gas phase, when the effect of the surface chemistry is ruled out. In these cases the pore size distribution assessment from the N_2 and CO_2 adsorption data stands as an additional tool for the textural characterization of carbon materials. A correct assessment of the micropore size distribution (MPSD) of the materials can be crucial to explain, for example, the maximum capacity, affinity and more complex phenomena, such as two-step isotherms, or the influence of the temperature in the adsorption process, as it will be further demonstrated in section 3.

2. Micropore size distribution assessment

A detailed characterization of activated carbons should include pore size analysis in the entire range of pores, and for this it is important to combine data from N_2 and CO_2 adsorption at, respectively, – 196 ºC and 0 ºC. Since the micropore volume constitutes the most important fraction of the surface area of activated carbons, the use of CO_2 instead of N_2 adsorption data has been repeatedly proposed as a better alternative due to the well-known diffusion limitations of N_2 in carbons with narrow micropores [4,8]. If fact, the assessment of the MPSD from CO_2 adsorption data is a key information, particularly when the adsorption of molecules of small dimensions is envisaged, since it may allow a deeper understanding of the diffusion and adsorption mechanism.

There are many methods to calculate the MPSD, most of them based on classical methods, *i.e.*, Horvath-Kawazoe, *t*-plot, and methods based on the theory of micropore volume filling (TMVF), namely the models of Dubinin-Radushkevich (DR), Dubinin-Radushkevich-Astakhov (DA) and Dubinin-Radushkevich-Stoeckli (DRS) [3-5]. The distribution of mesopores is generally made by methods based on the Kelvin equation, such as Barrett, Joyner and Halenda (BJH) or Broekhoff and de Boer (BdB), and their modifications, being however out of the scope of the present manuscript

In the 80's considerable progress was made on the understanding of fluid behaviour constrained by the presence of walls, which led to the application of the Density Functional Theory (DFT) to the adsorption phenomena [9-11]. From a mathematical approach, the DFT method applied to the calculation of the pore size distribution (PSD) is based on the integral of the individual isotherms of defined given sizes.

The most advanced form of this theory is called the non-local approach (NLDFT) that is based on calculating model isotherms that may be used to determine pore size distribution from gas adsorption data. Nowadays, the advanced methods based on NLDFT succeed in determining the pore size distribution in the entire range of pore sizes accessible to the adsorptive molecule [12,13].

However, the determination of the micropore size distribution remains a difficult problem for most activated carbons, given their highly developed micropore network. In fact, only few studies in the literature report the assessment of MPSD of activated carbons by the use of the more sophisticated NLDFT method applied to CO_2 adsorption data [14]. Moreover, these methods are difficult to implement due to their mathematical complexity, so, the majority of studies only present MPSDs assessed from the application of DRS equation what, as it will be discussed in the following, can lead to an inaccurate information.

In a study developed by Pinto and coworkers [15], the application of two variations of the DR equation to assess the micropore size distribution of carbon samples was discussed. The methodologies used for the fitting of the CO_2 adsorption data were the conventional DRS equation and a novel approach for fitting the integral adsorption equation for which the MPSDs are not constrained to a particular preassumed shape.

From the comparison of MPSD data obtained by these approaches for laboratory-made and commercial samples, the authors concluded that the results are highly dependent on the method used to make the adjustment of the experimental data, as it is clearly illustrated in Figure 2. Although the plots for samples AC1 and AC2 are relatively similar, significant differences were found between the results obtained by the two methods for the other two samples.

