

## Kinetics-thermodynamics integration for improved understanding of adsorption mechanisms: A critical perspective

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### Abstract

Adsorbates adsorption on adsorbent is a complex process and this study analyzed critically adsorption mechanisms using theoretical perspectives. Although considerable advances have been made in understanding the isolated role played by various system properties, theoretical developments have not been rigorous and they lag behind experimental and conceptual developments. Some of the experimental difficulties and theoretical complexities that are responsible for the slow development of a unifying adsorption model covering a range of adsorbates-adsorbent combinations have been analyzed critically from adsorption principle, experimental algorithms for obtaining adsorption and adsorption kinetics parameters as well as the adsorption parameters analysis using different adsorption, kinetic and thermodynamic models. the sudden decrease of adsorption densities of pH, temperature and adsorbent dosage after successive increase as been explained to be as a result of the effect of  $H^+$  and/or  $OH^-$  ions, intermolecular forces and/or weakening of the attractive forces due to excessive heat energy at higher temperature. The nexus between existing adsorption models such as Stern-Grahame and Equilibrium Constant ( $K_c$ ), Henry and Arrhenius laws, Langmuir isotherm and thermodynamic variables ( $\ln K_{eq}$ ,  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ ), Langmuir and Stern-Grahame's isotherm equations and pseudo first and second kinetic models were analyzed. The major individual contributions to the overall energy of adsorption have been identified and discussed for effective analysis of adsorption mechanisms and systems.

**Keywords:** Adsorption isotherm; Kinetic models; Thermodynamics; Arrhenius law; Adsorption density

### 1. Introduction

Adsorption of surfactants on solids in contact with solutions is important in controlling a variety of interfacial processes<sup>[1]</sup> such as detergency, flocculation, enhanced oil recovery, mineral flotation as well as solid/liquid separations. Adsorption is influenced by various interactions, among the solid, adsorbate, solvent and other dissolved species, such as electrostatic attraction, covalent bonding, hydrogen bonding or nonpolar interaction, lateral interactions between the adsorbed species and desolvation<sup>[2]</sup>.

Adsorption is a phenomenon that describes the interaction between two different phases that forms an interface layer by transfer of a molecule from a fluid bulk (liquid or gas) to a solid surface so, it is classified as a surface process. This layer is expressed by two kinds of interaction physical or chemical interactions. This process usually is reversible, and the reverse process is called desorption<sup>[3]</sup>.

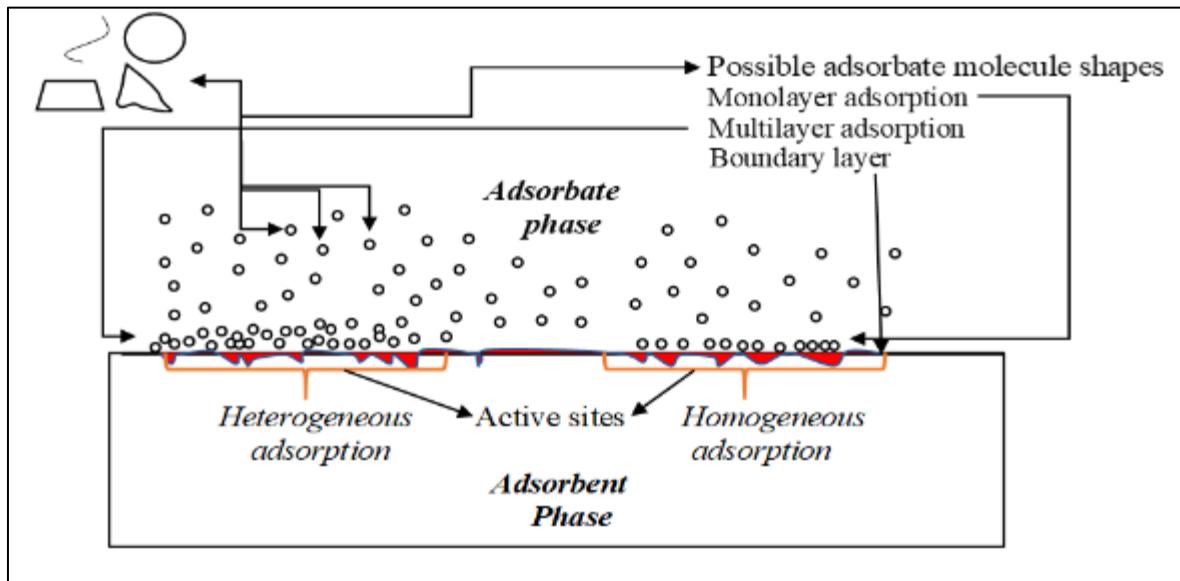
Kinetics or equilibrium adsorption studies are used to explain the adsorption mechanism and adsorption characteristics. Both thermodynamic and kinetic experimental results distinguish between physical adsorption and

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chemical adsorption. The results determine bonding type, binding specificity, temperature effect, enthalpy of the bonding process, concentration or pressure effect, saturation of the interfacial layer, and kinetics of the process [4].

## 2. Adsorption mechanism and principle

Adsorption of molecules occurs at active sites of the solid surface. The active sites are called homogeneous when they all contain the same energy potential. With different energy potentials the sites are said to be heterogeneous [5]. Molecules that are adsorbed are called adsorbate as represented in figure 1. In the adsorption process the molecule loses kinetic energy, making adsorption an exothermic process. The adsorbate, i.e. the molecules adhering to the surface of the adsorbent, may be considered to behave like a liquid. The reverse process of adsorption is called desorption [5]. This process is consequently endothermic; heat must be supplied to separate the adsorbate from the adsorbent.

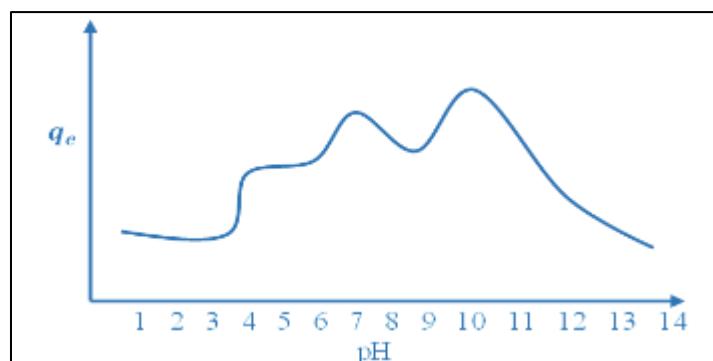


**Figure 1** Adsorbate adsorption mechanism

## 3. Factors that affect adsorption rate

### 3.1. pH of Adsorbate

pH is one of the most important parameters controlling adsorption of adsorbates in aqueous solutions. Normally, the adsorption of adsorbate increases as the pH shifts from low to high this is because pH is the most susceptible parameter in adsorption studies due to the fact that  $H^+$  is a strongly competing adsorbent [6]. This means that higher adsorption rate is observed at higher pH and vice versa as represented hypothetically in the graph of equilibrium adsorption ( $q_e$ , mg/g) versus pH.

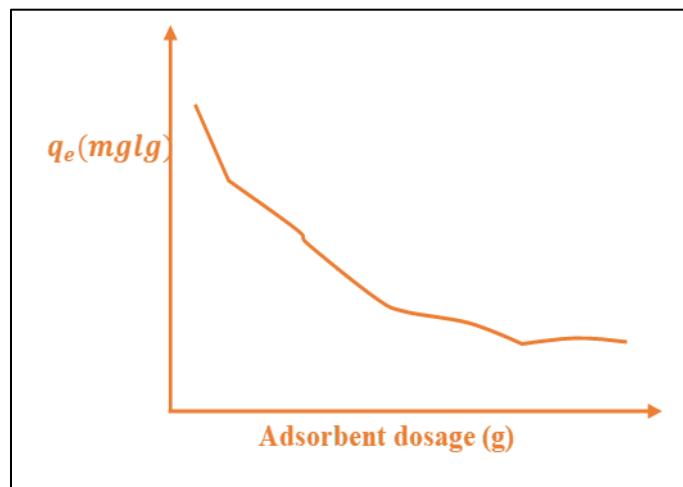


**Figure 2** Hypothetical effect of adsorbate pH on adsorption

Decrease in adsorption of adsorbates at pH>10 has been observed by some scholars [6-9]. The decrease in the formation of adsorbent-adsorbate bond at higher alkaline pH values may probably be attributed to an increase in electrostatic repulsion between the micelles and the negative adsorbent surface [9].

### 3.2. Adsorbent Dosage

Most experimental investigations showed that adsorption capacity of adsorbate adsorbed decreases with increasing adsorbent dosage as illustrated in figure 3.

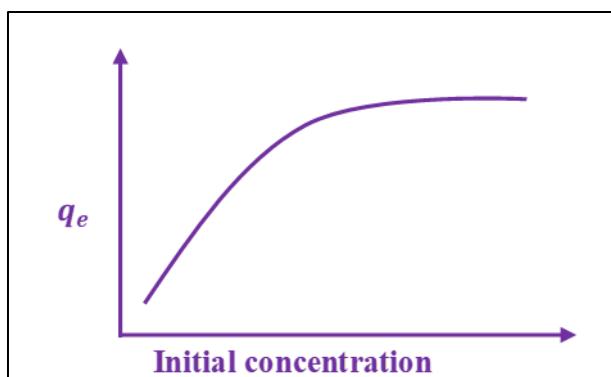


**Figure 3** Hypothetical effect of adsorbent dosage

The results base on the hypothetical figure 2 shows that increasing adsorbent dosage amount leads to decrease in adsorption capacity owing to the high bulk density and chemical resistance nature of adsorbent [6,10,11].

