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# An Adsorption Isotherm from a Micro-state Model

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**Abstract.** The present study is dedicated to the derivation of an alternative adsorption isotherm for liquid-solid interfaces from a micro-state model, where adsorption is predominantly of a chemical nature. We describe adsorption-desorption on a liquid-solid interface starting from a partition function. In the new model the surface site occupation number is controlled by the Pauli principle (monolayer condition) and additional an attractive or repulsive surface potential, which depends on the overall surface coverage (nonlinearity). The effective potential represents adsorbate adsorbent interaction, as well as an influence of adsorbate adsorbate interactions on the surface potential. A Langmuir equivalent isotherm is recovered in the limit of a weak potential. The proposed model and Langmuir's isotherm are compared using data of humic acid (HA) adsorption on Brazilian Oxisol soil samples. Both models parameterize the experimental data well, but only the new model seems to be self-consistent.

**Keywords:** adsorption isotherm, liquid-solid interface, micro-state model, humic acid, oxisol

## 1. Introduction

Adsorption is one of the main mechanisms that regulates mobility of chemical species and their geochemical cycles in the environment (Almendros, 1995; Kretschmar, 1997; Murphy et al., 1994; Senesi et al., 1997; Tipping, 1981; Wang et al., 1997). In order to understand rates of mineral phase dissolution and ion exchange processes, adsorption measurements represent a useful tool for investigating interactions with the microscopic surface structure. The question, as to which is the most appropriate isotherm equation for a given set of adsorption data, has been the principal issue in a variety of works (for a recent review see ref: Hinz, 2001). Knowing the adequate parametrization serves as a phenomenological classification of the interaction between adsorbent and adsorbate.

Since most adsorption equations (i.e., adsorption isotherms), as for instance the Langmuir, the van Bemmelen-Freundlich, the Frumkin-Fowler-Guggenheim, the Brunauer-Emmett-Teller model and others (for a more detailed description see for instance (Sparks, 1986; Sposito, 1989; Stumm, 1992)) are derived from a gas-solid adsorption hypothesis, consequently, their usefulness for liquid-solid interfaces may only be validated by direct comparison to experimental data. The present study is dedicated to the derivation of an alternative adsorption model for liquid-solid interfaces from a micro-state model.

Because of the considerable complexity of possible processes involved it seems convenient to motivate the model using general principles of statistical thermodynamics. A recent article about a revision of adsorption

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kinetics (Rudzinski and Panczyk, 2002) supports this reasoning, although in the present approach the principal argument is the partition function rather than time dependence of the adsorption process as given by the kinetic equation (see Rudzinski and Panczyk, 2002). The present model derivation starts from a description for adsorption-desorption on a liquid-solid interface by a partition function, which formally shows a similar mathematical structure as a nematic, smectic or cholesteric system (Garrod, 1995; Langer and Glotzer, 1997).

In distinction to gas-solid approaches the proposed model is characterized by a feedback of the adsorbate concentration to the surface adsorption capacity. A motivation and a more detailed description for the model structure of the partition function is given in Section 3. The resulting isotherm is then applied to some experimental data (Dick et al., 1999) and compared to Langmuir's approach (Section 4). In the conclusions a critical comparison between the two models is given, which allows us on the onehand understand why Langmuir's model is successful in parameterizing experimental data. On the other hand we indicate the physicochemical limits of the model and justify for the cases where a description beyond a mere parametrization of experimental data is desired, that a macro-state description based on a micro-states model is a useful alternative in order to relate statistical microscopic properties to the observed isotherm.

## 2. Adsorption Isotherms

The choice of Langmuir's model among other isotherms known from literature is justified by the fact that it is a model which can be understood from a microscopic motivation but is the simplest of a variety of models (Sposito, 1984). In fact, as shown by Sposito (1984), the van Bemmelen-Freundlich model, for example, may be understood as an integral over a continuum of Langmuir equations with a normal distribution for the logarithmic Langmuir parameter $\ln K_a$. Since the integral is a linear operation this modification does not alter qualitatively the comparison between the proposed model and established isotherms. Thus it shall be sufficient to compare the new isotherm to the Langmuir model.

Comparison of similarities and dissimilarities between the present and Langmuir's model may serve as a convenient starting point in a sequence of investigations dedicated to the question, whether there is a microscopic counterpart to the phenomenological classes of parametric isotherms given in the review article (Hinz, 2001). We are completely aware of the fact that such a challenge is in contradiction to the usual procedure of determining observable macro-states from micro-states, which has no unique inversion. However, a model micro-structure may shed further light on possible interaction properties of a liquid-solid interface. Our principal interest in this work is adsorption of substances which are (organic) molecules or even macromolecules. For these substances it is likely that the mutual non-interaction hypothesis of adsorbate molecules (Langmuir's hypothesis) no longer holds and one has to resort to approaches that permit the inclusion of interaction in order to obtain an (analytic) adsorption isotherm.

