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Role of the surface chemistry of the adsorbent on the initialization step of the water sorption process

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ABSTRACT

In this work, an equation for the prediction of the low pressure region of the water adsorption isotherms of activated carbons, based on their amount of surface groups, has been further developed in order to account for porous carbonaceous materials with an oxygen-rich surface chemistry. To attain this goal, highly hydrophilic carbon materials were selected and their surface chemistry was modified by several techniques (mainly thermal and plasma treatments) in order to obtain a series of samples with a surface oxygen content up to 45 wt%. Then, their water sorption isotherms were measured and the amount of surface groups obtained by fitting them by the proposed equation was compared with the one resulting from direct X-ray photoelectron spectroscopy (XPS) measurements. Based on the obtained results, it seems that beyond a certain concentration of surface oxygen, there is a change in the sorption mechanism (from clustering to layering) and consequently, on the size of the water cluster formed before the micropore filling. These findings have allowed us to go a step further in the modelling of this part of the water sorption isotherms and to find a correlation between the surface oxygen content and the water cluster size.

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1. Introduction

In recent years a number of experimental and simulation studies of adsorption of water in porous materials have appeared in the literature [1–6]. However, the mechanism of water adsorption is not yet fully understood and is still subject of discussion [1,4].

This work focuses on the low pressure range of the water sorption isotherms, prior to the start of micropore filling. The shape of the water isotherm is here affected by the specific interactions (hydrogen bonding) between the water molecules and the active sites on the carbon surface, followed by a water cluster growth (again by hydrogen bridging) on these initially bound water molecules. Thus, at very low loadings, water molecules adsorb around the functional groups at the edges of the graphene layers due to the strong electrostatic interactions, compared to the intermolecular

interactions and the interactions between water and the graphene layer. As the loading is increased, water clusters are formed around the functional groups and grow in size because of the greater electrostatic interactions between water molecules compared to the dispersive water-graphene interactions [7].

Based on previous works [8–11], where the above-described initiation and growth of the water clusters has been modelled, a Langmuir-type equation (Eq. (1)) was proposed to accurately fit the low-pressure range of the water adsorption isotherms [12]:

$$W = \frac{5[O+N][O+N](p/p_o)}{1+[O+N](p/p_o)} \qquad (1)$$

with W the amount of water adsorbed (g/g), p/p_0 the partial water pressure and $[O + N]$ the amount of surface (oxygenated and nitrogenated) complexes expressed as g/g_{carbon}. In this regard, X-ray Photoelectron Spectroscopy (XPS) is a suitable technique for measuring this last variable since it allows to quantify the functionalities located on the surface of the material (and not in the

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matrix), and therefore available to participate in the water sorption process [13].

In this first approach [12], the values of [O + N] obtained by fitting the water vapour isotherms of a considerable number of samples by Eq. (1) were compared with those resulting from XPS measurements and it was shown that the model gives good to excellent results for activated carbons with [O + N] up to 16%. However, when trying to apply it to materials with a richer surface chemistry, Eq. (1) does not seem to be valid in its present form.

In this work, and taking into account recent investigations where it was shown that oxygen groups play a dominant role on the water adsorption process [14,15], we have focused on the influence of these functionalities on the initialization mechanism. Specifically, it is necessary to determine if – in the case of materials with an oxygen-rich surface chemistry – the mechanism of micropore filling also proceeds through the formation of clusters of five water molecules [10,11] or, on the contrary, the equation should be modified as a function of oxygen content.

