

## Modeling adsorption isotherms with a hybrid Langmuir-multilayer approach for solid-liquid interfaces

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### Abstract

In this study, we investigate the boundaries of low and high concentration regimes for the BET equation, deriving a novel form for BET equation applied to liquids. The new isotherm form integrates the Langmuir model, which accounts for monolayer adsorption, with an additional term that explicitly describes the formation of multilayers over the initial monolayer. This perturbative approach offers a significant advantage by distinguishing the fraction of adsorbate in the first monolayer from that in subsequent multilayers. This differentiation is crucial for a more accurate representation of adsorption dynamics, as it provides deeper insights into the distribution of adsorbed molecules across different layers of the adsorbent surface. By refining the classic BET model, our proposed isotherm not only broadens the theoretical framework but also enhances the analytical tools available for the precise characterization of adsorption in liquid systems. This dual-terms interpretation allows for a more comprehensive understanding of adsorption processes, particularly in complex systems where multilayer formation is prevalent. The improved model can be applied to a wide range of practical scenarios, from environmental engineering to chemical manufacturing, offering a robust method for predicting and analyzing adsorption behavior.

*Keywords:* BET equation; Multilayer adsorption; Langmuir; Adsorption isotherms; Solid-Liquid adsorption.

### 1. Introduction

Adsorption in solid-liquid systems is crucial in various scientific and technological applications, such as water purification and catalyst optimization in chemical reactions [1]. Historically, the Brunauer-Emmett-Teller (BET) model has been fundamental in understanding multilayer adsorption on solid surfaces. This model, based on statistical assumptions, considers the formation of successive multilayers on an adsorbed monolayer [2]. However, the complexity of solid-liquid adsorption systems, characterized by diverse interactions and varying environmental conditions, often requires a more refined approach [3].

This study introduces a new equation that combines the Langmuir model with an additional term to account for multilayer adsorption on the initial monolayer. By addressing the dynamic coexistence of adsorbed layers, the equation offers a

more accurate representation of adsorption processes and enhances the modeling of experimental data.

The proposed equation is grounded in solid physical principles and aims to provide a comprehensive tool for characterizing adsorption isotherms in solid-liquid systems. The study discusses the derivation of the equation, its applicability, and the implications of its parameters, contributing to a deeper understanding of adsorption phenomena and advancing practical applications.

### 2. Theoretical development

Adsorption in solid-liquid systems has been extensively investigated due to its importance in various fields such as compound separation, water purification, and industrial processes. The BET model has traditionally been used to describe adsorption isotherms, considering the formation of multilayers over an adsorbed monolayer. However,

in this study, we present a new approach based on the linear combination of two distinct terms: the Langmuir equation, which describes monolayer adsorption, and an additional term that models multilayer adsorption.

The term  $q_{n>1}$  (multilayer adsorption) is introduced as an extension of the Langmuir model to capture the contribution of multilayers to the total adsorption. Its formulation is derived from physical considerations of the sequential adsorption of additional layers over the initial monolayer, incorporating parameters that reflect the interaction between the adsorbed layers.

*Derivation:*

The reduction of the BET equation to Langmuir in the limit of low concentrations and/or negligible  $K_M$  is already known [1,3]. Since  $K_M \ll 1$ , the product  $K_M \cdot C_{eq} \rightarrow 0$ .

$$q = q_m \frac{K_S C_{eq}}{(1 - K_M C_{eq})(1 - K_M C_{eq} + K_S C_{eq})} \quad (1)$$

And the equation 1 becomes the Langmuir equation:

$$q = q_m \frac{K_S C_{eq}}{(1 + K_S C_{eq})} \quad (2)$$

By definition,  $K_M = 1/C_{max}$ , where  $C_{max}$  is the highest possible concentration admitted by the model, where all additional adsorbate must be adsorbed onto the surface of the adsorbent, effectively leaving the liquid phase.

So, as  $C_{eq}$  increases,  $C_{eq} \rightarrow C_{max}$ , such that the term  $K_M \cdot C_{eq} \rightarrow 1$ . Simultaneously, with the increase in  $C_{eq}$ , the term  $K_S \cdot C_{eq}$  becomes dominant, implying:

$$\frac{K_S C_{eq}}{(1 - K_M C_{eq} + K_S C_{eq})} \rightarrow 1 \quad (3)$$

Then, at high concentrations, the equation 1 can be reduced to:

$$q = q_m \frac{1}{(1 - K_M C_{eq})} \quad (4)$$

At  $C_{eq} = 0$ , the equation gives  $q = q_m$  leading to deducing that the function gives the continuous multilayer adsorption over the first monolayer ( $q_m$ ) along the increasing  $C_{eq}$ .