Adsorption measurements are typically performed while the solute is in equilibrium with the adsorbent surface, i.e., the rate of adsorption of molecules onto the surface is counterbalanced by the rate of desorption of molecules back into the neighboring gas or liquid phase. In Langmuir's approach the equilibrium condition is implemented via the balance of the chemical potentials of an ideal gas and for adsorbed molecules derived from the Helmholtz free energy $\mu_g = \mu_a$. Further, the adsorbent surface is assumed to have a fixed number of localized sites $N_s$, where all sites are assumed to be equivalent and the surface is uniform. In Langmuir's approach the saturation coverage corresponds, to complete occupancy of these sites in form of a monolayer structure, whereas in the proposed model saturation does not necessarily imply in a complete monolayer coverage but depends on the intensity of the surface potential. Accordingly, the ability of a molecule to adsorb at a given site in Langmuir's approach is independent of the occupation of neighboring sites as a consequence of the classical limit of an ideal quantum gas. In the new model the occupation number is controlled by the Pauli principle, manifest in the Fermi-Dirac structure of the partition function, to be introduced below, and additional the attractive or repulsive surface potential, which depends on the overall surface coverage, to be discussed in Section 3.

According to Langmuir (1916), the resulting expression for the fractional coverage $f = \frac{N_a}{N_s}$ of $N_a$ adsorbate molecules on $N_s$ sites as a function of pressure $P$ is

$$f = \frac{P}{\frac{(2\pi m)^{\frac{3}{2}}}{h^3 \beta^{\frac{5}{2}} z_s} e^{-\beta \epsilon_{AE}} + P}, \qquad (1)$$

where $m$ stands for the molecule's mass, $h$ for Planck's constant, $z_s$ describes the surface partition function representing translational and vibrational movements of the adsorbed molecule on the surface of the solid, $\beta = (kT)^{-1}$ is the inverse of Boltzmann's constant times temperature and $\epsilon_{AE}$ the activation energy.

Formula (1) is usually used in parametric form when fitted to experimental data. To this end, the pressure, which is proportional to the adsorbate particle density, is replaced by the measured adsorbate concentration $x$. Then Eq. (1) changes to

$$y = f\ y_{\text{sat}} = \frac{x}{C^{-1} + y_{\text{sat}}^{-1}\ x}\ , \tag{2}$$

where $C$ is a product of Langmuir's equilibrium adsorption constant and the saturation capacity $y_{\text{sat}}$, which are adjusted to fit the data. Further, $y$ is the amount of adsorbed substance and $x$ the solute concentration. In the limit $x \to 0$, i.e., the low concentration limit $y \to Cx$, the behavior depends on the desorption velocity, which is proportional to $C$ and yields a measure for the mean probability per unit time of an adsorbed molecule to decouple from the adsorbent surface. In the saturation region the second parameter $y \to y_{\text{sat}}$ enters only, which shows that in the respective limits both fit parameters ($C$ and $y_{\text{sat}}$) decouple. Note, that the specific form of Eq. (1) or (2), respectively, is a consequence of the equilibrium constraint for the chemical potential of an ideal gas and of adsorbed molecules derived from the Helmholtz free energy $\mu_a = \mu_g$. The model to be derived in the next section differs with respect to this feature where as a consequence there arises a sensitivity for the saturation already present in the low $x$ limit, a manifestation of liquid-solid interface dynamics.

## 3. A Micro-State Model for Adsorption

From the revision of Langmuir's model one concludes that an alternative micro-state model has to contemplate quantum characteristics, which does not necessarily have a classical counterpart. Further the ideal gas hypothesis, useful for dilute systems only, shall be improved. Finally, the model has to mimic at least the basic features of a liquid solid interface. In order to motivate the new model we proceed in three steps. First, the equivalence is shown, arguing either with the adsorbed molecule number or with the adsorbent surface potential (next section). This relation will gain importance in the interpretation of the resulting isotherm to be derived in the subsequent section. Second, the partition function of the quantum system is motivated with both adsorption and desorption probabilities present and as a response to the Hamilton operator of the quantum many particle system. Last, the number of adsorbed molecules per adsorbent sites is derived in terms of the surface potential.

### *3.1. Equivalence Between Adsorbed Molecule Number and Surface Potential*

From the statistical point of view the micro-state is defined by the possible occupation of $N_s$ adsorbent sites by a given number of $N_a$ adsorbate molecules, which leads to the macro-state by determining the overall distribution of adsorbate on adsorbent sites. In terms of quantum mechanics the micro-state is defined by the set of occupation numbers $\{N_{pr}\}$ per phase space volume element specified by its position $r$ and momentum $p$ for identical adsorbate molecules. The occupation number for a specific macro-state in terms of the number of micro-states is $M = N_s!/(\prod_{p,r} N_{pr}!)$, where the product $\prod_{p,r} N_{pr}!$ extends over all possible positions and momenta, i.e., includes the whole phase space. The distribution has to be compatible with the total energy of the system $E = \sum_{pr} N_{pr} E_{pr}$ as well as the total adsorbate molecule number $N_a = \sum_{p,r} N_{pr}$. The energy $E_{pr}$ is the Hamiltonian eigenvalue for the phase space volume element specified by position $r$ and momentum $p$.

