

Research Article

Improper Estimation of Thermodynamic Parameters in Adsorption Studies with Distribution Coefficient K_D (q_e/C_e) or Freundlich Constant (K_F): Considerations from the Derivation of Dimensionless Thermodynamic Equilibrium Constant and Suggestions

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Adsorption processes often include three important components: kinetics, isotherm, and thermodynamics. In the study of solid–liquid adsorption, “standard” thermodynamic equilibrium constant (K_{Eq}^0 ; dimensionless) plays an essential role in accurately calculating three thermodynamic parameters: the standard Gibbs energy change (ΔG° ; kJ/mol), the standard change in enthalpy (ΔH° ; kJ/mol), and the standard change in entropy [ΔS° ; J/(mol × K)] of an adsorption process. Misconception of the derivation of the K_{Eq}^0 constant that can cause calculative errors in values (magnitude and sign) of the thermodynamic parameters has been intensively reflected through certain kinds of papers (i.e., letters to editor, discussions, short communications, and correspondence like comment/rebuttal). The distribution coefficient (K_D) and Freundlich constant (K_F) have been intensively applied for calculating the thermodynamic parameters. However, a critical question is whether K_D or K_F is equal to K_{Eq}^0 . This paper gives (1) thorough discussion on the derivation of thermodynamic equilibrium constant of solid–liquid adsorption process, (2) reasonable explanation on the inconsistency of (direct and indirect) application of K_D or K_F for calculating the thermodynamic parameters based on the derivation of K_{Eq}^0 , and (3) helpful suggestions for improving the quality of papers published in this field.

1. Introduction

In the studies of adsorption, adsorption thermodynamic plays an important role in estimating adsorption mechanism (physisorption or chemisorption). Adsorption processes in solid–liquid phases actually contain at least three important components: adsorbent (solid), adsorbate (solute), and water (solvent). However, the derivation of the standard thermodynamic equilibrium constant (K_{Eq}^0) is explained in many different ways in the literature [1–6]. When K_{Eq}^0 is applied for calculating the thermodynamic parameters (i.e., ΔG° , ΔH° , and ΔS°) of an adsorption process, the standard state conditions of this process must be defined [5, 7]. The misconception of such derivation can lead

to misapplying the relevant constants of adsorption equilibrium. As a result, the thermodynamic parameters are calculated without physical meanings. Therefore, it is necessary to give further discussion and considerable concerns on its derivation (K_{Eq}^0) in the field of adsorption (solid and liquid phases).

Recently, there are a remarkably increasing number of publications regarding the application of the distribution coefficient (K_D) [8–13] or the Freundlich constant (K_F) [14–17] as K_{Eq}^0 for calculating the thermodynamic parameters of a liquid–solid adsorption process. This is because the distribution coefficient obtained at different solution temperatures is often measured very fast and simply in laboratories. Meanwhile, the Freundlich model is more suitable for describing adsorption

processes that do not reach a strict plateau region in adsorption isotherms. In essence, adsorption isotherms describe the relationship: $q_e = f(C_e)$ [18]. Simultaneously, many scholars give some critical comments on this problem [7, 19–21]. The question is whether the thermodynamic parameters that are calculated based on the distribution coefficient or the Freundlich constant bring physical meanings. Notably, several relevant updated information is also provided herein.

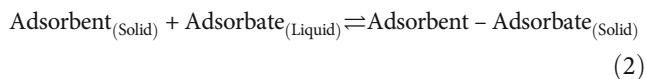
In any adsorption study, the amount of substance (adsorbate) adsorbed by solid material (adsorbent) at adsorption equilibrium (q_e ; mol/kg) is commonly calculated from Equation (1). The units of q_e (mol/kg) and C_e (mol/L) are used in this study based on previous suggestions [22–27]. Notably, the thermodynamic parameters need to be reported under the standard states [7, 28]. In this work, the superscript symbol ($^\circ$) represents the standard states, and the subscript abbreviation “Eq” means equilibrium. For convenience, the maximum adsorption capacity of adsorbent toward adsorbate (mol/kg) is abbreviated as MAC. The adsorption equilibrium constant of relevant model is abbreviated as AEC.

$$q_e = \frac{C_o - C_e}{m} V \quad (1)$$

where C_o and C_e (mol/L) are the concentrations of adsorbate at beginning and after adsorption equilibrium, respectively; m (kg) is the dried mass of adsorbent used; and V (L) is the volume of adsorbate solution.

2. Derivation of Standard Thermodynamic Equilibrium Constant

Adsorption process can be considered as a heterogeneous chemical equilibrium [2, 29–31]. Although this definition is always correct for all cases [3], it is acknowledged by the community in the field of adsorption. Therefore, chemical equilibrium between adsorption (\rightarrow) and desorption (\leftarrow) processes of adsorbate by adsorbent can be generally expressed as Equation (2) [21]. Detail discussion on this derivation has been reported by Lima and colleagues [21]. Early, some authors have reported other equations principally similar to Equation (2) [1, 32, 33].



In thermodynamics, the derivation of the thermodynamic equilibrium constant should be started from chemical potentials [2]. However, in this study, equilibrium constant is initially introduced to facilitate tracking by readers. Equilibrium constant is usually defined in the terms of activity (a ; unitless) rather than actual concentration in molar [2, 30, 34, 35].

The activities of the adsorption sites in adsorbent occupied by adsorbate ($a_{\text{Adsorbent-Adsorbate}}$), vacant adsorption sites in adsorbent ($a_{\text{Adsorbent}}$), and adsorbate in solution ($a_{\text{Adsorbate}}$) are defined in Equations (3), (4), and (5), respectively [5].

$$a_{\text{Adsorbent-Adsorbate}} = [\text{Adsorbent-Adsorbate}]_{\text{Eq}} \times \gamma_{\text{Adsorbent-Adsorbate}} \quad (3)$$

$$a_{\text{Adsorbent}} = [\text{Adsorbent}]_{\text{Eq}} \times \gamma_{\text{Adsorbent}} \quad (4)$$

$$a_{\text{Adsorbate}} = [\text{Adsorbate}]_{\text{Eq}} \times \gamma_{\text{Adsorbate}} \quad (5)$$

In the book, Crittenden et al. [36] defined “ $\{i\}$ = activity or effective concentration of ionic species, mol/L (M)”. This is because of its definition based on an equation ($\{i\} = \gamma_i [i]$) similar to Equation (5) by considering “ $[i]$ = concentration of ionic species in solution, mol/L (M)”. Ghosal et al. [33] reported the unit of activity was both mol/L and mg/L. However, in chemical thermodynamics, activity must be a dimensionless quantity by definitions and is dependent on the selection of standard states. Therefore, to obtain a strict correction, the concentrations (in molar) of the adsorbent–adsorbate [Adsorbent–Adsorbate], adsorbent [Adsorbent], adsorbate [Adsorbate] need to be reported corresponding to reference states [1, 27, 30, 37, 38]. Because both activity coefficient (γ) and activity (a) are dimensionless quantities (actually unitless) [30, 39], Equations (3), (4), and (5) are expressed as Equations (6), (7), and (8), respectively. The relevant information can be found in reference papers [27, 33], textbook [30], and IUPAC report [40].

$$a_{\text{Adsorbent-Adsorbate}} = \frac{[\text{Adsorbent-Adsorbate}]_{\text{Eq}}}{[\text{Adsorbent-Adsorbate}]^\circ} \times \gamma_{\text{Adsorbent-Adsorbate}} \quad (6)$$

$$a_{\text{Adsorbent}} = \frac{[\text{Adsorbent}]_{\text{Eq}}}{[\text{Adsorbent}]^\circ} \times \gamma_{\text{Adsorbent}} \quad (7)$$

$$a_{\text{Adsorbate}} = \frac{[\text{Adsorbate}]_{\text{Eq}}}{[\text{Adsorbate}]^\circ} \times \gamma_{\text{Adsorbate}} \quad (8)$$

where $\gamma_{\text{Adsorbent-Adsorbate}}$, $\gamma_{\text{Adsorbent}}$, and $\gamma_{\text{Adsorbate}}$ (dimensionless) are the corresponding activity coefficient of adsorbent–adsorbate, adsorbent, and adsorbate, respectively. The activity coefficient in the solid phase includes $\gamma_{\text{Adsorbent-Adsorbate}}$ and $\gamma_{\text{Adsorbent}}$ and that in the liquid phase is $\gamma_{\text{Adsorbate}}$.

Notably, the concentration of the solid phase of adsorbent–adsorbate [Adsorbent–Adsorbate] needs to be expressed in the term of surface coverage fraction (θ) that is the ratio of the number of occupied (or filled) adsorption sites to the number of total (or available) adsorption sites in adsorbent (Equation (9)). Similarly, the concentration of the solid phase of adsorbent [Adsorbent] is defined as the fraction of available adsorption sites in adsorbent ($1 - \theta$; Equation (10)) [1, 3–5, 37, 41].

$$[\text{Adsorbent-Adsorbate}]_{\text{Eq}} = \frac{\text{Number of filled adsorption sites}}{\text{Number of total adsorption sites}} = \theta \quad (9)$$

$$[\text{Adsorbent}]_{\text{Eq}} = \frac{\text{Number of vacant adsorption sites}}{\text{Number of total adsorption sites}} = 1 - \theta \quad (10)$$

After substituting Equations (9) and (10) into Equation (6)

and (7), Equations (11) and (12) are obtained, respectively.

$$a_{\text{Adsorbent-Adsorbate}} = \frac{\theta}{[\text{Adsorbent-Adsorbate}]^{\circ}} \times \gamma_{\text{Adsorbent-Adsorbate}} \quad (11)$$

$$a_{\text{Adsorbent}} = \frac{1 - \theta}{[\text{Adsorbent}]^{\circ}} \times \gamma_{\text{Adsorbent}} \quad (12)$$

According to IUPAC [42], the activity (a ; unitless) is defined as Equation (13). Therefore, the chemical potentials of the adsorbent ($\mu_{\text{Adsorbent}}$) and adsorbate ($\mu_{\text{Adsorbate}}$) are expressed as Equations (14) and (15), respectively. When adsorption process reaches equilibrium, the chemical potential of adsorbent-adsorbate ($\mu_{\text{Adsorbent-Adsorbate}}$) is given as Equation (16) [2, 34].

$$a = e^{\mu - \mu^{\circ}/RT} = \exp(\mu - \mu^{\circ}/RT) \quad (13)$$

$$\mu_{\text{Adsorbent}} = \mu_{\text{Adsorbent}}^{\circ} + RT \ln a_{\text{Adsorbent}} \quad (14)$$

$$\mu_{\text{Adsorbate}} = \mu_{\text{Adsorbate}}^{\circ} + RT \ln a_{\text{Adsorbate}} \quad (15)$$

$$\mu_{\text{Adsorbent-Adsorbate}} = \mu_{\text{Adsorbent-Adsorbate}}^{\circ} + RT \ln a_{\text{Adsorbent-Adsorbate}} \quad (16)$$

where R is the universal gas constant [8.31446]/(mol \times K)] and T is the absolute temperature of adsorption process in the kelvin unit with its symbol of K (kelvin = 273.15 + Celsius) [42]; μ is chemical potential (J/mol or kJ/mol) that is equal to ΔG ; μ° is standard chemical potential (equal to ΔG°) depending on the selection of the standard state [28]; and $\mu_{\text{Adsorbent}}^{\circ}$, $\mu_{\text{Adsorbate}}^{\circ}$, and $\mu_{\text{Adsorbent-Adsorbate}}^{\circ}$ are the standard chemical potentials of the adsorbent, adsorbate, and adsorbent-adsorbate in their standard states, respectively.