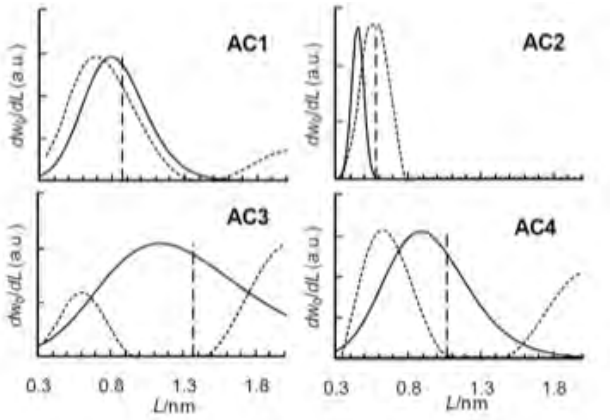

Figure 2. Micropore size distributions (MPSDs) of activated carbons obtained by fitting the DRS equation (solid line) and by the methodology proposed by Pinto *et al.* [15] (broken line). The vertical dashed line represents the weighted average micropore size of the distribution obtained by fitting the integral adsorption equation. Reprinted with permission from Ref. [15]. Copyright 2010 American Chemical Society.

Figura 2. Distribuciones del tamaño de microporos de carbones activos obtenidos mediante el ajuste de la ecuación DRS (línea continua) y por la metodología propuesta por Pinto *et al.* [15] (línea discontinua). La línea vertical discontinua representa el tamaño de microporo medio ponderado de la distribución obtenida mediante el ajuste de la ecuación de adsorción integral. Reimpreso con el permiso de la referencia. [15]. Copyright 2010 American Chemical Society.

The DRS equation gives a micropore size distribution that is a Gaussian average of the actual distribution, and it is only expected to give a good description of the actual distribution in cases where the activated carbons have relatively narrow and symmetric distributions, as in samples AC1 and AC2. So, the Gaussian-shaped distribution obtained from the DRS equation is not a suitable description for the MPSD of activated carbons for all cases.

From the practical point of view, it is preferable to use the fitting of the integral adsorption equation for

the determination of the MPSDs of carbon materials, since it does not assume a Gaussian distribution, and consequently allows to obtain more accurate pore size distributions. This method has been increasingly used in our group for the assessment of the MPSDs of activated carbons, and has enable us to interpret results of the adsorption of pharmaceuticals from liquid phase in a very straightforward way, as it will be highlighted in the following section.

The importance of using complementary data, and particularly the determination of MPSD, to assure a deeper characterization of activated carbons is exemplified in Figure 3 and Table 1 for three microporous carbons with similar type I(a) N_2 adsorption isotherms. Following the most common approach for characterizing porous materials, it is clear that carbons B and C have similar BET areas, while carbon A presents a slightly higher value, which are in accordance with the isotherms depicted in Figure 3(a). The type I(a) isotherms reveal the presence of a narrow micropore distribution and the quantification of the pore volumes presented in Table 1 corroborates this analysis. The volumes of micropores assessed from the application of the a_s method to the N_2 adsorption data allows, however, to gather more information regarding the amount of ultra and supermicropores in each sample. This volumes are also in agreement with the micropore volumes assessed by the DR method to both N_2 and CO_2 adsorption data. In fact, samples A and B present a higher volume of narrower micropores ($W_{DR\,CO2} > W_{DR\,N2}$), while sample C has a higher percentage of larger micropores.

Although all this discussion already points out the differences between these three microporous activated carbons, the further determination of the MPSD is even more informative, since the amout of micropores with different pore widths is clearly quantified (Figure 3(c)). In fact, this analysis reveals striking differences between these samples, with carbon A and B presenting monomodal distributions, centered at, respectively, 0.72 nm and 0.62 nm, and carbon C presenting a bimodal distribution with micropores with widths between 0.4 and 0.9 nm, and also higher than 1.2 nm. Regarding the samples with a monomodal distribution, carbon B has a sharper distribution (0.5 to 0.8 nm), characteristic of materials with molecular sieve properties, while carbon A has a wider micropore size distribution (0.5 to 1.4 nm).

