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Are the thermodynamic parameters correctly estimated in liquid-phase adsorption phenomena?

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ABSTRACT

Adsorption is a promising clean water technology process. Many materials both inorganic (such as zeolite, clays) and organic (such as residues from agricultural industry) have been used for wastewater decontamination. Among different pollutants, heavy metals and dyes are considered of great interest due to their toxicity. In order to develop an effective and accurate design model for the removal of pollutants from aqueous media, adsorption kinetics, thermodynamic and equilibrium data are essential basic requirements. This review article describes all the possible ways for estimating the thermodynamic parameters. Moreover, possible flaws are also highlighted. Meta data analysis was carried out and concluded that thermodynamic studies must be taken into consideration with caution since an enthalpy–entropy compensation was observed.

1. Introduction

The presence of various pollutants in the ecosystem has an alarming impact affecting the quality of life. Among them, heavy metal and dyes blame for their toxicity and carcinogenic effect on human and animal health. Based on the above, it is necessary to remove such pollutants from wastewaters and water. Compared to other purification technologies, adsorption is a promising process which is advantageous as low-cost operation, easily handling, without generation of secondary pollutants such as toxic sludge, providing high efficiency over a wide range of pollutants [1–25]. In order to organize, establish and understand an adequate design model for the removal of pollutants from aqueous media, isotherms, kinetics, desorption and thermodynamic studies are essential basic prerequisites.

Adsorption isotherms models are extensively used to provide information about the amount of adsorbed ion by a certain biomass and about the interaction between the adsorbents and adsorbate [26]. Those isotherms, which are a common name of equilibrium relationships, are essential for optimization of the adsorption mechanism pathways, expression of the surface properties and capacities of adsorbents, and productive design of the adsorption systems since they explain how pollutants interrelate with the adsorbent materials [27,28]. Explaining the phenomenon through which the preservation (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a persistent temperature and pH takes places, in broad-spectrum, an adsorption isotherm is an invaluable curve [29,30]. The mathematical association which establishes a significant role towards the modelling analysis, operational design and applicable practice of the adsorption systems is normally represented by plotting a graph between solid-phase and its residual concentration [31].

When the concentration of the solute remains unchanged as a result of zero net transfer of solute adsorbed and desorbed from sorbent surface, a condition of equilibrium is achieved. These associations between the equilibrium concentration of the adsorbate in the solid and liquid phase at persistent temperature are defined by the equilibrium sorption isotherms. Linear, favourable, strongly favourable, irreversible and unfavourable are some of the isotherm shapes that may form. Understanding of the mechanism of adsorption, surface properties, along with the extent of affinity of the adsorbents are delivered by the physicochemical parameters accompanied by the fundamental thermodynamic suppositions [32].

In terms of three basic approaches, an extensive diversity of equilibrium isotherm models (Langmuir, Freundlich, Brunauer–Emmett–Teller, Redlich–Peterson, Dubinin–Radushkevich, Temkin, Toth, Koble–Corrigan, Sips, Khan, Hill, Flory–Huggins and Radke–

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Prausnitz isotherm), have been framed in the past [33]. The first approach to be mentioned is kinetic consideration, while thermodynamics being the second one. A state of dynamic equilibrium with both adsorption and desorption rates in a balance is an adsorption equilibrium and a framework of deriving numerous forms of adsorption isotherm models is given by thermodynamics [34,35]. The key idea in the generation of characteristic curve is generally given by the third approach which is potential theory [36]. The alteration in the physical interpretation of the model parameters compels us to follow an interesting trend in the isotherm modelling which is the derivation in more than a single approach [37].

The amount of pollutant's uptake at equilibrium Q_e (mg/g) is calculated using the mass balance equation:

$$Q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where C_0 and C_e (mg/L) are the initial and equilibrium pollutant's concentration, respectively; V (L) is the volume of adsorbate (solution); m (g) is the mass of adsorbent.

In a recent review, Rangabhashiyam et al. [53] studied the use of two-, three-, four- and five-parametric isothermal models concluding that in case of two parameters isotherm model, Langmuir and Freundlich models have the best fitting. Langmuir isotherm assumes that all binding sites have equal affinity for the adsorbate, resulting to the formation of monolayer of adsorbed molecules, while Freundlich isotherm describes adsorption onto heterogeneous surfaces that provide adsorption sites of varying affinities.

Kinetics studies are another important tool to find the optimum condition for full-scale batch adsorption process [54]. Kinetic modelling reveals the mechanism of adsorption and potential rate-controlling steps such as mass transport or chemical reaction processes [54,55]. The most common are the pseudo-first and pseudo-second order kinetic equations.

Thermodynamic parameters provide further information about inherent energetic changes associated with adsorption process. The most common equations that related thermodynamic parameters such as change in free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) [56]. This note article attempted to shed light on the ways of the calculated thermodynamic approaches. Moreover, this work examines the relevance of the applied methods for calculating the thermodynamic parameters.

2. Results and discussion

2.1. Adsorption thermodynamics in equilibrium

2.1.1. Free energy Gibbs

The Gibbs free energy change (ΔG^0) is an indication of spontaneity of a chemical reaction and therefore is one of the most important criteria. It is calculated as follows:

$$\Delta G^0 = -RT\ln K \tag{2}$$

where R is the universal gas constant (8.314 J/mol K) and K is the equilibrium constant.