In essence, Gibbs energy change is initially introduced by American mathematician Josiah Willard Gibbs in the 1870's; 1839–1903). Although the appellation of the Gibbs "free" energy change has been widely used in the literature, it is not suitable or even not real [43]. The term recommended by IUPAC [42] is "the standard Gibbs energy change" for ΔG° . Therefore, the appellation of "free" is not used in this study. Similar to the Gibbs energy change of reaction (Equation (17)), the Gibbs energy change of adsorption process (ΔG_{ads}) is commonly expressed as Equation (18) [2]. By replacing Gibbs energy changes ($\Delta G_{\text{Adsorbent-Adsorbate}}$, $\Delta G_{\text{Adsorbent}}$, and $\Delta G_{\text{Adsorbate}}$) by chemical potentials ($\mu_{\text{Adsorbent-Adsorbate}}$, $\mu_{\text{Adsorbent}}$, and $\mu_{\text{Adsorbate}}$, respectively), Equation (18) becomes Equation (19).

$$\Delta G_{\text{reaction}} \text{ (or } \Delta_r G) = \Delta G_{\text{products}} - \Delta G_{\text{reactants}} \quad (17)$$

$$\Delta G_{\text{ads}} = \Delta G_{\text{Adsorbent-Adsorbate}} - (\Delta G_{\text{Adsorbate}} + \Delta G_{\text{Adsorbent}}) \quad (18)$$

$$\Delta G_{\text{ads}} = \mu_{\text{Adsorbent-Adsorbate}} - (\mu_{\text{Adsorbent}} + \mu_{\text{Adsorbate}}) \quad (19)$$

By substituting Equations (14)–(16) into Equation (19), Equation (20) is obtained.

$$\Delta G_{\text{ads}} = \mu_{\text{Adsorbent-Adsorbate}}^{\circ} - (\mu_{\text{Adsorbent}}^{\circ} + \mu_{\text{Adsorbate}}^{\circ}) + RT \ln \left(\frac{a_{\text{Adsorbent-Adsorbate}}}{a_{\text{Adsorbent}} \times a_{\text{Adsorbate}}} \right) \quad (20)$$

Similar to ΔG_{ads} , the standard Gibbs energy change of adsorption process ($\Delta G_{\text{ads}}^{\circ}$) is defined in Equation (21), so Equation (20) can be expressed as Equation (22) [2, 44]. In this equation, the so-called thermodynamic reaction quotient that is often used under non-equilibrium condition is defined as Equation (23).

$$\Delta G_{\text{ads}}^{\circ} = \mu_{\text{Adsorbent-Adsorbate}}^{\circ} - (\mu_{\text{Adsorbent}}^{\circ} + \mu_{\text{Adsorbate}}^{\circ}) \quad (21)$$

$$\Delta G_{\text{ads}} = \Delta G_{\text{ads}}^{\circ} + RT \ln Q \quad (22)$$

$$Q = \frac{a_{\text{Adsorbent-Adsorbate}}}{a_{\text{Adsorbent}} \times a_{\text{Adsorbate}}} \quad (23)$$

When adsorption reaches equilibrium, the numerical values of Q becomes K_{Eq}° [2, 44]. In this case, the standard dimensionless thermodynamic equilibrium constant (K_{Eq}° ; Equation (24)) is similar to the reaction quotient.

$$K_{\text{Eq}}^{\circ} = \frac{a_{\text{Adsorbent-Adsorbate}}}{a_{\text{Adsorbent}} \times a_{\text{Adsorbate}}} \quad (24)$$

Equation (24) was firstly reported by Graham [32] and then by many scholars [1, 5, 21, 22, 33]. When Equations (8), (11), and (12) are substituted into Equation (24), Equation (25) is obtained as follows:

$$K_{\text{Eq}}^{\circ} = \frac{((\theta/[\text{Adsorbent-Adsorbate}]^{\circ})\gamma_{\text{Adsorbent-Adsorbate}})}{((1 - \theta/[\text{Adsorbent}]^{\circ})\gamma_{\text{Adsorbent}}) \times \left(([\text{Adsorbate}]_{\text{Eq}}/[\text{Adsorbate}]^{\circ})\gamma_{\text{Adsorbate}} \right)} \quad (25)$$

The reference states for pure solvents and pure solids with a mole fraction are unity [30, 34]. According to IUPAC [40, 42, 45], the recommended value for the standard molality related to the standard thermodynamic quantities is 1 mol/kg. Therefore, $[\text{Adsorbent-Adsorbate}]^{\circ}$ and $[\text{Adsorbent}]^{\circ}$ are often assumed to be 1 mol/kg in most studies of adsorption [2, 5]. Meanwhile, the solid-phase activity coefficient ($\gamma_{\text{Adsorbent-Adsorbate}}$ and $\gamma_{\text{Adsorbent}}$) can be determined by the Wilson equation [46–51]. For example, in the adsorption study of metal ions (Zn^{2+} , Cu^{2+} , Cd^{2+} , and Na^{+}) using the cationic exchanger Amberlite IR-120, Valverde et al. [47] applied the Wilson equation and the Pitzer limiting law equation to determine the activity coefficient in the solid and liquid phases, respectively. However, for many adsorption cases, the solid-phase activity coefficient is not easy to be correctly estimated by the Wilson equation [51], especially for the case of adsorption isotherm (macroscopic equilibrium). Therefore, many scholars assumed that the activity coefficient of the occupied adsorption sites ($\gamma_{\text{Adsorbent-Adsorbate}}$) is similar to that of the vacant adsorption sites ($\gamma_{\text{Adsorbent}}$) when adsorption process reaches equilibrium [1, 22, 32]. Furthermore, Lin and Juang [35] assumed that the ratio ($\gamma_{\text{Adsorbent-Adsorbate}}/\gamma_{\text{Adsorbent}}$) was nearly maintained a constant under same experiment conditions when they applied

mass action law (microscopic equilibrium) for determining the thermodynamic equilibrium constant of ion exchange process. As a result of such discussion, Equation (21) can reduce to a simple form (Equation (26)) when adsorption process reaches equilibrium.

$$K_{\text{Eq}}^{\circ} = \frac{\theta}{(1 - \theta) \left([\text{Adsorbate}]_{\text{Eq}} / [\text{Adsorbate}]^{\circ} \right) \gamma_{\text{Adsorbate}}} \quad (26)$$

In essence, when adsorption process reaches equilibrium ($\Delta G_{\text{ads}} = 0$ and $Q = K_{\text{Eq}}^{\circ}$; Equation (22)), the standard Gibbs energy change of adsorption process is directly calculated from Equation (27) [2, 44, 52]. K_{Eq}° can be expressed as Equation (28).

$$\Delta G_{\text{ads}}^{\circ} \text{ (commonly expressed as } \Delta G^{\circ}) = -RT \ln K_{\text{Eq}}^{\circ} \quad (27)$$

$$K_{\text{Eq}}^{\circ} = e^{-\Delta G^{\circ}/RT} = \exp \left(\frac{-\Delta G^{\circ}}{RT} \right) \quad (28)$$

The fundamental thermodynamic relation of three thermodynamic parameters (ΔG° , ΔH° , and ΔS°) is commonly expressed as follows:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (29)$$

Assuming that the changes in ΔS° and ΔH° with temperatures are negligible, after substituting Equation (27) into Equation (29), the nonlinear (Equation (30)) and linear (Equation (31)) forms of the well-known van't Hoff equation (not Van't Hoff or van't Hoof equation) [1, 52–55] are achieved. The van't Hoff equation was initially proposed by the Dutch chemist who is Jacobus Henricus van't Hoff (1852–1911).

$$K_{\text{Eq}}^{\circ} = \exp \left(\frac{-\Delta H^{\circ}}{R} \times \frac{1}{T} + \frac{\Delta S^{\circ}}{R} \right) \quad (30)$$

$$\ln K_{\text{Eq}}^{\circ} = \left(\frac{-\Delta H^{\circ}}{R} \right) \times \frac{1}{T} + \frac{\Delta S^{\circ}}{R} \quad (31)$$

In adsorption studies, the surface coverage fraction (θ) is often defined as Equation (32) [1, 3, 5, 32, 33, 37, 41]. When $[\text{Adsorbate}]_{\text{Eq}}$ and $[\text{Adsorbate}]^{\circ}$ are expressed as C_e (mol/L) and C° (mol/L), respectively, Equation (26) becomes Equation (33).

$$\theta = \frac{q_e}{Q_{\text{max}}} \quad (32)$$

$$K_{\text{Eq}}^{\circ} = \frac{q_e/Q_{\text{max}}}{(1 - (q_e/Q_{\text{max}})) \times (C_e/C^{\circ}) \times \gamma_{\text{Adsorbate}}} \quad (33)$$

or another expression as follows:

$$q_e = \frac{Q_{\text{max}} C_e \left(K_{\text{Eq}}^{\circ} (\gamma_{\text{Adsorbate}}/C^{\circ}) \right)}{\left[1 + \left(K_{\text{Eq}}^{\circ} (\gamma_{\text{Adsorbate}}/C^{\circ}) \right) C_e \right]} \quad (34)$$

Based on Equation (34), the constant K_L (L/mol) is established

as Equation (35) or (36). The well-known Langmuir model is achieved as Equation (37). Equation (36) was recently reported by Lima and co-workers [2]. However, a similar form of this equation has been early published by some other scholars [1, 5, 22].

$$K_L = K_{\text{Eq}}^{\circ} \frac{\gamma_{\text{Adsorbate}}}{C^{\circ}} \quad (35)$$

$$K_{\text{Eq}}^{\circ} = \frac{K_L}{\gamma_{\text{Adsorbate}}} C^{\circ} \quad (36)$$

$$q_e = \frac{Q_{\text{max}} K_L C_e}{1 + K_L C_e} \quad (37)$$

where Q_{max} (mol/kg) that is the MAC is obtained when $C_e \rightarrow C_s$; K_L (L/mol) is the Langmuir adsorption equilibrium constant; and C_e (mol/L) and q_e (mol/kg) are previously defined in Equation (1). The parameter C_s (mg/L or mol/L) is defined as the solute solubility (or the liquid phase concentration at saturation). For example, Seifkar and Azizian [56] reported that the saturation concentration of methyl violet dye in liquid phase (C_s) was 33,000 mg/L.

Equation (36) describes the relationship between the constant K_L (L/mol) of the Langmuir model and the standard thermodynamic equilibrium constant K_{Eq}° . The constant K_L (L/mol) is more appropriate for calculating the thermodynamic parameters (ΔG° , ΔH° , and ΔS°) of the solid–liquid adsorption process with physical meanings. The units of adsorption isotherm that is the plot of q_e versus C_e should be presented as mol/kg versus mol/L, respectively [24, 27].

Clearly, the magnitude K_{Eq}° (Equations (36)) is not only strongly dependent on the Langmuir adsorption equilibrium constant K_L but also C° and $\gamma_{\text{Adsorbate}}$. According to IUPAC [40, 42, 45], “the recommended value for standard thermodynamic quantities is $C^{\circ} = 1 \text{ mol dm}^{-3}$ ” (or $C^{\circ} = 1 \text{ mol/L}$). In the adsorption studies of solid–liquid phases, the standard concentration (C°) is 1 mol/L as reported by many scholars [2, 5, 7, 8, 22, 27, 57–61].

Some authors suggested the effect of the activity coefficient of adsorbate ($\gamma_{\text{Adsorbate}}$) can be negligible under dilute ionic solution or non-ionic solute at low concentrations [5, 33]. Similarly, Hemond and Fechner [62] concluded that $\gamma_{\text{Adsorbate}}$ is very close to 1 within an ionic strength lower than 0.001 M; therefore, its effect can be ignored in freshwater environments. For example, Moreno-Marenco et al. [63] selected $\gamma_{\text{Adsorbate}}$ as unitary for the adsorption process of *n*-butylparaben onto activated carbon within initial adsorbate solutions from 0.10 to 1.03 mmol/L (without the presence of NaCl).

In contrast, the activity coefficient of charged adsorbates is commonly calculated according to the (extended) Debye–Hückel equation [8, 35, 37, 64]. Some other methods have been applied to estimate the activity coefficient in liquid phase such as the Pitzer method [35, 47, 51, 64] and Davies equation [35]. Each method often involves some limitations and is effective for a certain range of ionic strengths, so researchers should select what the best method for their investigations is.

For example, when ion exchange is a primary adsorption mechanism, Lin and Juang [35] compared the thermodynamic parameters of the adsorption process of Cu^{2+} ions by two

TABLE 1: Thermodynamic parameters for the process of Cu^{2+} adsorption by two resins (Chelex 100 and IRC 748) [35].

