

Modelling of water adsorption by activated carbons: effects of microporous structure and oxygen content

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Abstract

The present paper examines the adsorption of water by microporous carbons containing various amounts of surface oxygen and a smaller proportion of basic centres. The modelling of water adsorption for 293 and 310 K, using variable pore size distributions (PSD), confirms that the overall type IV isotherm is the sum of a type I isotherm associated with the specific interactions, and a type V isotherm reflecting the non-specific interactions. The principle of temperature invariance is followed by these isotherms, which indicates that modelling leads to the Dubinin–Astakhov equation.

The present approach allows the prediction of water adsorption near room temperature, on the basis of the PSD and the density of oxygen present on the surface area of the micropores. It is assumed, to a first and good approximation, that the pores are slit-shaped and the oxygen distribution is random.

Keywords: A. Activated carbon; B. Adsorption, modelling; D. Microporosity

1. Introduction

Due to their high sorptive capacity and their strong affinity for organic vapours [1], activated carbons are widely used in filtration technology. In such processes, water vapour is also present at relative pressures above 0.5–0.6 and its influence on mixed adsorption depends strongly on the amount of oxygen present on the surface. Typical and untreated activated carbons contain less than 1.5–2 mmol of oxygen per gram [2], which corresponds to a small fraction of the real surface area of the micropore walls [3]. Under these circumstances, the water adsorption isotherm is almost of type V [4–7], but selective treatments may increase the amount of oxygen. As a consequence, the water isotherm changes gradually to type IV and adsorption becomes important at relative pressures below 0.5.

In a previous study [8] based on modelling and dealing with adsorption of water in the absence of spe-

cific interactions, we showed that the type V isotherm depends essentially on the PSD of the carbon. This is due to the fact that in slit-shaped micropores the condensation pressure increases with the pore width L . A good agreement was also obtained, for example, with studies of Carrasco-Marin et al. [7] and of Stoeckli [5], dealing with the decomposition of the overall isotherms into type I and type V contributions.

In order to extend the possibility of predicting water adsorption by real activated carbons, we considered modelling based on Monte Carlo simulation [8–12]. This approach follows the same lines as previously [6], but includes the specific interactions between water and variable amounts of surface oxygen, as well as a limited number of basic sites, characterized by HCl titration. As shown earlier, basic sites contain little oxygen [3], but immersion calorimetry [3,5–7,13] indicates that their specific interactions with water are practically the same as those observed on average for the oxygen atoms in surface complexes (-10 kJ mol^{-1}). This means that these sites, which do not necessarily include all basic sites, can be considered as hydrophilic centres and may be included in calculations as equivalent oxygen sites. However, the

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Table 1
Main characteristics of the oxidized activated carbons

Carbon	W_o ($\text{cm}^3 \text{g}^{-1}$)	L_o (nm)	S_{mi} ($\text{m}^2 \text{g}^{-1}$)	S_e ($\text{m}^2 \text{g}^{-1}$)	E_o ($\text{m}^2 \text{g}^{-1}$)	$E_{\text{H}_2\text{O}(\text{I})}$ (kJ mol^{-1})	$E_{\text{H}_2\text{O}(\text{V})}$ (kJ mol^{-1})	n_1	n_2	[O] (mmol g^{-1})	[HCl] (mmol g^{-1})	[O]/ S_{tot} (atom nm^{-2})
DCG-5-ox	0.54	1.1	968	37	21.2	5.26	1.54	2	2.8	3.11	1.22	2.59
CMS-ox	0.25	0.75	580	28	26.1	6.4	4	2	4	6.3	0.1	6.34

concentration of basic sites [HCl], given by the equivalent amount of HCl needed for their titration does not exceed 0.8–1 meq g^{-1} in untreated carbons. Furthermore, their number decreases to 0.4–0.2 meq g^{-1} in typical oxidized active carbons [2]. This means that for the carbons used in the present study as references for the simulations (see Table 1), the basic sites represent only a fraction of the sites showing specific interactions with water. This is the case, in particular, for carbon CMS-ox. One may therefore either neglect the basic sites, or treat them as equivalent oxygen sites. Since the experimental isotherms reflect both interactions, the latter approach was adopted and simulations were based on a total number of equivalent sites $[\text{O} + \text{HCl}] = [\text{O}] + [\text{HCl}]$. It should also be pointed out that in the present work, all oxygen atoms are considered to be equivalent. This is substantiated by a detailed analysis [7] based on immersion calorimetry into water and taking into account the different types of surface groups (carboxylic, phenolic, lactone and basic).

