

# Sorption of organic compounds to activated carbons. Evaluation of isotherm models

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## Abstract

Sorption to ‘hard carbon’ (black carbon, coal, kerogen) in soils and sediments is of major importance for risk assessment of organic pollutants. We argue that activated carbon (AC) may be considered a model sorbent for hard carbon. Here, we evaluate six sorption models on a literature dataset for sorption of 12 compounds onto 12 ACs and one charcoal, at different temperatures (79 isotherms in total). A statistical analysis, accounting for differences in the number of fitting parameters, demonstrates that the dual Langmuir equation is in general superior and/or preferable to the single and triple Langmuir equation, the Freundlich equation, a Polanyi–Dubinin–Manes equation, and the Toth equation. Consequently, the analysis suggests the presence of two types of adsorption sites: a high-energy (HE) type of site and a low-energy (LE) type of site. Maximum adsorption capacities for the HE domain decreased with temperature while those for the LE domain increased. Average Gibbs free energies for adsorption from the hypothetical pure liquid state at 298 K were fairly constant at  $-15 \pm 4$  and  $-5 \pm 4$  kJ mol<sup>-1</sup> for the HE and LE domain, respectively.

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## 1. Introduction

Sorption of hydrophobic organic compounds (HOC) to soils and sediments can be dominated by adsorption to ‘hard carbon’ materials, such as black carbon (BC), coal, and kerogen (Allen-King et al., 2002; Huang et al., 2003; Cornelissen et al., 2005; Lohmann et al., 2005; Koelmans et al., 2006). The increased sorption will result in decreased HOC concentrations in organisms, and thus will reduce environmental risks of HOCs (Cornelissen et al., 2005; Koelmans et al., 2006).

This adsorption of HOCs most often has been quantified in terms of the Freundlich isotherm (mainly phenanthrene, see Cornelissen et al., 2005; Koelmans et al., 2006), or by in situ distribution coefficients for various compounds at a

single concentration (Cornelissen et al., 2005; Koelmans et al., 2006). However, much less work has been done to develop physical models for the explanation of adsorption of HOCs onto BC. It has been suggested that Langmuir affinities for adsorption onto BC can be estimated from solute solubility and entropy of melting (Van Noort, 2003). However, this estimate may describe only part of the BC adsorption process (Van Noort et al., 2004b), since several reports show that two different types of adsorption sites may be present (Al-Bahrani and Martin, 1976; Jonker et al., 2005; Sander and Pignatello, 2005; Vrind et al., 2006). For instance, a dual Langmuir model (DLM) (as well as a Polanyi–Manes model) was capable of describing adsorption of benzene, toluene, and nitrobenzene onto a charcoal (Sander and Pignatello, 2005). Furthermore, Vrind et al. (2006) found that a dual Langmuir equation very accurately described kinetics of adsorption and desorption for four organochlorine compounds on BC in a sediment. Although these reports suggest dual Langmuir

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sorption, systematic comparative evaluations of models are lacking due to the rarity of detailed isotherm data for BC.

At the molecular level, activated carbon (AC) may be considered a useful model for adsorption sites in BC, coal, and kerogen. The rationale for this is that molecular interactions between sorbates and the graphene (polycyclic aromatic) basal plane surfaces of AC perhaps closely resemble those of the other hard carbon types. This assumption is the basis of a recent adsorption model for BC (Van Noort, 2003) showing that adsorption onto an AC was comparable to adsorption onto environmental hard carbon.

AC sorption has been described by many types of isotherms representing various sorption models (Do, 1998) that differ in the number of empirical fitting parameters. While some progress has been made predicting AC adsorption isotherms (see Li et al. (2005) for a recent study on the prediction of aqueous AC isotherms based on the Polanyi–Dubinin–Manes model), the usually large number of empirical fitting parameters in many models prevents the development of simple equations, based on sorbate properties, for the prediction of AC adsorption. The Langmuir model is attractive as Langmuir affinity is an equilibrium constant and therefore directly related to the Gibbs free energy for sorption. However, differences in mutual orientations of adsorbing AC graphene basal planes may result in heterogeneous adsorption sites and thus to a poor fit of experimental sorption data to a single Langmuir equation.