### 3.3. Concentration of adsorbate

It has been asserted that increase in adsorbate concentration provides enough interface for adsorbates interaction with the adsorbent. An investigation on the effect of initial concentration on equilibrium adsorption capacity shows that increase in concentration of adsorbates molecules increases adsorbent's surface charge and driving more adsorption to take place [7] as represented in figure 4.

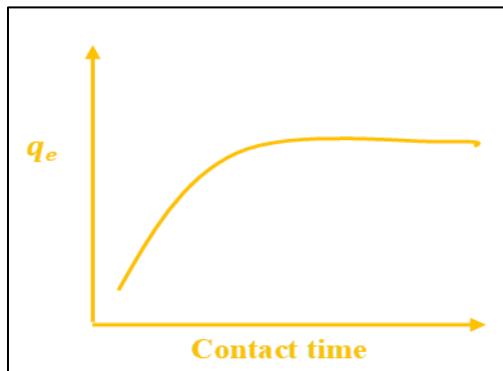


**Figure 4** Hypothetical effect of initial concentration

The plausible reason for this might be attributed to the fact that at lower initial adsorbate concentrations, sufficient adsorption sites are available for the adsorption of the adsorbent. Therefore, the fractional adsorption is independent of initial adsorbate concentration. However, at higher concentrations, the number of adsorbates is relatively higher when compared to the availability of adsorption sites. Hence, the percent adsorption of adsorbate depends on the initial adsorbate concentration and decreases with an increase in initial adsorbate concentration [8].

### 3.4. Contact time

The contact time is essential for the establishment of equilibrium during the adsorption process [9]. A general increase in adsorbates adsorption with contact time has been witnessed at the initial stage by most scholars [6,10,11]. A similar observation was noted in Elsayed et al.'s study in which the removal percent of heavy metal (adsorbate) increases along with the contact time [12] and figure 5 hypothetically represents the assertion:

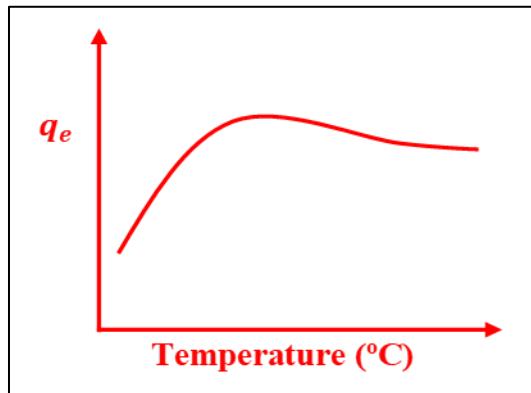


**Figure 5** Hypothetical effect of contact time

This may be due to the availability of greater adsorbent surface area at the opening of the adsorption of corresponding metal ions in the medium [13]. As the adsorption increases with increase in contact time, maximum adsorption time will be reached, which will result in static values, after which no further change in uptake will be observed and this may be due to the fact that the surface of adsorption sites is fully occupied, thereby reflecting the equilibrium point of the system [6]. This may also be because the remaining vacant sites are difficult to capture by the adsorbates due to the repulsive forces between the adsorbate present in solid and bulk phases.

### 3.5. Temperature

The adsorption of adsorbates is temperature dependent. The most common temperature range testified by most scholars is between 30 and 60 °C. The amount of adsorbate adsorbed increases gradually as temperature increases and optimum temperature of adsorption of adsorbate was observed between 40-60 °C [8,9,11,14]. Beyond optimum temperature there was a rapid decrease of adsorption as demonstrated in figure 6:



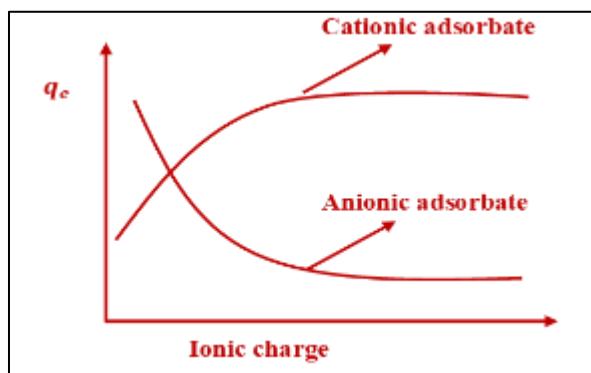
**Figure 6** Hypothetical effect of temperature

The decrease in adsorption with increase in temperature may be attributed to weak attractive forces between adsorbate and adsorbent and partly due to enhancement of thermal energies of adsorbate; thus, making the attractive forces between adsorbate and adsorbent insufficient to retain adsorbates at binding sites [14]. This could lead to desorption or cause adsorbate to bounce off surface of adsorbent instead of colliding and combining with it. Furthermore, Nwoko et al. [9] and Enajeme [6] affirmed that increase in adsorption capacity of adsorbate with temperature gave an endothermic process and it can be attributed to an increase in the number of active surface sites available for adsorption on the adsorbent or adsorbate of adsorbing species and, the decrease in the thickness of boundary layer surrounding the adsorbate. At a higher temperature the possibility of diffusion of adsorbates within the pore of the adsorbent may be

enhanced leading to higher adsorption density since diffusion is an endothermic process, greater adsorption will be observed at high temperature. Thus, the diffusion rate of ion in the external mass transport process increases with temperature.

### 3.6. Ionic Charge

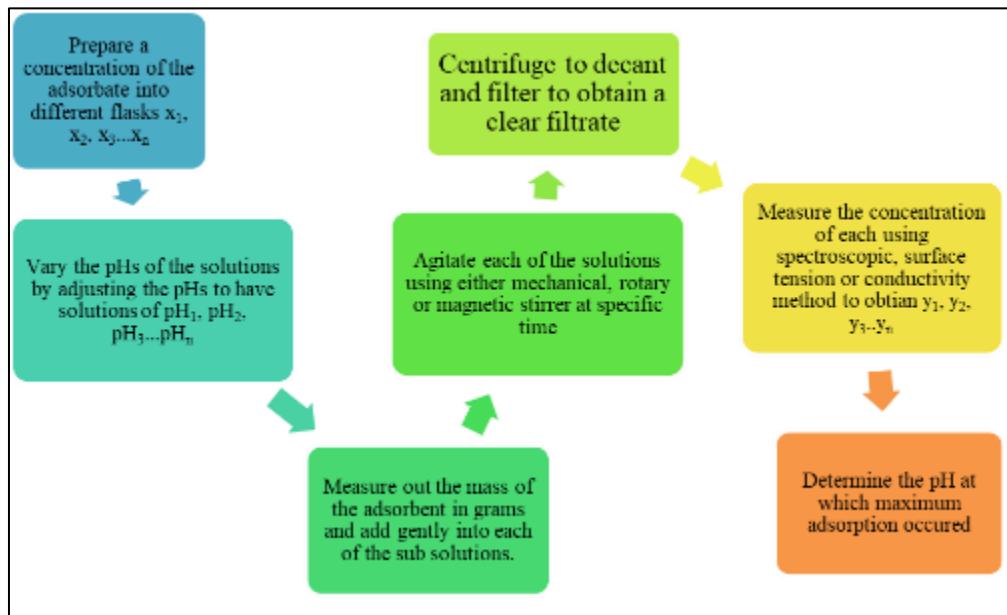
It is evidenced that at certain ionic concentration, equilibration is attained after which the rate of adsorption equals that of desorption. Until constant values are attained, adsorption capacity at this concentration showed that at the set point or concentration of equilibration is charge dependent. Equilibrium adsorption capacity ( $q_e$ ) values increased linearly for cationic spiked adsorbate adsorption [15]. The reverse case was observed for the anionic spiked adsorbate where equilibrium adsorption capacity decreases with increase in ionic charge. This is demonstrated in the hypothetical figure 7.



