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# Thermodynamic Alternative Calculations on a Published Work on Adsorption of Methyl Orange using Chitosan Intercalated Montmorillonite

Ain Aqilah Basirun[1], Adeela Yasid [1], Ahmad Razi Othman[2], Mohd Khalizan Sabullah[3], Mohd Izuan Effendi Halmi[4] and Mohd Yunus Abd Shukor[1]*

[1]Department of Biochemistry, Faculty of Biotechnology and Biomolecular Science Universiti Putra Malaysia,
43400 UPM Serdang, Selangor, D.E, Malaysia.
[2]Department of Chemical Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia,
43600 UKM Bangi, Selangor, D.E, Malaysia.
[3] Department of Biotechnology, Faculty of Science and Natural Resources, Universiti Malaysia Sabah,
88400 Kota Kinabalu Sabah.
[4]Department of Soil Management, Faculty of Agriculture Universiti Putra Malaysia,
43400 UPM Serdang, Selangor, D.E, Malaysia.

*Corresponding author:
Prof. Dr. Mohd Yunus Abd Shukor,
Department of Biochemistry,
Faculty of Biotechnology and Biomolecular Science
Universiti Putra Malaysia,
43400 UPM Serdang, Selangor, D.E, Malaysia.
Email: mohdyunus@upm.edu.my

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## ABSTRACT

Pollutant treatment methods are available for membrane isolation, exchange of ions, precipitation, transformation and biosorption. Biosorption has many positive aspects of all this technology, including low running costs, very effective toxicant detoxification at low concentrations, low levels of disposal materials. In many applications, adsorption plays an important role in concentrating useful compounds or eliminating contaminants. The thermodynamic parameters of the adsorption are often obtained from the relation between the adsorption constant ($K_C$ in Lmol$^{-1}$ unit) and the Gibbs free adsorption energy. When the van't Hoff plot for the temperature range 298.2 K to 328.2 K was plotted, a nonlinear curve was obtained with poor $R^2$ value ($R$=0.491). In order to calculate the ΔH° and ΔS° more accurately, the thermodynamics parameters were analysed at two processes: one between 298.2 and 301.2 K and another at between 301.2 and 328.2 K which gave a better $R^2$ values of 1.00 and 0.995, respectively. The ΔG°, ΔH° (kJ/mol) and ΔS° (kJ/mol×K) values for temperatures between 298.2 and 301.2 K and between 301.2 and 328.2 K were –29.4524, 14.65, 0.145 and –30.4787, –14.88 and 0.049, respectively. This paper depicts with the proposed workflow in the analysis of liquid-phase adsorption data from the data acquisition to data analysis and thermodynamics appropriate calculation of the dimensionless $K_C$ parameter.

## INTRODUCTION

Accumulation of dyes in wastewater from sectors such as fabrics manufacturing, paper, cosmetics, rubber and plastics has been found to be a major source of water contamination. Reactive dyes, anionic dye, are most widely used because of their vivid colors, excellent color speed and simple application. However, several reactive dyes are harmful to ecosystems and can cause direct harm to marine life. Since the dyes are structurally complex, are of synthetic origin and have high water solubility, it is difficult to remove them from the effluent using conventional physico-chemical and biological methods [1,2].

Today, adsorption separation in environmental engineering has become an aesthetic awareness and focus of nations worldwide, due to its low initial costs, simplicity of design, high efficiency, insensitivity to harmful substances and the complete removal of pollutants from aqueous solution.Natural polymers, like chitosan (CTS), have become more significant because of their biodegradable and indefensible natural properties in wastewater treatment. CTS, a natural biopolymer, contains amine functions, cationic behavior and is highly effective in the removal of anionic dyes [3,4].

There are several factors affecting the adsorption of dye were studied including the effect of temperature on liquid phase adsorption. An analysis of adsorption reaction temperature dependence provides helpful knowledge of changes in adsorption enthalpy and entropy. Temperature is a measure of the adsorption nature, whether it is an exothermic or an endothermic process. Currently, adsorption field has been enriched by a vast amount of studies published in different journals. Extensive research has been dedicated to sound understanding of adsorption isotherm and kinetics. However, a study on adsorption can only be meaningful and useful if it includes the structure as well as the dynamics of its different components, separately and interacting with each other. In this regard, it should be realised that a correct and extensive study on adsorption thermodynamics is desirable [5–7].

Thus, this chapter attempts to offer a better understanding of adsorption thermodynamics with special focus on its fundamental characteristics and mathematical derivations. In this study the published data from biosorption of dye (methyl orange) on the chitosan intercalated montmorillonite [2] is remodeled and recalculated the thermodynamics parameters correctly following the dimensionless equilibrium constant, Kc (without units) [8] and then regressed using nonlinear regression method and assessment of relationship between thermodynamic parameters, ΔG°, ΔH° and ΔS°. This discussion is in accordance with the assumption of the International Union of Pure and Applied Chemistry (IUPAC).