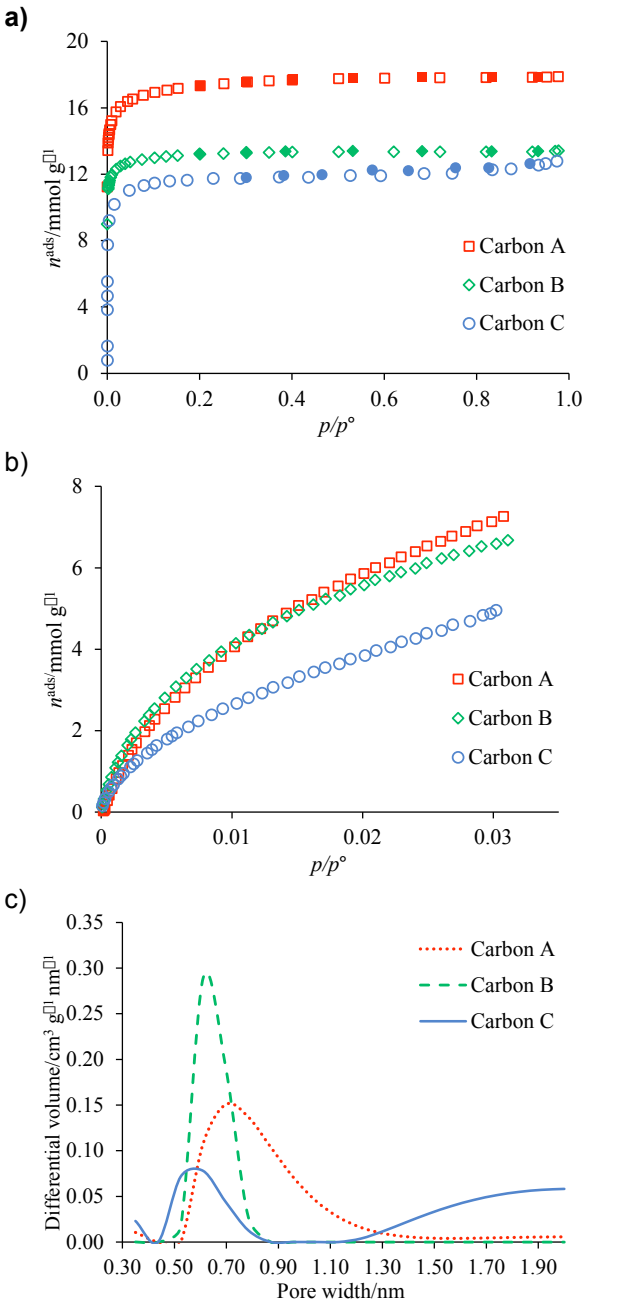

Figure 3. Textural characterization of three activated carbon samples: (a) N_2 adsorption-desorption isotherms at -196 ° C, closed symbols are desorption points; (b) CO_2 adsorption isotherms at 0 C; (c) micropore size distributions according to [15].

Figura 3. Caracterización textural de tres muestras de carbón activado: (a) isotermas de adsorción-desorción de N_2 a -196 ° C, símbolos cerrados son puntos de desorción; (B) isotermas de adsorción de CO_2 a 0 °C; (c) distribuciones del tamaño de microporos de acuerdo con [15].

Table 1. Nanotextural properties of three microporous activated carbons.

Tabla 1. Propriedades nanotexturales de tres carbones activos microporosos.

				α_S *method*			*DR equation*	
Materials	A_{BET} (m^2g^{-1})	V_{total} (cm^3g^{-1})	V_{meso} (cm^3g^{-1})	$V_{\alpha\,total}$ (cm^3g^{-1})	$V_{\alpha\,ultra}$ (cm^3g^{-1})	$V_{\alpha\,super}$ (cm^3g^{-1})	$W_{DR\,N2}$ (cm^3g^{-1})	$W_{DR\,CO2}$ (cm^3g^{-1})
Carbon A	1375	0.63	0.01	0.62	0.35	0.27	0.58	0.65
Carbon B	1053	0.47	0.00	0.47	0.30	0.17	0.46	0.52
Carbon C	907	0.43	0.03	0.40	0.16	0.24	0.40	0.27

