Atomistic calculation of adsorption in activated carbon with pore-size distribution

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A R T I C L E   I N F O

A B S T R A C T

We use molecular mechanics universal force field parameters to calculate single- and multicomponent adsorption of phenol, para-bromophenol, and m-cresol from the gas or liquid phase on activated carbon (AC). The carbon pores are modeled by shallow carbon nanotubes of various pore diameters. The effect of pore length is studied for the case of phenol. This calculation yields the Gibbs free energy change (ΔG) of adsorption which is used to predict the adsorption isotherm following reaction rate theory. The single-pore adsorption can be integrated to predict the overall adsorption if pore-size distribution is known. We show that the Freundlich adsorption isotherm may result from pore-size distribution coupled with a linear decline of ΔG with pore diameter. When the pore-size distribution of the carbon under study is not known, the adsorption of one species can be used to predict that of another on the same AC. We extend this methodology for the case of a bisolute adsorption system. Reasonable prediction of measured adsorption isotherms is demonstrated for single solute adsorption when both pore-size distribution and adsorbate–adsorbate interaction are taken into accounted. The suggested methodology is highly sensitive to the numerous parameters it requires.

1. Introduction

Activated carbon (AC) is a widely used adsorbent for separation of pollutants from the gas and liquid phases, but despite its wide use there is little atomic level understanding of adsorption of large organic molecules on AC. Knowing the adsorption isotherm is essential for many technological applications of activated carbon, and its prediction from basic principles may be used to replace experimentation and to optimize the adsorbent. Proper predictions of the adsorption properties of the system requires modeling of the adsorption isotherm for single-component as well as for competitive adsorption.

The activated carbon performance is influenced both by its surface chemistry and by the functional groups of the surface as well as by its porosity and pore distribution. The AC surface structure is highly complex and depends on the raw material used to produce it, the method of production, and pretreatment. Commercial active carbons commonly have a surface area of 800–1500 m^2/g, reaching as high as 2500 m^2/g [1]. This surface area is supplied mainly by micropores (with diameter <2 nm), while mesopores (2–50 nm) and macropores (>50 nm) contribute mainly to transport within the material. Several surface functional groups were identified including carboxyl, carbonyl, phenol, quinone, lactone, and lactol [2,3]. Nanoporous carbon is primarily made up of tightly curved individual carbon layers, including pores of typical size of 1 nm.

Completely closed carbon particles are also present. The carbon may have a fullerene-related structure in which pentagons and heptagons are distributed randomly throughout a hexagonal network [4,5].

Most previous atomistic simulations of adsorption on AC described the binding of small molecules from the gas phase on a single-sized slit-shaped pore model using the Grand Canonical Monte Carlo (GCMC) approach with spherical molecules described by the Lennard-Jones (LJ) potential. Yet several numerical studies of adsorption energies on carbon nanotubes (CNT) using molecular mechanics (MM) simulations were also reported [6–9]. In the present paper we use MM to characterize the adsorption on pores modeled as carbon nanotubes (NT) of various diameters and lengths. We use this information to predict the adsorption isotherm. We described these concepts and justify our approach below.

We represent the complex AC structure by a simple model composed only of micropores, represented by single wall carbon nanotubes (SWNT) of various diameters. The SWNT are graphene sheets wrapped into cylinders with 1–2 nm in diameter. There are three typical configurations for the SWNT: the "armchair," "zigzag," and "chiral". Carbon nanotubes are molecular tubes which now attract considerable attention.

Though a slit-shape model has been commonly used to represent an AC structure, its structural stability is usually not demonstrated computationally; it usually underestimates the molecule–AC interaction and various corrections have been suggested to correct it [10]. Several studies indicated that the adsorption on AC can be represented using a nanotube model [11–14]. Moreover,

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several studies on AC structure found that AC is composed of curved carbon layers, containing pentagonal rings which explain the porosity, due to curvature, and hardness while parallel grapheme layer are absent [4,5]. Based on these results Harris et al. claim "that the idea that microporous carbons have fullerene-like structure has important implications for the modeling of adsorption". In these cases a NT model may be a better representation for the real AC structure [5]. In addition, the adsorption in very narrow NT allows interaction from all directions and implies higher adsorption energy and allows adsorption even in very low concentrations. While AC may be more complex than the simple NT geometry, we show that the narrow pores used here are essential for predicting high loadings observed in adsorption from water, and for predicting high surface area.

This simple geometry represent an AC with a very high surface area of about 2500 m^2/g. Active carbon has a lower surface area either since the pores should be modeled by double-walled NT or since they incorporate meso and macropores as well.