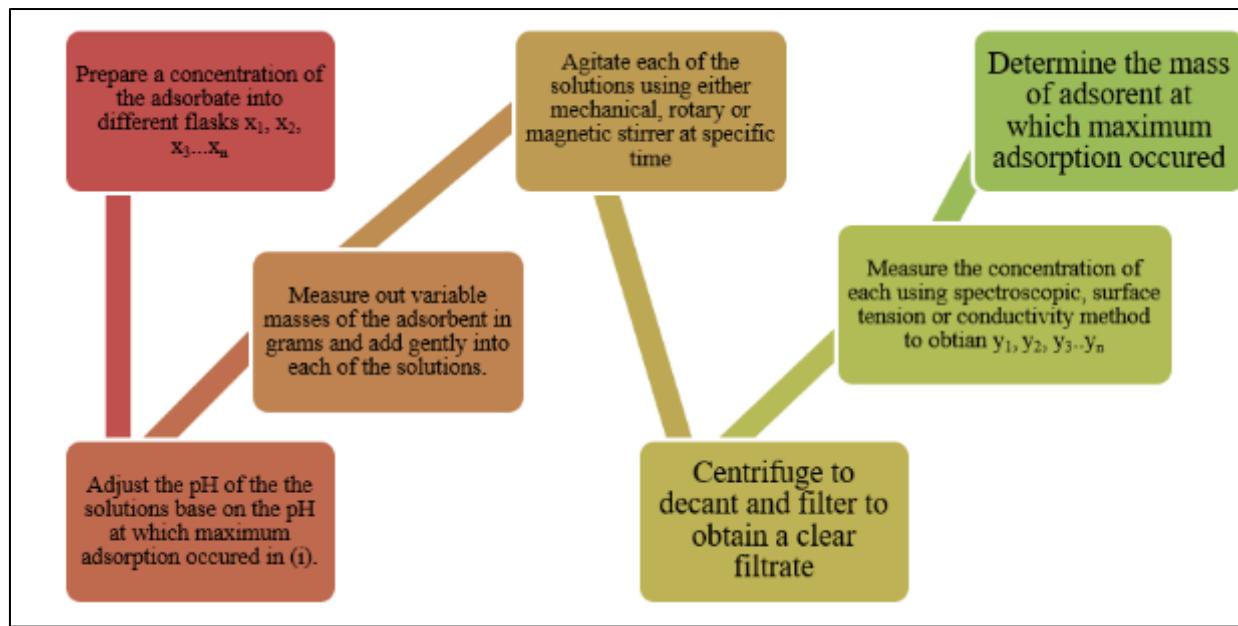
**Figure 7** Hypothetical effect of Ionic charge

## 4. Algorithms for obtaining adsorption experimental data

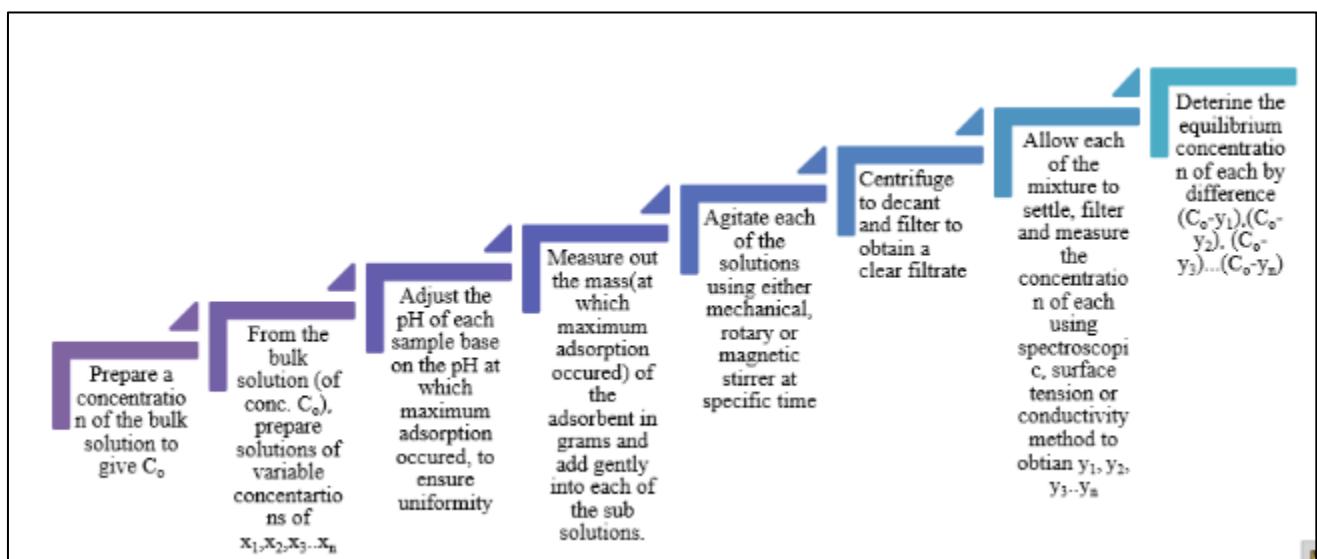
Obtaining adsorption experimental data involves carefully designed procedures and algorithms to analyze and interpret the interaction between adsorbates and adsorbents. Figures 8 to 15 show the algorithms and methods used for obtaining and analyzing adsorption data from experiments:



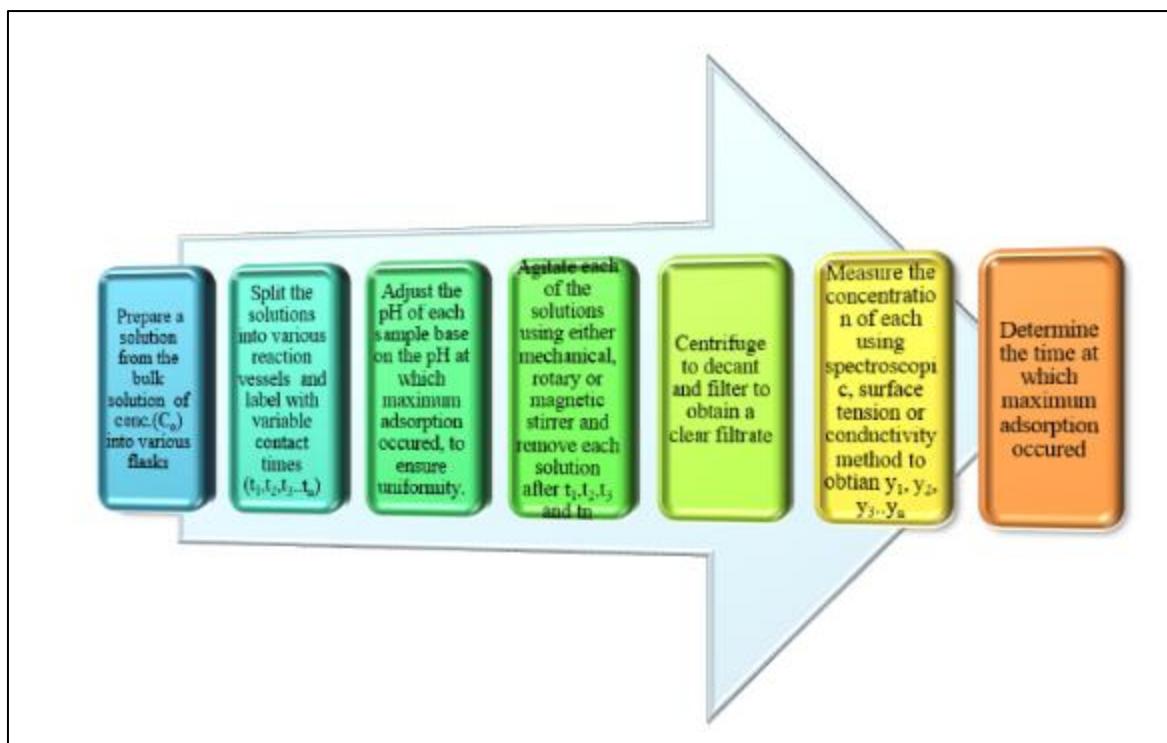
**Figure 8** Obtaining adsorption experimental data for the effect of Ph



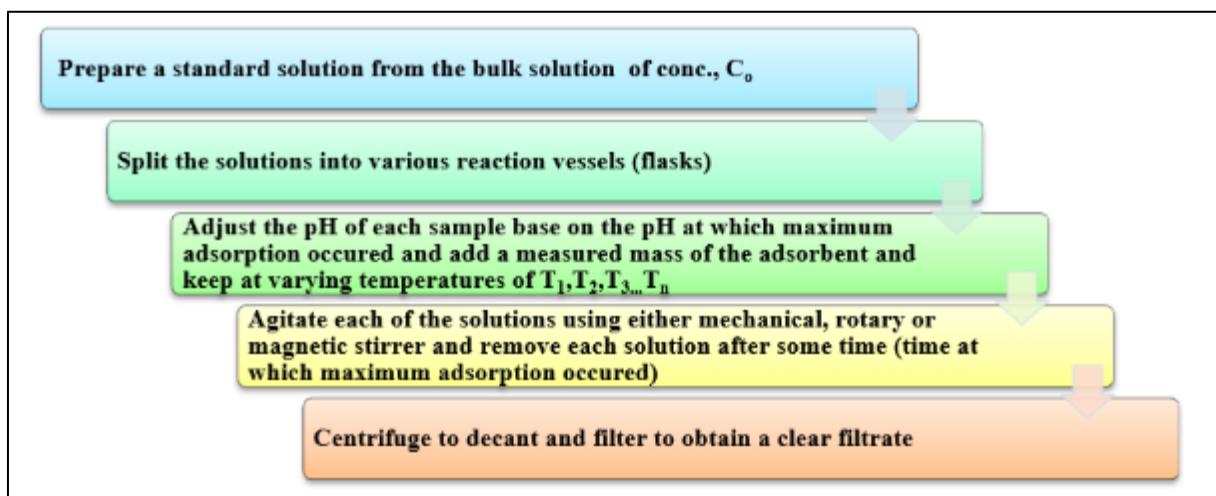
**Figure 9** Obtaining adsorption experimental data for the effect of Adsorbent dosage