In the present study, we (a) provide isotherm parameters for literature sorption datasets concerning 76 AC-sorbate combinations and three charcoal-sorbate combinations, and (b) we give the results of a statistical (ANOVA) analysis of the fit to six different sorption isotherms: the Freundlich, single Langmuir, dual Langmuir, triple Langmuir, Polanyi–Dubinin–Manes, and Toth equations. ANOVA analysis was applied to account for differences in the quality of fit, as well as for differences in the number of fitting parameters. Because we show that the dual Langmuir equation is in general statistically superior and/or preferable compared to the other model equations, we also explore the temperature dependence of the dual Langmuir maximum adsorption capacities and affinities.

## 2. Sorption models

The Freundlich model is an empirical model, with two fitting parameters:

$$q = K_F C^n \quad (1)$$

where  $q$  is the concentration sorbed,  $K_F$  is the Freundlich affinity coefficient,  $C$  is the solute concentration, either in water or in gas phase, and  $n$  is a measure for the heterogeneity of sorption sites. A disadvantage of this model is that it does not possess the correct Henry's law behavior: at infinitely low solute concentration the slope of the Freundlich isotherm is infinite (Terzyk et al., 2003). The Freundlich model can be considered as an infinite series of discrete Langmuir isotherms ( $i = \infty$  in Eq. (2)) (Sposito, 1984):

$$q = \sum_{n=1}^i \frac{b_n Q_{\max,n} C}{1 + b_n C} \quad (2)$$

where  $b_n$  is the Langmuir affinity constant, and  $Q_{\max,n}$  is the maximum adsorption capacity for site type  $n$ .

In the single Langmuir model ( $i = 1$  in Eq. (2); two fitting parameters), the sorbent has a uniform Gibbs free energy of adsorption for all sites. The dual Langmuir model ( $i = 2$  in Eq. (2); four fitting parameters) and the triple Langmuir model ( $i = 3$  in Eq. (2); six fitting parameters) assume two and three distinct types of sites, respectively.

In contrast to the Freundlich model, the Toth model, Eq. (3), possesses the correct Henry's law behavior (Terzyk et al., 2003). Like the Langmuir model, it assumes a maximum capacity of adsorption

$$q = \frac{Q_{\max} K_T C}{(1 + (K_T C)^t)^{1/t}} \quad (3)$$

In Eq. (3),  $K_T$  is the affinity constant and  $t$  is a measure for the surface heterogeneity of the activated carbon. When  $t$  is one, Eq. (3) reduces to the single site Langmuir model. The further  $t$  deviates from unity, the more heterogeneous the sorbent surface is.

From the Polanyi potential theory, mathematical functions such as the Dubinin–Astakhov equation and the Polanyi–Dubinin–Manes equation have been derived (Allen-King et al., 2002). These two equations can be represented by (three fitting parameters):

$$q = Q_{\max} \exp \left[ - \left( \frac{RT \ln(S/C)}{Z} \right)^d \right] \quad (4)$$

where  $S$  is the solubility in air (as vapor pressure) or in water.  $Z$  and  $d$  are empirical fitting parameters.  $R$  and  $T$  are the ideal gas constant and the system temperature, respectively.

## 3. Statistical evaluation of the fit to sorption equations

Experimental isotherm data points for 12 compounds on 12 different activated carbons at various temperatures and for three compounds on a charcoal were collected from the literature (Yun and Choi, 1997; Moon et al., 1998; Ryu et al., 1998; Benkhedda et al., 2000; Akkimaradi et al., 2001; Hindarso et al., 2001; Yun, 2001; Park et al., 2002; Yu et al., 2002; Zhang et al., 2002; Park and Moon, 2003; Sander and Pignatello, 2005), resulting in 79 isotherm data sets. Number of data points per isotherm ranged from 10 to 29. The six equations were fitted to the isotherms using non-linear least squares regression as available in SPSS (SPSS, Inc., Chicago, IL, USA). Data were unweighted because (a) higher concentrations are generally more accurate and (b) adsorbed concentrations spanned a narrow range: the ratio of the highest and the lowest adsorbed concentration ranged from 1.5 to 14, typically about 5 (see Fig. 1, and also Fig. S-1, Supplementary data) (Saez and Rittman, 1992). Visual inspection of the fits

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