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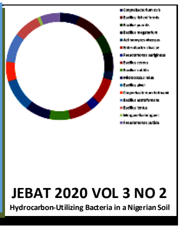

Re-evaluation of Thermodynamic Parameters using Dimensionless Langmuir Constants from Published Data on Glyphosate Adsorption onto Activated Carbon Loaded with Manganese and Iron

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ABSTRACT

Effect of temperature on the adsorption process will be reflected in the thermodynamic parameters. These data provide information on the efficiency of the adsorption process. Thus, an appropriate calculation for the thermodynamic parameter is crucial in adsorption research. In this paper, thermodynamic parameter data from a previously published paper on glyphosate adsorption onto AC/Mn/Fe was re-evaluated using the newly proposed method based on dimensionless equilibrium constant (K_c) derived from Langmuir sorption method. The recalculated results are as follows; entropy, $\Delta S°$=224.04 J mol^{-1}, enthalpy, $\Delta H°$ =39.97 kJ mol^{-1} and the range of Gibs fee energy for the five investigated temperature (5 °C, 15 °C, 25 °C, 35 °C and 45 °C) were $\Delta G°_{278.15K}$ = -22.26 kJ mol^{-1} and $\Delta G°_{318.15K}$ = -32.52 kJ mol^{-1}. Recalculated value of thermodynamics presented in this paper is mostly beyond the original data. Significant differences were observed in the sign and magnitude of $\Delta S°$ and the value of $\Delta G°$ of the tested temperature. Interestingly, the actual experiment was well represented by the recalculated results. Here we suggested the alternative calculation for thermodynamic parameters using the dimensionless equilibrium constant K_c.

INTRODUCTION

Glyphosate or N-(phosphonomethyl) glycine ($C_3H_8NO_5P$; CAS 1071-83-6) is an active ingredient in many herbicides effective in controlling weeds. In line with the increasing trend in glyphosate usage, its residue has been detected in water bodies including a stream, surface water, groundwater, and seawater[1–4]. Therefore, numerous treatment technologies involve conventional methods such as biological treatment, physicochemical treatment, and reverse osmosis have been developed for the removal of glyphosate from the polluted environment. Advanced oxidation process (AOP) including UV treatments, photocatalytic or electrochemical treatments has also been proposed as an alternative to the conventional method [5–7].

Adsorption onto activated carbon is often considered the most economical, non-toxic, and effective method for removing organic compounds in aqueous solutions. Several studies have explored various sources of activated carbon for glyphosate removals such as commercial coconut-shell AC[8] and waste-derived activated carbon for example waste newspaper [9], an oil palm frond [10] and *Eucalyptus camaldulensis* bark [11]. To further improve its efficiency, granular activated carbon (GAC) was hybrid with graphene oxide and $MnFe_2O_4$ in a fixed-bed column for glyphosate adsorption [12]. Besides, other magnetic particles for example manganese ferrite ($MnFe_2O_4$), iron oxide (Fe_3O_4) was also loaded or impregnated into AC and tested for their glyphosate adsorption capacity [13–15].

Thermodynamic parameters are the output of the adsorption process. They provide essential information in chemical engineering technologies and overall uptake of adsorbate onto the adsorbents since adsorption is a temperature-dependent process [16,17]. The thermodynamic parameter provides details on energy changes and describes the spontaneity of the process. These parameters are also necessary for interpreting adsorption behaviours (i.e., physisorption, ion exchange, or chemisorption) that reflect the efficacy of adsorption. It is, therefore, important to calculate these parameters accurately.

The acceptable equilibrium constant is the key to the correct calculation of ΔG^{θ}, ΔH^{θ}, and ΔS^{θ}. Accurate calculation of these thermodynamic parameters is highly dependent on the equilibrium constant, K_c [17,18] which is strongly influenced by the estimation methods [19]. For accurate determination of thermodynamic parameter, the equilibrium constant (K_c) must be dimensionless [20]. This specification also complies with the requirements of the International Union of Pure and Applied Chemistry which stated that the standard equilibrium constant ($K°$) for calculating Gibbs free energy change ($\Delta G°$) must be a dimensionless parameter [17,21].