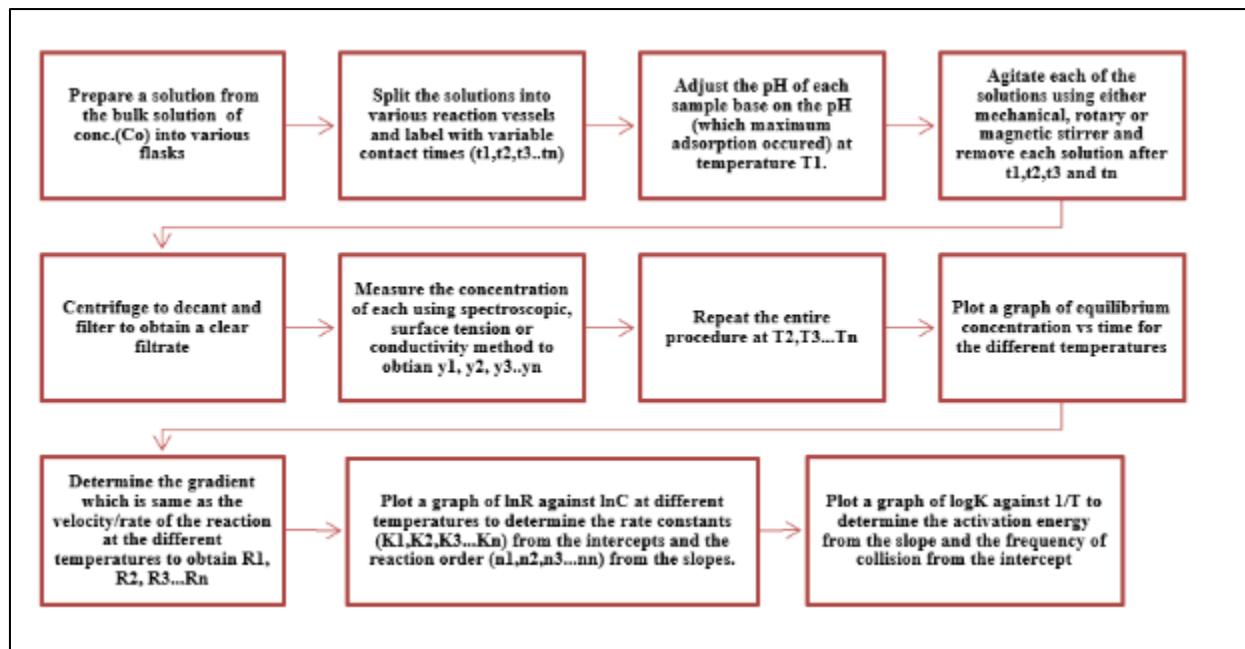
**Figure 10** Obtaining adsorption experimental data for the effect of initial concentration



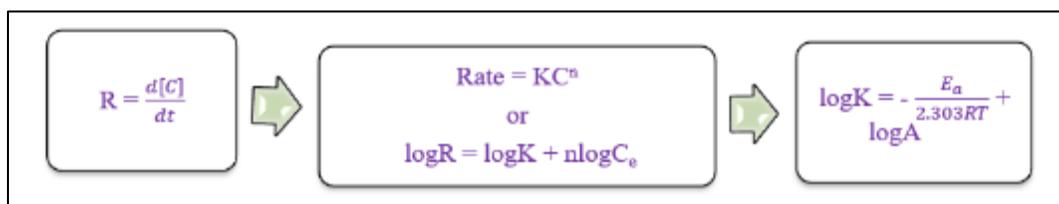
**Figure 11** Obtaining adsorption experimental data for the effect of contact time



**Figure 12** Obtaining adsorption experimental data for the effect of temperature

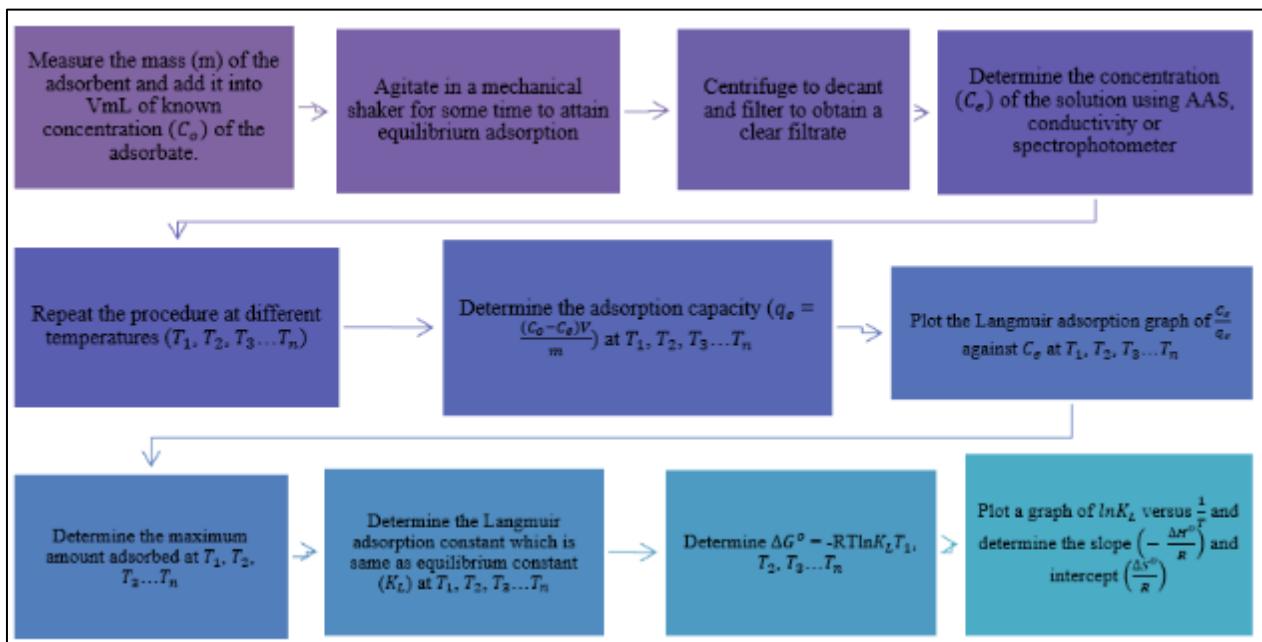


**Figure 13** Determining Parameters for Arrhenius Equation



**Figure 14** Equations for determining the Arrhenius effect of temperature on adsorption rate

## 5. Experimental procedures for determining thermodynamic parameters (from langmuir isotherm constant)



**Figure 15** Experimental procedures for determining thermodynamic parameters

## 6. Adsorption isotherm models

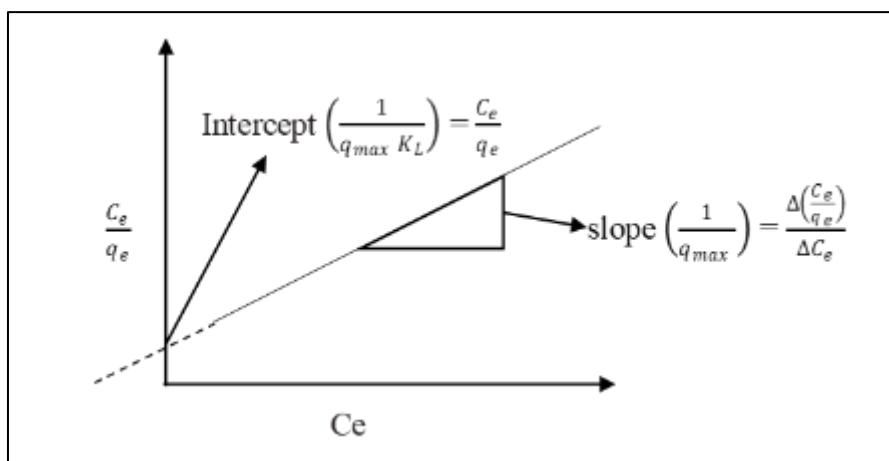
An isotherm is a functional expression for the variation of adsorption relative to the concentration of adsorbate in the bulk solution at constant temperature [16]. Isotherm usually explains the relationship between the concentration of adsorbate at solid phase in relation to its concentration at equilibrium phase. In this research, five isotherms were used to model equilibrium data obtained [15]. Adsorption isotherms are basic requirement for the design of adsorption system [17]. It is basically imported to describe how solute interacts with biosorbent, and it is critical for optimizing the use of adsorbent. Equilibrium relationships between sorbents and sorbates are described by sorption isotherms which give the capacity of a sorbent for a sorbate [18]. Isotherms can be deduced by designing batch reactors at fixed temperatures. It describes the relation of between the adsorbate retained by the activated carbon and the adsorbate equilibrium concentration [16].

### 6.1. Langmuir Adsorption Isotherm

The Langmuir model can be presented by the equation (1) below<sup>8</sup>.

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{1}{q_{max}} C_e \quad \dots \dots \dots \quad 1$$

Where:  $q_{max}$  is the monolayer adsorption capacity of the adsorbent, i.e. the maximum amount adsorbed;  $K_L$  is the Langmuir adsorption constant;  $C_e$  is the equilibrium adsorbate concentration in the solution and  $q_e$  is the equilibrium adsorbate concentration on adsorbent. Values of  $q_{max}$  and  $K_L$  are calculated respectively from the slope and the intercept of the plot of  $\frac{C_e}{q_e}$  against  $C_e$ .