First, families of model isotherms were generated for slit-shaped micropores of widths L between 0.6 and 1.5 nm and containing variable amounts $[\text{O} + \text{HCl}]$ of oxygen and oxygen equivalent sites on their walls (0, 2.2 and 5 atoms per nm^2). In a second stage, overall isotherms were calculated, using the same PSDs as previously [8], which shows the influence of the oxygen content on water adsorption. It was also established, that the overall isotherms fulfil the requirement for temperature invariance and consequently that modelling is in agreement with Dubinin's theory [14–17], as found experimentally [18–20]. Finally, adsorption isotherms were calculated for real carbons, of known PSDs and oxygen contents. As shown below, this test was successful, which offers the possibility of predicting with a good accuracy the water adsorption isotherms of a given carbon on the basis of its PSD and the $[\text{O} + \text{HCl}]$ content.

The present approach presents similarities with the work of Muller et al. [12] on water adsorption by activated carbons. However, we consider the problem from a different side, in particular the correlation with Dubinin's theory extended to water adsorption [18].

2. Theoretical

2.1. Water adsorption isotherms and Dubinin's theory

The fundamental aspects have been presented in detail in the first paper [8] and in the recent study by

Stoeckli [3] and consequently we shall limit ourselves to the essential.

It has been shown that the adsorption of water by carbons follows Dubinin's theory [14–17], which is based on the thermodynamic potential $A = RT \ln(p_o/p)$. The fundamental equation is the so-called Dubinin–Astakhov (DA) equation

$$N_a = N_{ao} \exp[-(A/E)^n] \quad (1)$$

where N_a is the amount adsorbed at relative pressure p/p_o and temperature T ; N_{ao} is the limiting amount filling the micropore volume $W_o = N_{ao}V_m$, assuming that V_m is close to the molar volume in the liquid state, and E is the so-called characteristic energy of the system.

In the case of water adsorbed on carbons containing oxygen and equivalent [HCl] sites, both specific and non-specific interactions are present and the overall isotherm is a sum of type I and type V isotherms. Both are given by Eq. (1), but with different values of E and n and the overall isotherm is

$$N_a = N_{ao}(\text{I}) \exp[-(A/E_{\text{H}_2\text{O}(\text{I})})^{n_1}] + N_{ao}(\text{V}) \times \exp[-(A/E_{\text{H}_2\text{O}(\text{V})})^{n_2}] \quad (2)$$

As shown earlier [5,7], $N_{ao}(\text{I})$ corresponds to the sum of surface oxygen [O] (0.5–9 mmol g^{-1}) and the basic surface groups [HCl].

Parameters $E_{\text{H}_2\text{O}(\text{I})}$ and $E_{\text{H}_2\text{O}(\text{V})}$ are related to the characteristic energy E_o of the carbon, obtained with the benzene isotherm (Benzene is a non-specific reference vapour). As shown elsewhere [13–17,21], including modelling [22], E_o is also an inverse function of the average pore size, L_o . This indicates that both the specific and the non-specific contributions to water adsorption depend on the structure of the carbon. As shown by Stoeckli [5],

$$E_{\text{H}_2\text{O}(\text{I})} = (0.29 \pm 0.02)E_o \quad (3)$$

and, in the absence of specific surface groups, one obtains the limiting value

$$E_{\text{H}_2\text{O}(\text{V})} = (0.059 \pm 0.08)E_o \quad (4)$$

It was also shown that $E_{\text{H}_2\text{O}(\text{V})}$ depends to some extent on the primary interactions. Neglecting the basic groups, the correlation

$$E_{\text{H}_2\text{O}(\text{V})} = E_o[0.06 + 6 (\text{kJ/mol})[\text{O}] / (E_o N_{ao}(\text{H}_2\text{O})(1 + \alpha T)\Gamma(1 + 1/n_2))] \quad (5)$$

can be established. It follows the approach described in detail in an earlier study dealing with the specific inter-

actions between short alcohols and surface oxygen groups of a variety of activated carbons [23]. Logically, this correlation should be confirmed by modelling water adsorption in the presence of surface oxygen (see below).