T (K)	Chelex 100 resin				IRC 748 resin			
	K_{Eq}°	ΔG°	ΔH°	ΔS°	K_{Eq}°	ΔG°	ΔH°	ΔS°
1. Based on the extended Debye–Hückel equation								
288	0.00258	14.27	39.65	88.11	0.00283	14.05	40.81	92.83
298	0.00439	13.45	$(y = -4769x + 10.6)$		0.00494	13.16	$(y = -4908x + 11.2)$	
308	0.00793	12.39	$(r^2 = 0.9974)$		0.00833	12.26	$(r^2 = 0.9996)$	
318	0.01200	11.69			0.01420	11.25		
2. Based on the Davies equation								
288	0.00354	13.51	39.50	90.23	0.00387	13.30	40.67	94.99
298	0.00602	12.67	$(y = -4751x + 10.9)$		0.00676	12.38	$(y = -4892x + 11.4)$	
308	0.01080	11.60	$(r^2 = 0.9978)$		0.01140	11.46	$(r^2 = 0.9997)$	
318	0.01640	10.87			0.01930	10.44		
3. Based on the Pitzer method								
288	0.00389	13.29	39.94	92.52	0.00424	13.08	41.40	98.24
298	0.00661	12.44	$(y = -4804x + 11.1)$		0.00743	12.15	$(y = -4980x + 11.8)$	
308	0.01200	11.33	$(r^2 = 0.9976)$		0.01260	11.20	$(r^2 = 0.9993)$	
318	0.01830	10.58			0.02180	10.11		

Note: The unit of ΔG° (kJ/mol), ΔH° (kJ/mol), and ΔS° [J/(mol·K)]; the information in parenthesis indicating the van't Hoff equation; and the activity coefficient of the cations in the aqueous phase in K_{Eq}° calculated by different methods (using the extended Debye–Hückel equation, Davies equation, and Pitzer method).

chelating ion exchange resins (Chelex 100 and IRC 748). The authors applied the extended Debye–Hückel limiting law, Davies equation, and Pitzer method to determine the activity coefficient of the cations in the aqueous phase. The result (Table 1) demonstrated that the signs of thermodynamic parameters (ΔG° , ΔH° , and ΔS°) calculated based on the activity coefficients (determined by three methods) are the same, and their magnitudes are nearly identical.

Notably, all ΔG° values in Table 1 are positive. A question is whether the following conclusion (the adsorption was a non-spontaneous process) can be obtained. In essence, the sign of ΔG is often used as a criterion to evaluate the spontaneity of an adsorption process: ($-\Delta G$) spontaneous and ($+\Delta G$) non-spontaneous [24, 31, 43, 65–67]. A similar information is found in the textbook [55]: “*the sign of $\Delta_r G$ and not that of $\Delta_r G^{\circ}$ determines the direction of reaction spontaneity*”. However, in the literature, the spontaneity of adsorption processes is frequently reached based on the sign of ΔG° (Equation (27)) [12, 14, 16, 33, 37, 59, 63, 68–71].

Xiaofu et al. [67] suggested that “*it may not be appropriate to use ΔG° as a parameter for discussing the spontaneity of a reaction*”. They noted “ ΔG° for a reaction can be either positive, negative or zero” as follows: $\Delta G^{\circ} > 0$ (when $K_{\text{Eq}}^{\circ} < 1$), $\Delta G^{\circ} < 0$ ($K_{\text{Eq}}^{\circ} > 1$), and $\Delta G^{\circ} = 0$ ($K_{\text{Eq}}^{\circ} = 1$). Similarly, based on the equilibrium position of a given reaction (i.e., $A_{\text{Reactant}} \rightleftharpoons B_{\text{Product}}$), Shahwan [31] strongly concluded that “*the criterion of spontaneity of sorption must be based on ΔG , not on ΔG°* ”. Figure 1 shows that ΔG° can be negative, positive, or zero depending on the magnitude of K_{Eq}° [31, 38]. Under a given temperature, when K_{Eq}° is higher than unity, ΔG° (in Equation (27)) will be negative, and vice versa. Similarly, Lima et al. [66] suggested that negative ΔG° values (because of $K_{\text{Eq}}^{\circ} > 1$) imply

that Equation (2) tends to proceed in the forward direction (adsorption). In this case, “*adsorption is thermodynamically favourable to takes place*” [66].

Some researchers [3, 5] debated that “ ΔG° sign gives no information on the spontaneity of the process in non-standard conditions”. However, they suggested that the spontaneity of adsorption (based on ΔG°) is strongly dependent on the selection of the standard state [3, 5]. For instance, Salvestrini et al. [72] investigated the adsorption process of diclofenac onto activated carbon at different temperatures (288, 298, 308, 298, and 318 K) and reported the positive values of ΔG° (5.8, 7.6, 7.7, and 10.1 kJ/mol, respectively). This is because they selected 1 mg/g for solid phase and 1 mg/L for solute (as the standard states) and applied them for calculating K_{Eq}° derived from the Langmuir constant (Table 2). If the selected standard states are 1 mol/kg for solid phase and 1 mol/L for solute, the ΔG° values will be negative (Table 2). The concluded suggested the sign of ΔG° is also strongly dependent on the selected standard state and then the magnitude of K_{Eq}° (i.e., $K_{\text{Eq}}^{\circ} > 1$ leading to $\Delta G^{\circ} < 0$; Equation (27). The selection of standard states does not affect the sign and magnitude of ΔH° (Table 2). However, there is not any convincing reason to explain why the authors [72] selected the standard states (1 mg/g for solid phase and 1 mg/L for solute) instead of 1 mol/kg and 1 mol/L. In the literature, other researchers [4] selected the different values for the standard state of adsorbate (i.e., 1 mg/L, 1 g/L, 1 mmol/L, and 1 mol/L; Table 3) when they applied Equation (36) for describing the relationship between K_L and K_{Eq}° . Another opinion is regarded to the solubility of adsorbate. Saeed et al. [73] selected the standard state of dye C as the solubility value of methylene blue dye

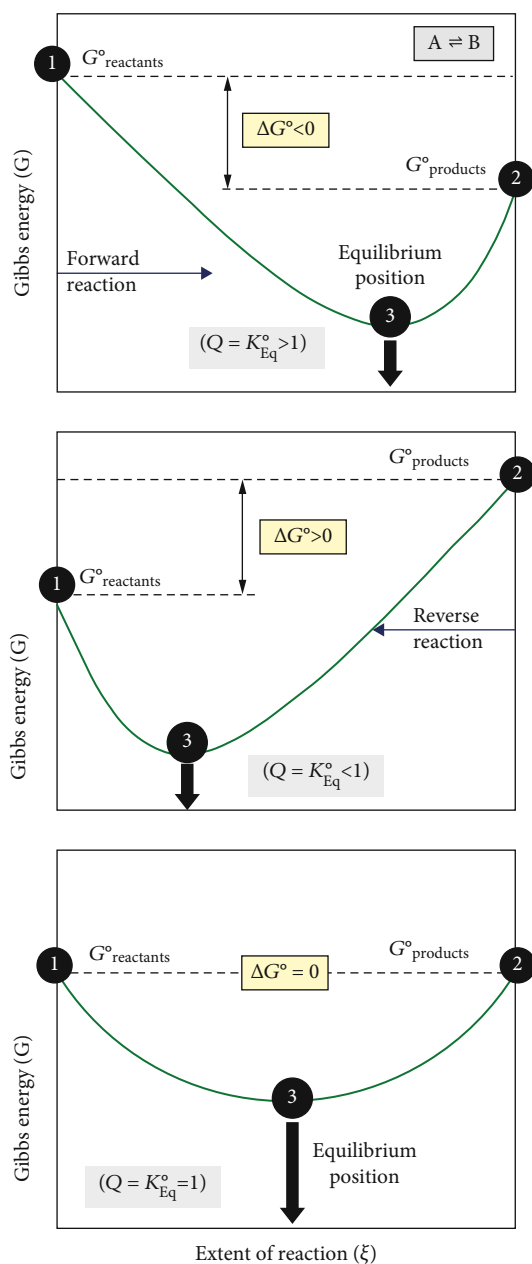


FIGURE 1: Gibbs energy (G) as function of the extent of reaction (ξ) for describing ΔG° (negative, positive, or zero). Adapted from the literature [31] with some modification.

at a given temperature, for example, 43,210 mg/L, 60,010 mg/L, and 83,430 mg/L at 298 K, 308 K, and 318 K, respectively. They explained that the value C° (1 mol/L \approx 319,850 mg/L) is overwhelmingly higher than the solubility of methylene blue dye. In essence, the standard state C° must be 1 mol/L as defined by IUPAC [40, 42, 45]. Therefore, scholars cannot freely select the value for the standard state C° .

To sum up, the standard thermodynamic equilibrium constant (K_{Eq}°) is always dimensionless (without any unit). This conclusion has been defined by the International Union of Pure and Applied Chemistry [39]. In fact, K_{Eq}° is dimensionless because the activity (a) in Equation (24) is dimen-

sionless. From Equation (27), the units of three parameters (ΔG° , R , and T , respectively) are kJ/mol, kJ/(mol \times K), and K; therefore, $\ln K_{\text{Eq}}^\circ$ (or K_{Eq}°) must be dimensionless. Those discussions have been also stated by many scholars [21, 33, 52, 74, 75]. Adsorption processes in solid–liquid phases (i.e., the adsorption of phenol by active carbon) actually contain at least three important components: adsorbent (active carbon that is solid), adsorbate (phenol that is solute), and water (solvent). K_{Eq}° should be only dependent on temperatures, but K_L is dependent on the concentrations of adsorbate. In addition, none of all experimental conditions of adsorption are conducted under strict standard conditions. Therefore, it is not easy to accurately determine the so-called “standard” thermodynamic parameters in liquid–phase adsorption systems. The so-called standard thermodynamic equilibrium constant might be obtained by considering some assumptions such as the standard references for pure solid and pure liquid phases being 1 mol/kg and 1 mol/L. Under such assumptions, the relationship between K_{Eq}° and K_L can be expressed as Equation (36).

3. Some Mistakes Regarding the Application of the Langmuir Constant for Calculating the Thermodynamic Parameters

The first problem involves the standard state for adsorbate concentration (C°) in Equation (36). Some researchers directly applied K_L (L/mg) as K_{Eq}° for calculating the thermodynamic parameters. In this case, the C° is tacitly selected as 1 mg/L [72]. This problem of this selection on the magnitudes (both sign and value) of thermodynamic parameters (i.e., Table 3) has been discussed in Section 2 and in the literature [4, 22, 23, 33].

Recently, Najafloo et al. [76] applied the Langmuir constant for calculating the thermodynamic parameters of Pb adsorption by cellulose sulfate/chitosan aerogel. To convert K_L from a dimensional constant to dimensionless one, they introduced a new conversation (Equation (38)). Clearly, this is a basic mistake. The authors understood incorrectly the unit of K_L that is liter per milligram of adsorbent (solid). The correction must be liter per milligram of adsorbate (solute). The unit of symbol m (defined in Equation (1)) is milligram of adsorbent (solid). The mass of adsorbate (in milligram) is remarkably different to that of adsorbent.

$$K_{\text{Eq}}^\circ = K_L \left(\frac{\text{L}}{\text{mg}} \right) \times \frac{m}{V} \left(\frac{\text{mg}}{\text{L}} \right)? \quad (38)$$

Reddy et al. [77] defined the equilibrium constant K (as Equation (39)) and applied it as K_{Eq}° for calculating the thermodynamic parameters of the adsorption of potential toxic metals ions onto the modified-biosorbent (derived from *Moringa oleifera* leaves). They expected that the constant K has a unit of L/g. Its unit is similar to that of the distribution coefficient K_D or the Henry constant. Therefore, the thermodynamic parameters (Table 4) calculated based on this constant K do not bring physical meanings compared to those

TABLE 2: Thermodynamic parameters for diclofenac adsorption onto F400 activated carbon [72].

T (K)	Selected standard states ($C^{\circ}=1$ mg/L?)				Selected standard states ($C^{\circ}=1$ mol/L)			
	K_L (L/mg)	ΔG°	ΔH°	ΔS°	K_L (L/mol)	ΔG°	ΔH°	ΔS°
288	0.087	5.85	-30.85	-127.5	25765	-24.33	-30.85	-22.75
298	0.047	7.58	$(y=176.8x - 0.532)$		13919	-23.65	$(y=3710.6x - 2.7361)$	
308	0.050	7.68	$(r^2=0.8629)$		14807	-24.60	$(r^2=0.8558)$	
318	0.022	10.10			6515	-23.23		

Note: The unit of ΔG° (kJ/mol), ΔH° (kJ/mol), and ΔS° [J/(mol·K)]; the information in parenthesis indicating the van't Hoff equation.