**Figure 16** Hypothetical Langmuir adsorption isotherm

The hypothetical Langmuir adsorption isotherm as seen in figure 16, has been asserted not to have a negative slope, nor intercept, and adsorption increased as amount adsorbed at equilibrium ( $q_e$ ) increases [6,8,9,11]. Hence, in most cases a positive interaction between adsorbent and adsorbate molecules. The residual plots showed no pattern or trend; a sign of good fitting.

### 6.2. Equilibrium adsorption capacity ( $q_e$ )

The equilibrium adsorption capacity ( $q_e$ ) is the amount of adsorbate adsorbed per gram of adsorbent at equilibrium (mg/g) obtain from equation 2:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad \dots \dots \quad 2$$

Where  $C_0$  = initial concentration of adsorbate (mg/L),  $C_e$  = equilibrium concentration (mg/L),  $V$  = volume of solution (L) and  $m$  = mass of adsorbent (g).

- **Monolayer adsorption capacity ( $q_{max}$ ):** A relatively high adsorption capacity suggests that significant number of molecules were adsorbed from the solution.

- **Langmuir adsorption constant ( $K_L$ ):** The Langmuir adsorption constant value shows the degree of affinity between adsorbate and adsorbent and that the adsorption process is either favorable or not [9]. The value of  $K_L$  indicates that the behavior of the isotherm is described as unfavorable adsorption ( $K_L > 1$ ), linear adsorption ( $K_L = 1$ ), no adsorption ( $K_L = 0$ ), and favorable adsorption ( $0 < K_L < 1$ ) [3].

### 6.3. Freundlich Adsorption Isotherm

Freundlich isotherm is used for modeling the adsorption on heterogeneous surfaces [16,19,20]. The equation of the Freundlich adsorption model is expressed in equation 3.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \dots \dots \dots \quad 3$$

Where  $K_F$  is a constant related to the adsorption capacity (Freundlich constant) and  $\frac{1}{n}$  is an empirical parameter related to the adsorption intensity. Values of  $K_F$  and  $n$  are calculated from the slope and the intercept of the plot of  $\log q_e$  vs.  $\log C_e$  as shown in Figure 17.

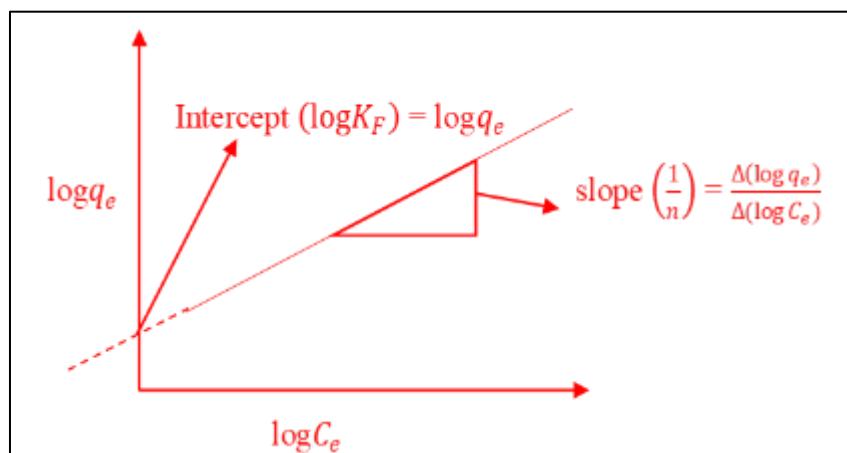


Figure 17 Freundlich hypothetical isotherm

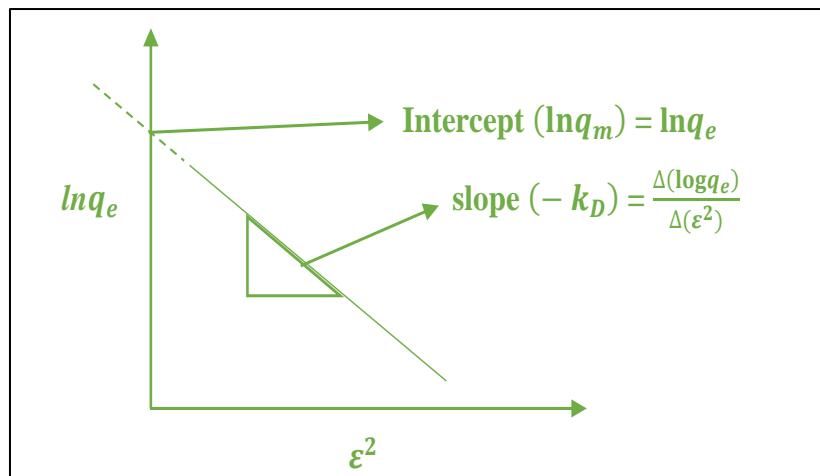
- **Heterogeneity of the adsorbent surface ( $\frac{1}{n}$ ):** The when  $1/n$  value is less than 1, it indicates a heterogeneous surface with a variety of adsorption sites, suggesting that the adsorption process is complex and may involve multiple mechanisms [9]. It has been noted that if the value of  $1/n$  was between 0 and 1, it indicates the adsorbents prepared are favourable for adsorption of the adsorbate under the conditions used in the study [6].
- **Freundlich constant ( $K_F$ ):** It is a key parameter in the Freundlich isotherm which reflects the capacity of the adsorbent to adsorb the solute and higher values of  $K_F$  values mean greater adsorption capacity, suggesting a stronger interaction between the adsorbent and adsorbate [6]. It is also used in comparing the effectiveness of various adsorbents for a particular contaminant.

### 6.4. Dubinin-Radushkevich (D-R) isotherm

D-R isotherm is commonly used to describe the sorption isotherms of single solute systems. The D-R isotherm is expressed as [21]

$$\ln q_e = \ln q_m - k_D \varepsilon^2 \quad \dots \dots \dots \quad 4$$

Where  $q_e$  is the adsorbate concentration (mg/L) that is adsorbed per unit mass of adsorbent,  $q_m$  is the D-R adsorption capacity (mg/L),  $k_D$  is the constant related with adsorption energy ( $mol^2 k/J^2$ ) and  $\varepsilon$  is the Polanyi potential [21].



**Figure 18** D-R Adsorption hypothetical isotherm

As it is seen in Fig.18, the D-R plot hypothetically yields a straight line. In the D-R isotherm, the values of the adsorption capacities  $q_m$ , adsorption energy constants  $k_D$  and the main adsorption energies E can be calculated for adsorbate adsorption. Low values of adsorption energy show that the adsorption has a physical nature.

**$k_D$  constant ( $\text{mol}^2 \text{J}^{-2}$ ):** The  $k_D$  constant in the D-R isotherm is related to the adsorption energy. It is connected to the mean free energy of adsorption (E), which provides insight into adsorption mechanism [20] given as

$$E = \frac{1}{\sqrt{-2k_D}} \quad \dots \quad 4.1$$

**Polanyi potential ( $\varepsilon$ ):** The polanyi potential ( $\varepsilon$ ) is a measure of the adsorption potential energy represented mathematically as:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad \dots \quad 4.2$$

Where, R is the gas constant ( $\text{kJK}^{-1} \text{mol}^{-1}$ ) and T is the temperature (K).

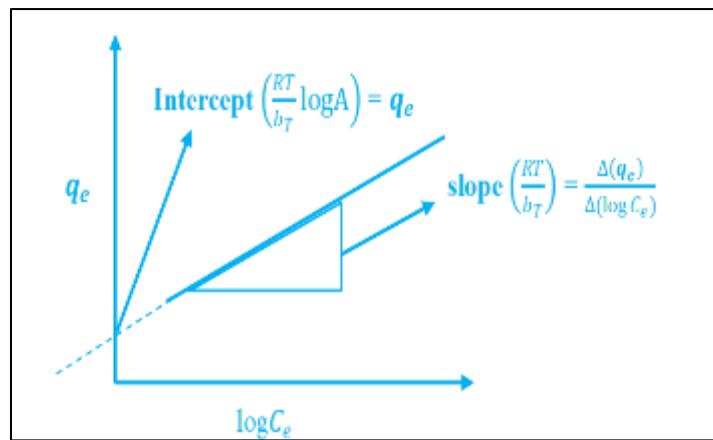
### 6.5. Temkin Adsorption Isotherm

The Temkin adsorption isotherm is a mathematical model that describes the adsorption of molecules onto a surface. The mathematical expression for Temkin's model is given by:

$$q_e = B \ln(A) + B \ln(C_e) \quad \dots \quad 5$$

$$q_e = \frac{RT}{b_T} \ln(A) + \frac{RT}{b_T} \ln C_e \quad \dots \quad 5.1$$

Where; A is Temkin isotherm equilibrium binding constant ( $\text{L/g}$ ),  $C_e$  is equilibrium concentration ( $\text{mg/L}$ ),  $q_e$  is the amount of adsorbate in the adsorbent at equilibrium ( $\text{mg/g}$ ), R is universal gas constant ( $8.314 \text{ J/mol.K}$ ) and T is temperature (K). Figure 19 presents a hypothetical linear graph of  $q_e$  against  $\log C_e$ .



**Figure 19** Temkin Adsorption isotherm

### 6.5.1. Temkin isotherm equilibrium binding constant ( $A$ )

The Temkin isotherm equilibrium binding constant value indicates degree of adsorption capacity (low, moderate or high) and how adsorbent can effectively remove adsorbates from the solution [22].