It should also be pointed, out that the validity of Eqs. (1) and (2) has been confirmed for organic adsorbates and for water, by the agreement between the experimental and the calculated enthalpies of immersion $\Delta_i H$ of the carbons into water. The latter is a thermodynamic consequence of Dubinin's theory given by [16,17]

$$\Delta_i H \text{ (J/g)}_{\text{mi}} = -N_{\text{ao}} E (1 + \alpha T) \Gamma (1 + 1/n) \quad (6)$$

where α is the expansion coefficient of the liquid filling the micropores and Γ is the tabulated 'Gamma' function (for $1.5 < n < 5$, it varies between 0.88 and 0.92). A small correction has to be applied for the wetting of the external (non-microporous) surface S_e of the carbon.

Finally, studies based on the correlation between E_o and the average micropore-width [21], the enthalpy of immersion of phenol from dilute aqueous solutions [3] and the modelling of CO_2 adsorption [22], show that the actual surface area of the micropore walls S_{mi} can be estimated with a good approximation.

2.2. PSDs in activated carbons

As described previously [22], the PSD of a microporous carbon can be obtained from the analysis of the CO_2 adsorption isotherm at 273 K, using model isotherms. The latter are obtained from Monte Carlo simulations, assuming slit-shaped micropores. Simultaneously, and provided that the access to the micropores is not restricted by external 'gate' effects, the PSD can also be derived from the enthalpies of immersion of the carbon into liquids with molecular dimensions between 0.4 and 1.5 nm. For the carbons considered in the present and the earlier studies, one observes a good correlation between the PSDs obtained from these two independent techniques [22].

2.3. Modelling of water adsorption isotherms in oxidized carbons

Adsorption isotherms in single slit-shaped carbon pores were calculated by grand canonical Monte Carlo (GCMC) simulation, as described in the relevant publications [8–11]. The method is essentially the same as that used in our previous publication [8], and a detailed description of the implementation of the GCMC algorithm for water adsorption studies is also available [24]. In the GCMC method, the volume, temperature and chemical potential are kept constant, while the total number of molecules is allowed to fluctuate. By calculating the pressure from the chemical potential (using the Peng–Robinson equation of state), adsorption iso-

therms can be obtained in a form (adsorbed density versus pressure in the bulk phase) that is comparable to experiments.

Water is represented by the SPC/E potential, with parameters taken from Berendsen et al. [25], and long-range electrostatic interactions are accounted for by using the method of Heyes and van Swol [26]. The simulation cell is rectangular, bounded in the z direction by the pore walls and replicated in the x and y directions by using periodic boundary conditions. The length of the simulation cell in the directions parallel to the wall was 3 nm, which is sufficient to avoid any finite-size effects [27]. The walls are sheets of graphite, composed of Lennard-Jones centres that are spread out uniformly over the whole area. Interactions between this smooth graphite wall and a Lennard-Jones adsorbate centre are described by the 10-4-3 potential of Steele [28]. As discussed above (see Section 1), the oxygenated sites of the active carbon and the equivalent [HCl] sites may be represented, formally and to a good approximation, by an single type of oxygen. In the present case, we chose a carbonyl groups, as modelled by the OPLS potential for C=O groups in aminoacids [29]. This model comprises a Lennard-Jones centre and a negative charge for the oxygen atom, as well as a positive charge located on the carbon atom in the basal plane of graphite (as described in [30]). In this paper, the carbonyl sites were distributed randomly on the surface of the carbon micropores. Cross-species Lennard-Jones parameters were calculated from the Lorentz–Berthelot combining rules.

3. Experimental

For the present study, two oxidized activated carbons were used, CMS-ox and DCG-5-ox. They have been characterized by a variety of techniques [16–19] and their main structural and chemical properties are given in Table 1. These carbons were chosen in view of the fact that their PSDs (see Figs. 4 and 5) have been determined unambiguously and that their water adsorption isotherms show clear deviations from the basic type V isotherm observed at low oxygen contents. These isotherms were determined at 293 and 310 K, as described elsewhere [16,18], following outgassing at temperatures not exceeding 100 °C, in order to prevent the destruction of the surface complexes.