In this study, the published thermodynamic data on glyphosate adsorption onto manganese and iron-loaded activated carbon (GAC/Mn/Fe) experiment by Yamaguchi et al. reevaluated based on the appropriate adsorption thermodynamics calculation. [23]. It is no doubt that this paper is beneficial to the researchers working in the area of glyphosate adsorption. However, it was stated that the value of equilibrium constant K_c was obtained from the intercept on the ordinate of the plot $\ln(q_e/C_e)$ against q_e [24]. This method is also known as distribution coefficient method, where K_c is defined by the Equation (1). This method is originally proposed by [25] and developed from the method of [26].

$$\mathrm{Kc} = \frac{q_e}{Ce} \qquad \text{(Eq. 1)}$$

Although this approach has been widely used for calculating thermodynamic parameters in the literature, the main concern is the units of K_c or K_d (distribution coefficient method) in Eq. 1 are L/g as Ce has units of mg/L and qe has units of mg/g. Since these units vary significantly, they are not appropriate to use directly as the equilibrium constant for the calculation of thermodynamic parameter, $\Delta G°$, $\Delta H°$, and $\Delta S°$ [20,27]. Thus, K_c can be obtained as dimensionless by multiplying K_L by the molecular weight of adsorbate (g/mol), 1000 and then 55.5 [28]. Therefore, here we propose the reevaluation of [22] thermodynamic parameters calculation based on the equilibrium constant, K_c (dimensionless) derived from the Langmuir constants newly suggested calculation by [23]

MATERIALS AND METHODS

Data acquisition and fitting

Glyphosate adsorption isotherm data (Figure 1) from a published work [22] were downloaded, and the value of data plotted in the figure was extracted using the digitisation tool in the Curve Expert Professional 2.6 software [29]. The data generated by the digitisation process were then inserted and fitting for non-linear regression of the Langmuir isotherm model. Curve fitting was also done using the Curve Expert Professional 2.6 software [29]. The adsorption isotherm was reproduced by plotting the Q_e in mol kg^{-1} over C_e in mol L^{-1} unit value.

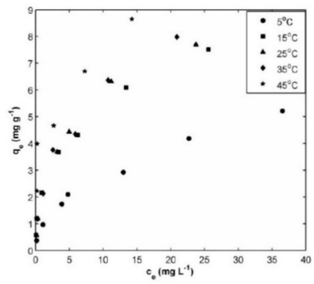

Fig.1. Glyphosate adsorption isotherms on GAC/Mn/Fe.(80 mL glyphosate solution (20 mg/L), 800 mg adsorbent, at 25°C, 150 rpm, pH=3.8, and t= 0 - 48 h) adapted from [22].

Determination of the equilibrium constant, K_L and conversion to a dimensionless parameter, K_c

The equilibrium constant, K_c used for thermodynamic parameter calculation was derived from Langmuir constant, K_L. The Langmuir equation [30] was derived for the gas-solid interface but has been widely applicable in the solid liquid as well [31] The Langmuir equation is as follows:

$$q_e = \frac{q_{\mathrm{m}} K_L C_e}{1+K_L C_e} \qquad \text{(Eq. 2)}$$

Where,

q_{m} (mg/g) is the Langmuir maximum adsorption capacity; K_{L} (L/mg) is the Langmuir constant; C_e (mg/ L), is the equilibrium concentration of the compounds in the solution (mg/L).

Equilibrium constant, K_L derived from equation 2 was converted to the dimensionless form by multiplying K_L by the molecular weight of adsorbate (g/mol), 1000 and then 55.5 (Eq 2) [28]

$$\mathrm{K_c} = 169.07 \times 55.5 \times 1000 \times \mathrm{K_L} \qquad \text{(Eq. 3)}$$

Where,

55.5 is the number of moles of pure water per liter and the term of 169.07 x 55.5 x 1000 x $\mathrm{K_L}$ is dimensionless. Note that Mw of glyphosate =169.07 g mol^{-1}