### 6.5.2. The $b_T$ Constant

The positivity or negativity of  $b_T$  shows that the adsorption process is either exothermic or endothermic. It also reflects strong interaction between adsorbate and adsorbent implying the advantageousness of the adsorption process [11].

## 7. Adsorption kinetic and kinetic models

Adsorption kinetic isotherm is a curve (or line) that describes the rate of retention or release of a solute from an aqueous environment to solid-phase interface. Pseudo-first and pseudo-second order models are the mostly utilized kinetic models, but in this study, and intraparticle diffusion and Elovich models are in addition explained.

## 7.1. Pseudo-First order

It is also known as Lagergren model. It describes the adsorption of solute onto adsorbent following the first order mechanism. It is also varied under low pressure adsorption and under high sorbent dosage. The plots of  $\ln(q_e - q_t)$  versus  $t$  gives a straight-line graph. The values of the rate constants  $K_1$  and theoretical equilibrium adsorption capacities  $q_e$  (theoretical) at different concentrations and temperatures can be calculated from the slopes and intercepts of the linear plots [6] as represented in figure 19. The pseudo-first order equation is given by

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad \dots \dots \dots \quad 6.0$$

where  $q_t$  = Concentration of adsorbate adsorbed (in mg/g) onto adsorbent at time  $t$  which can be calculated from the mass balance equation

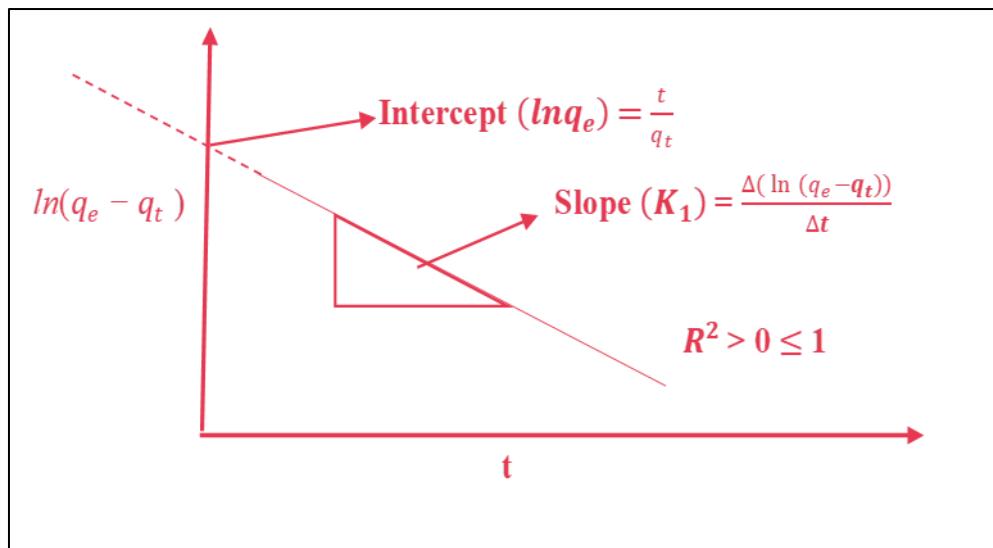
$q_t = \frac{(C_0 - C_t)V}{m}$  where  $C_0$ ,  $C_t$ ,  $V$  and  $m$  are initial conc. of adsorbate in adsorbent, concentration of adsorbate at time  $t$ , volume of the solution and mass of adsorbent, respectively.

$q_e$  = Equilibrium adsorption capacity (mg/g)

When  $t$  is equal to the equilibrium contact time,  $C_t = C_e$  and hence  $q_t = q_e$  and the amount of adsorbate adsorbed at equilibrium,  $q_e$  is calculated using the equation.

$k_1$  = Rate constant in per minute: It is always inversely proportional to the initial concentration of the solute and this is because a longer time is required for a large initial solute concentration.

The plots of  $\ln(q_e - q_t)$  versus  $t$  give a straight line graph with slope  $K_1$  and intercept  $\ln q_e$ . Consider figure 20, a hypothetical pseudo-first order isotherm.

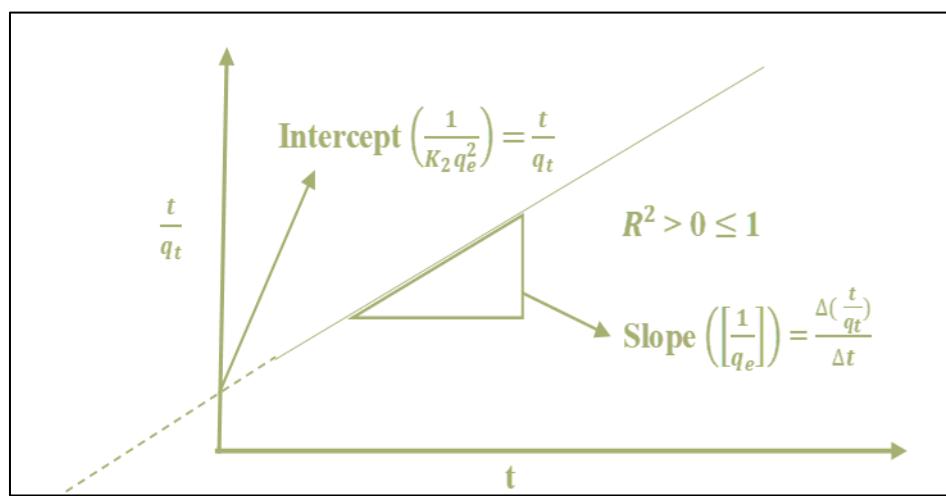
**Figure 20** Hypothetical pseudo-first order isotherm

### Pseudo-Second order

The pseudo-second order is used to determine the equilibrium value of adsorbents and rate constant. This model assumes that the rate of adsorption of solute(adsorbates) is proportional to the available sites on the adsorbent. The reaction rate is dependent on the amount of solute on the surface of the adsorbent and the driving force ( $q_e - q_t$ ) is proportional to the number of active sites available on the adsorbent [6]. The equation can be represented as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left[ \frac{1}{q_e} \right] t \quad \dots \dots \dots \quad 7.0$$

The chemisorption step is assumed to be the rate-determining step in the pseudo-second order. The plot of  $\frac{t}{q_t}$  versus  $t$  gives a straight-line graph. Values of  $K_2$  and  $q_e$  can be calculated from the slope,  $\left[ \frac{1}{q_e} \right]$  and intercept,  $\frac{1}{K_2 q_e^2}$ . A hypothetical graph for pseudo-second order isotherm can be represented in figure 21.

**Figure 21** Hypothetical pseudo-second order isotherm

When the solute concentration is low, the equation explains the adsorption mechanism more than any other kinetic model. However, at high initial concentration, pseudo first order model is favoured.

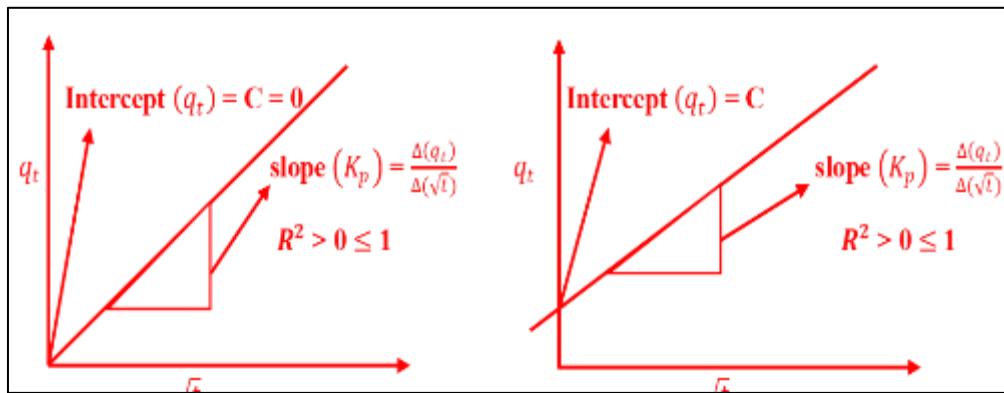
## 7.2. Intraparticle diffusion

It is also called Weber and Morris Model [23]. The model is widely applied to examine the rate limiting step during adsorption. The adsorption of solutes/adsorbates in a solution involves mass transfer (film diffusion), surface diffusion and pore diffusion. Film diffusion is an independent step whereas surface and pore diffusion may occur simultaneously [9]. The intraparticle diffusion model can be expressed mathematically as:

$$q_t = K_p \sqrt{t} + C \quad \dots \dots \dots \quad 8.0$$

$K_p$  = Rate constant in mg/g.min

$C$  = boundary layer of thickness, and it determines the boundary layer effect. The higher the value, the greater the effect. If  $C = 0$ , Intraparticle diffusion controls the adsorption process and if  $C \neq 0$ , and the plot gives multiple linear sections, these sections correspond to different mechanisms that control the adsorption process.