To extract the contribution of only n layers with  $n > 1$ , we need to subtract  $q_m$  from the equation:

$$q_{n>1} = q_m \frac{1}{(1 - K_M C_{eq})} - q_m \quad (5)$$

$$q_{n>1} = q_m \left[ \frac{1}{(1 - K_M C_{eq})} - 1 \right] \quad (6)$$

$$q_{n>1} = q_m \frac{K_M C_{eq}}{(1 - K_M C_{eq})} \quad (7)$$

Now we can approximate the multilayer BET equation by a linear combination of the monolayer Langmuir equation (eq. 2) and the  $n > 1$  multilayer equation (eq. 7), that becomes:

$$q = q_m \left[ \frac{K_S C_{eq}}{(1 + K_S C_{eq})} + \frac{K_M C_{eq}}{(1 - K_M C_{eq})} \right] \quad (8)$$

To interpret the equation, the first term (Langmuir) is a function that goes from zero to one (which represents the complete monolayer formation), while the second term (multilayers) goes from zero to infinity, adding up to the first layer. The  $q_m$  consists in a scale factor of the function, that gives the magnitude of the function to fits the physical units used experimentally.

In fact, after the presented approximations and algebraic manipulations, equation 8 remains an identity of the BET equation (eq. 1). This can be deduced from the proposition below.

*Proposition 1:* the BET equation (1) is equal to equation (8) since the monolayer equilibrium constant term  $K_S$  is a composite constant for BET, taken as an apparent equilibrium constant  $K_S^\dagger$  added with the multilayer equilibrium constant  $K_M$ , according to the equation:

$$K_S = K_S^\dagger + K_M \quad (9)$$

While the monolayer constant for equation 8 is, in fact,  $K_S^\dagger$ .

*Proof of proposition 1:*

Assume the equation 8 present an apparent monolayer equilibrium constant:

$$q = q_m \left[ \frac{K_S^\dagger C_{eq}}{(1 + K_S^\dagger C_{eq})} + \frac{K_M C_{eq}}{(1 - K_M C_{eq})} \right] \quad (10)$$

$$K_S^\dagger = K_S - K_M \quad (11)$$

$$q = q_m \left[ \frac{(K_S - K_M) C_{eq}}{(1 + (K_S - K_M) C_{eq})} + \frac{K_M C_{eq}}{(1 - K_M C_{eq})} \right] \quad (12)$$

With a simple algebraic rearrangement:

$$q = q_m \left[ \frac{(1 - K_M C_{eq})(K_S C_{eq} - K_M C_{eq}) + (1 - K_M C_{eq} + K_S C_{eq})K_M C_{eq}}{(1 - K_M C_{eq})(1 - K_M C_{eq} + K_S C_{eq})} \right] \quad (13)$$

$$q = q_m \left[ \frac{K_S C_{eq} - (1 - K_M C_{eq} + K_S C_{eq})K_M C_{eq} + (1 - K_M C_{eq} + K_S C_{eq})K_M C_{eq}}{(1 - K_M C_{eq})(1 - K_M C_{eq} + K_S C_{eq})} \right] \quad (14)$$

The equation 8 becomes exactly the BET equation:

$$q = q_m \left[ \frac{K_S C_{eq}}{(1 - K_M C_{eq})(1 - K_M C_{eq} + K_S C_{eq})} \right] \quad (15)$$

*Isotherms that deviate from the ideal form of the BET function:*

Besides, when an adsorption isotherm presents multilayer formation but does not fit properly with BET equation, many factors can produce such deviations. The modular characteristic of equation 8 for BET isotherm shows useful to perform adaptations in the isotherm model, such as insert a new parameter “ $n$ ” as an exponential factor to modulate de rate of multilayer formation along the increase of equilibrium concentration, as follows:

Using the multilayer form in equation 6, the equation 8 can be written in the following form:

$$q = q_m \left[ \frac{K_S C_{eq}}{(1 + K_S C_{eq})} + \frac{1}{(1 - K_M C_{eq})} - 1 \right] \quad (16)$$

Now, we can modify the denominator of the term related to the multilayer formation, to modulate the magnitude of the response to change in equilibrium concentration:

$$q = q_m \left[ \frac{K_S C_{eq}}{(1 + K_S C_{eq})} + \frac{1}{\sqrt[n]{1 - (K_M C_{eq})^n}} - 1 \right] \quad (17)$$

Is important to note that this adaptation is just empirical and serves to fit the model to specific experimental data. However, this adaptation preserves the accuracy of some important physical meanings of the equation such as the values of monolayer capacity  $q_m$  and the values of equilibrium constants. If the experimental data does not agree perfectly with the original BET equation, numerical solutions will estimate wrongly all the parameters, trying to better fit the data at the limits of high multilayer formation.

Fun fact: despite the multilayer part of the equation has absolutely no relation with relativity, when coefficient  $n = 2$ , the equation assumes the same format of Lorentz factor ( $\gamma$ ) [4].