From the experimental point of view one is interested in the distribution of macro-states $M$, where only the most probable of them is suitable for comparison with observation. Under the above mentioned constraints $M$ may be determined by the use of the Lagrange multiplier method and maximizing the logarithmic function $L$ (Schwabl, 2000),

$$\begin{aligned} L &= \ln M + \beta\mu \sum_{p,r} N_{pr} - \beta \sum_{p,r} N_{pr} E_{pr} \\ &\Rightarrow \frac{\partial L}{\partial N_{pr}} = 0 \end{aligned} \tag{3}$$

where $\mu$ is the chemical potential. The last equation determines the phase space distribution $N_{pr} = e^{-\beta(E_{pr}-\mu)}$ for adsorbate molecules with momentum and position $(p, r)$.

For many dilute systems (i.e., gas solid interfaces), interaction terms, such as two-body forces or effective interactions determined from a mean field approximation (Schwabl, 2000), may be neglected. An essential step towards a liquid-solid interface description is the inclusion of at least an effective surface potential $\pm\kappa V$, where the sign indicates whether the contribution is repulsive or attractive. Effective potential in this context means, that adsorbate adsorbent interaction, as well as the influence of adsorbate adsorbate interactions on the surface potential are present (to be detailed in the next paragraph). Here $\kappa$ denotes the interaction strength which depends on the physicochemical nature of adsorbate and adsorbent surface, and $V = V(r)$ the spatial dependence of the surface potential. In general $V$ may depend on the momenta and positions of the molecules, though measurements are typically conducted when the liquid and solid phases are in a stationary state and thus $V(p, r)$ reduces to $V(r)$. The occupation number including the potential term is then

$$N_{pr}^{\pm} = e^{-\beta(E_{pr}-\mu\pm\kappa V)}, \qquad (4)$$

The potential $V$ may be understood as an average potential representing the influence of the remaining $N_a - 1$ molecules on one adsorbate molecule that tends to adsorb on ($-$ sign), or to desorb ($+$) from a surface site.

We illustrate this by an example taken from a Monte Carlo Simulation for a liquid-solid interface: As a starting point, a fixed number of $N_s$ surface sites are distributed randomly on a surface. Additionally a total number of $N$ molecules is supplied, which is understood as the sum of $N_a$ adsorbed molecules on surface sites and the remaining $N_r$ molecules in the liquid phase. Consequently, the surface system is characterized by a grand canonical ensemble with $N_a$ subject to fluctuations. The inter-adsorbate interaction is then setup by a repulsion dominated Lenard-Jones potential, which mimics Pauli's exclusion principle. The same potential type serves for the adsorbate adsorbent interaction, but with a balanced attractive and repulsive contribution in order to permit bound quantum states. The net potential, which enters into the Schrödinger Hamiltonian is then the sum over all adsorbate-adsorbate and all adsorbate-adsorbent interactions.

Next, the initial condition is setup by a homogeneous volumetric distribution of molecules, represented as free particle solutions with momentum distribution according to Maxwell. Equilibrium is implemented in the Monte Carlo procedure by a standard procedure in literature known as detailed balance criterion (Rapaport, 1997; Thijssen, 1999). The simulation is then controlled by the transition probabilities, which are calculated scanning repetitively the first to the last particle in a random sequence and determining the probability of changing or maintaining the particle's quantum state. The procedure is repeated until the energy of the system stabilizes. Possible microscopic changes of the system are then transitions from a free state to a free state, a bound to a bound state, a free to a bound state and vice versa. The simulation is then performed for various $N$. In Fig. 1 is shown a configuration with $\frac{N_a}{N_s} = \frac{1}{2}$.

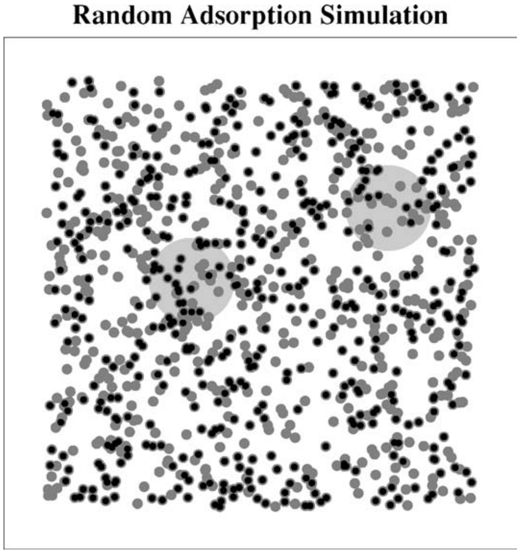

*Figure 1.* Simulation of 500 randomly adsorbed molecules on 1000 adsorbent sites.