The Freundlich adsorption isotherm has been widely applied in describing experimental adsorption of organic pollutants in aqueous solutions, including that of phenol and phenolic compounds [15–18]. The Freundlich isotherm has been originally accounted for by Langmuir adsorption while an exponential distribution of adsorption energies is assumed. Our atomistic calculations show how ΔG varies with pore diameter. This approach can be used to integrate the adsorption over all pore sizes, when their distribution is known. The Freundlich isotherm can approximately describe the calculated isotherm when a certain pore-size distribution is accounted for, while the behavior in a single pore diameter follows the Langmuir adsorption isotherm. This description is exact only when the distribution accounts for all pore sizes, while in practice the smaller pores are excluded. While adsorbate–adsorbate repulsion can account for this behavior [15,19,20] this explanation does not apply here since for phenol, the model adsorbate used here, the adsorbate–adsorbate interaction is attractive.

Previous work by this group used atomistic calculations to study the single-component adsorption of phenol on shallow single-size SWNT with various diameters and functional groups [21]. This work showed that the adsorption of phenol on most functional groups is thermodynamically unstable at room temperature and most of the adsorption is contributed by micropores and graphite planes [21].

The present work extends this study to active carbon with pore-size distribution as well as to the case of unknown pore-size distribution. We also extend the study to long SWNT, so that the adsorption is 3-D in nature and to carbon with multicomponent adsorption.

This work suggests a computational chemistry methodology to predict adsorption properties on well-defined structures. The first part of this work deals with single-component adsorption and is incorporates the following steps:

1. Characterizing the structure of the adsorbent and calculating the maximal capacity of adsorption of a certain component.
2. Calculation of the change in the thermodynamic properties (enthalpy, entropy, and Gibbs free energy) of adsorption, and when necessary the energetic barrier to adsorption. We show that in general ΔG may vary with fractional occupancy.
3. Using this information to calculate the adsorption equilibrium of a NT in contact with a gas phase of known (partial) pressure of adsorbent, using known kinetic theory for calculation of adsorption and desorption probabilities. This will lead to several problems in 3-D adsorption as discussed and addressed below. When ΔG varies with fractional occupancy we should incorporate this dependence to the calculation or choose to show the effect of the maximal and the minimal ΔG.

4. Evaluating the adsorption isotherm by assuming a simple Langmuir isotherm for each pore size and then averaging for a certain pore-size distribution The gas–solid adsorption equilibrium is translated to liquid–solid equilibrium, using gas–liquid solubility data (i.e., Henry constant).

The estimation of adsorption of two or more competing species requires more data than those of a single component: current practice for such isotherms is to apply the multicomponent Langmuir isotherm, which applies to a single-sized pore with no adsorbate–adsorbate binary interactions, or the multicomponent Freundlich (see derivation by Sheindorf et al. [15,16]). Methods that attempt to predict the multicomponent adsorption from single-component data often fail to predict the isotherm in cases where adsorbate–adsorbate interaction occurs [15,16,18]. The Freundlich multicomponent isotherm requires single-component data as well as a competition coefficient which had to be determined experimentally.

In the second part of this work we apply the molecular mechanics methodology to predict the multispecies competitive adsorption on AC with a certain pore-size distribution.

The structure of this work is the following: We study first the single-component gas-phase adsorption of phenol, for which we describe the energy dependence on pore size and length in detail. We then study *m*-cresol and *para*-bromophenol (PBP) adsorption, before studying coadsorption of phenol with each of the other molecules. The work was motivated by our interest in adsorption on AC [15,16] and regenerative procedures using catalytic agents that were deposited on the AC [22,23].

2. Computational methods

The adsorption of the model adsorbents, phenol, *m*-cresol, and *para*-bromophenol, on activated carbon is governed by van der Waals and Coulomb interactions. To represent van der Waals interactions, we applied molecular mechanics (MM) modeling using the universal force field (UFF) parameters of Rappe and co-workers [24–27]. This approach was proven to accurately represent both short- and long-range interactions in the absence of chemical interactions. While adsorption is usually studied using GCMC simulations with simplified Lennard–Jones potentials [28], there are several numerical studies of adsorption energies on CNT using MM simulations [6–9]. The MM approach yields a better description of the interaction of large (phenol) molecules with other molecules and with the walls, at the expense of the system size. GCMC can handle larger samples, but use relatively simpler potential description (LJ).

All calculations were performed using the Gaussian 03 package from Gaussian Inc. and Arguslab 4.0.1 by Planaria software.

The geometries were fully optimized in all calculations in order to reach the lowest energy configuration. It should be emphasized here that throughout this work it was assumed that there is infinite time for equilibration and that the minimum energy configuration of the system was reached. The minimum energy geometries were determined to be true minima by the absence of imaginary frequencies in the calculated vibrational spectrum. Thermodynamic parameters of the adsorption were calculated, using the Gaussian 03 package, as the difference between the corresponding values of the system with optimal position of a molecule inside a nanotube and those of the corresponding separated components. For example, for calculating ΔG for adsorption of a single phenol molecule on a NT the Gibbs free energy values were calculated separately for phenol, for the "empty" NT, and for the corresponding system of "phenol inside the NT" and then the ΔG for the system was calculated as $\Delta G = G_{(phenol+NT)} - G_{(phenol)} - G_{(NT)}$. Similarly for