For this reason, different porous carbonaceous materials with an oxygen-rich surface chemistry and almost negligible nitrogen content were selected. Therefore, the [O + N] factor of Eq. (1) will be labelled as [O] hereinafter. Among the studied materials are activated carbons, resorcinol-formaldehyde carbonaceous resins (which present high surface oxygen contents difficult to achieve with activated carbons) and cements. The four main reasons behind the selection of the latter are: i) the carbonaceous nature of the materials with ii) high oxygen contents due to the high relative presence of hydrates and oxides within their composition. However, the final oxygen and carbon content can also vary from sample to sample depending on the preparation procedure, hydration time, the use of additives, the drying method, etc [16]. Moreover, iii) they can be considered as porous materials, with specific surface areas around 80–140 m^2/g (but also dependent on the previously mentioned parameters) [17]. This porosity is mainly due to the formation of the calcium-silicate-hydrate phase during the hydration of the cement, which contains a network of fine pores called gel pores [18]. Finally, iv) including cements in our study will allow us to broaden the applicability of the model towards a wider variety of porous carbonaceous materials.

Moreover, the surface chemistry of some of the parent materials was modified by thermal and plasma treatments (described in the experimental section) in order to obtain a series of samples with an increasing surface oxygen content of 17–45 wt%. Then, their water sorption isotherms were measured and the initial equation was modified according to the obtained results.

Summing up, the present study provides further insights on the role played by the surface oxygen groups on the initialization step of the water vapour sorption process in porous carbonaceous materials and, consequently, it has allowed us to go a step further in the modelling of the water sorption isotherms.

2. Experimental

Carbonaceous resins (samples CR70 and CR85) were prepared following the same experimental procedure [19,20] (sol-gel polymerization of resorcinol and formaldehyde in water, using sodium carbonate as catalyst) but with different gelation temperatures (70 and 85 °C, respectively). This synthesis method leads to carbon materials with a surface rich in polar and reactive oxygen groups [21,22]. Specifically, samples CR70 and CR85 are characterized (Table 1) by a very similar and high oxygen content (~31 wt%), an almost negligible nitrogen content ($\leq$0.05 wt%). They also present a highly developed porosity (S_{BET} = 489 and 591 m^2/g, respectively). Then, sample CR70 was further submitted to thermal treatments under nitrogen atmosphere (50 mL/min) at 200, 450 and 700 °C for

Table 1
Surface chemistry characterization of the carbonaceous resins (CR70 and CR85).

	XPS (wt%)		
	C	N	O
CR70	64.5	0.01	30.9
CR85	65.5	0.05	31.9

1 h in order to selectively remove its surface groups and thus obtaining three materials (CR70 H200, CR70 H450, CR70 H700) with intermediate oxygen contents.

CR70, CR70 H450 and activated carbon 362 (which was the activated carbon with the highest surface oxygen content selected for the previous study [12] and with a S_{BET} = 1076 m^2/g) were also subjected to plasma treatments in argon and oxygen atmospheres (samples PAr and PO2, respectively) in a cylindrical dielectrical discharge plasma reactor (Model Femto, version 3, Diener Electronic, Germany). The gas pressure was kept at 0.8 mbar and the applied power was 100 W. This technique offers potential advantages for the surface modification of carbon materials while preserving their textural properties [23,24].

Finally, two cement pastes with different water-to-cement ratios were made and cast [17]. The cement used was CEM I 52.5 N and the standard used for the mixing procedure was EN 196-1. The chemical and phase composition of the cement can be found elsewhere [17,25]. After one day of storage in a relative humidity of 95 $\pm$ 5% and a temperature of 20 $\pm$ 2 °C, the samples were stored in water at 20 $\pm$ 2 °C for a minimum period of 6 months to ensure a stable formation of the cementitious matrix. Prior to testing, the samples were ground and sieved (500–1000 μm). The nomenclature given to these samples is CP followed by a number which stands for their water-to-cement ratio.