$\boldsymbol{A_{BET}}$- Apparent surface area, estimated from the N_2 isotherms, applying the BET equation in the range 0.05 < *p/p*°< 0.15 [3]; $\boldsymbol{V_{total}}$- Total pore volume, evaluated at *p/p*° = 0.975 in the N_2 adsorption isotherms at -196 °C [6]; $\boldsymbol{V_{meso}}$- Mesopore volume, obtained from the difference between V_{total} and $V_{\alpha\,total}$; $\boldsymbol{V_{\alpha\,total}}$, $\boldsymbol{V_{\alpha\,ultra}}$, $\boldsymbol{V_{\alpha\,super}}$- Total micropore volume, ultramicropore volume (width less than 0.7 nm), and supermicropore volume (width between 0.7 and 2 nm), obtained from the application of the α_S method applied to the N_2 adsorption data, taking as reference the isotherm reported by Rodríguez-Reinoso *et al.* [7]; $\boldsymbol{W_{DR\,N2}}$ and $\boldsymbol{W_{DR\,CO2}}$- Micropore volume analyzed using the Dubinin–Radushkevich formulism to the N_2 and CO_2 adsorption data [3].

3. MPSD for deeper insights into the adsorption of pharmaceuticals onto activated carbons

In this section, examples illustrating the importance of MPSD as a tool for obtaining a deeper insight into the adsorption mechanism of pharmaceutical compounds by activated carbons, will be presented. In all the cases, the MPSD of the porous carbons was obtained from CO_2 adsorption data, according to the method described by Pinto *et al*. [15]. The molecular structure and information regarding the critical dimensions of the pharmaceutical compounds for which the adsorption mechanism onto activated carbons will be discussed in the following sections are displayed in Figure 4.

3.1 Ibuprofen

Regarding the ibuprofen adsorption onto activated carbons prepared from industrial pre-treated cork, a deeper characterization of the microporosity revealed to be necessary for the interpretation of the obtained results [17], since the correlation of the different ibuprofen uptakes for samples with similar microporous volumes ($V_{\alpha\ total}$) was not so straightforward. For example, for three activated carbons with $V_{\alpha\ total}$ between 0.27 and 0.32 $cm^3\ g^{-1}$, removal efficiencies ranging from 16 % to 69 % were obtained, being the higher removal attained for the sample with the intermedium $V_{\alpha\ total}$ value. The surface chemistry of two of these samples assessed by the determination of the pH at the point of zero charge (pH_{PZC}) is similar – pH_{PZC} ~ 5 – but samples presented distinct removal efficiencies (16% and 33%).

Given the critical dimension of ibuprofen, 0.72 nm, and that no restriction to the diffusion of ibuprofen into larger micropores is likely to occur, the diffusion towards the adsorption active sites has proved to be dependent of the presence of larger micropores. The uptake trend was also dependent on the MPSDs of the samples, pointing out that ibuprofen adsorption occurs mainly in pores with widths between 0.72 and around 1.40 nm. Besides, according to the MPSDs, the sample with the higher percentage of micropores between these widths (44%), *i.e.*, close to the ibuprofen critical dimensions, presents the higher value for the Langmuir constant (K_L), a measure of the adsorption affinity.

The effect of surface chemistry was also considered, but no enhanced adsorption was observed for samples presenting the most favorable electrostatic interaction (neutral carbons surface or positively charged – solution pH > pH_{PZC} – and ibuprofen in the anionic form), being then possible to conclude that for the adsorption of ibuprofen onto this set of carbons, texture stands as the determinant parameter controlling the process.

3.2 Caffeine

On the opposite of what was observed for ibuprofen adsorption, to justify the adsorption mechanism of caffeine onto activated carbons, both texture and surface chemistry have to be taken into account [18,19].