## MATERIALS AND METHODS

### Data acquisition

Data from Figure 1 from a published work [2] were downloaded and processed using the software Webplotdigitizer 2.5 [9] which digitizes the scanned figure into a comma separated data. This method has been utilized by many researchers and acknowledged for its reliability [10,11]. The generated data were then inputted into the curve-fitting software CurveExpert Professional software (Version 1.6) utilizing the Marquardt algorithm. The adsorption isotherm was replotted with the unit of $C_e$ and $q_e$ in mol/l and mol/Kg, respectively [12,13].

### Calculation on dimensionless equilibrium constant $K_L$

The Langmuir equation (**equation 1**) was initially derived from a kinetic study and the subsequently from a thermodynamic study. Accurate estimation of thermodynamic parameters is directly dependent on precise analysis of the equilibrium constant between two phases, *K<sub>C</sub>*.

$$q_e = \frac{q_{mL} K_L C_e}{1 + K_L C_e} \qquad \textbf{(Eqn. 1)}$$

Derived $K_c$ from Langmuir was converted to dimensionless form using **equation 2** and being used in **equation 4** as follows [14]:

$$K_C = 10104 \times 55.5 \times 1000 \times K_L \qquad \textbf{(Eqn. 2)}$$

where the fact 55.5 is the number of moles of pure water per liter and the term of 10104 x 55.5 x1000 x KL is dimensionless. The molecular weight of methyl orange is 10104 gmol$^{-1}$.

The relationship of dimensional $K_L$ with unitless equilibrium constant of $K_C$ is described in **equation 3** where, $K_L$ (L/mol) is the Langmuir constant, C° is the selected standard of adsorbate (C°=1 mol/L); γ (dimensionless) is the activity coefficient of CTS in solution [15].

$$K_C \approx \frac{K_L\left(\frac{L}{mol}\right) \times C^{\circ}\left(\frac{mol}{L}\right)}{\gamma} \qquad \textbf{(Eqn. 3)}$$

The laws of thermodynamics were applied in the calculation of adsorption thermodynamics parameters (ΔG°, ΔH° and ΔS°) using the van't Hoff equation. When adsorption reaches equilibrium, the free energy change (ΔG) is nearly zero. **equation 3** becomes **equation 5** that has been commonly used to compute ΔG° (standard Gibbs energy change).

$$\Delta G^{\circ} = -RT\ln K_C \qquad \textbf{(Eqn. 4)}$$

$$\ln K_C = \frac{-\Delta H^{\circ}}{R} \times \frac{1}{T} + \frac{\Delta S^{\circ}}{R} \qquad \textbf{(Eqn. 5)}$$

The universal gas constant, R is 0.00831 kJ/mol×K.

The relationship between ΔG°, ΔH° and ΔS° of an adsorption process is express as follows:

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

## RESULTS AND DISCUSSION

Isotherms, kinetics, and thermodynamics studies play an important role in thoroughly understanding the adsorption process of organic and inorganic compounds in aqueous solutions. In the three studies, the thermodynamic adsorption is essential in consideration of the types and mechanisms of the adsorption process under variations of the solution temperature. The thermodynamics can effectively exhibit adsorption mechanisms through a series of the adsorptive equilibrium experiments under different temperatures and various initial adsorbate concentrations as well as fixed optimal conditions (pH of the solution, the adsorbent's particle size, ionic strength, and solid/liquid ratio) [5,16]

The absorption thermodynamics data from a published work [2] on the biosorption of methyl orange by chitosan intercalated montmorillonite were analysed using another thermodynamic alternative calculation approach by Nguyen's method [15]. Gathering the information, the units of adsorption isotherms (the plot of $q_e$ against $C_e$) must be presented as mol/Kg ($q_e$) and mol/L ($C_e$) as shown in **Fig. 1**.

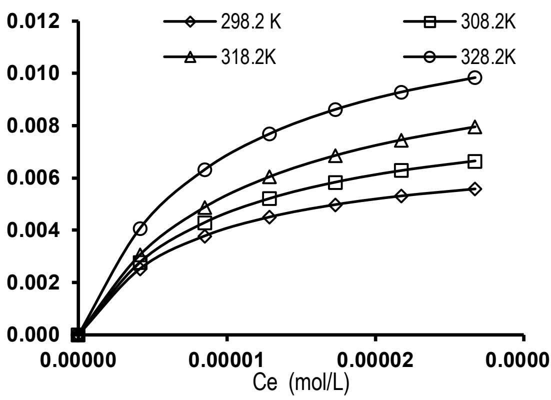

**Fig. 1.** Equilibrium adsorption isotherm of methyl orange onto chitosan intercalated montmorillonite at various temperature. Recalculation of equilibrium constant Kc, into dimensionless form. The values of Kc (unitless) are listed in **Table 1**.