The relationship between K_L (with the unit) with the equilibrium constant, K_c (without unit) is described in equation 4 where K_L (L/mol) is the Langmuir constant; $C°$ is the selected standard state of adsorbate ($C°$ =1 mol/L); γ (dimensionless) is the activity coefficient of adsorbate (glyphosate) in solution [23]

$$K_c \approx \frac{K_L\left(\frac{L}{mol}\right) \times C^{\circ}\left(\frac{mol}{L}\right)}{\gamma} \qquad (4)$$

Estimation of adsorption thermodynamics parameters

For the thermodynamic study, [22] were conducted batch-adsorption experiments in the same conditions but varying the temperature (5 °C, 15 °C, 25 °C, 35 °C and 45 °C) and the initial concentration of glyphosate (5, 10, 20, 30, 40, 60 and 80 mg/L). The stirring was continued until reaching the equilibrium time, 24 hours.

In this study, K_c values (dimensionless) obtained from the Langmuir constant at several temperatures were used to calculate the thermodynamic parameters and substitute in the van't Hoff linear equation. The thermodynamic parameters were computed according to the laws of thermodynamics using the following equations. The Gibbs energy, $\Delta G°$ (kJ mol^{-1}) was calculated from Eqs. (5) and (6). The relationship between $\Delta G°$ and $\Delta H°$and $\Delta S°$ is described in Eq. 6.

$$\Delta G^{\circ} = -RT \ln K_c \qquad \text{(Eq. 5)}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \qquad \text{(Eq. 6)}$$

The well-known van't Hoff equation (Eq. 7) is obtained by substituting Eq. (5) into Eq. (6). The values of ΔH° (kJ mol^{-1}) and ΔS° (J mol^{-1}) were obtained from the slope and intercept of a linear plot between ln K_c and 1/T.

$$LnK_c = \frac{-\Delta H^{\circ}}{R} \times \frac{1}{T} + \frac{-\Delta S^{\circ}}{R} \qquad \text{(Eq. 7)}$$

Where,

T is the absolute temperature (K), *R* is the universal gas constant (8.314 J mol-1 K-1), and K_c is the thermodynamic equilibrium constant.

RESULTS AND DISCUSSION

The thermodynamic parameters data from the published work on glyphosate adsorption on GAC/Mn/Fe [22] were recalculated based on the dimensionless approach [23]. The effect of various solution temperatures (5 ºC, 15 ºC, 25 ºC, 35 ºC, 45 ºC) on the process of glyphosate adsorption onto AC/Mn/Fe is presented in **Fig. 2**. The result of calculated adsorption isotherm was presented in the plot of q_e (mol/ kg) over C_e (mol/L) in order to be consistent with physical definitions [23]. Results showed that adsorption capacity increases with temperature increasing from 5 °C (278.15K) to 45 °C (318.15 K). The phenomenon is related to the process of enlargement pore network of GAC within the increasing temperature that promoted increasing the amount of glyphosate adsorbed onto GAC/Mn/Fe through common pore-filling mechanism [32].

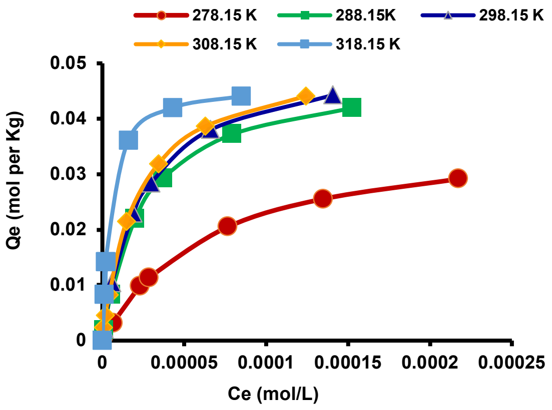

Fig. 2. Effect on solution temperature on adsorption process of glyphosate onto GAC/Mn/Fe. Calculated data from Langmuir isotherm model

In the present work, we adopted the Langmuir sorption model for determination of K_c. The K_L values have been calculated from the Langmuir isothermal data by fitting it using a non-linear equation. This model has been extensively used to describe sorption at equilibrium. It is mostly due to its simplicity and ability to describes the process at the microscopic level, in terms of sorption energy and monolayer coverage [33]. In comparison, the original published work [22] used the distribution coefficient method to determine thermodynamic parameter where Kc was calculated from the intercept on the ordinate of the plot ln (q_e/C_e) against q_e. Due to the differences approach used to determine the K_c value, the Langmuir constant obtained from the adsorption isotherm analysis by [22] was used for comparison with our result (**Table 1**).