Caffeine is a compound with a critical dimension of ~ 0.45 nm, so, it will have less steric constrains to the diffusion than ibuprofen. In fact, literature data reveals higher adsorption capacity for activated carbons with higher micropore volume, particularly if large

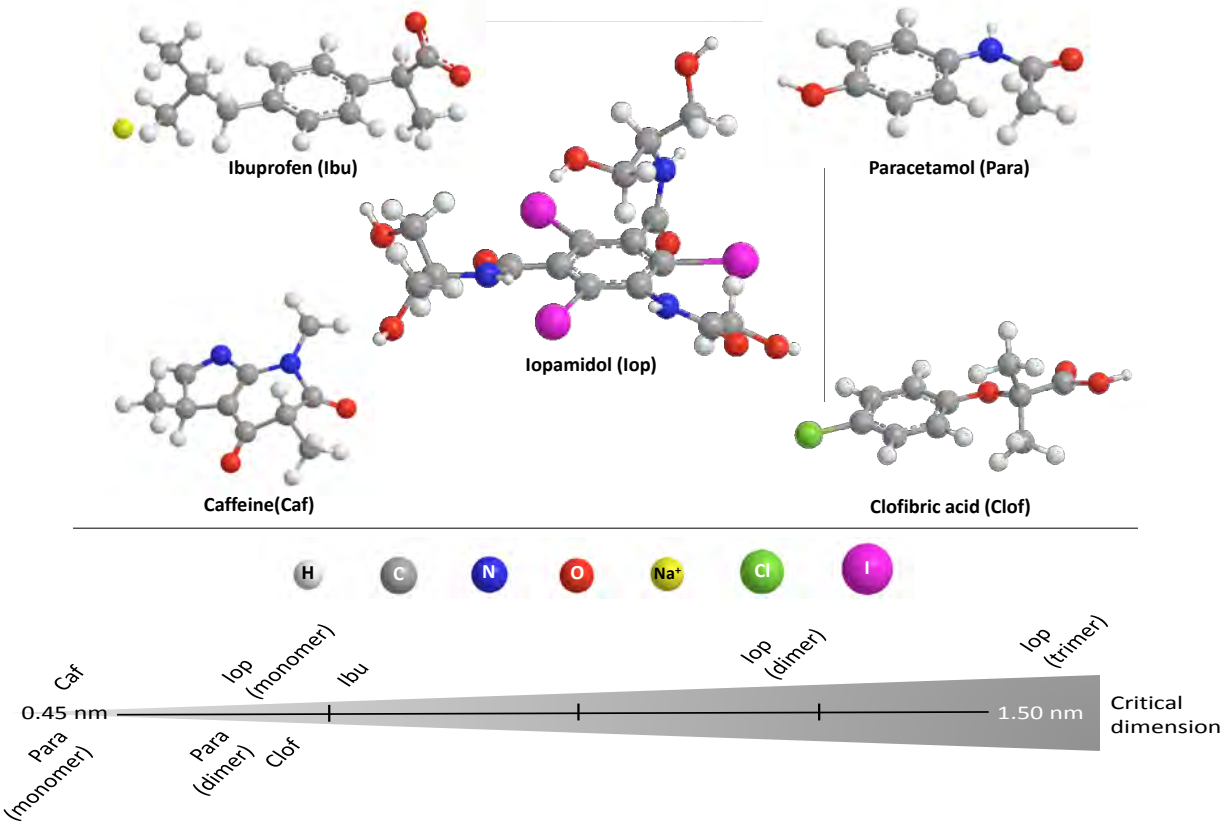

Figure 4. Molecular structure and scale highlighting the trend of the critical dimensions of the mentioned pharmaceutical compounds (see ref. [16] and references cited in the following topics for more detailed data). For paracetamol and iopamidol, the critical dimensions of their aggregates are also presented.

Figura 4. Estructura molecular y escala que destaca la tendencia de las dimensiones críticas de los compuestos farmacéuticos mencionados (véase la ref. [16] y las referencias citadas en los siguientes temas para obtener información más detallada). Para el paracetamol y el iopamidol, se presentan también las dimensiones críticas de sus agregados.

amounts of pores with apertures close to the critical dimensions of caffeine are present, and consequently a more efficient packing of the molecules is possible. The adsorption affinity values obtained for caffeine adsorption onto char-derived, rapeseed-derived and commercial activated carbons cannot be explained considering only the MPSD of the samples. Actually, besides the textural parameters, the adsorption affinity of caffeine seems to be also controlled by the surface chemistry of the carbons, most possible due to the high percentage of lone electron pairs in the caffeine molecule.