The performed simulations permit the following observations:

1. If a surface site is empty, then the superposition of all potential terms is effectively attractive and adsorption decreases the system's energy, which rises the respective transition probability. There is, however, a chance for the molecule to remain in the liquid phase which as a consequence maintains the total energy.
2. An adsorbate molecule in the liquid phase is repelled from a site, if the site is occupied. In this case the net potential tends to rise the system's energy, which in turn suppresses the probability for adsorption. In zones where the density of adsorbed molecules is low, adsorption probability is higher in comparison to zones with a higher density.
3. A molecule occupying a surface site may desorb or maintain its state with a probability, which is controlled by the total energy of the system. With increasing $N$ the steady state equilibrium between

adsorption and desorption is characterized by an increasing desorption rate.

A steady state of the simulation shows a spatial distribution of randomly adsorbed molecules forming some sort of irregular pattern (see Fig. 1), where the white background represents the surface with its 1000 adsorbent sites (light spots) and the dark spots are 500 adsorbed molecules on some of the sites. The light disks indicate two regions with different densities in adsorbed molecules. The disk to the left has got 34 adsorbent sites with 22 adsorbed molecules whereas to the right one finds 32 adsorption sites with 13 of them occupied. Independent simulations always show this phenomenon with high/low density zones in different locations as indicated by the disks in Fig. 1.

In the language of statistical thermodynamics this effect may be formalized by an attractive effective potential $-\kappa V$ for the lower density contribution, whereas accumulation of adsorbate molecules leads to a repulsive potential $+\kappa V$ in the respective region. In general, the total adsorbate molecule number and the total number of adsorbent sites is huge so that one may consider the adsorbent site distribution as well as the adsorbate distribution over the surface as homogeneous on a macroscopic scale which permits one to treat the potentials as mean interactions. The contributions with either sign distinguishes the considered system from a dilute one. A combination of an adsorption desorption probability defines the underlying statistics of the model.

Adsorption experiments typically determine the adsorbed quantity $N_a$ of adsorbate on adsorbent sites independent of the molecular momentum, which is obtained by integrating out the momentum distribution,

$$N_a^{\pm} = e^{\beta\mu}\left(\frac{2\pi}{m\beta}\right)^{\frac{3}{2}} e^{\mp\beta\kappa V}. \tag{5}$$

If we assume that the most probable distribution is dominant and represents the observable equilibrium distribution for adsorbed molecules, then the molecule density varies with the mean potential $\pm\kappa V$. Equation (5) is the announced equivalence between the average potential energy and the molecule density.

### 3.2. An Adsorption-Desorption Quantum Partition Function

If an occupied site does not permit the occupation by a second molecule the relevant occupation quantum numbers for any site are $N_k \in \{0, 1\}$. This may be interpreted as a Pauli exclusion principle on the molecular level or in other words reflects the influence of occupied sites on the adsorption probability and is the reason for saturation. For the quantum system the number of ways $M_k$ of distributing the $N_k$ indistinguishable molecules belonging to the quantum state $Q_k$ is given by the binomial coefficient $M_k = \frac{Q_k!}{(Q_k - N_k)!N_k!}$, and consequently the total number of micro-states corresponding to a macro-state is $M = \prod_k M_k$.

The most probable distribution of states is again determined using the function $L$, which also includes the afore mentioned constraints

$$L = \ln M + \beta\mu \sum_k N_k - \beta \sum_k N_k \epsilon_k. \tag{6}$$

Using Stirling's approximation for optimizing Eq. (6) yields the average (de)occupation number of a single particle quantum state $\epsilon_k$ at equilibrium—the Fermi-Dirac distribution.

$$\bar{N}_k^{\pm} = \frac{1}{e^{-\beta(\epsilon_k - \mu \pm \kappa V)} + 1} = \frac{1}{\beta}\frac{\partial \log z_k}{\partial \mu} \tag{7}$$

From Eq. (7) one recognizes the adsorption-desorption partition function for a single adsorption site

$$z = \frac{1}{1 + e^{-\beta(\epsilon - \mu - \kappa V)}} \frac{1}{1 + e^{-\beta(\epsilon - \mu + \kappa V)}}. \tag{8}$$

In the last step to follow the momentum distribution is integrated out and the fractional coverage of the surface, or the ratio of adsorbed molecules to the number of adsorption sites is determined from the partition function in terms of the surface potential.

### 3.3. The Adsorption Isotherm

In Langmuir's approach and others (Sposito, 1984) the isotherm was specified by $T$ and $P$, whereas in the proposed model equilibrium is determined in terms of $T$ and $\mu$. One may evaluate the chemical potential $\mu$ per particle of the liquid from an integration of the Gibbs-Durham relation if the equation of state is known (note, that the present case allows an approximation maintaining the result even independent of the specific form of the chemical potential). Once $\mu$ and $T$ of the liquid are specified, it is equivalent to argue in terms of the surface potential instead of molecule number in order to quantify adsorption.