TABLE 3: Thermodynamic parameters for adsorbing phenol onto bispyridinium dibromides-modified montmorillonites.

T (K)	K_L	C°	K_{Eq}°	Thermodynamic parameters			Remarks
				ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° [J/(mol·K)]	
1. Case 1 (the units of K_L and C° are L/mg and mg/L)							
298	0.0156 L/mg	1 mg/L	0.0156	10.31	-14.48	-83.21	Modified and reported by [4]
313	0.0116 L/mg	1 mg/L	0.0116	11.59			
328	0.0091 L/mg	1 mg/L	0.0091	12.80			
2. Case 2 (the units of K_L and C° are L/mmol and mmol/L)							
298	1.467 L/mmol	1 mmol/L	1.467	-0.95	-14.48	-45.43	[4]
313	1.096 L/mmol	1 mmol/L	1.096	-0.24			
328	0.860 L/mmol	1 mmol/L	0.86	0.41			
3. Case 3 (the units of K_L and C° are L/g and g/L)							
298	15.59 L/g	1 g/L	15.59	-6.81	-14.48	-25.78	[4]
313	11.65 L/g	1 g/L	11.65	-6.39			
328	9.14 L/g	1 g/L	9.14	-6.03			
4. Case 4 (the units of K_L and C° are L/mol and mol/L)							
298	1467 L/mol	1 mol/L	1467	-18.06	-14.48	12.01	Originally published by [68]
313	1096 L/mol	1 mol/L	1096	-18.22			
328	860 L/mol	1 mol/L	860	-18.43			

TABLE 4: Thermodynamic parameters for adsorbing potential toxic metals ions by the modified-biosorbent.

	As reported by Reddy et al. [77]						As re-calculated by the author				
	Q_m (mg/g)	K_L (L/mg)	K (L/g)	ΔG°	ΔH°	ΔS°	K_L (L/mol)	K_{Eq}°	ΔG°	ΔH°	ΔS°
1. For adsorbing Cd(II)											
293 K	159.8	0.027	4.317	-3.56	14.61	61.89	3035	3035	-19.53	11.96	107.4
303 K	166.2	0.03	4.987	-4.05	$(r^2=0.9740)$		3372	3372	-20.47	$(r^2=0.9574)$	
313 K	171.4	0.037	6.341	-4.81			4159	4159	-21.69		
2. For adsorbing Cu(II)											
293 K	146.9	0.024	3.525	-3.07	12.33	52.61	1525	1525	-17.86	7.26	85.88
303 K	151.3	0.028	4.236	-3.64	$(r^2=0.9964)$		1779	1779	-18.85	$(r^2=0.8954)$	
313 K	167.9	0.029	4.869	-4.12			1843	1843	-19.57		
3. For adsorbing Ni(II)											
293 K	138.0	0.021	2.899	-2.59	10.00	42.94	1232	1232	-17.34	3.47	71.01
303 K	148.8	0.022	3.273	-2.99	$(r^2=0.9961)$		1291	1291	-18.05	$(r^2=0.999)$	
313 K	163.9	0.023	3.769	-3.45			1350	1350	-18.76		

Note: The unit of ΔG° (kJ/mol), ΔH° (kJ/mol), and ΔS° [J/(mol·K)].

on the Langmuir constant K_L (Table 4).

$$K(\text{L/g}) = Q_{\max} \left(\frac{\text{mg}}{\text{g}} \right) K_L \left(\frac{\text{L}}{\text{mg}} \right) \quad (39)$$

4. Derivation of the Distribution Coefficient and whether It Is Suitable for Applying the Calculation of Thermodynamic Parameters

Fifty years ago, Biggar and Cheung [78] developed the simple method for estimating the thermodynamic parameters of picloram adsorption by different soils. This method was later modified by Khan and Singh [79] for calculating the thermodynamic parameters of carbofuran adsorption by Sn(IV) arsenosilicate cation exchanger. The method modified by Khan and Singh [79] has been intensively applied in the literature later for calculating the thermodynamic parameters [9–12, 80]. Many researchers directly applied the distribution coefficient (K_D ; Equation (40)) as the standard thermodynamic equilibrium constant (K_{Eq}°) for calculating the thermodynamic parameters [7, 9, 10, 12]. In contrast, some others had converted the unit of K_D before it was applied for the calculation [80–82]. A critical question whether both cases (direct and indirect) are appropriate for obtaining the thermodynamic parameters consistent with physical meanings is also discussed in this paper.

According to Khan and Singh [79], the K_D value was obtained by plotting $\ln(q_e/C_e)$ versus q_e and extrapolating to zero q_e . The q_e and C_e parameters are defined in Equation (1). After that, a straight-line fitted into the experimental data (with a high r^2 value), and the intersection of the straight-line with the vertical axis provided the value of K_D . Clearly, the K_D value must be obtained from the different adsorbate concentrations of an adsorption isotherm [7]. The distribution coefficient K_D obtained from this method still has a certain unit such as L/g or L/kg as described in Equation (40) or Equation (41), respectively.

$$K_D = \frac{q_e}{C_e} = \frac{\text{mg/g}}{\text{mg/L}} = \frac{\text{L}}{\text{g (of adsorbent that is solid)}} \quad (40)$$

$$K_D = \frac{q_e}{C_e} = \frac{\text{mol/kg}}{\text{mol/L}} = \frac{\text{L}}{\text{kg (of adsorbent that is solid)}} \quad (41)$$

where C_e and q_e is defined in Equation (1), and their units— C_e (mg/L) and q_e (mg/g)—are selected in this section because they are the most common use in the literature.

A typical example expressing the idea of Khan and Singh [79] is provided by taking the full adsorption isotherm of methylene green dye by commercial activated carbon [24]. The full adsorption isotherm (the points of the equilibrium adsorption data: $n = 19$) is expressed in Figure 2(a). Based on the idea of Khan and Singh [79], the author continuously divided the full adsorption isotherm into two regions that (1) one is the adsorption isotherm containing outer points ($n = 7$) and (2) another is the adsorption isotherm obtained

by removing the outers ($n = 12$). The values K_D (linear method) and K_L (non-linear method) calculated based on the three regions are provided in Table 5. Table 6 indicates the thermodynamic parameters of the adsorption process calculated based on K_D and K_L . Although the sign of ΔG° , ΔH° , and ΔS° calculated based on K_D are relatively similar that based on K_L , their magnitudes based on K_D and K_L are different. An important question is how to define the standard state (i.e., C°) for K_D in Equation (40) or (41). This is because ΔG° , ΔH° , and ΔS° are defined as the standard thermodynamic parameters for an adsorption process. Notably, $\gamma_{\text{Adsorbate}}$ cannot be ignored in several adsorption cases (i.e., Table 1), but it is not defined in two equations: Equations (40) and (41).

However, many researchers commonly do the adsorption study at only one initial adsorbate concentration (C_0) and directly applied the q_e and C_e values (examined at different temperatures) for calculating K_D values [9, 10]. This is misconception from the method proposed by Khan and Singh [79]. Based on the raw data in Figure 2 [24], Table 7 shows the K_D values and the thermodynamic parameters were calculated at each adsorbate concentration under different temperatures. At one initial adsorbate concentration, after equilibrium adsorption, C_e and q_e values are obtained. The K_D value is differently calculated based on those C_e and q_e . The thermodynamic parameters obtained based on the K_D (in this table) do not bring any physical meanings.

In general, Equation (40) can be expressed as the one-parametric Henry model (Equation (42)). In this case, the Henry constant (K_H ; L/g) is equal to the distribution coefficient (K_D ; L/g). In essence, the Henry model is a specific case of the Freundlich model (Equation (43)) when the exponent n of the Freundlich model is unity. Moreover, when the concentration of adsorbate in solution (~infinite dilution) is extremely low (this means K_L and $C_e \ll 1.0$), the Langmuir model (Equation (44)) reduces to the linear Henry model (Equation (45)). Therefore, the constant K_D might be obtained when the concentrations of adsorbate in solution (C_e) after adsorption are very low [5, 7]. However, under this situation, the adsorption sites available in adsorbent are not fully covered by adsorbate. This means that adsorption process does not reach equilibrium in two phases (solid and liquid). Figure 3 that shows the different shapes of adsorption isotherm in solid-liquid phases adapted from the reference [83]. The constant K_H or K_D is identified in an unsaturated adsorption region in Figure 3. Under this region, the adsorbing sites available in adsorbent are not fully covered (or occupied) by adsorbate.

$$q_e = K_H C_e \text{ (Henry model)} \quad (42)$$

$$q_e = K_F C_e^n \text{ (Freundlich model)} \quad (43)$$

$$q_e = \frac{Q_{\max} K_L C_e}{1 + K_L C_e} \text{ (Langmuir model)} \quad (44)$$

$$q_e = Q_{\max} K_L C_e = K_H C_e \text{ (with } K_H = Q_{\max} \times K_L) \quad (45)$$

$$K_D = \frac{q_e}{C_e} = Q_{\max} K_L \text{ (obtained from Equation (44), when } C_e \rightarrow 0) \quad (46)$$

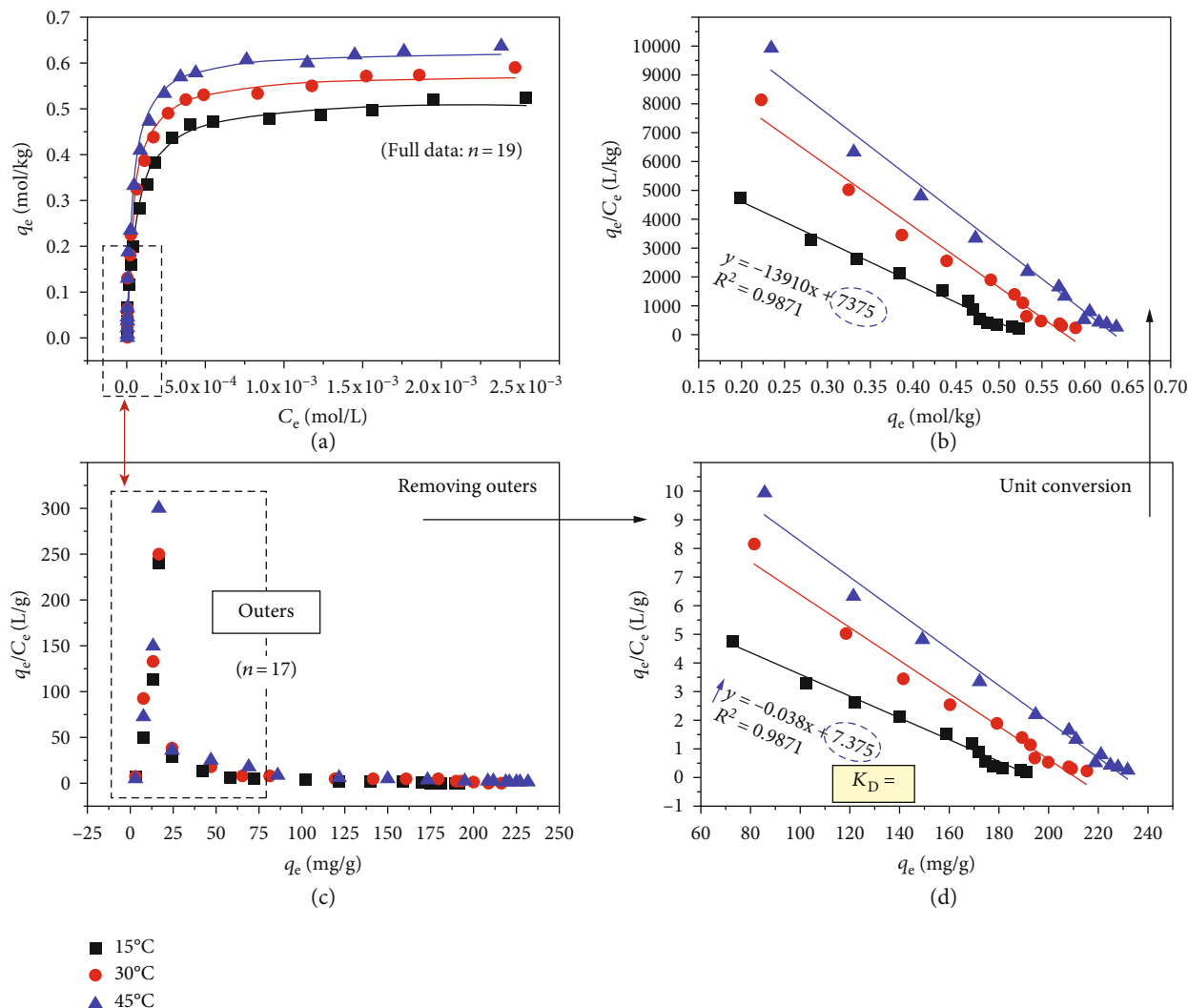


FIGURE 2: (a) Adsorption isotherm of methylene green dye onto commercial activated carbon [24]; and (b)–(d) the different plots of q_e/C_e vs. q_e for determining constant K_D .