3.3 Paracetamol

The influence of the MPSD of carbons obtained from a residue produced from pine gasification (fly ash), in the adsorption process of paracetamol was also demonstrated [18,20], and allowed to rationalize the unexpected lower adsorption affinities of the lab-made carbons.

In these works the authors obtained lower adsorption affinities for the activated carbons presenting the maximum of the MPSDs aligned with the critical dimensions of paracetamol molecule (~ 0.46 nm), what is not commonly observed. However, if considering also the existence of paracetamol dimers in solution, with slightly higher critical dimensions (~ 0.66 nm), both maximum adsorption capacities and affinities could be related with the MPSD of the materials. In another study, sucrose-derived activated carbons were also tested for paracetamol adsorption [16] and once again the MPSD allowed to justify the adsorption capacities. As it is clearly illustrated in Figure 5, the maximization of the adsorption capacity for paracetamol occurs in the materials presenting a larger volume of micropores with dimensions between 0.5 and 1.1 nm.

Following this research topic the authors investigated the influence of the temperature (20–40 °C) in the adsorption process of paracetamol onto activated carbons with distinct MPSD [21] and proved that paracetamol oligomers were formed in the presence of the activated carbon. Once again the MPSD of the adsorbents allowed to explain the temperature dependence observed. The sample presenting a continuous MPSD obeys to the expected thermodynamic behaviour for a simple adsorption process (higher adsorption capacity at lower temperature), while for materials with the maximum of the MPSD centered near the critical dimensions of the species or when the MPSD is not continuous, the maximum adsorption capacity increases when temperature changes from 20 ºC to 40ºC. This finding was rationalized considering stronger adsorbent–adsorbate interactions that promote changes in the oligomers conformations, allowing better diffusion and packing of these larger species during adsorption. This results could not be explained just considering the energy gain associated with the temperature increase.

3.4 Iopamidol

Iopamidol is a voluminous molecule for which more steric hindrance during the adsorption process onto microporous activated carbons can be expected. In order to elucidate the parameters controlling the adsorption of this molecule, activated carbons with different pore network were already tested [16,22].

The results obtained with two sets of samples were very distinct and unexpected, since two-step isotherms were obtained for lab-made samples, while commercial materials presented type I curves [22]. These results could only be explained correlating the MPSDs of the carbons with theoretical and experimental data that revealed the existence of iopamidol aggregates in solution, with obviously increasing critical dimensions (i.e. monomer ~ 0.6 nm, dimer ~ 1.2 nm and trimer ~ 1.5 nm), and the dependence of this aggregation with concentration. The two-step isotherms were only observed for lab-made samples where micropores with widths between 1.2 and 2 nm are absent, and consequently the diffusion of larger species towards the adsorption site is hindered. The second step of the isotherms corresponds to the adsorption of the dimer and trimer species in larger porosity.