*Determine when a given fraction of the surface is covered by the adsorbate:*

Following the Langmuir theory, the full surface coverage of the adsorbent will be reached only at infinite concentration. However, eventually there will be a need to determine when a certain fraction of the surface is covered by the adsorbate, e.g., for a 95% of available surface coverage, the following equality must be truth:

$$\frac{K_S C_{eq}}{1 + K_S C_{eq}} = 0.95 \quad (18)$$

rewrite the right side as rational fraction:

$$\frac{K_S C_{eq}}{1 + K_S C_{eq}} = \frac{19}{20} \quad (19)$$

$$C_{eq(0.95)} = \frac{19}{K_S} \quad (20)$$

thus, for 50% coverage the solution will be as follows:

$$C_{eq(0.5)} = \frac{1}{K_S} \quad (21)$$

The same logic can be used to any fraction ( $\theta$ ) of monolayer coverage and knowing  $K_S$  is possible to estimate de surface coverage at any equilibrium concentration  $C_{eq(\theta)}$ :

$$C_{eq(\theta)} = \frac{\theta}{K_S(1 - \theta)} \quad (22)$$

*Performance comparison of BET isotherm against Langmuir-Freundlich isotherm type (the case of Sips model):*

Models that incorporate additional parameters to modulate the adsorption curve, such as the exponent in the Langmuir-Freundlich equation, often achieve a good fit to experimental data [5]. However, they can produce estimated parameters that challenge the physical interpretation of the phenomena involved. For example, an estimate of a very high maximum adsorption capacity ( $q_m$ ) might not be supported by experimental results and could even exceed the observed values. Moreover, the disparity between the model's estimated values and the experimental data often calls into question the validity of the fit achieved. Examples based on experimental data from literature fitted for Sips model, and recalculated for BET model, are shown in Table 1 and Figure 1.

Table 1. Isotherms presented in the literature where adsorption is modeled according to the Sips model, compared with the application of the BET model from this work.

Isotherm	Parameters			REF
Sips	$q_m$ (mg g <sup>-1</sup> )	$K_{Sips}$	$n$	[6]
	175.2	0.024	0.541	
BET	$q_m$ (mg g <sup>-1</sup> )	$K_S$	$K_M$	This work
	129.9	0.056	$1.63 \times 10^{-4}$	
Sips	$q_m$ (mg g <sup>-1</sup> )	$K_{Sips}$	$n$	[7]
	210.01	2.53	0.31	
BET	$q_m$ (mg g <sup>-1</sup> )	$K_S$	$K_M$	This work
	112.37	765.8	0.396	

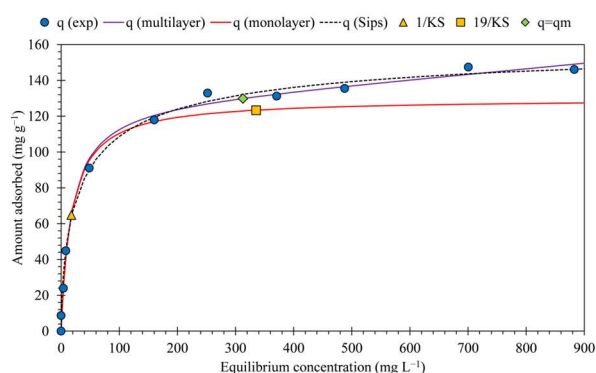


Figure 1. Adsorption isotherm of MB (Methylene Blue) in A-CNF/DT. Experimental data published by Radjai et al. [6].

In his original article, Sips elegantly describes the distribution of adsorption energies on catalyst sites [8]. However, upon deeper exploration of isotherm models, the assumption that the Freundlich isotherm best characterizes the adsorption process (as suggested in equation 7 of the original article) begins to falter. Later, in equation 10, the issue becomes more apparent where a modification of the original Freundlich equation is introduced to better align it with observed reality. At this point, a hybrid Langmuir/Freundlich equation emerges, which is widely used in the literature to fit experimental isotherm data [5]. However, its application often has only a limited connection to the energy distribution on sites as originally deduced by Sips. The Langmuir/Freundlich isotherm, known as the Sips isotherm, more closely resembles a Langmuir isotherm with an adjustable parameter that fits the curve under various conditions, rather than necessarily representing an isotherm for sites with different energies.

## 4. Conclusions

The proposed equation was compared to experimental data from adsorption isotherms for various solid-liquid systems, demonstrating excellent agreement. The equation's ability to describe adsorption under different experimental conditions underscores its robustness and versatility. Additionally, the analysis of the equations provided valuable insights into the nature of multilayer adsorption, offering deeper information about the relative contributions of monolayer and multilayer adsorption to the overall adsorption process.

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