TABLE 5: The calculating results for the constants K_D and K_L based on Figure 2.

T (K)	K_D (L/g)	When q_e (mg/g) vs. C_e (mg/L)			K_D (L/kg)	When q_e (mol/kg) vs. C_e (mol/L)		
		r^2	K_L (L/mg)	adj- R^2		r^2	K_L (L/mol)	adj- R^2
1. Full adsorption isotherm ($n=19$)								
288	71.50	0.2886	0.0440	0.9869	71500	0.2886	16068	0.9869
303	85.12	0.3511	0.0588	0.9901	85121	0.3511	21435	0.9901
318	92.93	0.3137	0.0706	0.9899	92926	0.3137	25751	0.9899
2. The outer region ($n=7$)								
288	97.79	0.1035	0.5427	0.8392	97794	0.1035	197972	0.8391
303	117.0	0.1581	0.5177	0.8635	116973	0.1581	188892	0.8635
318	123.9	0.1043	0.3270	0.8668	123897	0.1043	119318	0.8668
3. After removing the outer region ($n=12$) used for calculating the thermodynamic parameters								
288	7.375	0.9871	0.039	0.9961	7375	0.9871	14130	0.9961
303	12.17	0.9765	0.053	0.9952	12101	0.9765	19494	0.9952
318	14.50	0.9846	0.059	0.9977	14502	0.9846	21631	0.9977

TABLE 6: Thermodynamic parameters of the dye adsorption process (Figure 2) calculated based on K_D and K_L .

T (K)	When q_e (mg/g) vs. C_e (mg/L)					When q_e (mol/kg) vs. C_e (mol/L)				
	K_D (L/g)	K_L (L/mg)	ΔG°	ΔH°	ΔS°	K_D (L/kg)	K_L (L/mol)	ΔG°	ΔH°	ΔS°
1. Calculated based on K_D										
288	7.375	—	-4.785	17.29	77.02	7375	—	-21.33	17.29	134.4
303	12.17	—	-6.295	$(r^2=0.9425)$		12101	—	-23.68	$(r^2=0.9464)$	
318	14.50	—	-7.071			14502	—	-25.33		
2. Calculated based on K_L										
288	—	0.039	-22.88	10.89	117.5	—	14130	-22.88	10.89	117.5
303	—	0.053	-24.88	$(r^2=0.9347)$		—	19494	-24.89	$(r^2=0.9346)$	
318	—	0.059	-26.39			—	21631	-26.39		

Note: The unit of ΔG° (kJ/mol), ΔH° (kJ/mol), and ΔS° [J/(mol·K)]; the information in parenthesis indicating the van't Hoff equation; assuming K_D as K_{Eq}^o by Khan and Singh [79]; K_L (L/mol) being considered as K_{Eq}^o (when $C^*=1$ mol/L).

where K_H (L/g) is the Henry constant; Q_{max} (mg/g) is the Langmuir maximum adsorption capacity of an adsorbent under optimal operation conditions (pH, contact time, etc.) at a constant temperature; K_L (L/mg) is the Langmuir equilibrium constant; K_F is the Freundlich constant (mg/g)/(mg/L)ⁿ, and n is the exponent of the Freundlich model ($0 < n < 1$).

As shown in Equation (40), K_D is a dimensional coefficient, with a common unit being L/g. Therefore, it cannot be directly applied as the constant K_{Eq}^o for calculating the thermodynamic parameters. This problem has been intensively discussed in the literature [2, 7, 18–21, 84–86].

Some authors recommended to convert the unit of K_D (L/g) into K_{Eq}^o (no unit) by simply multiplying K_D value by 1000 (Equation (47)) [82, 87]. The author considered the density of pure water (ρ_{water}) is ~1.0 g/mL (equal to 1000 g/L). Such idea has been followed by some other researchers [70, 71, 75, 81]. Unfortunately, this suggestion is not correct, and the mistake has been thoroughly discussed elsewhere [2, 5, 58]. In fact, as shown in Equation (40), the unit of K_D is liters of solution per grams of adsorbent (not adsorbate!), so Equation (47) is misconception. This problem has been early identified and discussed by Liu [1].

$$K_{Eq}^o = K_D \times \rho_{water} = \frac{L}{g \text{ (of adsorbent)}} \times 1000 \frac{g \text{ (of water)}}{L} \quad (47)$$

Several other authors tried to convert the unit of K_D (L/g) into K_{Eq}^o (no unit) using Equation (48) or (49) [11, 12, 88]. A critical comment on this conversion method has been published by some authors [7, 89]. Similarly, Lima and co-workers [2] suggested that the K_D values obtained from Equation (48) or (49) cannot be applied as K_{Eq}^o for calculating the thermodynamic parameters.

$$K_{Eq}^o = K_D \times \left(\frac{m}{V}\right) = \left(\frac{q_e}{C_e}\right) \times \left(\frac{m}{V}\right) = \frac{L}{g \text{ (of adsorbent)}} \times \frac{g \text{ (of adsorbent)}}{L \text{ (of adsorbate)}} \quad (48)$$

$$K_{Eq}^o = K_D \times \left(\frac{m}{V}\right) = \left(\frac{q_e}{C_e}\right) \times \left(\frac{m}{V}\right) = \frac{(C_o - C_e)V}{C_e \times m} \times \frac{m}{V} = \frac{C_o - C_e}{C_e} \quad (49)$$

Furthermore, Zhou [80] recommended to apply Equation (50) and Equation (51) to convert the unit of K_D (L/g) into K_{Eq}^o (no unit). However, those two methods have not received the concerns and agreements of the communities in the field. The main reason of the disagreement has been thoroughly analysed by Rahmani-Sani and colleagues [90]. This is also main reason why the distribution coefficient K_D (not true adsorption equilibrium constant) cannot be used as the standard thermodynamic equilibrium constant K_{Eq}^o for calculating the thermodynamic parameters. The thermodynamic parameters that are calculated based on the distribution coefficient K_D do not bring physical meanings. An analogous conclusion has been claimed by some other scholars [1, 2, 5, 20, 21].

$$K_D = \frac{\Gamma \times a_{SA}}{C_e} = \frac{(kg/m^2) \times (1/m)}{kg/m^3} = \frac{kg/m^3 \text{ (of solid)?}}{kg/m^3 \text{ (of liquid)?}} \quad (50)$$

$$K_D = \frac{\Gamma}{t_{thickness} \times C_e} = \frac{kg/m^2 \text{ (of solid)?}}{m \times (kg/m^3 \text{ (of liquid)?})} \quad (51)$$

where Γ (kg/m²) is surface concentration; a_{SA} (1/m) is the surface area (m²) available for adsorption per unit volume (m³); C_e (mg/L or kg/m³) is the equilibrium concentration of adsorbate; and $t_{thickness}$ (m) is the thickness of the by Zhou adsorbed layer. The information was reported as reference [80].

On the basis of the Henry model (Equation (42)), Sawafta and Shahwan [91] proposed a method to estimate thermodynamic equilibrium constant of the adsorption process of methylene blue in water and water–ethanol solution by iron nanoparticles. The authors rearranged Equation (1) to obtain C_e as Equation (52), and the Henry model (Equation (42)) will become Equation (53). After rearranging, Equation (54) is obtained. The parameters (q_e , C_o , m , and V) in Equation (54) have been defined in Equation (1). They reported

TABLE 7: Thermodynamic parameters of the dye adsorption process (Figure 2) calculated based on K_D obtained at each initial adsorbate concentration under different temperatures.

C_o (mg/L)	When q_e (mg/g) vs. C_e (mg/L)						When q_e (mol/kg) vs. C_e (mol/L)												
	288 K	303 K	318 K	ΔG°	ΔH°	ΔS°	r^2	288 K	303 K	318 K	ΔG°	ΔH°	ΔS°	r^2					
Lowest	6.59	6.83	6.83	-4.52	-4.84	-5.08	0.90	18.85	0.774	6591	6824	6824	-21.06	-22.24	-23.34	0.90	76.27	0.774	
	50.64	92.55	73.71	-9.40	-11.41	-11.37	9.87	67.96	0.408	50640	92535	73700	-25.94	-28.81	-29.63	9.87	125.4	0.408	
	112.5	132.3	149.1	-11.31	-12.31	-13.23	7.17	64.19	0.996	112471	132354	149095	-27.85	-29.71	-31.50	7.17	121.6	0.996	
	239.7	249.6	299.8	-13.12	-13.91	-15.08	5.61	64.84	0.861	239742	249593	299814	-29.66	-31.31	-33.34	5.61	122.3	0.861	
	29.67	35.40	36.02	-8.12	-8.99	-9.48	4.98	45.69	0.838	29674	35402	36020	-24.66	-26.39	-27.74	4.98	103.1	0.838	
	12.27	16.78	24.94	-6.00	-7.10	-8.50	17.96	83.04	0.991	12267	16778	24936	-22.54	-24.51	-26.77	17.96	140.5	0.991	
	6.70	8.47	17.18	-4.55	-5.38	-7.52	23.70	97.41	0.907	6695	8470	17177	-21.09	-22.79	-25.78	23.70	154.9	0.907	
	4.75	8.13	9.93	-3.73	-5.28	-6.07	18.85	78.80	0.948	4748	8132	9930	-20.27	-22.68	-24.33	18.85	136.2	0.948	
	3.27	5.02	6.31	-2.83	-4.06	-4.87	16.77	68.29	0.979	3266	5016	6306	-19.38	-21.47	-23.13	16.77	125.7	0.979	
	2.61	3.43	4.81	-2.30	-3.11	-4.15	15.41	61.37	0.992	2615	3431	4806	-18.84	-20.51	-22.42	15.41	118.8	0.992	
	2.12	2.55	3.33	-1.80	-2.36	-3.18	11.42	45.78	0.982	2121	2551	3332	-18.34	-19.76	-21.45	11.42	103.2	0.982	
	1.51	1.88	2.20	-0.99	-1.58	-2.08	9.53	36.57	0.997	1512	1876	2199	-17.53	-18.99	-20.35	9.53	94.01	0.997	
	1.15	1.39	1.66	-0.34	-0.83	-1.35	9.36	33.64	0.999	1150	1389	1663	-16.88	-18.23	-19.61	9.36	91.08	0.999	
	0.86	1.08	1.33	0.35	-0.20	-0.75	10.98	36.89	0.999	862	1082	1329	-16.19	-17.60	-19.02	10.98	94.32	0.999	
	0.53	0.64	0.79	1.53	1.14	0.61	10.39	30.67	0.994	527	637	795	-15.01	-16.26	-17.66	10.39	88.11	0.994	
	0.39	0.47	0.52	2.23	1.93	1.73	7.06	16.83	0.993	396	465	521	-14.32	-15.47	-16.54	7.02	74.13	0.995	
	0.32	0.38	0.42	2.74	2.46	2.27	7.25	15.70	0.997	319	375	426	-13.80	-14.93	-16.01	7.37	73.55	0.998	
	0.27	0.31	0.36	3.18	2.97	2.73	7.45	14.82	0.999	265	308	355	-13.36	-14.44	-15.53	7.41	72.13	0.999	
Highest	0.21	0.24	0.27	3.78	3.61	3.49	6.57	9.73	0.998	206	239	268	-12.76	-13.79	-14.78	6.65	67.42	0.998	
Some summaries																			
Average	25.06	29.87	33.66	-2.91	-3.64	-4.31	10.59	46.90		25056	29866	33658	-19.45	-21.05	-22.57	10.60	104.4		
Minimum	0.21	0.24	0.27	-13.12	-13.91	-15.08	0.90	9.73	0.408	206	239	268	-29.66	-31.31	-33.34	0.90	67.42	0.408	
Maximum	239.7	249.6	299.8	3.78	3.61	3.49	23.70	97.41	0.999	239742	249593	299814	-12.76	-13.79	-14.78	23.70	154.9	0.999	
Median	2.61	3.43	4.81	-2.30	-3.11	-4.15	9.53	45.69		2615	3431	4806	-18.84	-20.51	-22.42	9.53	103.1		