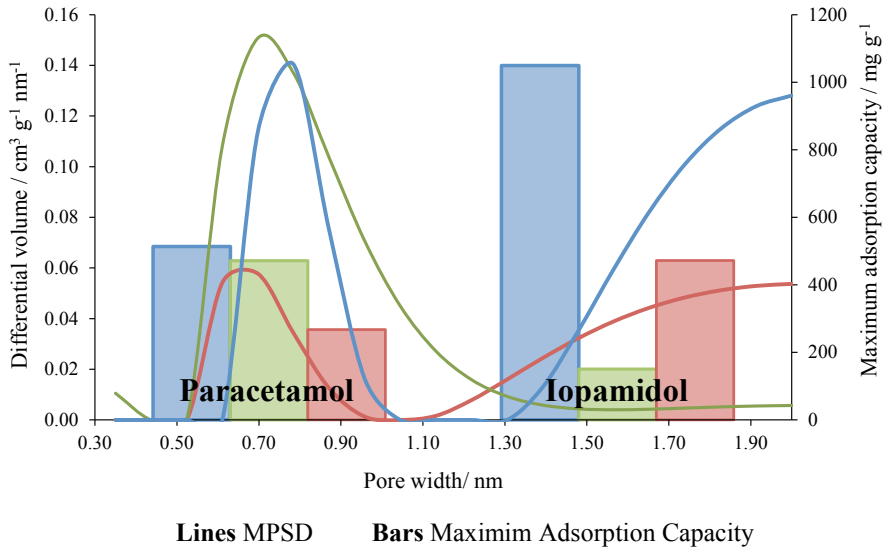

Figure 5. Relation between the micropore size distribution (MPSD) of three activated carbons and their maximum adsorption capacity for paracetamol and iopamidol. Lines represent the micropore size distribution while bars correspond to the maximum adsorption capacity for each pharmaceutical compounds.

Figura 5. Relación entre la distribución del tamaño de microporos (MPSD) de tres carbones activados y su capacidad de adsorción máxima de paracetamol y iopamidol. Las líneas representan la distribución del tamaño de microporo mientras que las barras corresponden a la capacidad máxima de adsorción para cada un compuesto farmacéutico.

The importance of the MPSD in the adsorption of iopamidol is also clearly illustrated in the results obtained with sucrose-derived activated carbons [16]. The initial adsorption rate is higher for the material with a well-developed mesopore network, a trend also observed in the previous example. On the other hand, the adsorption capacity of the carbon presenting the higher volume of pores with widths higher than 1.3 nm overcomes by far the performance of the other tested carbons, as it is shown in Figure 5. Thus, to maximize iopamidol adsorption, activated carbons must present a MPSD with a high percentage of pores with apertures larger than 1.3 nm.

3.5 Clofibric acid

In a work that aimed to evaluate the effect of solution pH and water hardness in clofibric acid adsorption onto two commercial activated carbons, the MPSDs also contributed to explain the results in hard water at pH 8 [23].

Independently of the water hardness degree, the increase of solution pH from 3 to 8 lead in all cases to a lower removal of clofibric acid, since the deprotonated clofibric acid specie present at pH 8 has a much higher solubility. However, at pH 8, when changing from deionized water to hard water, the maximum adsorption capacity increases, being the most pronounced effect observed for the carbon presenting the larger volume of wider micropores. These data were reasoned considering calcium complexation with clofibrate anion, as exposed by molecular modeling and conductivity studies, that allows the adsorption of clofibric acid entities as $CaClof_2$ or $CaClof^-$. The most noticeable effect, observed for the carbon with the larger volume of micropores with apertures higher than 1.1 nm, was related with the possibility of accommodating more entities, thus amplifying the enhancement of clofibric acid adsorption in hard water.

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6. References

[1] Brunauer S; Emmett PH and Teller E. Adsorption of gases in multimolecular layers. Journal of the American Chemical Society 1938; 60:309-319.

[2] Thommes M, Kaneko K, Neimark AV, Olivier JP, Rodríguez-Reinoso F, Rouquerol J and Sing KSW. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). Pure and Applied Chemistry 2015; 87:1051-1069.

[3] Gregg SJ, Sing KSW. Adsorption, Surface Area and Porosity. 2nd ed. London: Academic Press Inc.; 1982.

[4] Rouquerol F; Rouquerol J; Sing K, Llewellyn P and Maurin G. Adsorption by Powders and Porous Solids - Principles, Methodology and Applications (2nd ed). Academic Press 2014.

[5] Marsh, H and Rodríguez-Reinoso, F. Activated Carbon, Elsevier 2006.

[6] Gurvich L, J. Soc. Phys.-Chim. Russe, 1915; 47:805-827.

[7] Rodríguez-Reinoso F, Martin-Martinez JM, Prado-Burguete C and McEnaney B. A standard adsorption isotherm for the characterization of activated carbons. J. Phys. Chem., 1987; 91:515-516.

[8] Choma J and Jaroniec M. Characterization of Nanoporous Carbons by Using Gas Adsorption Isotherms. In: Bandosz TJ. Ed. Activated Carbon Surfaces in Environmental Remediation, Volume 7, Elsevier 2006, p 107-158.

