



# Re-evaluation of the century-old Langmuir isotherm for modeling adsorption phenomena in solution

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## ABSTRACT

One of the first reported equations to describe adsorption at equilibrium is the Langmuir model (*J. Am. Chem. Soc.* 1918, 40, 1361–1403). Initially, the model was used to describe adsorption from the gas phase, along with adsorption from the liquid phase. Herein, the shortcomings of the Langmuir model for adsorption processes from liquid phase are revealed. This study reports a revised form of the Langmuir isotherm model that provides further insight on the nature of adsorption and desorption processes in condensed phases. This approach is anticipated to provide a theoretical background for universal calculation of the adsorption thermodynamic parameters. We also provide an overview of the methods that use the Langmuir equilibrium constant for calculation of thermodynamic parameters of adsorption and source of their limitations are highlighted.

## 1. Introduction

Adsorption is an effective and facile method for pollutant removal from wastewater and gas streams due to its low infrastructure and operational cost, especially for the use of sustainable and recyclable materials. Adsorption has great potential for application in various fields such as catalysis, filtration, gas storage, protein purification, and chemical separations. Due to the broad scope of industrial applications of adsorption-based phenomena, further experimental and theoretical studies are vital to develop this field to its full potential. There are many studies aimed at describing adsorption processes at kinetic [1–7] and equilibrium [8] conditions. Since the pioneering work of Langmuir [9], a variety of classical models have been proposed [10–15] that include the Langmuir-Freundlich [16] and Toth [17] (for heterogeneous surfaces), the Temkin [18] model for systems with adsorbate-adsorbate interactions, the Frumkin [19] model for systems with adsorbate-adsorbate interactions, among other types of models. The AV-isotherm [20,21] for adsorption with two different configurations of an adsorbate, multi-site occupancy adsorption isotherm [22,23], and a multilayer adsorption isotherm for heterogeneous surfaces [24] were recently proposed.

In spite of the increasing number of recent developments for modeling equilibrium adsorption phenomena, the Langmuir isotherm remains popular. Up to now, many publications ( $> 10^4$ ) have been reported for the study of equilibrium adsorption using this model, especially for liquid phase systems. However, some assumptions are not

met for the Langmuir model in certain systems, and reveals the need to modify this isotherm model in a revised form [25,26]. A noteworthy report on the modification of the Langmuir model by Sohen et al. [25] considered the effect of solution concentration ( $C$ ) on both of adsorption and desorption rate equations. Although the primary assumption for this model was logical, the role of solution concentration on desorption rate was unclear. Therein, the simplest polynomial function,  $C^n\theta$  was taken as desorption rate (where  $n$  is the level of desorption dependence on concentration and  $\theta$  is the surface coverage) [25]. In other studies [27–29], the Langmuir isotherm constant was modified for estimation of adsorption thermodynamic parameters: Gibbs energy ( $\Delta G_{ad}^\circ$ ), entropy ( $\Delta S_{ad}^\circ$ ) and enthalpy ( $\Delta H_{ad}^\circ$ ). The change in Gibbs energy of adsorption is calculated by using Eq. (1):

$$\Delta G_{ad}^\circ = -RT \ln K^\circ \quad (1)$$

$R$  is the universal gas constant,  $T$  is absolute temperature and  $K^\circ$  is the dimensionless adsorption equilibrium constant. Also, the Gibbs energy of adsorption relates to entropy and enthalpy of adsorption by Eq. (2):

$$\Delta G_{ad}^\circ = \Delta H_{ad}^\circ - T \Delta S_{ad}^\circ \quad (2)$$

Substitution of Eq. (1) in Eq. (2) yields the van't Hoff equation:

$$\ln K^\circ = \frac{\Delta S_{ad}^\circ}{R} - \frac{\Delta H_{ad}^\circ}{RT} \quad (3)$$

As mentioned above, the Langmuir adsorption equilibrium constant ( $K_L$ ) was used instead of the adsorption equilibrium constant ( $K^\circ$ ) to

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**Table 1**

Adsorption thermodynamic parameters derived from Langmuir isotherm constant with different units for adsorption of phenol onto HMBP-Mt (reference [33]). The “\*” denotes the unit that was used in this reference.

	$K_L$			$\Delta G_{ad}^\circ$ (KJ/mol)	$\Delta H_{ad}^\circ$ (KJ/mol)	$\Delta S_{ad}^\circ$ (J/(mol K))
	T(K)	Value	Unit			
Adsorption of phenol onto HMBP-Mt [33]	298	0.016	L/mg	10.31	-14.48	-83.21
	313	0.012	L/mg	11.59		
	328	0.009	L/mg	12.80		
	298	1.47	L/mmol	-0.95	-14.48	-45.42
	313	1.10	L/mmol	-0.24		
	328	0.86	L/mmol	0.41		
	298	15.59	L/g	-6.81	-14.48	-25.77
	313	11.64	L/g	-6.39		
	328	9.14	L/g	-6.03		
	298	1467	*L/mol	-18.06	-14.48	12.01
	313	1096	*L/mol	-18.21		
	328	860	*L/mol	-18.43		

estimate thermodynamic parameters of adsorption. However, the calculation of thermodynamic parameters of adsorption by the Langmuir equilibrium constant is faced by challenges since the values of  $K_L$  reported in many studies have variable units (L/mol, L/g, L/mg, L/mmol, etc) were used to estimate adsorption thermodynamic parameters [30–33]. Since obtained thermodynamic parameters depend on the units for  $K_L$ , there is non-uniformity concerning the reported thermodynamic values, where some typical examples [30–33] are shown in Tables 1 and (S1). Accordingly, it can be seen that the magnitude of thermodynamic parameters changes in accordance with the variable units for  $K_L$ . Therefore, judging whether the adsorption process is spontaneous or nonspontaneous is largely affected by the unit scale of  $K_L$ . In some cases the value of  $\Delta S_{ad}^\circ$  is positive or negative depending on choice of units (Table 1)!