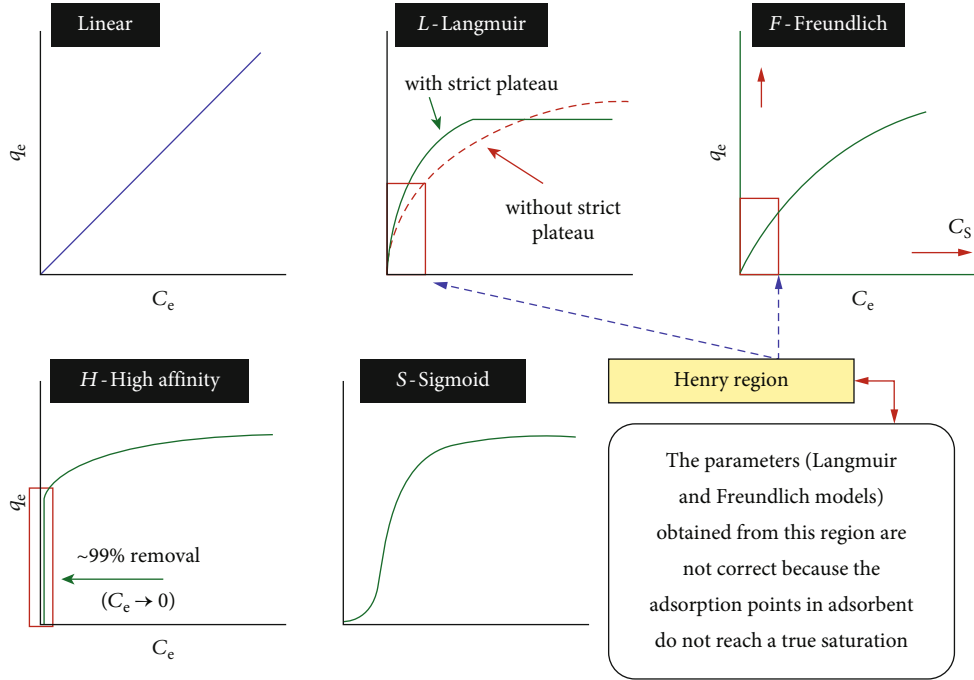


FIGURE 3: Different shapes of the adsorption isotherms classified by Moreno-Castilla [83].

that the K_H constant as obtained from the plot of q_e vs. C_o (in Equation (54) that is a linear form as $y = ax + b$) is dimensionless and equal to thermodynamic equilibrium constant. The K_H value is determined from the slope of Equation (54). A critical question is what the meanings of the y -intercept of this linear equation is. In addition, when the unit of q_e (mg/g) and C_o (mg/L) is introduced in Equation (54), Equation (55) is obtained. Clearly, the unit of K_H (Equation (55)) still be L/g that is similar to K_D (L/g) as early discussed. Therefore, the method that was recently proposed by Sawafta and Shahwan [91] for determining the constant (that is similar to K_D ; so it cannot be equal to so-called thermodynamic equilibrium constant) is not suitable for calculating the thermodynamic parameters.

$$C_e = C_o - \frac{q_e}{V} m \quad (52)$$

$$q_e = K_H \times C_e = K_H \times \left(C_o - \frac{q_e}{V} m \right) \quad (53)$$

$$q_e = \frac{K_H}{1 + (K_H/V)m} C_o \quad (54)$$

$$\frac{\text{mg}}{\text{g}} = \left(\frac{K_H}{1 + K_H \times (\text{g of adsorbent/L})} \right) \times \frac{\text{mg}}{\text{g}} \quad (55)$$

Recently, Chen et al. [92] gave a new definition for the distribution coefficient. This new coefficient is named as “the standard equilibrium constant” (K_D°). The relationship between K_D and K_D° is shown in Equation (56). The authors [92] defined two parameters (q° and C° , respectively) as the standard states of solution in the solid and liquid phases. The authors assumed that q° and C° are 1 mol/kg and 1 mol/L. They concluded that K_D° is calculated from Equation (56) is dimensionless. Unfor-

tunately, the definition of the standard equilibrium constant (K_D°) is incorrect from beginning. Lima et al. [21] commented that the term of q° in Equation (56) does not exist in the science and the literature. From Equation (56), Lima et al. [21] estimated that q° is obtained from Equation (57) although Chen et al. [92] did not provide this equation. If C_o° and C_e° are 1 mol/L, q° will be zero (i.e., 0 mol/kg). This means that K_D° is a value undetermined or tending to the infinite according to the concept of functional limit [21].

$$K_D^\circ = \frac{q_e/q^\circ}{C_e/C^\circ} = K_D \times \frac{C^\circ}{q^\circ} \quad (56)$$

$$q^\circ = \frac{C_o^\circ - C_e^\circ}{m^\circ} V^\circ \quad (57)$$

where C° and q° that are defined by Chen et al. [92] are the standard states of solution in liquid and solid, respectively.

To sum up, the (direct and indirect) applications of the distribution coefficient (K_D ; Equation (40) or (41)) as the standard thermodynamic equilibrium constant (K_{Eq}° ; Equation (26)) for calculating the thermodynamic parameters of solid-liquid adsorption process are not feasible and thus should be avoided because of the unit problem and other aforementioned reasons (i.e., it is not true adsorption equilibrium constant). The equilibrium constant of some adsorption models (i.e., K_L from the Langmuir model) can be applied as the thermodynamic equilibrium constant by appropriately considering [Adsorbate] $^\circ$ and $\gamma_{\text{Adsorbate}}$ (Equation (26)).

TABLE 8: Thermodynamic parameters of the adsorption process of methylene blue onto hydrogels.

T (K)	K_F^* (L/mg)?	K_L^* (L/mg)	K_{Eq}^o	van't Hoff equation	Thermodynamic parameters		
					ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° [J/(mol × K)]
1. Based on the Freundlich constant (incorrect)							
295	12.38*	—	3939592	$y = -1188x + 19.19$ ($r^2 = 0.9191$)	-37.25*	9.87	159.6
305	13.17*	—	4212840		-38.68*	(0.14*)?	(2.3*)?
315	15.93*	—	5094315		-40.45*		
2. Directly based on the Freundlich constant (incorrect)							
295	12.38*	—	12.38*	$y = -1188x + 6.52$ ($r^2 = 0.9191$)	-6.16	9.87	54.17
305	13.17*	—	13.17*		-6.54		
315	15.93*	—	15.93*		-7.25		
3. Directly based on the Langmuir constant (incorrect)							
295	—	0.00392*	0.00392	$y = -2692x + 3.53$ ($r^2 = 0.9139$)	13.59	22.38	29.37
305	—	0.00454*	0.00454		13.68		
315	—	0.00702*	0.00702		12.99		
4. Based on the Langmuir constant (correct)							
295	—	0.00392*	1254	$y = -2691.6x + 16.21$ ($r^2 = 0.9139$)	-17.50	22.38	134.8
305	—	0.00454*	1452		-18.46		
315	—	0.00702*	2245		-20.21		

Note: *Results are reported by the author [97]. The exponent n is 0.9843 at 295 K, 1.0095 at 305 K, and 1.0572 at 315 K [97].

5. Feasibility of Applying the Freundlich Constant (K_F) for Calculating Thermodynamic Parameters?

Unlike, the Langmuir model, the Freundlich model (Equation (43)) is an earliest empirical equation without physical meanings [93]. From Equation (43), the unit of the Freundlich constant K_F that is (mol/kg)/(mol/L) ^{n} is correctly obtained in Equation (58). Some authors made a mistake in presenting the unit of K_F as L/mol (or L/mg) or even mol/g (or mg/g [77, 85]) without considering the magnitude of its exponent. This mistake has been discussed elsewhere [94, 95]. Only the case of its exponent $n = 1$ (a linear isotherm), the unit of K_F reduces from (mol/kg)/(mol/L) ^{n} to L/kg and K_F will be equal to K_H . For example, when $n = 1$, Chao et al. [96] reported the K_F values (1023, 442, 252, 199, 120 L/kg) for adsorbing organic compounds (propylbenzene, ethylbenzene, toluene, benzene, trichloromethane) by titanate nanotubes modified with octadecyltrichlorosilane were inversely proportional to their water solubilities (55, 152, 515, 1780, 7900 mg/L, respectively).

$$K_F = \frac{q_e}{C_e^n} = \frac{(\text{mol/kg})}{(\text{mol/L})^n} \quad (58)$$

Húmpola and co-workers [69] applied the Freundlich constant K_F as the constant K_{Eq}^o for calculating the thermodynamic parameters of the adsorption process of phenol onto different kinds of activated carbon. However, they reported the incorrect unit as [(mol^(1- n) × L ^{n})/g]. Although the authors reported the thermodynamic equilibrium constant in Equation (27) was L/mol, they did not provide detail information how to convert

the unit of K_F from [(mol^(1- n) × L ^{n})/g] to L/mol. A similar mis-application of K_F for calculating the thermodynamic parameters of the adsorption of Co²⁺ ion by chitosan-aluminium oxide composite was reported by Ma et al. [17].

Salunkhe [97] applied the constant K_F for calculating the thermodynamic parameters of the adsorption process of methylene blue by hydrogels. The authors have a mistake regarding the unit of K_F (L/mg). They converted the unit K_F from L/mg to L/mol and then applied it as K_{Eq}^o for calculating the thermodynamic parameters (Table 8). The correct thermodynamic parameters for this process should be calculated based on K_L (Table 8).

In 2015, Ghosal and Gupta [16] introduced the relationship between K_{Eq}^o and K_F (mg/g)/(mg/L) ^{n} as Equation (59) by considering the mass of water per litre (actually, it is the density of pure water ρ_{water} ; g/L). This might be the first paper on this unit conversion because they did not give any reference for this idea and equation. The idea of using ρ_{water} to convert K_F from dimensional to dimensionless based on the previous publication of Milonjić [87]. The authors [16] reported that the K_{Eq}^o constant obtained from Equation (59) is dimensionless. Many authors have applied Equation (59) for calculating the thermodynamic parameters [14, 15, 98, 99].

It is necessary to verify whether the K_{Eq}^o constant calculated from Equation (59) is actually dimensionless. The analysis results (Equations (60)–(63)) demonstrated that the information in Equation (59) is completely error. This is because of the significant difference among the mass of adsorbent (solid), adsorbate (solute), and water (solvent). This problem has been identified by other authors [65, 100]. Therefore, the thermodynamic parameters calculated based on the Freundlich constant

TABLE 9: Thermodynamic parameters of the adsorption process of phenol onto hydroxyapatite.