Dynamic water vapour sorption (DVS) isotherms of all the studied materials were performed in a gravimetric water sorption analyzer (Aquadyne DVS, Quantachrome). Before the sorption experiments, the activated carbons and carbonaceous resins were outgassed under temperature (120 °C) and vacuum (10^{-5} Torr) for 24 h. In the case of cement pastes, and in order to preserve their microstructural properties, the samples were prepared for the analysis using a solvent-exchange-method in isopropanol followed by vacuum drying at 20 °C as further detailed in Ref. [17]. The amount of surface-oxygenated groups of the materials was measured by XPS, under high vacuum conditions, using an ESCA S-probe VG monochromatic spectrometer with an Al Kα X-ray source (1486 eV), recorded with a spot size of 250 μm by 1000 μm and analyzed using Casa XPS software package. It bears emphasizing again that it is the surface (and not the total) oxygen, the only one able to interact with the water molecules during the first stages of the water sorption process. Hence, XPS is a more appropriate technique than elemental analysis to evaluate the oxygen located on the surface of the carbonaceous materials (moreover taking into account that during the plasma treatment only the external surface of the samples is being modified [23,24]). In the case of cement-bound materials, also the theoretical surface oxygen content was calculated. Finally, the porous character of the samples was verified by means of N$_2$ adsorption at 77 K.

3. Results

First of all, characteristic water isotherms of the three groups of carbonaceous materials studied herein are shown in Fig. 1a. As it can be observed, they present different shapes and water uptakes according to their textural properties and surface chemistry. As it has been indicated before, the water sorption process is initially
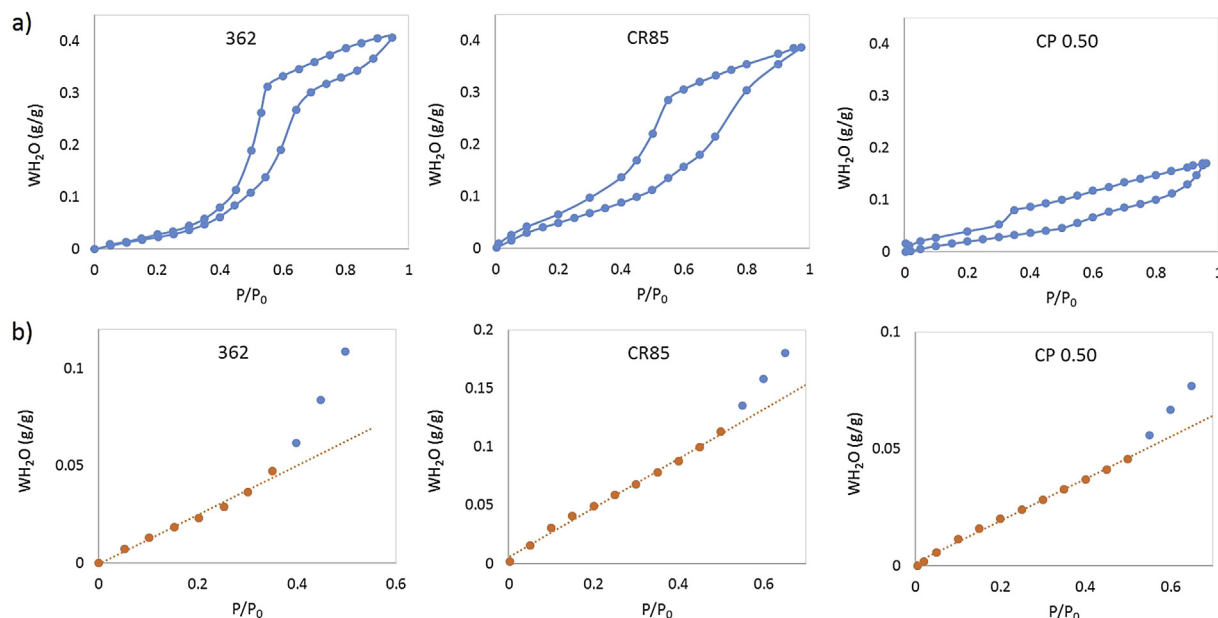
Fig. 1. Complete (a) and low-pressure range (b) water isotherms of samples: 362, CR85 and CP 0.50. (A colour version of this figure can be viewed online.)

driven by the hydrogen bonding between the water molecules and the surface functionalities and the subsequent cluster growth. Thus, in the range of the water isotherm fitted by the proposed equation (Fig. 1b), only the surface chemistry of the material, and not its textural properties, is playing a role.

