



# Molecular simulation and experiments of water adsorption in a high surface area activated carbon: Hysteresis, scanning curves and spatial organization of water clusters



Lev Sarkisov<sup>\*</sup>, Alessio Centineo, Stefano Brandani

*Institute for Materials and Processes, School of Engineering, The University of Edinburgh, EH9 3JL, UK*

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## ABSTRACT

Despite decades of research, quantitatively accurate molecular models of water sorption on activated carbons remain elusive, while many phenomena are not properly understood even qualitatively. Here we focus specifically on scanning phenomena. Scanning isotherms, obtained by reversing either adsorption or desorption process before the closure of the hysteresis loop, have been recently explored as a sensitive experimental probe for structural characterization of activated carbons and at the same time have been subject of several competing theories of adsorption. We employ adsorption experiments and molecular simulations to understand the nature of the states along the adsorption and scanning curves for water at 308 K in a high surface area activated carbon, Maxsorb. The molecular model considered here is based on a random packing of fullerene-like fragments, functionalized with carboxylate groups. The model is able to reproduce reasonably well the shape of the adsorption and scanning desorption isotherms. We investigate spatial organization, structure, size and interaction between the clusters on the adsorption branch. Furthermore, we show that the scanning desorption isotherm consists of a series of states of the system where a single cluster of water shrinks in size as water evaporates from its surface, before it finally disintegrates into separate smaller clusters.

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## 1. Introduction

Adsorption of water on activated carbons has been subject of numerous theoretical and experimental studies [1]. From the industrial perspective, presence of water vapour needs to be taken into account in many gas separation processes, including natural gas sweetening, carbon capture and volatile organic compounds removal from air streams. Design and optimization of these processes would significantly benefit from having accurate, predictive models of water adsorption in porous materials. Water adsorption has been also proposed as a method for characterization of oxygen groups on the surface of porous carbons [2–4], and as a general characterization method [5,6], complementing the arsenal of more traditional physical adsorption characterization techniques based on nitrogen and argon adsorption at cryogenic conditions and carbon dioxide adsorption at 273 K.

Furthermore, more recently, Velasco et al. attempted to link

hysteresis and scanning sorption behaviour of water in activated carbons with the topology and surface chemistry of the material [7]. It emerges from this study that water scanning behaviour is sensitive to both surface chemistry and structure of the activated carbon, and in this capacity it could be seen as a promising technique for porous material characterization. The principal challenge, however, in the interpretation of the water adsorption hysteresis and scanning isotherms in activated carbons is lack of a molecular level description of the states of the system and confined water along these isotherms. This defines the remit of the current article: to develop a molecular model of an activated carbon capable of generating a reasonably realistic adsorption isotherm and scanning curves for water; and, using this model, to explore the nature and spatial organization of the adsorbed states along the scanning curves. For this we adopt a variant of a previously developed model of a high surface area activated carbon based on a random packing of fullerene-like fragments functionalized with oxygen edge groups [8,9]. However, to justify selection of this model as a starting point in our endeavours, it is instructive to briefly review the current state-of-the-art in theoretical studies of water adsorption in activated carbons.

<sup>\*</sup> Corresponding author.

E-mail address: [Lev.Sarkisov@ed.ac.uk](mailto:Lev.Sarkisov@ed.ac.uk) (L. Sarkisov).

Firstly, it is important to recognize that predictive, accurate molecular models of water adsorption in activated carbons remain largely elusive, although some promising directions started to emerge [10]. This situation stems from two principal challenges. The first challenge is associated with the very complex internal structure of activated carbons [11]. Construction of a molecular model of an activated carbon can be guided by the available data from neutron and X-ray scattering experiments, data on porosity and surface area, reference adsorption results used for model calibration; however there is no single and consistent strategy for this process and different approaches proposed over the years vary substantially in the effort required for their adoption and in the quality of the predicted adsorption data, even for light gases such as carbon dioxide and methane. This is in stark contrast with the field of zeolites, where, in the absence of ambiguity about the structure of the material, accurate models for adsorption for light gases, alkanes, aromatics and other species have been developed over the years (see for example, Ref [12–14]). The second challenge is associated with the very nature of the adsorbate itself. Many models of water have been proposed over the years [15,16]. Yet, within the range of reasonably simple, transferrable and computationally tractable models (based on rigid structures and point charges), none of the models maintains consistent accuracy across the whole phase diagram [15]. Even at ambient conditions, accuracy of these models still needs substantial improvement in the prediction of bulk properties, such as saturated vapour pressure, let alone quantitative predictions of water adsorption. Not surprisingly, prediction of water adsorption has been very challenging for all types of materials, including the crystalline ones (see, for example, Ref [17]).