T (K)	K_L (L/mg)	K_{Eq}^o	Thermodynamic parameters		
			ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o [J/(mol × K)]
1. As reported by Lin et al. [101] using Equations (64)–(66)					
293	—	—	−2.03	6.48	29.0
313	—	—	−2.26		27.9
333	—	—	−2.32		26.4
2. As recalculated based on K_L (suggested)					
293	0.1225*	12145	−22.91	12.34	120.0
313	0.1482*	14693	−24.97		
333	0.2264*	22445	−27.74		

Note: *Values are reported by the author [101].

are not true and do not have physical meanings [24, 65, 100].

$$K_{Eq}^o = K_F \times \rho_{\text{water}} \times \left(\frac{1}{\rho_{\text{water}}/1000} \right)^{(1-n)} \quad (59)$$

$$K_{Eq}^o = \left(\frac{\text{mg of adsorbate/g of adsorbent}}{(\text{mg of adsorbate/L})^n} \right) \times \left(\frac{\text{g of water}}{\text{L}} \right) \times \left(\frac{1}{\text{g of water/L} \times 1000} \right)^{(1-n)} \quad (60)$$

$$K_{Eq}^o = \left(\frac{\text{mg of adsorbate}}{\text{g of adsorbent}} \right) \times \left(\frac{\text{L}}{\text{mg of adsorbate}} \right)^n \times \left(\frac{\text{g of water}}{\text{L}} \right) \times \left(\frac{\text{L}}{\text{mg of water}} \right)^{(1-n)} \quad (61)$$

$$K_{Eq}^o = \left(\frac{\text{mg of adsorbate}}{\text{g of adsorbent}} \right) \times \left(\frac{\text{g of water}}{\text{L}} \right) \times \left(\frac{\text{L}}{\text{mg of adsorbate}} \right)^n \times \left(\frac{\text{L/mg of water}}{(\text{L/mg of water})^n} \right) \quad (62)$$

$$K_{Eq}^o = \left(\frac{\text{mg of adsorbate}}{\text{g of adsorbent}} \right) \times \left(\frac{\text{g of water}}{\text{L}} \right) \times \left(\frac{\text{L}}{\text{mg of water}} \right) \times \left(\frac{\text{L}}{\text{mg of adsorbate}} \right)^n \times \left(\frac{\text{mg of water}}{\text{L}} \right)^n \quad (63)$$

Lin et al. [101] applied Equations (64)–(66) for calculating the thermodynamic parameters of the adsorption process of phenol by hydroxyapatite solid. They calculated ΔH^o based on the plot of $\ln(1/C_e)$ vs. $1/T$ in Equation (64). The unit of K_F reported by Lin et al. [101] is L/mg. ΔG^o was directly calculated based on the exponent of the Freundlich model. Their result in Table 9 is doubtfully.

$$\ln \frac{1}{C_e} = \frac{\ln K_F - \Delta H^o}{RT} \quad (64)$$

$$\Delta G^o = -nRT \quad (65)$$

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} \quad (66)$$

6. Considering Other Adsorption Equilibrium Constants Related to Adsorption Isotherms

Apart from the constant K_L (L/mol) of the Langmuir model that can be applied for calculating the thermodynamic parameters of various adsorption processes, several other constants from the some adsorption isotherm models have

been also considered as K_{Eq}^o for calculating the thermodynamic parameters [21, 63].

Recently, Lima et al. [102] initially gave some new ideas on applying other constants of the adsorption isotherms for calculating the thermodynamic parameters of adsorption process in solid–liquid phases. The most important consideration is the unit of those constants that must be expressed as L/mol (as the constant K_L). In this case, those constants are defined as the adsorption equilibrium constants, and they can be used to replace K_L in Equation (36) for calculating the thermodynamic parameters. From those ideas, Tran et al. [24] successfully applied the constants of various adsorption models (i.e., the Langmuir, Liu, Sips, Toth, Khan, Hill, Redlich–Peterson, Radke–Prausnitz, and Koble–Corrigan models) for calculating the thermodynamic parameters of adsorbing methylene green (MG) dye by commercial activated carbon (CAC) (Table 10). Those models possess the features of the Freundlich and Langmuir models.

Among those models, the Langmuir–Freundlich model (or the Liu model) have been intensively applied for calculating the thermodynamic parameters. It is hard to verify the original paper for the Langmuir–Freundlich model. In the literature, this model is often expressed in different forms. However, the most common form is expressed as Equation (67). Some authors found that this form (Equation (67)) is similar to the Liu model (Equation (68)) [24, 102]. The relationship between two models is expressed in Equation (70). When summing Equation (69) into Equation (67), the Langmuir–Freundlich model will become the Liu model. Therefore, it can be concluded that the Liu model and Langmuir–Freundlich model are the same fundamentals and derivations.

$$q_e = \frac{Q_{LF}(K_{LF}C_e)^{n_{LF}}}{1 + (K_{LF}C_e)^{n_{LF}}} \quad (67)$$

$$q_e = \frac{Q_{Liu}C_e^{n_{Liu}}}{(K_{Liu})^{n_{Liu}} + C_e^{n_{Liu}}} \quad (68)$$

$$K_{LF} = \frac{1}{K_{Liu}} \quad (69)$$

$$q_e = \frac{Q_{LF}(1/K_{Liu})^{n_{LF}}(C_e)^{n_{LF}}}{1 + (1/K_{Liu})^{n_{LF}}(C_e)^{n_{LF}}} = \frac{Q_{LF}(C_e)^{n_{LF}}}{(K_{Liu})^{n_{LF}} + (C_e)^{n_{LF}}} \quad (70)$$

$$K_{Liu(eq)} = \frac{1}{K_{Liu}} \quad (71)$$

where $Q_{Liu} = Q_{LF}$ (mol/kg) is the MAC of the models; K_{Liu} (mol/L) is the Liu constant; $K_{Liu(eq)}$ (obtained from Equation (71)) = K_{LF} (L/mol) is the adsorption equilibrium constant of the Liu and Langmuir–Freundlich models; and n_{LF} (dimensionless) = n_{Liu} is the exponents of the Langmuir–Freundlich and Liu models.

In 2003, Liu and coworkers [103] initially developed a general model derived from a thermodynamic approach (Equation (68)). The equilibrium constant $K_{Liu(eq)}$ of this model is appropriate for calculating the thermodynamic parameters, and so it is then applied by many scholars [24, 104, 105]. Surprisingly, the authors reported the constant K_{Liu} without any

TABLE 10: The thermodynamic parameters of the adsorption process of methylene green dye using commercial activated carbon calculated based on various adsorption equilibrium constants of the isotherm models [24].

T (K)	K_{Model}	n_{model}	K_{Eq}°	ΔG°	Thermodynamic parameters			
					Linear method ΔH°	ΔS°	Non-linear method ΔH°	ΔS°
1. Langmuir model: $K_{\text{Model}} = K_L$ (L/mol)								
288	16,068	—	16,068	-23.19	12.01	122.3	11.68	121.24
303	21,435	—	21,435	-25.12				
318	25,752	—	25,752	-26.85				
2. Langmuir–Freundlich model: $K_{\text{Model}} = K_{\text{LF}}$ (L/mol)								
288	13,734	0.7430	13,734	-22.81	11.73	120.1	118.87	0.9729
303	18,313	0.7558	18,313	-24.73				
318	21,767	0.7394	21,767	-26.41				
3. Liu model: $K_{\text{Model}} = K_{\text{Liu}}$ (mol/L)								
288	72.81×10^{-6}	0.7429	13,735	-22.81	11.72	120.1	118.86	0.9726
303	54.59×10^{-6}	0.7558	18,318	-24.73				
318	45.94×10^{-6}	0.7394	21,767	-26.41				
4. Sips model: $K_{\text{Model}} = K_{\text{Sip}}(\text{L/mol})^{1/n_{\text{Sips}}}$								
288	1192	0.7435	13,815	-22.80	11.71	120.0	11.38	118.95
303	1671	0.7561	18,331	-24.71				
318	1628	0.7403	21,881	-26.42				
5. Khan model: $K_{\text{Model}} = K_{\text{Khan}}$ (L/mol)								
288	21,579	0.9579	21,579	-23.90	16.73	141.1	16.51	140.01
303	31,070	0.9503	31,070	-26.06				
318	41,688	0.9429	41,688	-28.13				

Note: The unit of ΔG° , ΔH° and ΔS° was kJ/mol and J/(mol \times K), respectively.

unit [103, 106]. However, as analyzed in Equation (72), the unit of the constant K_{Liu} must be mol/L (when considering $q_e = \text{mol/kg}$ and $C_e = \text{mol/L}$). This is consistent with its unit expressed in Equation (69). The authors [103, 106] did not provide a strict limitation for the exponent n_{Liu} of this model. They reported the n_{Liu} value of 0.52 for adsorbing Cu^{2+} , 1.02 for adsorbing Zn^{2+} , and 1.2 for adsorbing Cd^{2+} by aerobic granules [103]. However, Lima et al. [102] suggested that this exponent must be a positive value ($n_{\text{Liu}} > 0$). The relationship between K_{Eq}° and $K_{\text{Liu}(\text{eq})}$ is expressed as Equation (73) [24, 102]. Some researchers have applied $K_{\text{Liu}(\text{eq})}$ as K_{Eq}° for calculating the thermodynamic parameters of some adsorption processes (Table 10) [24, 104].

$$\frac{\text{mol}}{\text{kg}} = \frac{(\text{mol/kg}) \times (\text{mol/L})^{n_{\text{Liu}}}}{(K_{\text{Liu}})^{n_{\text{Liu}}} + (\text{mol/L})^{n_{\text{Liu}}}} \quad (72)$$

$$K_{\text{Eq}}^{\circ} = \frac{K_{\text{Liu}(\text{eq})}}{\gamma_{\text{Adsorbate}}} C^{\circ} \quad (73)$$

Because the Langmuir–Freundlich model has the same form to the Liu model, the name of two models should be integrated and called as the Liu model. The name of the Langmuir–Freundlich model should be considered as the general adsorption isotherm models combining the characteristic of the Langmuir model and Freundlich model. The isotherm models (Sips, Khan, etc.) that can reduce to the Langmuir or

the Freundlich model under specific conditions are called as the Langmuir–Freundlich typed model.

Another feasible consideration is the Sips model [107]. In nature, it is one of the typical Langmuir model-typed equation. Assuming one adsorbate is occupied by the adsorbing sites n of adsorbent. On the average, the Sips model for adsorbing under liquid–solid phases is given as Equation (74). Lima et al. [102] suggested that the exponent of this model should be in a strict range ($0 < 1/n_{\text{Sips}} \leq 1$). When $n_{\text{Sips}} = 1$, this model reduces to the Langmuir model. The adsorption equilibrium constant of this model $K_{\text{Sips}(\text{eq})}$ (L/mol) is defined as Equation (75) that can be used as K_{Eq}° (Equation (76)) for calculating the thermodynamic parameters (Table 10) [24, 102].

$$q_e = \frac{Q_{\text{Sips}} K_{\text{Sips}} C_e^{1/n_{\text{Sips}}}}{1 + K_{\text{Sips}} C_e^{1/n_{\text{Sips}}}} \quad (74)$$

$$K_{\text{Sips}(\text{eq})} = \sqrt[1/n_{\text{Sips}}]{K_{\text{Sips}}} \quad (75)$$

$$K_{\text{Eq}}^{\circ} = \frac{K_{\text{Sips}(\text{eq})}}{\gamma_{\text{Adsorbate}}} C^{\circ} \quad (76)$$

where Q_{Sips} is the MAC of Sips model (mol/kg); K_{Sips} is its constant (L/mol) $^{1/n_{\text{Sips}}}$; n_{Sips} is its exponent (dimensionless).

Similar to the Langmuir models, the unit of the AEC of Khan model (K_{Khan}) is L/mol. However, the constant K_{Khan}

is independent on its exponent. The exponent n_{Khan} should be higher than zero. Therefore, it is possible to directly apply it as K_{Eq}° for calculating the thermodynamic parameters (Table 10) [24, 102]. In 1997, Khan et al. [25] modified their previous model (proposed for describing the adsorption data of multi-components) and then applied it for describing the adsorption behavior of phenol, *p*-nitrophenol, or *p*-chlorophenol in single solution by activated carbon. This modified model is commonly known as the Khan model (Equation (77)). When $n_{\text{Khan}} = 1$ this model is mathematically equivalent the Langmuir model. Khan et al. [25] reported that n_{Khan} (in both their current study and extracted from the literature) for adsorbing various single organic adsorbates in water ranged from 0.55 to 5.84. However, it is necessary to set the limitation for this exponent.

$$q_e = \frac{Q_{\text{Khan}} K_{\text{Khan}} C_e}{(1 + K_{\text{Khan}} C_e)^{n_{\text{Khan}}}} \quad (77)$$

where Q_{Khan} is the MAC estimated by the Khan model (mol/kg); K_{Khan} is the AEC of this model (L/mol); and n_{Khan} is its exponent (dimensionless).

7. Some Suggestions for Improving the Quality of Papers Published in This Field

Science and technology are always changing. Some traditional methods or previous comments might be suitable and correct at the publication time. However, in the future, they might be not appropriate or even not correct.

It is notable that none of all publications in high-impact journals are always correct. In essence, a manuscript submitted to the journal needs to undergo a reviewing process. The submitted work is often accepted for publication only based some peoples: reviewers and editors (but not all researchers in the field). Sometimes, some people who are named as experts are beginners (i.e., doctoral students); meanwhile, other people have never committed themselves to do experiments on adsorption or write the papers in this field.

Therefore, the present author has some suggestions for beginners. When researchers (less experienced) start to do experiments and explain their data, they should wonder whether the methods, information, and results in the published papers or the books are appropriate for their current studies. In fact, beginners often follow or directly use the previously published methods of their groups/labs for their current works; for example, in the case of applying the unit conversion of the Freundlich constant [16]. As earlier discussed, none all publications prove correct information and accuracy method; therefore, open-minded beginners should read more and more papers (especially textbooks) published from different author groups and publishers. Importantly, researchers should give more updated citations when writing their manuscripts. This is an effective way to avoid the repeat of the similar mistakes discussed by other scholars in the literature [108].