As described elsewhere [6], carbon DCG-5-ox has also been characterized by a combined technique based on a variable preadsorption of n -nonane, followed by immersion into water. This leads to the conclusion that, to a first and good approximation, the hydrophilic sites (oxygen atoms and basic HCl equivalents) are distributed uniformly over the surface of the micropores.

4. Results and discussion

4.1. Modelling

In a first stage, modelling was carried out for water adsorption at 293 and 310 K in slit-shaped micropores of widths between 0.4 and 1.0 nm. The pore widths (L) estimated from adsorption methods refer to the “accessible space”, which can be defined in several ways. As before [8], H is the pore width defined in the simulations, and refers to the space between the centres of carbon atoms of opposing walls. The correction of 0.24 nm suggested by Everett and Powl [31] ($L = H - 0.24$ nm), and used in this paper, leads to a good agreement, but a number of authors also use the value of 0.34.

The model isotherms were calculated on the basis of the simulated single pore isotherms and the PSD. This is achieved by multiplying the pore volume obtained from the PSD for a given pore width (V_i) by the molar density adsorbed in the corresponding pore (ρ_i), and then performing a summation over all pore widths. This can be represented by the following equation:

$$N_a \text{ (mmol g}^{-1}\text{)} = \sum_i \rho_i \text{ (mmol cm}^{-3}\text{)} \times V_i \text{ (cm}^3 \text{g}^{-1}\text{)} \quad (7)$$

As observed previously for the adsorption by pure carbons, the water isotherm is characterized by a sharp condensation at a relative pressure p/p_s , which depends on the pore-width L (condensation occurs first in the smaller pores). However, as illustrated by Fig. 1, for a pore of a given width (in the present case $L = 1.0$ nm), an increase in the surface density of oxygen reduces the condensation pressure. This means that water adsorption depends on both the micropore width and the oxygen density on the surface. This feature is reflected in real activated carbons, where the overall isotherm depends on the PSD and the oxygen content. As before, we used formal PSDs given by a discrete Gaussian with

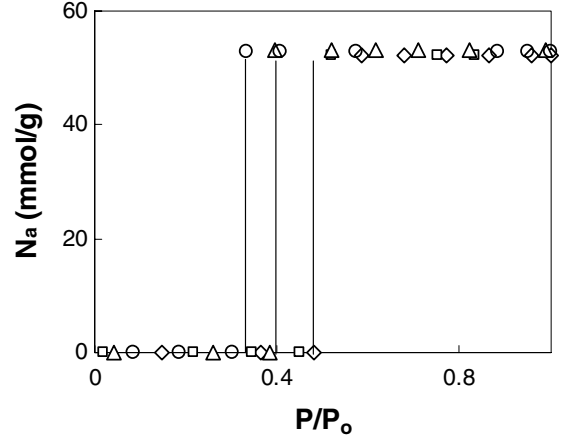


Fig. 1. Stepwise model isotherms for 293 K obtained for a pore of $L = 1.0$ nm and containing 0 (\diamond), 2.2 (Δ), and 5 (\circ) oxygen sites per nm^2 (random distribution).

blocks of 0.1 nm, centered at L_o and normalized to $1 \text{ cm}^3 \text{g}^{-1}$,

$$dW/dL = (1/\sigma\sqrt{2\pi}) \exp[-(L - L_o)^2/2\sigma^2] \quad (8)$$

Fig. 2 shows the evolution of water adsorption isotherms at 293 K for a model carbon with $L_o = 1.0$ nm and $\sigma = 0.2$ nm, with uniform oxygen densities of 0, 2.2 and 5 atoms per nm^2 (or 0, 40 and 90 atoms in the unit cell of $2 \times 9 \text{ nm}^2$). As the oxygen density increases, the overall isotherm is shifted towards the origin, as expected, and gradually changes from a pure type V isotherm to an increasingly steeper type IV. A similar pattern is observed for the distribution centered at $L_o = 0.7$ nm.