This interval can be easily delimited since once the non-specific interactions prevail over the specific ones or, in other words, the pore filling begins, there is an upswing in the water isotherm (see Fig. 1b) that cannot be fitted by the proposed Langmuir-type equation [12]. In this way, the upper limit has to be determined independently for every sample, and it does not necessarily coincide with the closure of the hysteresis loop, as we know water sorption sometimes exhibits low pressure hysteresis [26].

3.1. Carbon materials with high oxygen contents

Bearing in mind that in the earlier study [12] the validity of Eq. (1) was only verified for activated carbons up to 16 wt% O, the first step in the current investigation was to check its suitability for other carbon materials within that surface oxygen content range. For this reason, sample CR70 was pyrolyzed at high temperature (700 °C), aiming at considerably lowering its surface oxygen content. Hence, sample CR70H700, with a surface oxygen content of 9.1 wt% (XPS analysis), was obtained. Subsequently, its water sorption isotherm was measured and the fit of Eq. (1) is shown in Fig. 2. There it can be seen that at relative pressures lower than 0.4, the model assuming a cluster size of 5 water molecules perfectly matches the experimental adsorption data and, as expected, the fitting is getting worse as the non-specific interactions (pore filling) take over from the specific interactions and the cluster formation. In fact, the estimated [O] value from the water isotherm is 8.9 wt%, which is in perfect agreement with the surface oxygen content measured by XPS. This result further confirms the validity of the initially proposed model for carbonaceous materials (not only activated carbons) with low and moderate surface oxygen contents (<16 wt% O).

Once this has been proven, we could move to the second (and main) objective of this research: to evaluate the model for the prediction of the low pressure range of the water sorption
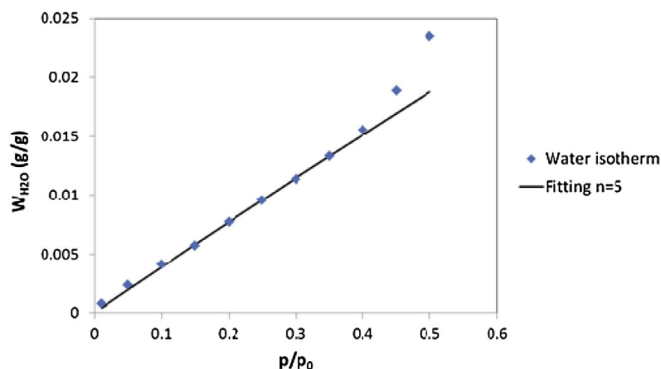

Fig. 2. Fit of the water sorption isotherm of sample CR70 H700 with Eq. (1) assuming a cluster size of 5 water molecules. (A colour version of this figure can be viewed online.)

isotherms of highly hydrophilic carbon materials. To attain this goal, the water isotherms of the: i) parent carbonaceous resins (CR70 and CR85), ii) thermally modified CR70 at 200 and 450 °C and iii) plasma treated samples, were measured. In this way, a series of carbons with surface oxygen contents ranging from 17 to 42% in weight were analyzed. Then, the amount of surface oxygen calculated by the fitting with Eq. (1) was compared with the one resulting from direct XPS measurements (Table 2). There, it can be seen that for all the samples the oxygen contents estimated from the water sorption isotherm are lower than the XPS ones and the difference between both values increases with the hydrophilicity of the studied material. Therefore, the proposed model, assuming that a water cluster of 5 molecules (n = 5) is formed before the micropore filling, seems not to be valid for this kind of materials.

Considering this premise, the next step was to reverse the fitting procedure, taking into consideration the experimental oxygen content and calculating the size of the water cluster (n parameter). In this regard, n values between 4.6 and 1.1 were obtained (Table 2). Thus, again it can be noticed that there is a progressive fall in the n parameter value when analyzing samples with increasing surface oxygen content. It is also important to mention here that we have also reversed the fitting procedure for the activated carbon with the

Table 2
Comparison of the surface oxygen contents obtained by XPS and modelling of the water isotherms of the parent and modified carbon materials; as well as the n parameter for reverse fitting.