Negative or positive values of ΔG^0 confirm the spontaneity (or no-spontaneity) of adsorption process. ΔH^0 (enthalpy change) provides information about the energy release (exothermic process) or consumption (endothermic process) during adsorption process. Another thermodynamic parameter namely ΔS^0 (entropy change) depending on the sing, indicates if the randomness increases (positive values) or decreases (negative values), during adsorption procedure. Thermodynamic studies were calculated based on many equations as described in Table 1. In the majority of adsorption studies, authors, without explanation use one of these equations and plots and the final decision of the most suitable plot was proved by correlation coefficients (R^2) values. In order to calculate the thermodynamic parameters, adsorption data from two or more temperatures are bare necessities. (See Table 2.)

Table 1
Lists of adsorption isotherms (non-linear forms).

Isotherm	Non-linear form	Reference
Langmuir	$Q_e = \frac{Q_m K_L C_e}{1+K_L C_e}$	[38]
Freundlich	$Q_e = K_F(C_e)^{1/n}$	[39]
Dubinin–Radushkevic	$Q_e = (Q_s)e^{-k_{DR}\varepsilon 2}$	[40]
Tempkin	$Q_e = (\frac{RT}{b_T})\ln(A_T C_e)$	[41]
Flory–Huggins	$\frac{\theta}{C_0} = K_{FH}(1-\theta)^{n_{FH}}$	[42]
Hill	$Q_e = \frac{Q_{S_H} C_e^{n_H}}{K_D + C_e^{n_H}}$	[43]
Redlich–Peterson	$Q_e = \frac{K_R C_e}{1+a_R C_e^{g}}$	[44]
Sips	$Q_e = \frac{K_S C_e^{\beta_S}}{1+a_S C_e^{\beta_S}}$	[45]
Toth	$Q_e = \frac{K_T C_e}{(a_T + C_e)^{1/t}}$	[46]
Koble–Corrigan	$Q_e = \frac{A C_e^n}{1+B C_e^n}$	[47]-
Khan	$Q_e = \frac{Q_s b_K C_e}{(1+b_K C_e)^{a_K}}$	[48]
Radke–Prausnitz	$Q_e = \frac{a_{RP} r_R C_e^{\beta_R}}{a_{RP} + r_R C_e^{\beta_R - 1}}$	[49]
BET	$Q_e = \frac{Q_s C_{BET} C_e}{(C_s - C_e)[1+(C_{BET}-1)(C_e/C_s)]}$	[50]
FHH	$\ln(\frac{C_e}{C_s}) = -\frac{\alpha}{RT}(\frac{Q_s}{Q_e d})^r$	[51]
MET	$Q_e = Q_s\left(\frac{kC_e}{\ln(C_s - C_e)}\right)^{1/3}$	[52]

In case of ΔG^0 estimation, it is necessary to estimate K (equilibrium constant) variable. There are conflicting approaches regarding the appropriate units of K constant. According to Liu [57], if we use for ΔG^0 estimation the K_L as equilibrium constant (obtained from Langmuir model), the correct units of K_L are L/mol. On the other hand, ΔG^0 is wrongly estimated leading to misunderstandings by using others units (such as L/mg). In another work published by the same author [58], it was concluded that the calculation of ΔG^0 from Langmuir isotherm by equation (K_L in L/mol) is feasible for (i) neutral adsorbates or adsorbates with very weak charge, and (ii) dilute solutions of charged adsorbate; whereas for charged adsorbate solution at high concentration the effect of the activity coefficient needs to receive the appropriate attention. Then the free energy Gibbs is calculated by $\Delta G^0 = -RT\ln\left[\frac{K_L}{\gamma_e} x(\frac{mol}{L})\right]$ (γ_e is the activity coefficient). On the contrary, Milonjic [59] supports that the equilibrium constant K is wrongly presented with units in many works due to the fact that ΔG^0 unit is J/mol and RT is also J/mol. As a result, the K variable must be dimensionless. Milonjic recommended to recalculate the K as dimensionless by multiplying it by 55.5 (number of moles per litre of solution). So, the Gibbs equation takes the

Table 2
Thermodynamic modelling equations.

Expression	Equation form	Plot
Gibbs	${}^a\Delta G^0 = -RT\ln(K_L)$ ${}^b\Delta G^0 = -RT\ln(\frac{Q_e}{C_e})$ ${}^c\Delta G^0 = -RT\ln(K)$ ${}^d\Delta G^0 = -RT\ln(K_0)$	–
Van't Hoff	$\ln(b_L) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$	$\ln(b_L)$ vs $\frac{1}{T}$
	$\ln(\frac{Q_e}{C_e}) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$	$\ln(\frac{Q_e}{C_e})$ vs $\frac{1}{T}$
	$\ln K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$	$\ln(K)$ vs $\frac{1}{T}$
	$\ln(K_0) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$	$\ln(K_0)$ vs $\frac{1}{T}$
Clausius–Clapeyron	$\Delta H^0 = R\frac{T_1 \times T_2}{T_2 - T_1}\left(\frac{\ln(C_{e_1})}{\ln(C_{e_2})}\right)$	–

C_e (mg/L) and Q_e (mg/g) are the equilibrium liquid phase concentrations and amount of solute adsorbed at equilibrium, respectively; a: b_L in (L/mol) from Langmuir model; b: Q_e/C_e is the ratio where Q_e is adsorbed dye at concentration (mg/L) and C_e is the residual dye concentration in the solution (mg/L); c: $K = Q_m X b_L$ calculated from Langmuir constants (Q_m) is the maximum adsorption capacity in mg/g and b_L units in L/mg; d: K_0 can be evaluated by plotting $\ln(Q_e/C_e)$ versus q_e by extrapolating to $Q_e = 0$.