This procedure can also be repeated with the model isotherms corresponding to a temperature of 310 K and it leads to a similar pattern. Moreover, as illustrated by Fig. 3, it appears that the overall isotherms obtained for $T = 293$ and 310 K, with PSDs centered at 0.7 and 1.0 nm ($\sigma = 0.2$ nm and 2.2 oxygen atoms nm^{-2}), lead to single characteristic curves for plots of N_a versus

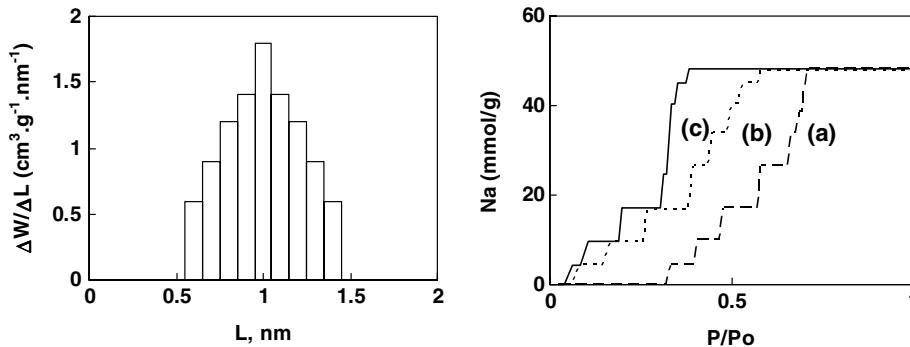


Fig. 2. Evolution of the water adsorption isotherm at 293 K in a model carbon with a Gaussian PSD ($W_o = 1 \text{ cm}^3 \text{g}^{-1}$, $L_o = 1.0$ nm, $\sigma = 0.2$ nm) (left), containing 0 (a), 2.2 (b) and 5 (c) oxygen atoms per nm^2 (uniform densities but random distribution of the sites).

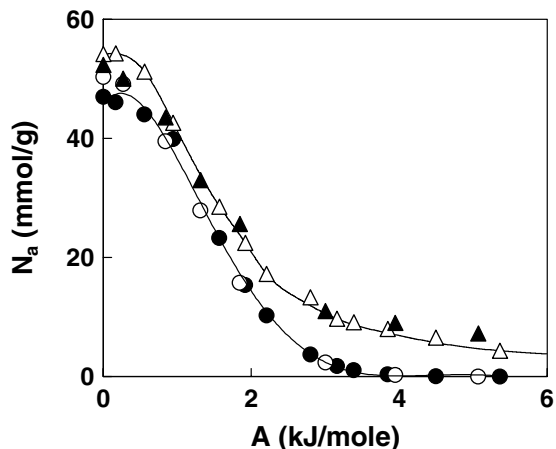


Fig. 3. Characteristic curves for water adsorption isotherms at 293 K (○ △) and 310 K (● ▲), in model carbons where $W_0 = 1 \text{ cm}^3 \text{ g}^{-1}$; Gaussian PSDs with $L_0 = 0.7$ (○ ●) and 1.0 nm (△ ▲), and $\sigma = 0.2 \text{ nm}$.

$A = RT \ln(p_s/p)$. This means that the requirement for temperature invariance, postulated by Dubinin's theory and observed experimentally for water adsorption by microporous carbons with variable degrees of oxidation [3,5–7,20], is also fulfilled by modelling. Basically, this indicates that modelling validates the application of

Dubinin's theory to water adsorption suggested some years ago by Stoeckli et al. [18]. This aspect will be developed in the next section.

4.2. Comparison of simulated and experimental isotherms

The techniques outlined above were used in connection with experimental water adsorption isotherms on carbons DCG-5-ox and CMS-ox, measured both at 293 and 310 K. These carbons have well-defined PSDs, determined from CO_2 adsorption at 273 K and/or from enthalpies of immersion into liquids of different molecular dimensions. As shown in Fig. 4 and 5, one observes a good agreement between the simulated and experimental isotherms, assuming random distributions of oxygen atoms and oxygen-equivalents of basic centres. For carbons DCG-5-ox and CMS-ox, this amounts to, respectively, 2.59 and 6.34 atoms per nm^2 . However, variations of the surface density cannot be ruled out, and in the case of carbon DCG-5-ox an even better agreement can be obtained for the initial part of the isotherm if one assumes a density of 2.2 atoms per nm^2 in the pores of $L < 0.8 \text{ nm}$ and 5 atoms per nm^2 for $L > 0.8 \text{ nm}$ (The total amount of [O + HCl] centres remains constant). Such variations have been suggested for certain carbons by the changes in the enthalpies of