Sample	[Oxygen] (wt%)		n parameter
	XPS	H$_2$O isotherm	
362	16.9	16.2	4.6
CR70 H450	17.8	16.2	4.2
362 PO2	21.9	19.5	4.3
CR70 H200	24.3	20.2	4.0
CR70 H450 PO2	27.8	22.0	3.7
362 PAr	29.5	22.5	3.6
CR70	30.9	21.9	3.5
CR85	31.9	22.1	3.4
CR70 PAr 1	35.9	25.7	2.6
CR70 PAr 2	37.4	24.7	2.2
CR70 H450 PAr	39.6	20.6	1.9
CR70 PO2	41.9	19.5	1.1

highest surface oxygen content that was included in the previous study (362) and we have found out that an n-value of 4.6 is more suitable. For the rest of the activated carbons, with lower amounts of oxygenated complexes on their surface, an n-factor of 5 is still applicable.

These results indicate that beyond a certain concentration of surface oxygen (ca. 16 wt%) there is a gradual change in the water adsorption mechanism from clustering to layering. Considering the fact that oxygen-water interactions are always stronger than water-water interactions, water molecules will first bind to the oxygen groups located on the surface of the material, and only once there are no more available functionalities, the cluster formation and growth will begin. This phenomenon, enhanced by steric effects, will have an influence on the size of the water cluster formed before the micropore filling.

3.2. Cement pastes

As mentioned in the experimental section, two cement pastes with different water-to-cement ratios were prepared (CP 0.50 and CP 0.30). The high oxygen content (Table 3) of these materials also allowed us to go a little bit further in our study in terms of oxygen content. In addition, the absence of nitrogen within their composition (Table 3) helps us, once more, to separately study the effect of the surface oxygen complexes.

In Table 3 it is shown that the differences between the experimental (XPS) and the calculated values (Eq. (1) with n = 5) for the surface oxygen contents are even more pronounced for these types of materials. Thus, when calculating the number of molecules in the water cluster by fixing the [O]$_{XPS}$, the obtained values are lower than unity. However, and even though XPS has a penetration depth of only a few nanometers [27], it is highly probable that not all the oxygen quantified by this technique is available to participate in the adsorption mechanism. A plausible reason is that the complex structure of cements, and more precisely, the presence of bridging and non-bridging oxygen [28], hinders the selective quantification
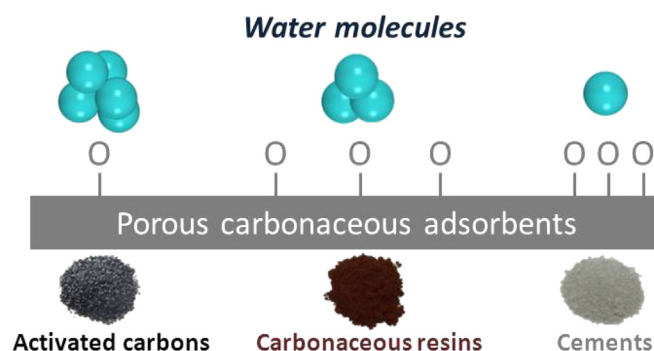
of surface oxygen groups. Furthermore, the theoretical oxygen content was calculated through the chemical composition of the CEM I 52.5 N cement [17,25] and slightly higher values than the experimental ones were obtained (46.6 and 52.3% wt O for samples CP 0.50 and CP 0.30, respectively). This result points out to the possibility that the difference between the experimental and the theoretical oxygen contents corresponds to the oxygen located in the inner cement matrix. But, even if XPS somehow slightly overestimates the amount of surface oxygen complexes playing a role in the water sorption phenomenon, the calculated number of molecules in the water cluster (n) will be only marginally influenced and will certainly not go up much (n ≤ 1). According to this, it seems that there is an incomplete surface coverage and pore filling in these cementitious materials is not preceded by cluster formation of the water molecules. This is probably due to the much less hydrophobic nature of the pore walls compared to activated carbons. A schematic illustration of the herein obtained results is shown in Fig. 3.