Table 1. Comparison of equilibrium constants obtained from Langmuir curve fitting.

T (K)	Original data [22]	Recalculated data
	K_L (mg L^{-1})	Kc, (dimensionless)
278.15	0.085	15251.52
288.15	0.217	41024.41
298.15	0.239	41729.65
308.15	0.278	47353.89
318.15	0.490	219556.96

The calculated *Kc* value vary greatly compared with the original values for example, Kc value for temperature 278.15 K was 15251.52 compared to 0.085 in original data. This finding is in agreement with the results obtained by Tran et al., (2016) and [31] where the high *Kc* value was observed using the dimensionless Langmuir constant method compared to the distribution coefficient method. Other researchers also adopted a similar approach. For instance, the study of Cu(II) sorption on chitosan [34] and cationic dye adsorption on hydrochars of winery and citrus juice industries [35]. It should be realised that directly calculated from the coefficient of distribution without taking into account the dimensionality of the constant of equilibrium may result in incorrect calculations [19].

The plot of ln K against 1/T (van't Hoff) of glyphosate adsorption onto GAC/Mn/Fe showed in **Fig. 3**. The plot of ln K against T^{-1} would theoretically yield a straight line, which allows the calculation of ΔH° and ΔS° from its slope and interception [18]. **Fig. 2** indicates that the estimation method in this paper fits well with the experimental data (R^2 = 0.8052). The correlation coefficient (R^2) of van't Hoff equation is also a determining factor in selecting the optimal derivation for K_c [19]. The value of ΔH° and ΔS°cannot be adequately calculated from van't Hoff equation if the R^2 value is too low [23]. Thus, in this case, the ΔH° and ΔS° can be directly estimated from the slope and interception of the plot (**Fig. 2**).

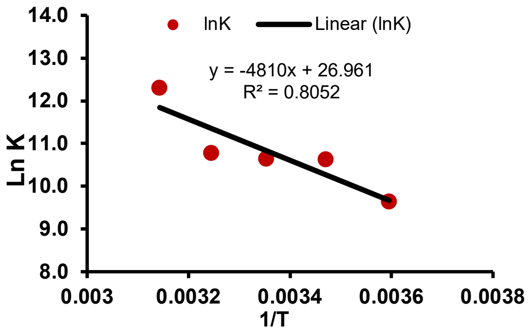

Fig. 3. The van't Hoff plot of glyphosate adsorption on GAC/Mn/Fe. K value is the Langmuir constant calculated from the Langmuir adsorption model. The reaction has been studied at five different adsorption temperatures 278.15 K, 288.15K and 298.15 K, 308.15 K, 318.15K

Table 2 summarise the comparison of thermodynamic parameters values from the reported work [22] and re-evaluated data. Compared to the findings of Yamaguchi et al., the recalculated ΔG° values are more negative for all temperatures under investigation. ΔG° calculated using both methods had the same sign but except for the lowest temperature (278.15 K) in the original data.

The negative values of (ΔG°) for all the investigated temperatures implied the spontaneous nature of glyphosate adsorption onto GAC/Mn/Fe without any further requirement (i.e. energy or heating) [23]. However, the magnitude of these parameters differed considerably depending on the applied constants. These results agree well with existing studies on glyphosate adsorption onto other carbonaceous or magnetic materials [11,36–38]

A positive value of standard adsorption enthalpy ($\Delta H°$=39.97 kJ mol^{-1}) reflected an endothermic adsorption process of glyphosate adsorption on GAC/Mn/Fe which was supported by the phenomenon that the glyphosate adsorption capacities increased with the increase of adsorption temperature as presented in **Fig. 2**. In an endothermic process, the adsorbate species has to displace more than one water molecule for their adsorption, resulting in the endothermicity of the adsorption process. Therefore $\Delta H°$ will be positive [39]. This result is in line with the original data ($\Delta H°$=20.924 kJ mol^{-1}), but the higher value was observed in recalculated data