**Figure 22** Hypothetical Intra-particle diffusion isotherm

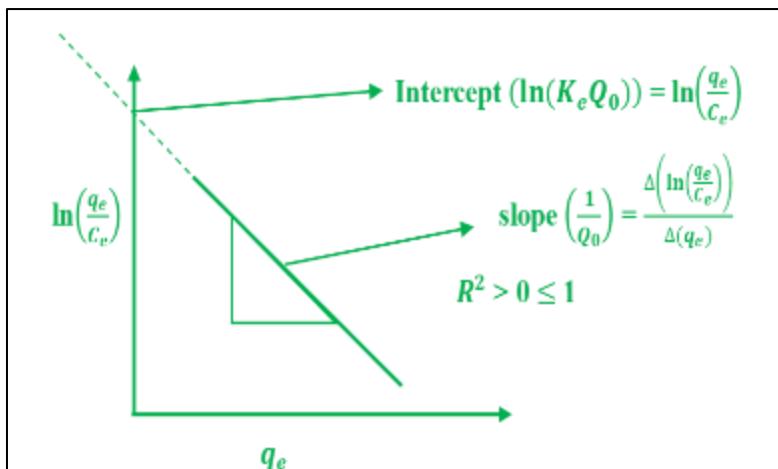
It has also been asserted similarly that, If the line passes through the origin, it is the rate determining step in the adsorption process. But, if the plot is of multi linear plots, then several steps are involved in the adsorption process like film diffusion and intra particle diffusion [9] represented in the hypothetical graphs in figure 22.

## 7.3. Elovich Adsorption Isotherm

The Elovich model is rooted in kinetic principles, suggesting that adsorption sites increase exponentially as more molecules are adsorbed, implying a multilayered adsorption process and the equation is given by:

$$\ln\left(\frac{q_e}{C_e}\right) = \ln(K_e Q_0) - \left(\frac{1}{Q_0}\right) q_e \quad \dots \dots \dots \quad 9.0$$

The values of  $Q_0$  and  $K_e$  in mg/g and  $min^{-1}$  respectively, represents the maximum adsorption capacity of the adsorbent and adsorption rate constant.



**Figure 23** Hypothetical Elovich's isotherm

### 7.3.1. Adsorption capacity ( $Q_0$ )

A high adsorption capacity implies that the adsorbate was successfully adsorbed on the adsorbent from the solution.

### 7.3.2. Adsorption Rate constant ( $K_e$ )

Low value of  $K_e$  suggests that the desorption rate is slow, implying that the adsorbed molecules are strongly bound to the adsorbent surface.

## 8. Determination of best fit adsorption and kinetic model

models are usually subjected to accuracy tests using model performance indicators (error functions) such as coefficient of determination ( $R^2$ ) and Chi square ( $\chi^2$ ), all in a bid to determine the model that fits the experimental data best.

## 8.1. Correlation coefficient ( $R^2$ )

The correlation coefficient or coefficient of determination represents the variance about the mean, it is used to analyze the fitting degrees of kinetic models with experimental data [24]. The coefficient of determination ( $R^2$ ) is defined by the following equation. The applicability of each model is determined by comparing the correlation coefficients. The higher the value of correlation coefficients, the better will be the goodness of fit [9].

$$R^2 = \frac{\sum (q_{ecal} - q_{mexp})^2}{\sum (q_{ecal} - q_{mexp})^2 + (q_{ecal} - q_{mexp})^2} \quad \dots \quad 10.0$$

$q_{ecal}$  = amount of adsorbate obtained by kinetic isotherm models ( $mg\text{g}^{-1}$ )

$q_{mexp}$  = average of  $q_{exp}$  ( $mgg^{-1}$ )

$q_{exp}$  = amount of adsorbate adsorbed by adsorbent during the experiment ( $mg\text{g}^{-1}$ )

## 8.2. Chi-Square Test ( $\chi^2$ )

This function is very important in the determination of the best fit for experimental data obtained from sorption procedures. It can be obtained by judging the sum square difference between experimental and calculated data, with each square difference divided by its corresponding values [25-27]. The value of this function can be evaluated from the following expression;

$$\sum_{i=1}^n \frac{(q_{ecal} - q_{emeans})^2}{q_{emeans}} \dots 11.0$$

Ebelegi et al. [24] evaluated the predictive performance of the f-mexp modified equation for the modeling of adsorption kinetics of experimental systems using chi square ( $\chi^2$ ), and results revealed that the f-mexp equation can fit the experimental data very well over the whole adsorption range.

## 9. Thermodynamics of adsorption reactions

One of the most important and fruitful applications of thermodynamics is the analysis of chemical equilibria, where thermodynamics can be used to determine the temperature and pressure that optimize the products of a given chemical reaction [7,25-27]. No industrial process would ever be undertaken without a thorough thermodynamic analysis of the chemical reactions involved, with adsorption inclusive.

### Graphical Dimensions for determining Thermodynamic parameters

There are two graphical dimensions for obtaining thermodynamic parameters base on two equations. The first graphical dimension utilizes the equations 12.1 and 12.2:

$$\Delta G_{ads}^o = -RT \ln K_{eq} \quad \dots \dots \dots \quad 12.1$$

$$\Delta G_{ads}^o = \Delta H^o - T\Delta S^o \quad \dots \dots \dots \quad 12.2$$

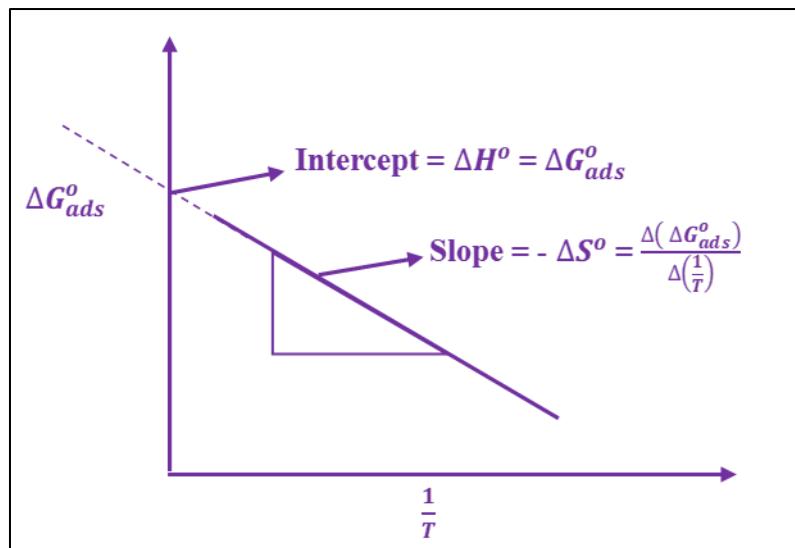
Where R is gas constant ( $8.314 \text{ Jmol}^{-1}\text{K}^{-1}$ ) and T is absolute temperature in Kelvin, R is the gas constant and  $K_{eq}$  can be obtained from  $\frac{q_e}{c_e}$  [8,9,28]. The modality for obtaining the first graphical dimension thermodynamic parameters is represented in figures 24 and 25.

When the equilibrium constant ( $K_{eq}$ ) at different temperatures,  $T_1, T_2, T_3 \dots T_n$  is determined,

and the values of  $\Delta G_{ads}^o$  at different temperatures,  $T_1, T_2, T_3 \dots T_n$  is determined using  $\Delta G_{ads}^o = -RT \ln K_{eq}$

A graph of  $\Delta G_{ads}^o$  against T can be used to determine  $\Delta S^o$  and  $\Delta H^o$  from the slope and intercept respectively base on the equation  $\Delta G_{ads}^o = \Delta H^o - T\Delta S^o$  as demonstrated in figure 25.

**Figure 24** First dimension-1 for determining thermodynamic parameters



**Figure 25** Graphical dimension-1 for determining thermodynamic parameters

The second graphical dimension also utilizes two equations (13.1 and 13.2):

$$\Delta G_{ads}^o = -RT \ln K_{eq} \quad \dots \quad 13.1$$

$$\ln K_{eq} = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad \dots \quad 13.2$$

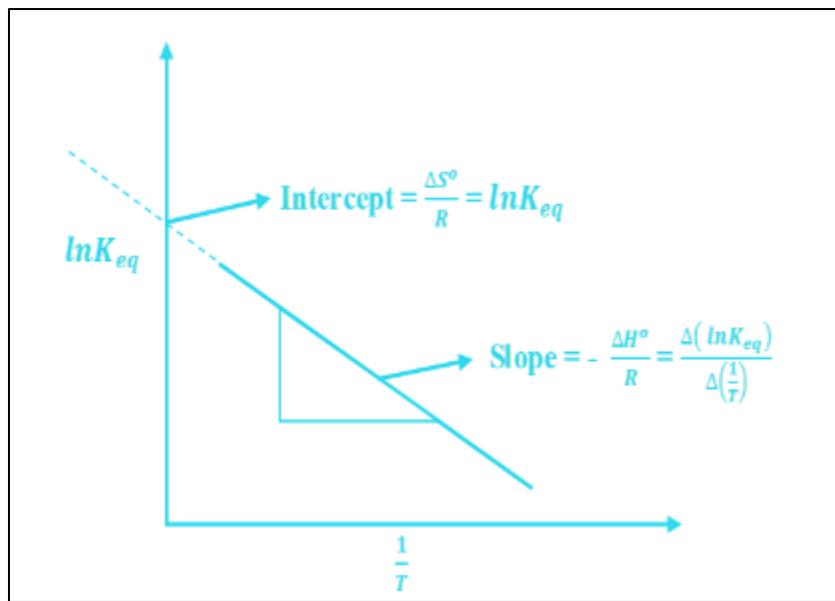
Where R is gas constant ( $8.314 \text{ Jmol}^{-1}\text{K}^{-1}$ ) and T is absolute temperature in Kelvin, R is the gas constant and  $K_{eq}$  can be obtained from  $\frac{q_e}{c_e}$  [6]. The modality for obtaining the second graphical dimension thermodynamic parameters is represented in figures 26 and 27.