Using Eq. (7) and integrating over the allowed momentum configurations of the molecules the grand partition function reads $Z = z^{N_s}$,

$$\ln Z = N_{ph.s.} \int \left\{ \ln\left(1 + e^{-\beta(\epsilon+\kappa V-\mu)}\right) + \ln\left(1 + e^{-\beta(\epsilon-\kappa V-\mu)}\right)\right\} p^2\, dp, \tag{9}$$

where the quantum mechanical normalization of phase space is known to be $N_{ph.s.} = \frac{4\pi}{h^3}$. The integral in Eq. (9) extends over all momentum eigenvalues of possible quantum states multiplied by a logarithmic weight factor. In other words Eq. (9) represents the logarithm of the sum over the entire quantum state density times its occupation probabilities, which serves as the key quantity from which $N_a$ and $N_s$ may be derived. Thus the mean number of adsorption sites and adsorbed molecules is

$$N_s = \frac{1}{\beta}\frac{\partial \ln Z}{\partial \mu}, \quad \text{and} \quad N_a = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}. \tag{10}$$

The variation of the occupied quantum state density with the chemical potential is then proportional to the number of adsorption sites, whereas, according to the already shown equivalence between potential energy and molecule density, the number of adsorbed molecules is then given by the variation of the occupied quantum state density with the surface potential.

Note, that $\ln Z$ and $N_s$ are even functions in $\kappa V$ whereas the mean number of adsorbed molecules $N_a$ is odd. In most of the laboratory experiments, the condition $\beta^{-1} = kT \ll \epsilon \pm \kappa V - \mu$ holds and upon substitution of the potential by its expectation value $\bar{V}$ yields the approximation which factorizes the leading order term in $\bar{V}$ and the remaining momentum integral,

$$N_s = N_{ph.s.}(e^{\beta\kappa\bar{V}} + e^{-\beta\kappa\bar{V}})\left(\int e^{-\beta(\epsilon-\mu)}\right) p^2\, dp \tag{11}$$

and accordingly

$$N_a = N_{ph.s.}\kappa(e^{\beta\kappa\bar{V}} - e^{-\beta\kappa\bar{V}})\left(\int e^{-\beta(\epsilon-\mu)}\right) p^2\, dp. \tag{12}$$

Recalling, that the mean potential is a measure for the number of adsorbed molecules per number of adsorbate sites or the fractional surface occupation $f$ times a constant, then Eqs. (11) and (12) yield

$$\frac{N_a}{N_s} = \kappa \tanh(\beta\kappa\bar{V}). \tag{13}$$

In order to reproduce a gas-solid isotherm we introduce a further approximation. For gas adsorption the surface potential $V$ is typically short ranged so that the average potential $\bar{V}$ is weak. This permits to replace the *tanh* function by a Padé approximant (a rational function) (Baker and Graves-Morris, 1996) which renders Eq. (13) an expression equivalent to the Langmuir isotherm.

$$\frac{N_a}{N_s} \approx \kappa \frac{\beta\kappa\bar{V}}{1 + \beta\kappa\bar{V}} \tag{14}$$

Note, that as a consequence of the approximation the even, odd dependence of $N_s$ and $N_a$ on $\kappa V$ is lost, reducing the expression to a simple potential dependence.

The isotherm (13) may be compared to experimental data, where one may again introduce a parametric form,

$$y = y_{\text{sat}} f = y_{\text{sat}} \tanh(Bx), \tag{15}$$

which is the liquid-solid interface adsorption isotherm. The discussion of the next section is dedicated to a comparison of Langmuir's and the proposed model using some experimental data of humic acid adsorption on Oxisol.

## 4. Model Validation

As of particular interest we consider humic acid (HA) adsorption on Brazilian Oxisol soil samples as discussed in detail elsewhere (Dick et al., 1999). Untreated and $NH_4$-Oxalate treated soil samples were used as adsorbent, whereas humic acids from a South Brazilian coal (HAc) and from a Brazilian Mollisol sample (HAs) were employed as adsorbate. The humic acids were extracted with $0.5\frac{mol}{\ell}$ $NaOH$ solution, according to the procedure reported in Swift (1996). The chemical composition of the adsorbates were determined by elemental analysis and additional $^{13}C{-}NMR$ spectroscopy gave further information about types and proportions of the $C$-functional groups contained.

The samples were further analyzed by Diffuse Reflectance Infrared Fourier Transformed spectroscopy (DRIFT) before and after adsorption, which showed that in both adsorbents adsorption was of a chemical nature where the ligand exchange reaction between the carboxyl groups and the mineral surfaces was a predominant mechanism. The HAc was adsorbed in greater quantity than the HAs in both adsorbents, because of a higher aromatic character and a higher carboxyl content in its molecule. In terms of the proposed model this means, that values for $\kappa$ of HAs shall always be smaller than the corresponding ones of HAc.