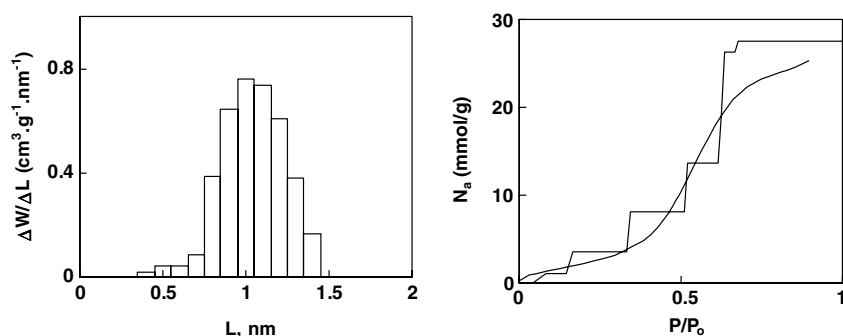


Fig. 4. Simulated (steps) and experimental (—) water adsorption isotherm on carbon DCG-5-ox. The calculations based on the experimental PSD (left) and model isotherms containing respectively 2.2 and 5 atoms per nm^2 for pore widths below and above 0.8 nm.

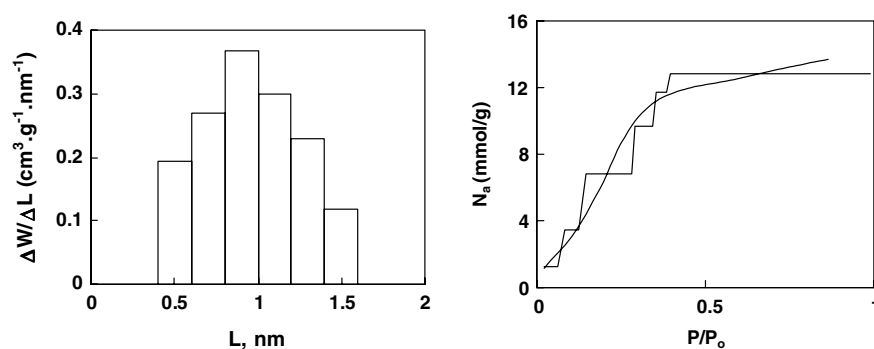


Fig. 5. Simulated (steps) and experimental (—) water adsorption isotherm on carbon CMS-ox at 293 K. The calculations are based on the experimental PSD (left) and model isotherms with 5 oxygen atoms per nm^2 .

immersion into water, following the preadsorption of increasing amounts of *n*-nonane or *n*-undecane [32] (For a uniform density, the enthalpy shows a linear decrease with preadsorption). However, the origin of the change in density cannot be explained at this stage.

5. Conclusions

The present study shows that the adsorption isotherm of water on a given activated carbon can be predicted by way of modelling, on the basis of the PSD and the oxygen + HCl equivalent content alone. To a first and good approximation, one may assume that the oxygen-containing complexes and the basic centres are randomly distributed on the surface, with a fixed density. However, the model may be refined by considering a variable density and/or a correlation between the adsorption centres. This requires further information on the carbon and the use of techniques such as immersion calorimetry combined with the preadsorption of an *n*-alkane [32]. The model of ideally slit-shaped micropores and the exact location of the oxygen atoms may be questioned and must be examined again, in particular in the light of new structural models for the micropores, as put forward recently by Py et al. [33]. However, the present study suggests that good results can be obtained, for example to take into account the role of water in the case of industrial filtration.

It is also interesting to point out that simulations based on different PSD are in agreement with the empirical extension of Dubinin's theory to water adsorption [5,18]. This is confirmed by the fact that calculations for different temperatures show that the requirement for temperature invariance of the so-called characteristic curve is fulfilled, at least over a certain range of temperature.

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