Furthermore, a parameter with dimensional units is not expressed reliably in logarithm coordinates. As well, the requirements of the International Union of Pure and Applied Chemistry (IUPAC) for estimation of  $\Delta G_{ad}^\circ$  should use a dimensionless  $K^\circ$  term [34]. More recently, further attention to this problem has led to other proposed methods to address the above shortcoming [27,29,35–40]. The lack of a unified method for estimation of thermodynamic parameters represents an important knowledge gap in this field, as evidenced by limited theoretical background to address this issue.

As outlined above, the Langmuir adsorption isotherm was derived for gas phase adsorption processes with subsequent application for liquid phase systems. Uncertainty regarding the “applicability of the Langmuir isotherm to adsorption processes from the liquid phase” has been noted. In this study, we provide a new insight into applicability of the Langmuir isotherm model for liquid phase adsorption processes. The approach described herein leads to an improved theoretical basis for estimation of adsorption thermodynamic parameters.

## 2. Theoretical background

Nearly a century ago, Langmuir [9] proposed a seminal adsorption isotherm theory that used a kinetic approach to describe a reversible adsorption and desorption process for “A” species from the gas phase



where “V” and “ $A_{ad}$ ” are the vacant and occupied sites, respectively.  $k_a$

and  $k_d$  are the rate constants of adsorption and desorption, respectively. The respective rate and rate constants in parentheses for the adsorption ( $r_a, k_a$ ) and desorption ( $r_d, k_d$ ) steps are defined below:

$$r_a = k_a p(1-\theta) \quad (5)$$

$$r_d = k_d \theta \quad (6)$$

where  $p$  is the pressure and  $\theta$  is the surface coverage.  $\theta = q/q_m$ , where  $q$  and  $q_m$  are the adsorbed amount per unit mass of adsorbent and the monolayer adsorption capacity, respectively.

At equilibrium, Eqs. (5) and (6) yield the Langmuir isotherm model since  $r_a = r_d$ .

$$\theta_e = \frac{K_L p_e}{1 + K_L p_e} \quad \text{or} \quad q_e = \frac{q_m K_L p_e}{1 + K_L p_e} \quad (7)$$

The subscript “e” denotes an equilibrium state and  $K_L$  ( $k_a/k_d$ ) is the Langmuir equilibrium constant. The Langmuir model for gas phase processes was applied for adsorption from solution by replacing the pressure term with solute concentration ( $C$ ) by the following equations:

$$r_a = k_a C(1-\theta) \quad (8)$$

$$r_d = k_d \theta \quad (9)$$

At equilibrium,  $r_a = r_d$ , two forms of the Langmuir model are defined by equation (10).

$$\theta_e = \frac{K_L C_e}{1 + K_L C_e} \quad \text{or} \quad q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (10)$$

## 3. Modification of Langmuir model

A revised form of the Langmuir isotherm can be obtained by revision of Eq. (9). Inspection reveals that the rate of desorption is proportional to the fraction of available vacant sites ( $1 - \theta$ ), along with the concentration of solute ( $C$ ) in solution. The forward adsorption process approaches zero as the available vacant sites become occupied by the adsorbate. As the surface sites of the adsorbent are saturated by the solute  $\theta = 1$ , there are no available vacant sites for adsorption. The term  $(1 - \theta)$  in Eq. (8) serves as a limiting factor for the forward kinetic adsorption process. In Eq. (9), the rate of desorption depends on the surface coverage ( $\theta$ ), where the concentration of solute has no effect on desorption. It follows that there is uncertainty concerning the effect of solute concentration on the desorption rate. Based on statistical rate theory [4,41–43], the driving force for desorption is related to a difference in chemical potential ( $\mu_s - \mu_b$ ) of “A” species in adsorbed phase ( $\mu_s$ ) and the solution phase ( $\mu_b$ ). Thus, bulk concentration is an effective parameter on the desorption process. To achieve a better understanding of the desorption process, three types of systems are considered in Fig. 1; adsorbents with similar surface coverage are brought into contact with solutions containing an adsorptive at variable concentration. According to the Langmuir model, the rate of desorption for these systems in Fig. 1 should be similar since the rate of desorption is proportional to  $\theta$  and each system has a similar  $\theta$ -value. By contrast, the solute chemical potential in solution ( $\mu_b$ ) differs for each system. The tendency of ad-species to be desorbed is higher in the systems with lower bulk concentration (lower  $\mu_b$ ; Fig. 1a). Similarly, the tendency of ad-species for desorption differs for the systems in Fig. 1b, c. Since, the bulk concentration of solute in the liquid phase was not addressed by the conventional Langmuir kinetic model, where similar desorption rates are predicted in Fig. 1.

To this end, it should be mentioned that the rate of adsorption (forward process) is proportional to the number of available vacant sites on the surface of adsorbent. The rate of forward process approach zero once the adsorbent surface is saturated by an ad-layer. By contrast, desorption is inversely related to adsorption processes where adsorbates are transferred from the adsorbed state to bulk solution. In the case of desorption processes, the concentration of solute in bulk

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