For example, in 2009, Shuibo and co-workers [109] directly applied the Langmuir constant K_L (L/mg) for calculating the thermodynamic parameters of the process of ura-

nium (VI) adsorption in water using the hematite-based adsorbent. In the same year, Milonjić [82] wrote a comment work on this direct application and suggested a conversion relation (Equation (78)). The author considered the density of pure water (ρ_{water}) is ~ 1.0 g/mL (equal to 1,000,000 mg/L or 10^6 mg/L). This equation has been then applied by many scholars [98, 110–112]. However, ten years later, Zhou and Zhou [58] published a comment paper to analyse the feasibility of the previous comment made by Milonjić [82]. Zhou and Zhou [58] concluded that Equation (78) is certainly error because the difference between the mass of adsorbate and water (Equation (79)). Table 11 shows the comparison of the thermodynamic parameters that are obtained from (1) directly applying K_L (L/mg) as K_{Eq}° [109] and (2) indirectly applying K_L (L/mg) by the unit conversions [58, 82].

$$K_{\text{Eq}}^{\circ} = K_L \times 10^6 \quad (78)$$

$$K_{\text{Eq}}^{\circ} = K_L \times 10^6 \rho_{\text{water}} = \left(\frac{\text{L}}{\text{mg of adsorbate}} \right) \times 10^6 \left(\frac{\text{mg of water}}{\text{mL}} \right) \quad (79)$$

Another example is the modified Langmuir model (Equation (80)) that was proposed by Azizian and co-workers [4]. As discussed in Section 2, the constant K_{Eq}° is obtained by assuming that the standard state (or reference state) for pure liquids and pure solids is 1 mol/L and 1 mol/kg, respectively. However, some authors did not agree to this assumption [4, 5, 72]. Therefore, Azizian and co-workers [4] developed a revised form of the Langmuir isotherm using the aspect of adsorption and desorption kinetics. The authors concluded that the modified Langmuir constant (K_{ML}) in Equation (80) is a dimensionless quantity. Therefore, they suggested that K_{ML} can be directly applied for calculating the thermodynamic parameters. However, the theory on derivation of K_{ML} from thermodynamics aspects is missed. Different scholars made two comments on some problems of the modified Langmuir model [113, 114]. Unlike K_L , the constant K_{ML} does not dependent on the units of q_e and C_e used (Table 12) [24]. This constant (dimensionless) is a different principle to the adsorption equilibrium (dimensional such as L/mol) related to adsorption isotherm models such as the Langmuir, Lui, Sips, and Khan models. In addition, a question is how the authors can define activity coefficient for adsorbate (solute) in Equation (25). Therefore, the direct application of K_{ML} for calculating the thermodynamic parameters should be done with a thorough consideration because it might not be suitable for all cases of adsorption studies [24].

$$q_e = \frac{Q_{\text{ML}} K_{\text{ML}} C_e}{(C_s - C_e) + K_{\text{ML}} C_e} \quad (80)$$

where C_s is the saturation concentration of solute in bulk phase that is previously defined in Equation (37); Q_{ML} (mol/kg) is the modified Langmuir MAC of adsorbent; and K_{ML} (dimensionless) is the modified Langmuir constant.

Some uncertain conclusions or questionable statements should be not continued to use in this field. For example, in

TABLE 11: Comparison of thermodynamic parameters for the adsorption process of U(VI) on hematite obtained from different calculation methods.

T (K)	K_{Eq}°	ΔG°	Linear method (Eq. (31))		Non-linear method (Eq. (30))	
			ΔH°	ΔS°	ΔH°	ΔS°
1. K_L(L/mg) as the original report by Shuibo et al. [109]						
293	1.01	-0.0242	5.081	17.25	5.295	17.95
305	1.03	-0.0750				
318	1.19	-0.4599				
2. K_L(L/mg) $\times 10^6$ as the comment by Milonjić [82]						
293	1,010,000	-33.68	5.081	132.11	5.295	132.8
305	1,030,000	-35.11				
318	1,190,000	-36.99				
3. K_L(L/mol) as the comment by Zhou and Zhou [58]						
293	240,400	-30.18	5.087	120.2	5.301	120.9
305	245,200	-31.47				
318	283,300	-33.19				

Note: The unit of ΔG° (kJ/mol), ΔH° (kJ/mol), and ΔS° [J/(mol \times K)]; and thermodynamic parameters recalculated based on the literature [58, 82, 109].

TABLE 12: Comparison of relevant parameters of the Langmuir and modified Langmuir models obtained from different units (q_e and C_e) of the plots of MG adsorption isotherm by CAC [24].

	Adsorption isotherm		
	q_e (mg/g) vs. C_e (mg/L)	q_e (mmol/g) vs. C_e (mmol/L)	q_e (mol/kg) vs. C_e (mol/L)
1. Langmuir model			
Q_L	211.2 mg/g	0.578 mmol/g	0.578 mol/kg
K_L	0.059 L/mg	21.44 L/mmol	21435
adj- R^2	0.990	0.990	0.990
red- χ^2	69.4	5.2E-04	5.2E-04
2. Modified Langmuir model			
Q_{ML}	210.6 mg/g	0.577 mmol/g	0.577 mol/kg
K_{ML}	588.4	588.4	588.4
adj- R^2	0.990	0.990	0.990
red- χ^2	69.4	5.2E-04	5.2E-04

1998, Gupta [115] investigated the adsorption of nickel and copper ions using activated slag. The author concluded that “positive values of entropy (ΔS°) reflect the affinity of the adsorbent material for the metal ions and suggest some structural changes in adsorbate and adsorbent”. The doubtful conclusion (positive values ΔS° suggest some structural changes in adsorbate and adsorbent) is drawn without supported by relevant experimental data (i.e., comparing the structure of adsorbent before and after adsorption). Other researchers have early commented on above conclusions; for example: “the positive entropy change during adsorption is the result of structural changes to the solute or adsorbent or the release of other ions by an ion exchange mechanism by the solute, without experimental or theoretical proof” [26]. However, many other researchers have cited the paper of Gupta for similar conclusions such as “the positive values of ΔS confirm a high prefer-

ence of Methylene Blue molecules for the NLP surface and suggest possibility of some structural changes or readjustments in the Methylene Blue-NLP adsorption complex” [13]. Reddy et al. [77] concluded that “the positive values of ΔS° show increased randomness at the solid/solution interface with some structural changes in the sorbate (hydrated metal ions) and biosorbent”.

Another example is the information on the sign of ΔH° . In a review article, Hu et al. [116] concluded that “the value of K_L should decrease with the increase in temperature since adsorption was usually an exothermic process ($\Delta H^{\circ} < 0$)”. This conclusion is proposed without any experimental data supported. The value of K_L can increase or decrease when solution temperatures increase [26]. For example, the constants K_L of the adsorption process of phenol onto hydroxyapatite increased from 0.1225 L/mg to 0.2264 L/mg when the temperatures

increased from 293 K to 333 K; as a result, the adsorption process was endothermic ($\Delta H^\circ > 0$; +12.34 kJ/mol; Table 9) [101]. In contrast, the constants K_L of the adsorption process of diclofenac adsorption onto F400 activated carbon decreased from 0.087 L/mg to 0.022 L/mg ($\Delta H^\circ < 0$; -30.85 kJ/mol; Table 2) when the temperature increased from 288 K to 318 K [72].

Lastly, Luo et al. [68] wrote “the ΔG° value is in the range of 0 to -20 kJ/mol and -80 to -400 kJ/mol for physical and chemical adsorptions, respectively. In this study, the ΔG° values are close to -18 kJ/mol, indicating that the adsorptions are mainly physical in nature”. Conclusions regarding physisorption or chemisorption must be proposed based on the magnitude of the standard change in enthalpy ΔH° , not standard Gibbs energy change ΔG° . In general, chemisorption (i.e., $\Delta H^\circ > 80$ kJ/mol [104]) has a higher magnitude of ΔH° than physisorption. ΔH° value for covalent bonds (chemisorption) is often in the range 200–800 kJ/mol [117], while that for hydrogen bonds (physisorption) is lower than 40 kJ/mol [118].

8. Conclusions

The general form of standard dimensionless thermodynamic constant K_{Eq}° of the solid–liquid adsorption is fully expressed as Equation (25). Under some assumptions, Equation (25) decreases to Equation (26) and then commonly expressed as Equation (36): $K_{Eq}^\circ = (K_L/\gamma_{Adsorbate})C^\circ$. It is necessary to define or calculate two important parameters: $\gamma_{adsorbate}$ (dimensionless) and C° (1 mol/L by definition). Adsorption equilibrium constants are applied in Equation (36) must be dimensional (their units must be L/mol like the Langmuir adsorption equilibrium constant). The plot of adsorption isotherm should be presented as q_e (mol/kg) versus C_e (mol/L) in studying adsorption thermodynamics. The non-linear technique is always applied for calculating the relevant parameters of adsorption isotherm models. The adsorption equilibrium constants (i.e., K_L , $K_{LF} = K_{Liu(eq)}$, $K_{Sips(eq)}$, and K_{Khan}) of the Langmuir, Langmuir–Freundlich or Liu, Sips, and Khan models can be considered as K_{Eq}° and applied for calculating the thermodynamic parameters of adsorption process: so-called standard Gibbs energy change (ΔG° ; kJ/mol), standard enthalpy change (ΔH° , kJ/mol); and standard entropy change [ΔS° ; J/(mol \times K)]. The non-linear form of the van't Hoff equation should be applied for calculating ΔH° and ΔS° to minimize some error functions. The negative value of ΔG° does not imply that adsorption processes occur spontaneously. The sign of ΔG° indicates the magnitude of K_{Eq}° . Mechanism involved in chemisorption is considered based on the magnitude of ΔH° (>80 kJ/mol), not ΔG° .

The distribution constant (K_D) and Freundlich constant (K_F) are not a true adsorption equilibrium constant. They are not equal or converted to K_{Eq}° . Thermodynamic parameters calculated based on K_D and K_F do not bring physical meanings. The constant K_D is often used of an analyte in two immiscible solvents such as water and *n*-octanol (hydrophobic). The application of K_D or K_F for calculating the thermodynamic parameters should be avoided. The author hopes that this paper will be helpful for other researchers in this filed.

Abbreviations

K_{Eq}° : —:	Standard thermodynamic equilibrium constant
C° : mol/L:	Standard concentration of adsorbate (or solute)
ΔG° : kJ/mol:	Standard Gibbs energy change
ΔG : kJ/mol:	Gibbs energy change
ΔH° : kJ/mol:	Standard change in enthalpy
ΔS° : J/(mol \times K):	Standard change in entropy
R : J/(mol \times K):	Universal gas constant
T : K:	Absolute temperature of adsorption process
C_e : mol/L:	Adsorbate concentrations in solution after adsorption equilibrium
q_e : mol/kg:	Amount of adsorbate adsorbed by solid material after adsorption equilibrium
K_D : L/kg:	Distribution coefficient
K_F : (mol/kg)/(mol/L) ^{<i>n</i>} :	Freundlich constant
a : —:	Activity
γ : —:	Activity coefficient
$\gamma_{Adsorbate}$: —:	Activity coefficient of adsorbate (~1.0 under dilute conditions)
μ : kJ/mol:	Chemical potential
θ : —:	Surface coverage fraction
ρ_{water} : g/L:	Density of pure water
K_L : L/mol:	Adsorption equilibrium constant of the Langmuir model
K_{Liu} : mol/L:	Adsorption constant of the Liu model
$K_{Liu(eq)}$: L/mol:	Adsorption equilibrium constant of the Langmuir model
K_{Sips} (L/mol) ^{1/<i>n</i>_{Sips}} :	Adsorption constant of the Sips model
$K_{Sips(eq)}$: L/mol:	Adsorption equilibrium constant of the Sips model
K_{Khan} : L/mol:	Adsorption equilibrium constant of the Khan model
K_{ML} : —:	Adsorption constant of modified Langmuir model

Data Availability

All data, models, and code generated or used during the study appear in the submitted article.

Conflicts of Interest

The author declares no conflicts of interest involved in the publication of this paper.

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