Finally, when representing the calculated n-values versus the oxygen content determined by XPS (wt%) of all the studied materials, and also including the activated carbons that were used in the previous work [12], it is clear that all the samples (including the cements) follow the same descending trend (Fig. 4). Moreover, it is possible to obtain a simple numerical fitting, based on a third degree polynomial function (inset in Fig. 4). In this regard, the obtained numerical parameters seem to be logical since the n-value tends to be 5 as the surface oxygen content is decreased, which is the number of water molecules forming the cluster before the micropore filling for those activated carbons with an oxygen content lower than 16 wt%. And also the order of the function (power of 3) is in agreement with the fact that an increasing three-dimensional hindering is taking place as the surface oxygen content is increased.

Summarizing, it was found that when the surface oxygen content of porous carbonaceous materials is higher than 16 wt%, the calculated n-values begin to progressively decrease, being ≤1 in the case of the samples with the highest oxygen contents (cements). These results indicate that in those materials with very high surface oxygen contents, steric effects become important, thus having also an influence on the size of the water cluster formed before the micropore filling. Consequently, for highly hydrophilic carbon materials it is necessary to adapt the value of the cluster size (n) in order to predict the first part of the water sorption isotherms using independent surface oxygen measurements (e.g. XPS).

4. Conclusions

This work provides further insights into the influence of the

Table 3
XPS analysis of the cement pastes included in this study (CP 0.50 and CP 0.30), and surface oxygen content and n parameter calculated from the fitting of their water sorption isotherms.

	XPS (wt%)					H$_2$O isotherm	
	C	S	Ca	Si	O	O (wt%)	n value
CP 0.30	17.0	2.0	30.7	6.2	44.2	12.3	0.5
CP 0.50	20.0	1.6	28.3	6.8	43.4	14.0	0.6

Fig. 3. Schematic illustration of the influence of the surface oxygen content on the water cluster size. (A colour version of this figure can be viewed online.)
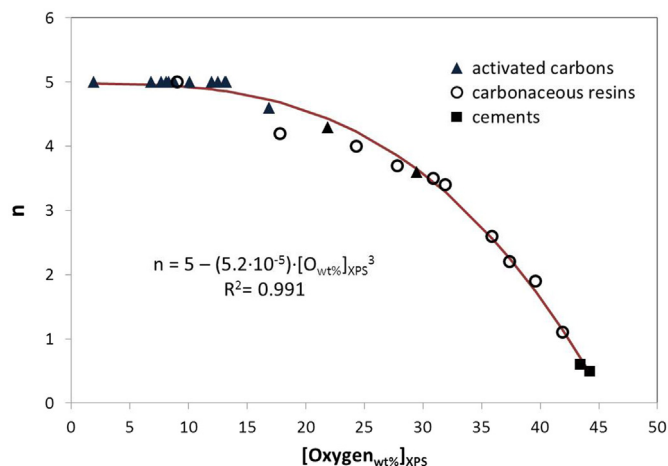
Fig. 4. Modelling of the influence of the surface oxygen content on the cluster size. (A colour version of this figure can be viewed online.)

surface oxygen content of porous carbonaceous materials on the mechanisms prevailing at the beginning of the water sorption process.

It has been shown that beyond a certain concentration of surface oxygen content (~16 wt%), there is a change in the sorption mechanism (from clustering to layering), enhanced by steric effects. Hence, the size of the water cluster, formed before the micropore filling starts, steadily decreases from the initial value of 5. Furthermore, the presence of very high amounts of oxygenated groups on the surface of the sample (i.e. cements) inhibits the occurrence of water-water interactions and therefore the formation of water clusters.

Therefore, Eq. (1) is valid if n is adapted as a function of the oxygen content (wt%) according to the function: $n = 5 - (5.2 \cdot 10^{-5}) \cdot [O]_{XPS}^3$.

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