The $NH_4$-oxalate treatment resulted in an Oxisol sample with higher specific surface area $\sigma_t = 140.9\frac{m^2}{g}$ in comparison to the untreated Oxisol with $\sigma_u = 66.1\frac{m^2}{g}$ (Dick et al., 1999). The higher $\sigma_t$ in the treated sample has its origin in the break-up of micro-aggregates by the oxalate treatment caused by the extraction of the cementing portion of iron oxides, that bonded the particles together.

$$\frac{\sigma_u}{\sigma_t} \approx \frac{1}{2} \tag{16}$$

The difference $\Delta\kappa = \kappa(treated) - \kappa(untreated)$ for the HAc and HAs samples, which is proportional to the difference in the saturation concentrations, is a measure for the effect of the adsorbed oxalate that created hydrophobic adsorption sites, for the exposure of more reactive sites after the treatment and for the lower pH value.

The adsorption isotherms were determined at 25°C and the experimental data were fitted using Langmuir's model and the parametrization by the hyperbolic tangent (see Fig. 2). In order to validate and compare both models the Maximum Likelihood method (Tanner, 1996) was employed. The results are shown in Table 1. In the untreated soil systems both models compete in reproducing the experimental data, whereas in the treated systems the present model shows the better parameter correlation with the data (see Table 1). One may see from Fig. 2 that the slope in the Langmuir model is always larger than the one found by the hyperbolic tangent fit. Also the saturation value was found to be larger in all four cases. Taking the saturation value $y_{\text{sat}}^{(i)}$ for the untreated ($u$) and the treated samples ($t$), one may

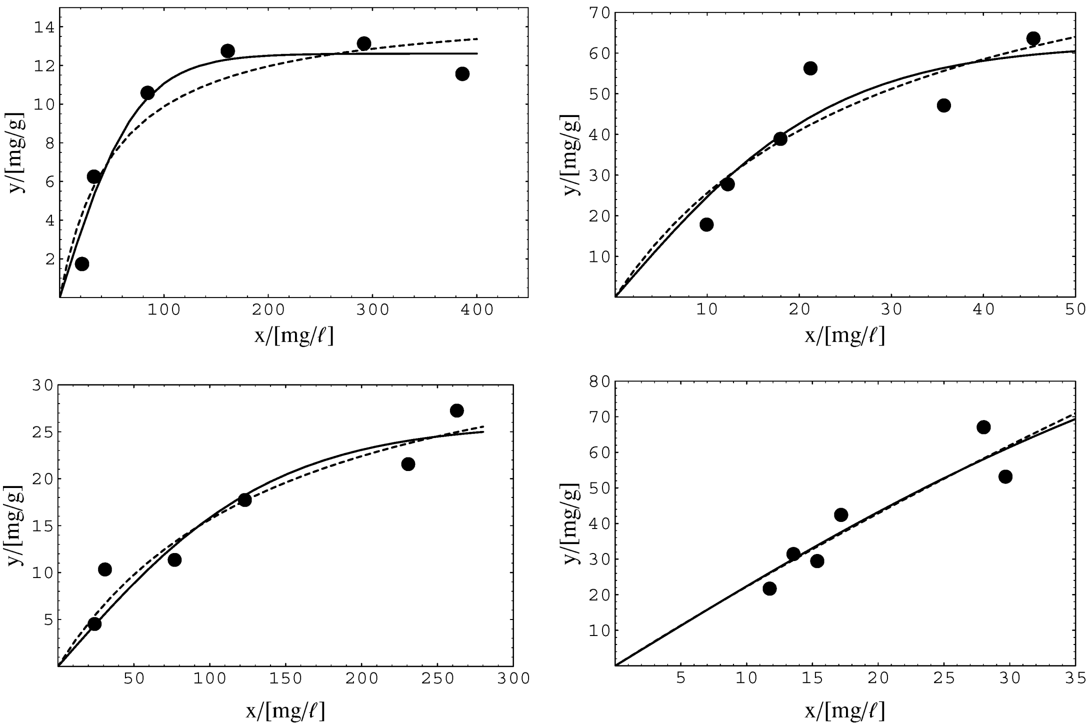

*Figure 2.* Adsorption isotherms for natural oxisol (left) and after ammonium oxalate treatment (right). The upper figures show the data for the Mollisol sample and the lower ones for a coal sample. In all figures the ordinate shows the adsorbed quantity of humic acid per weight of soil sample, the coordinate gives the equilibrium humic acid concentration per volume of solution. The solid lines represent the hyperbolic tangent parametrization $y = y_{\text{sat}} \tanh(Bx)$ whereas the dashed lines correspond to the Langmuir parametrization $y = \frac{x}{C^{-1} + y_{\text{sat}}^{-1} x}$.