**Table 1**. Comparison of original Langmuir constant (with unit) and recalculate dimensionless equilibrium constant $K_C$ derived from Langmuir isotherm replot

| T (K) | $K_L$(L/mol) (Original data) | $K_C$ (dimensionless) |
|---|---|---|
| 298.2 | 316.08 | 131208.5 |
| 308.2 | 391.45 | 108797.3 |
| 318.2 | 439.90 | 89948.38 |
| 328.2 | 600.17 | 106486.2 |

The viability and spontaneity of an adsorption process are calculated by thermodynamic parameters. They are also important for the evaluation of adsorbents (i.e. physisorption, ion exchange or chemisorption) [2,7]. The exact measurement of these thermodynamic parameters absolutely depends on the equilibrium constant of the $K_C$. In calculating thermodynamic parameters, particularly free energy Gibbs, many authors make use of constants derived from different isothermal models, partition constants and distribution coefficient. According to the IUPAC, the Gibbs free energy change (after ΔG°) must be determined by a normal balance constant $K_C$ for calculating Gibbs free energy change.

**Table 2** summaries the calculating performance of the parameters of thermodynamics for whole the adsorption process. Based on the van't Hoff plot in **Fig. 2**, the negative values of standard Gibbs free energy (– ΔG°) which is differ with original data suggest that the process of methyl orange adsorption onto CTS occurred spontaneously without the requirement of energy or heat. The conversion to dimensionless gives ΔG° values ($\Delta G° > 20$) indicated the adsorption happened is chemisorption as adsorption with ΔG° values ranging from −400 to −80 kJ/mol corresponds to chemisorption [7,12]. In comparison with original data, the negative value of ΔG° is remained except the value is slightly higher that could change the perspective of nature of adsorption system from physisorption to chemisorption.

Because the $R^2$ value ($R^2 = 0.491$) of the van't Hoff equation is too low, the ΔH° and ΔS° values cannot be adequately calculated from such equation. In addition, the adsorption capacity and the equilibrium constant $K_C$ did not follow the order of temperatures, such as 298.2 K < 308.2 K < 318.2 K< 328.2 K. Therefore, this study follows the solution reported in Nguyen [15] whereby the thermodynamics parameters were analysed at two processes: one at (298.2 – 301.2 K) and another at (301.2 – 328.2 K) as constructed in **Fig. 3** (A) & (B).

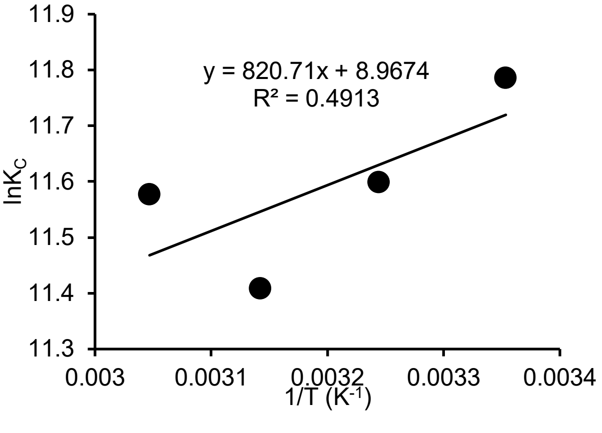

**Fig. 2.** van't Hoff plot of for the removal of methyl orange by chitosan intercalated montmorillonite

**Table 2.** Comparison between recalculated thermodynamics parameters using dimensional $K_C$ and original result.

| T(K) | $K_C$ | ΔG° (kJ/mol) | ΔH° (kJ/mol) | ΔS° (kJ/(mol.K)) |
|---|---|---|---|---|
| 298.2 | 131208 | -29.20 | -6.82 | +0.0742 |
| 308.2 | 108797 | -29.70 | | |
| 318.2 | 89948 | -30.16 | | |
| 328.2 | 106486 | -31.58 | | |

Result from original published work [2]

| T(K) | $K_L$(L/mol) | ΔG° (kJ/mol) | ΔH° (kJ/mol) | ΔS° (kJ/(mol.K)) |
|---|---|---|---|---|
| 298.2 | 316.08 | -14.27 | +16.55 | +0.055 |
| 308.2 | 391.45 | -15.30 | | |
| 318.2 | 439.90 | -16.10 | | |
| 328.2 | 600.17 | -17.50 | | |

Based on replot as suggested by Nguyen's method (**Fig. 4**), the parameters of Δ*H*° and Δ*S*° of adsorption thermodynamics at 298.2 – 308.2 K and 308.2 – 328.2 K were calculated as shown in **Table 3.** Generally, the slope of van't Hoff plot defines the system either it is exothermic (negative slope) or endothermic (positive slope). Clearly, an increase in solution temperature from at 298.2 to 308.2 K, the maximum adsorption capacity of CTS significantly decreased. This is might be caused by two feasible reasons which are a continuing increase in enlarging pore network of CTS was not favorable to adsorbed dye molecules [13,15] and desorption phenomenon resulted from the weak adsorption interaction during the adsorption process. The result is well consistent with the Δ*H*° value.