[9] Tarazona P, Marconi UMB and Evans R. Phase equilibria of fluid interfaces and confined fluids. Non-local versus local density functionals. Mol Phys 1987; 60:573-595.

[10] Seaton NA, Walton JPRB and Quirke N. A New Analysis Method for the Determination of the Pore Size Distribution of Porous Carbons from Nitrogen Adsorption Measurements. Carbon 1989; 27:853-861.

[11] Lastoskie C, Gubbins KE and Quirke N. Pore Size Distribution Analysis of Microporous Carbons: A Density Functional Theory Approach. J Phys Chem 1993; 97:4786-4796.

[12] Jagiello J and Olivier JP. 2D-NLDFT Adsorption Models for Carbon Slit-Shaped Pores with Surface Energetical Heterogeneity and Geometrical Corrugation. Carbon 2013; 55:70-80.

[13] Jagiello J and Olivier JP. Carbon Slit Pore Model Incorporating Surface Energetical Heterogeneity and Geometrical Corrugation. Adsorption 2013; 19:777-783.

[14] Falco C, Marco-Lozar JP, Salinas-Torres D, Morallón E, Cazorla-Amorós D, Titirici MM and Lozano- Castelló D. Tailoring the porosity of chemically activated hydrothermal carbons: Influence of the precursor and hydrothermal carbonization temperature. Carbon 2013; 62(0):346-355.

[15] Pinto ML, Mestre AS; Carvalho AP and Pires J. Comparison of methods to obtain micropore size distributions of carbonaceous materials from CO_2 adsorption based on the Dubinin-Radushkevich isotherm. Ind Eng Chem Res 2010; 49:4726-4730.

[16] Mestre AS, Tyszko E, Andrade MA, Galhetas M, Freire C and Carvalho AP. Sustainable activated carbons prepared from a sucrose-derived hydrochar: remarkable adsorbents for pharmaceutical compounds. RSC Adv 2015; 5:19696–19707.

[17] Mestre AS, Pires RA, Aroso I, Fernandes EM, Pinto ML, Reis RL, Andrade MA, Pires J, Silva SP and Carvalho AP. Activated carbons prepared from industrial pre-treated cork: Sustainable adsorbents for pharmaceutical compounds removal. Chem Eng J 2014; 253:408–417.

[18] Galhetas M, Mestre AS, Pinto ML, Gulyurtlu I, Lopes H and Carvalho AP. Chars from gasification of coal and pine activated with K_2CO_3: Acetaminophen and caffeine adsorption from aqueous solutions. J Colloid Interface Sci 2014; 433: 94-103.

[19] Batista MKS, Mestre AS, Matos I, Fonseca IM and Carvalho AP. Biodiesel production waste as promising biomass precursor of reusable activated carbons for caffeine removal. RSC Adv 2016; 6:45419-45427

[20] Galhetas M, Mestre AS, Pinto ML, Gulyurtlu I, Lopes H and Carvalho AP Carbon-based materials prepared from pine gasification residues for acetaminophen adsorption. Chem Eng Journal 2014; 240:344-351.

[21] Galhetas M, Andrade MA, Mestre AS, Kangni-foli E, Villa de Brito MJ, Pinto ML, Lopes H and Carvalho AP. The influence of the textural properties of activated carbons on acetaminophen adsorption at different temperatures Phys Chem Chem Phys 2015; 17:12340-12349.

[22] Mestre AS, Machuqueiro M, Silva M, Freire R, Fonseca IM, Santos MSCS, Calhorda MJ, Carvalho AP. Influence of activated carbon porous structure on iopamidol adsorption. Carbon 2014; 77:607-615.

[23] Mestre AS, Nabiço A, Figueiredo PL, Pinto ML, Santos MSCS and Fonseca IM. Enhanced clofibric acid removal by activated carbons: Water hardness as a key parameter. Chem Eng Journal 2016; 286:538-548