Although there is no quantitative molecular model of water adsorption in activated carbons, we do have a fairly good qualitative understanding of the processes. At low pressures, water molecules associate with the individual polar surface groups; the water clusters initiated in this fashion grow in size and at some point start to coalesce with each other. Depending on the structure of the carbon material, this coalescence process may occur in several stages. This picture was originally proposed by Gubbins and co-workers using graphitic slit pores decorated with surface groups as a simple model of an activated carbon and later revisited and confirmed in several subsequent works [1,18–22].

Hysteresis and scanning phenomena require a model that goes beyond a single, slit shaped pore. Two alternative classes of activated carbon models have been proposed that are not based on the slit pore presentation. In the first class, construction of the model of a porous microstructure aims either to reflect the actual process of activated carbon formation or capture essential structural characteristics such as the radial distribution function between carbon atoms (see for example, Ref. [23]). This type of reconstructive methods typically lead to complex, disordered models of carbon microstructure. In the second class of models a similar overall effect of structural disorder and heterogeneity is achieved by considering a system of randomly packed structural elements, representing reasonably realistic fragments of stacked graphite layers [24–27]. These non-slit pore models of activated carbons so far have been used predominantly to provide a qualitative explanation for the observed adsorption phenomena and only recently attempts to extend them to quantitative adsorption predictions have been made [8,9].

In the context of water adsorption, these non-slit pore models confirm the original picture proposed by Gubbins and co-workers. For example, Liu and Monson explored a model of BPL activated carbon based on a random packing of carbon platelets, or disks, decorated with polar surface groups [26]. Again, adsorption of water starts at these groups, followed by formation of clusters of

various sizes in different compartments of the model. Interestingly, this model is able to reproduce very realistic adsorption isotherms, including the hysteresis loop. Although water scanning curves have not been explored in this model (or for that matter in any other model), realistic hysteresis loops observed by Liu and Monson suggest that this class of models is a promising starting point to explore scanning adsorption behaviour.

Hence, our starting point is the model of a high surface activated carbon based on a random packing of curved, fullerene-like fragments of carbon sheet decorated with polar surface groups [8,9]. Previously, this kind of model has been used to investigate carbon dioxide and methane adsorption in Maxsorb activated carbon (or MSC-30) and adsorption of multicomponent mixtures, relevant for carbon capture processes [8,9]. A similar model has been also recently employed by Wang et al. with a focus on the role of surface groups on carbon dioxide/methane separation factors [28]. In the historical perspective, this model indeed stems directly from the studies of Liu and Monson [26] and Segarra and Gland [24] before them, based on simplified or coarse-grained models of graphitic fragments. However, explicit representation of the molecular structure of the fragments provides a more flexible way to control and explore various properties of the fragments such as geometry, location and type of the surface groups. It also makes it possible to use reasonably accurate off-the-shelf force fields without excessive re-parameterization and explicitly include charge distribution within the fragment. Several other similar fragment-based models have been proposed recently [29–31], however water adsorption, including hysteresis and scanning phenomena, have not been explored in them, most likely due to prohibitive computational cost, as will be discussed later in the article.

The remaining article is organized as follows. After the methodology section, we first present experimental data for water adsorption in MSC-30 at 308 K and place our findings in the context of the previous experimental studies on similar materials. We will then compare the experimental results with simulations. The model proved to be computationally very costly (we will touch upon this issue in the Conclusion section) and, as a result, comprehensive optimization of the model to reproduce experimental results could not be performed at this stage. Therefore, the comparison between the model and experimental data is still qualitative (or rather semi-quantitative as we present results in reduced units of pressure, and in experimental units of loading and the simulation isotherms operate in the correct ranges of those variables). Using the results from molecular simulations we investigate properties of the water clusters along adsorption and scanning isotherms. Molecular visualization provide additional insights on the state of the system along these paths.

## 2. Methodology

### 2.1. Experiments: characterization and water adsorption

The porous material used in this study has already been used and characterized in our previous work [8]. The BET surface area and the pore volume measured for the Maxsorb MSC-30 are respectively 3179 m<sup>2</sup>/g and 1.33 cm<sup>3</sup>/g. The characterization and activation of the sample have been performed on a Quantachrome Autosorb IQ apparatus coupled with the Quantachrome ASiQwin software for the automated acquisition and reduction of the data. The pore size distribution (see the SI) and the micropore volume have been calculated QSDFT method [32].

The experimental equilibrium isotherms have been measured on a Quantachrome Aquadyne DVS gravimetric water sorption analyser. The instrument is a gravimetric system which operates at atmospheric pressure and constant temperature under different

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