*Table 1.* Maximum Likelihood parameter fits of the proposed and Langmuir's model. The model errors refer to hypothesis testing at the 95% confidence level (CL).

| | | | | Model | |
|---|---|---|---|---|---|
| # | Soil system | Quantity | Units | Tanh | Langmuir |
| $S_1$ | HAs | Slope at $x = 0$ | in $\frac{\ell}{g}$ | 0.13 | 0.29 |
| | on natural | Saturation $y_{\text{sat}}^{(1)}$ | in $\frac{mg}{g}$ | 12.6 | 15.2 |
| | oxisol | Model error (95% CL) | in % | 7.5 | 12.3 |
| $S_2$ | HAs | Slope at $x = 0$ | in $\frac{\ell}{g}$ | 2.62 | 3.45 |
| | on treated | Saturation $y_{\text{sat}}^{(2)}$ | in $\frac{mg}{g}$ | 62.3 | 102.0 |
| | oxisol | Model error (95% CL) | in % | 8.2 | 10.7 |
| $S_3$ | HAc | Slope at $x = 0$ | in $\frac{\ell}{g}$ | 0.18 | 0.26 |
| | on natural | Saturation $y_{\text{sat}}^{(3)}$ | in $\frac{mg}{g}$ | 25.9 | 39.4 |
| | oxisol | Model error (95% CL) | in % | 9.3 | 9.0 |
| $S_4$ | HAc | Slope at $x = 0$ | in $\frac{\ell}{g}$ | 2.26 | 2.32 |
| | on treated | Saturation $y_{\text{sat}}^{(4)}$ | in $\frac{mg}{g}$ | 119.7 | 555.6 |
| | oxisol | Model error (95% CL) | in % | 5.0 | 39.2 |

verify that for the hyperbolic tangent parametrization the HAs adsorbate ratio shows approximately the same value as the respective HAc ratio,

$$\frac{y_{\text{sat}}^{u}}{y_{\text{sat}}^{t}}(HAs) \approx \frac{1}{5} \approx \frac{y_{\text{sat}}^{u}}{y_{\text{sat}}^{t}}(HAc)\ . \tag{17}$$

One may expect an approximately equal value since the treatment changed the soil surface, whereas the adsorption mechanism is related to the humic acid adsorbate on the soil adsorbent, which remains the same. The ratios determined with the Langmuir model differ by approximately a factor of two.

$$\frac{y_{\text{sat}}^{u}}{y_{\text{sat}}^{t}}(HAs) \approx \frac{1}{7} \approx 2 \times \frac{y_{\text{sat}}^{u}}{y_{\text{sat}}^{t}}(HAc) \tag{18}$$

A second test to compare and validate the models may be drawn from the ratio of the adsorbate dependent desorption probabilities for the untreated and treated soil systems, respectively. Desorption probability is proportional to the derivative of the isotherm in $\bar{V}$ or $P$, respectively. The expressions for the hyperbolic tangent (Eq. (13)) and Langmuir isotherm (see Eq. (1)) are

$$\frac{df}{d\bar{V}} = \beta\kappa^2 \operatorname{sech}^2(\beta\kappa\bar{V}),$$
$$\frac{df}{dP} = \frac{\Gamma}{(\Gamma + P)^2} \quad \text{with} \quad \Gamma = \frac{(2\pi m)^{\frac{3}{2}}}{h^3 \beta^{\frac{5}{2}} z_s} e^{-\beta\epsilon_{AE}}. \tag{19}$$

Recalling that the adsorption process is a steady state equilibrium, one may argue that, the larger the quantity of adsorbed molecules becomes the more possibilities arise for desorption, which should increase desorption probability. Further, the closer the adsorption is to its saturation region, the larger will be the desorption contribution to the steady state equilibrium. Especially, if one compares the desorption contribution for a given solute concentration, then adsorption in the untreated sample is closer to saturation than in

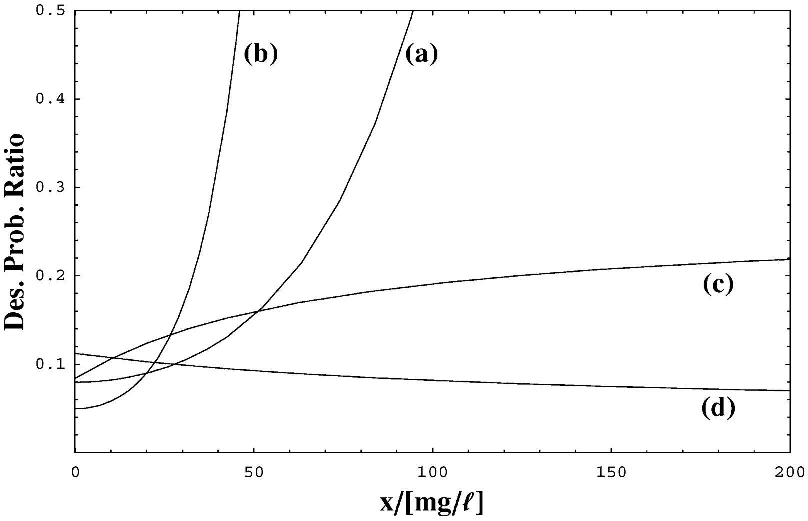

*Figure 3.* Desorption Probability Ratios of the untreated to the treated samples for the hyperbolic tangent ((a) and (b)) and Langmuir ((c) and (d)) parametrization for the best fit parameter set from Table 1. (a) and (c) show the ratios for the samples $S_1/S_2$, (b) and (d) for $S_3/S_4$.