A positive value of the standard adsorption enthalpy (Δ*H*° = 14.65 kJ/mol) confirms that the adsorption was endothermic reaction. However, a further increasing in temperature to 328.2 K, there was an increase in adsorption capacity at a higher temperature because the phenomenon of enlargement pore network of CTS within the increasing temperature simulate to increase the amount of dye adsorbed onto CAC through common pore-filling mechanism [17].

The present of heat or energy caused an increase in the mobility of dye molecules and an increase in the number of active adsorption sites with an increase in temperature. Because the contribution of weak van der Waals in the adsorption process, the standard adsorption enthalpy change was negative and low magnitude (Δ*H*° = −14.88 kJ/mol).
A similar result reported by the authors has resulted in an increase in temperature, resulting in a reduction in the dye viscosity leading to the increase in adsorption capability of the molecule across the external boundary layer and in the inner pores of CTS adsorbents as a result [2].

The positive entropy changes ΔS° of adsorption is similar to original data because the randomness of the adsorbates after adsorption would be increase in less viscosity of dye solution due to increase in temperature. Besides, the positive value of ΔS° might be because the adsorption occurs in two consecutive steps: desorption of the adsorbed water and adsorption of the adsorbate.

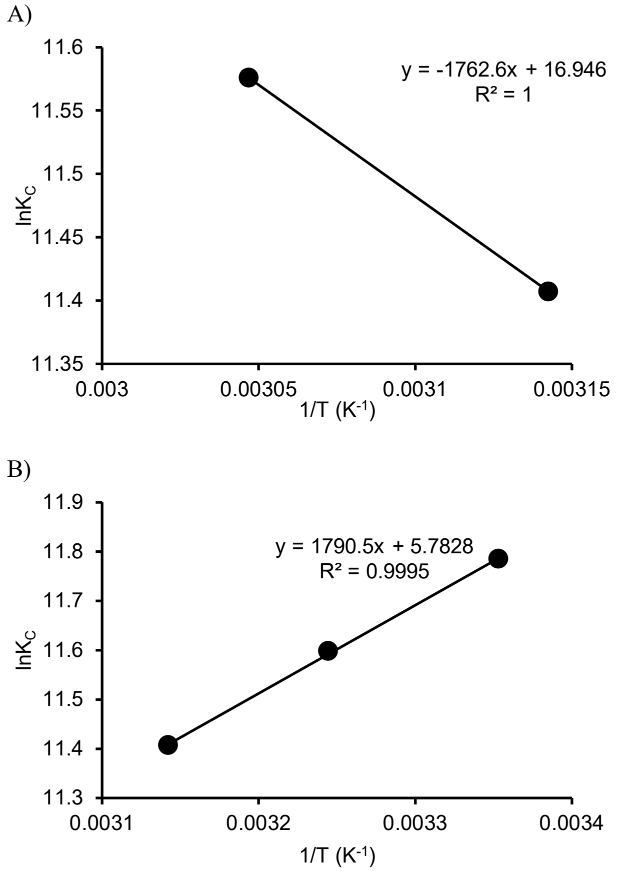

**Fig. 3.** Two set of van't Hoff plot calculated based on two operations temperature. A) 298.2 – 301.2 K and B) 301.2 – 328.2 K

**Table 3.** Thermodynamic parameters of methyl orange by CTS intercalated montmorillonite at two operation temperatures.

| T (K) | ΔG° (kJ/mol) | ΔH° (kJ/mol) | ΔS° (kJ/mol×K) |
|---|---|---|---|
| 298.2-318.2 | -29.4524 | 14.65 | 0.145 |
| 318.2-328.2 | -30.4787 | -14.88 | 0.049 |

## CONCLUSION

In conclusion, for adsorption thermodynamics, the equilibrium constant ($K_C$) must be dimensionless regardless of using Langmuir equilibrium isotherms or partition/distribution coefficient method. The optimal method for calculating thermodynamic parameters should be appropriately selected according to the data from the adsorption equilibrium experiment. Notably, it is inaccurate to calculate the thermodynamic parameters from an experiment that shows nonlinear van't Hoff plot and a more suitable analysis would be to split the data to two temperature ranges.

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