Table 2: Thermodynamic parameters for the adsorption of glyphosate onto GAC/Mn/Fe

T (K)	Original data [22] *Kc* Coefficient distribution method			Recalculated data Kc (dimensionless) Langmuir constants		
	$\Delta G°$ (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1})	$\Delta G°$ (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1})
278.15	0.527			-22.26		
288.15	- 0.281			-25.43		
298.15	- 0.970	20.924	-73.250	-26.36	39.97	224.04
308.15	- 1.275			-27.57		
318.15	- 2.606			-32.52		

Previous literature also reported on the similar reaction of glyphosate adsorption process [32,36]. It is generally accepted that, when $\Delta H°$ is in the range of (5–10) kJ mol^{-1}, the adsorption mechanism is physisorption. When it is in the range (30–70) kJ mol$^{-1,}$ [32] or very high ~40-400 kJ mol^{-1}[40] the adsorption belongs to chemisorption; i.e., a chemical bond is formed between the adsorbate and the surface [32]. Since the value of $\Delta H°$ ~40 kJ mol^{-1}, we proposed that the adsorption process in this study is chemisorption. This result is consistent with the fact that a chemical adsorption process usually occurs at high temperature [33,41] and the adsorption capacity generally increases with the temperature range [19]. Our recommendation undermines the original work suggesting that the adsorption process is neither fully physical nor fully chemical [22].

The results for the entropy ($\Delta S°$) signs and magnitudes of the thermodynamic parameters contradict the reported data. Our calculation methods resulted in the positive value ($\Delta S°$=224.04 J mol^{-1}) while Yamaguchi et al., reported negative value ($\Delta S°$= -73.250 J mol^{-1}). The positive value of $\Delta S°$ represents the affinity of the adsorbent to the adsorbate species. Furthermore, the positive value of ΔS implies increased randomness at the solid/solution interface with specific structural changes in the adsorbate and adsorbent. The value also correlates to an increase in the degree of freedom of the adsorbed species, indicating that this adsorption process is irreversible and corresponds to a dissociative mechanism [36,37,39]

In the other hand, the negative value of $\Delta S°$ indicates that the adsorption process is enthalpy oriented. The negative value of entropy ($\Delta S°$) also implies a decreased disruption of the solid/liquid interface during the adsorption process, which allows the adsorbate ions/molecules to escape from the solid phase to the liquid phase. Consequently, the amount of adsorbate that can be adsorbed would decrease [39]. Thus, the negative value of $\Delta S°$ reported in the original work differs from the actual experimental results that showed increasing adsorption capacity.

In response to different standard states, both the coefficient distribution method and the Langmuir model are likely to give different values of specific thermodynamic parameters (Salvestrini et al., 2014). It is now realised that the direct substitution of the KL values to the Van't Hoff plot and the substitution of the values $\Delta S°$ and $\Delta H°$ was led to errornous. As argued by [42], theoretically the equilibrium constant should be a dimensionless or unitless quantity [34],

CONCLUSION

Here, we adopted a newly proposed methods to re-evaluate the thermodynamic parameter published data on glyphosate adsorption onto GAC/Mn/Fe reported. The use of dimensionless form of K_c derived from Langmuir constant for thermodynamics calculation resulted in different entropy sign (ΔS) and different magnitude in all of the thermodynamic parameters. This result is finally led to a different interpretation of thermodynamic adsorption in this study. Adsorption of glyphosate onto GAC/Mn/Fe was reported as spontaneous (ΔG° < 0), endothermic (ΔG° >0) and promoted by rising temperature. Based on the magnitude of $\Delta H°$ and comparison with previous literature on glyphosate adsorption, we suggested that the mechanism of adsorption involve chemisorption. The appropriate approach for determining equilibrium constant, K_c for adsorption thermodynamic parameter calculation could prevent misuse and propagating of the wrong information in the field of adsorption thermodynamics. However, it is essential to follow the procedures for calculating adsorption thermodynamic parameters and carefully scrutinizing the method for converting the K value to a dimensionless form.

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