the treated one, which means that desorption shall increase more rapidly in the untreated sample than in the treated one. As a consequence one expects that the desorption probability ratio for the untreated to the treated sample shall rise with increasing adsorbate concentration. The model predictions may be verified using the best parameter sets of the experimental data fits for the respective models and soil samples. The result for the ratios of the soil systems $S_1/S_2$ and $S_3/S_4$ in the hyperbolic tangent parametrization show the expected behavior (see Fig. 3), whereas the respective Langmuir ratios look different. If one assumes that the effect of the soil treatment by oxalate does primarily affect the surface structure and has less or no effect on the adsorption mechanism, as indicated by the DRIFT spectra, then one expects that the ratio of the desorption probabilities shall increase. The hyperbolic tangent isotherm confirms this behavior, whereas the Langmuir model contradicts this hypothesis.

## 5. Conclusions

In the present study a micro-state model based adsorption isotherm for liquid-solid interfaces was discussed. Although adsorption processes in natural soil systems have to be considered as rather complex, we believe to have shown with our example that micro-state models for up to now existing phenomenological isotherms may shed further light on significant process properties. Our micro-state model was designed for adsorption scenarios where adsorption is predominantly of a chemical nature. We are completely aware of the fact that adsorption data from natural soil systems are likely to show a larger dispersion in comparison to results from synthetic experiments. Nevertheless a comparison of the model prediction of two microscopically motivated models (the Langmuir model and our proposal) showed, that although both seem to represent experimental data well, the new model is self-consistent. One reason may be attributed to the fact that in approaches in the spirit of Langmuir, the specific form of the isotherm results from a constraint (equilibrium condition for the chemical potentials) rather than a dynamical property (relation of the adsorbed quantity to the adsorbent site occupation dependent interaction potential).

Experimental findings indicate that in both untreated and treated adsorbents, humic acid adsorption is of a chemical nature (ligand exchange reaction between the carboxyl group and the mineral surface). If the principal effect of the oxalate treatment resulted in the break-up of micro-aggregates, then one expects that the ratio of the saturation values for the humic acid from a Mollisol for the untreated to the treated adsorbent shows the same ratio as the values of humic acid from coal. The fact that the ratio of the untreated to the treated system is smaller than the corresponding specific area ratios likely indicates that the treatment enlarges the surface in a fractal like fashion. An experimental verification may be conducted measuring data with different adsorbent grain sizes. The relation of grain size to the specific surface ratio is then equivalent to box counting, usually employed to determine the fractal Hausdorff dimension, which characterizes the increase of reactive adsorbent sites. Using the model prediction, this idea is further supported by the comparison of the adsorbate concentration dependent desorption probability, which for our model shows a rise with increasing desorption possibility. The mentioned constraint in Langmuir's approach is responsible for a weak increase or even a decrease in the desorption probability, which may be understood from the fact that the specific adsorbent density per effective area enters only in the range of small adsorbate concentrations and contributes less or almost nothing with increasing concentration.

We believe that with the present discussion we realized a first step in a direction where the set of phenomenologically known isotherms may be justified from micro-state models, which may open pathways for a further characterization and understanding of relevant properties in the question of adsorption processes.

## Nomenclature

| | |
|---|---|
| $f$ | Fractional surface coverage $(0 \leq f \leq 1)$; |
| $P$ | Gas pressure |
| $m$ | Molecular mass |
| $h$ | Planck's constant |
| $\beta = (kT)^{-1}$ | Inverse Boltzmann's constant times temperature |
| $z_s$ | Surface partition function |
| $\epsilon_{AE}$ | Activation energy |
| $y_{\text{sat}}$ | Saturation capacity |
| $x$ | Adsorbate concentration |
| $C = k_L\ y_{\text{sat}}$ | Langmuir isotherm parameter (Langmuir's equilibrium constant $k_L$ times saturation capacity) |
| $M$ | Number of macro-states |
| $\mu$ | Chemical potential |
| $N_{pr}$ | Number of adsorbate molecules with momentum $p$ and position $x$ |

| | |
|---|---|
| $N_s$ | Number of adsorbent sites |
| $N_a$ | Number of adsorbate molecules |
| $E_{pr}$ | Energy eigenvalue for particles with phase space coordinates $(p, r)$ |
| $V$ | Effective surface potential |
| $\kappa$ | Interaction strength |
| $Q_k$ | Number of quantum states with quantum number $k$ |
| $M_k$ | Macro-states with quantum number $k$ |
| $N_k$ | Number of indistinguishable molecules |
| $z$ | Partition function |
| $Z$ | Grand partition function |
| $N_{ph.s.}$ | Quantum mechanical phase space |
| $\sigma$ | Specific surface area |
| $B = \beta\kappa$ | Hyperbolic tangent isotherm parameter. |

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