When the equilibrium constant ( $K_{eq}$ ) at different temperatures,  $T_1, T_2, T_3 \dots T_n$  is determined

A graph of the natural log of equilibrium constant ( $\ln K_{eq}$ ) against  $\frac{1}{T}$  will give a slope of  $\Delta H_{ads}^o$  and intercept of  $\Delta S_{ads}^o$  base on the equation:

$$\ln K_{eq} = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \text{ as demonstrated in figure 27.}$$

**Figure 26** Dimension-2 for determining thermodynamic parameters



**Figure 27** Graphical dimension-1 for determining thermodynamic parameters

## 10. Kinetics and thermodynamic nexus for adsorption mechanism

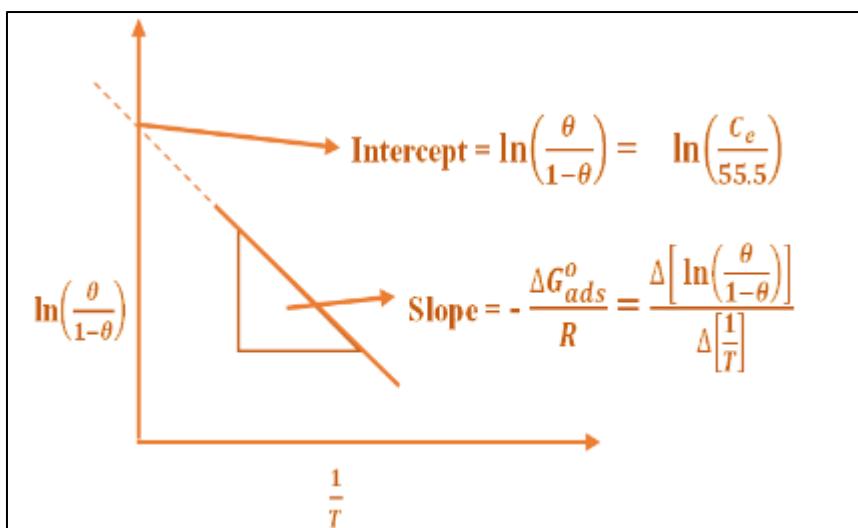
### 10.1. Nexus between Stern-Grahame and Equilibrium Constant ( $K_c$ )

Adsorption of surfactants at the solid/liquid interface is usually described by the Stern-Grahame equation [29], which may be written in the form:

$$\frac{\theta}{1-\theta} = \frac{C_e}{55.5} e^{-\frac{\Delta G_{ads}^0}{RT}} \quad \dots \quad 14.1$$

$$\ln\left(\frac{\theta}{1-\theta}\right) = \ln\left(\frac{C_e}{55.5}\right) - \frac{\Delta G_{ads}^0}{RT} \quad \dots \quad 14.2$$

where  $\theta$  is the fraction of surface sites occupied,  $C_e$  is the equilibrium concentration of surfactant and  $\Delta G_{ads}^0$  is the standard free energy of adsorption. A graph of  $\ln\left(\frac{\theta}{1-\theta}\right)$  against  $\frac{1}{T}$  will give a slope of  $-\frac{\Delta G_{ads}^0}{R}$  and intercept  $\ln\left(\frac{C_e}{55.5}\right)$  as demonstrated in the hypothetical figure 28.



**Figure 28** Hypothetical plot for determining  $\Delta G_{ads}^0$  from Stern-Grahame's equation

It is also known that [28]:

$$\Delta G^\circ = -RT\ln K_c \quad \dots \quad 14.3$$

$$\ln K_c = -\frac{\Delta G^\circ}{RT} = -\frac{(\Delta H^\circ - T\Delta S^\circ)}{RT} \quad \dots \quad 14.4$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \dots \quad 14.5$$

the Stern-Grahame equation can be re-written as:

$$\ln\left(\frac{\theta}{1-\theta}\right) = \ln\left(\frac{c_e}{55.5}\right) + \ln K_c \quad \dots \quad 14.6$$

$$K_c = \left(\frac{\theta}{1-\theta}\right) \cdot \left(\frac{c_e}{55.5}\right) \text{ at } T_1, T_2, T_3, \dots, T_n \quad \dots \quad 14.7$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \dots \quad 14.8$$

A plot of  $\ln K_c$  against  $\frac{1}{T}$  will give a slope  $-\frac{\Delta H^\circ}{R}$  and intercept of  $\frac{\Delta S^\circ}{R}$  [28]. A hypothetical graph of this can be equated to that in figure 26.

#### 10.1.1. Standard free energy of adsorption ( $\Delta G_{ads}^\circ$ )

The standard free energy change ( $\Delta G^\circ$ ) is a crucial thermodynamic parameter in adsorption processes because it provides direct insight into the feasibility, spontaneity, and nature of the adsorption of adsorbates onto an adsorbent [30]. Negative values of the standard free energy change mean the adsorption reaction is spontaneous and if the values fall within the range of -20 to 0 kJ/mol it indicates physisorption and outside this range, it indicates chemisorption [8,9,11,31].

#### 10.1.2. Standard enthalpy of reaction ( $\Delta H^\circ$ )

The standard enthalpy change ( $\Delta H^\circ$ ) is a fundamental thermodynamic parameter that provides insight into the heat effects, mechanism, and interaction strength during the adsorption of an adsorbate onto an adsorbent [32]. When the standard enthalpy for any adsorption reaction is small (i.e., within the range of -5 to 40 kJ/mol) it is considered to be of a physical interaction (van der Waals) and weak. But when the standard enthalpy is large (i.e., within the range of 40 to 80 kJ/mol), it is considered to be of a chemical adsorption/bonding and strong [33-36].

#### 10.1.3. Standard entropy of reaction ( $\Delta S^\circ$ )

The standard entropy change ( $\Delta S^\circ$ ) in adsorption quantifies the change in disorder when an adsorbate transfers from a bulk phase (gas or solution) to being bound on a surface.  $\Delta S^\circ$  offers valuable insights into molecular freedom, mechanisms, and spontaneity of adsorption [11].

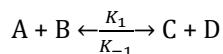
### 10.2. Nexus between Stern-Grahame and Arrhenius law (Activation Energy)

Arrhenius law on effect of temperature on equilibrium constant states that:

$$\frac{d\ln K_c}{dT} = \frac{\Delta E}{RT^2} \quad \dots \quad 15$$

Where  $K_c$  = expressed in terms of equilibrium constant,  $\Delta E$  = energy change accompanying the reaction,  $R$  = gas constant and  $T$  = temperature. For experimental and graphical applicability, equation 15 is reduced to equation 16.1 through 15.1 to 16 presented below:

Considering a second order reaction as thus:



Forward rate =  $K_1[A][B]$  so that  $K_1$  = rate constant for forward reaction

Backward rate =  $K_{-1}$  [C][D] so that  $K_{-1}$  = rate constant for backward reaction

At equilibrium we will have;

$$K_1[A][B] = K_{-1}[C][D] \quad \dots \quad 15.1$$

$$\frac{[C][D]}{[A][B]} = \frac{K_1}{K_{-1}} = K_c \quad \dots \quad 15.2$$

Substitute the value of  $K_c$  into equation 15;

$$\frac{d \ln K_c}{dT} = \frac{\Delta E}{RT^2} \quad \dots \quad 15.3$$

$$\frac{d \ln(\frac{K_1}{K_{-1}})}{dT} = \frac{\Delta E}{RT^2} \quad \dots \quad 15.4$$

$$\frac{d \ln K_1}{dT} - \frac{d \ln K_{-1}}{dT} = \frac{\Delta E}{RT^2} \quad \dots \quad 15.5$$

Equation 14.5 may be split as two equations such that;

$$\frac{d \ln K_1}{dT} = \frac{E_1}{RT^2} + C \quad \dots \quad 15.6$$

$$\frac{d \ln K_{-1}}{dT} = \frac{E_{-1}}{RT^2} + C \quad \dots \quad 15.7$$

Where  $E_1 - E_{-1} = \Delta E$  and  $C$  = integration constants. Experiments show that  $C$  can be set equal to zero (Letort, 1937), so that equation 15.6 or 15.7 may be written as;

$$\frac{d \ln K_{ads}}{dT} = \frac{E_a}{RT^2} \equiv d \ln K_{ads} = \frac{E_a}{RT^2} dt \quad \dots \quad 15.8$$

$$\int d \ln K_{ads} = \frac{E_a}{R} \int T^{-2} dt \equiv \ln K_{ads} = \frac{E_a}{R} \left[ \frac{T^{-2+1}}{-2+1} \right] + A \quad \dots \quad 15.9$$

$$\ln K_{ads} = \frac{E_a}{R} \left[ \frac{T^{-1}}{-1} \right] + A \equiv \ln K_{ads} = - \frac{E_a}{R} \left[ \frac{1}{T} \right] + A \quad \dots \quad 16$$

$$\ln K_{ads} = - \frac{E_a}{RT} + A \equiv K_{ads} = A e^{-\frac{E_a}{RT}} \quad \dots \quad 16.1$$

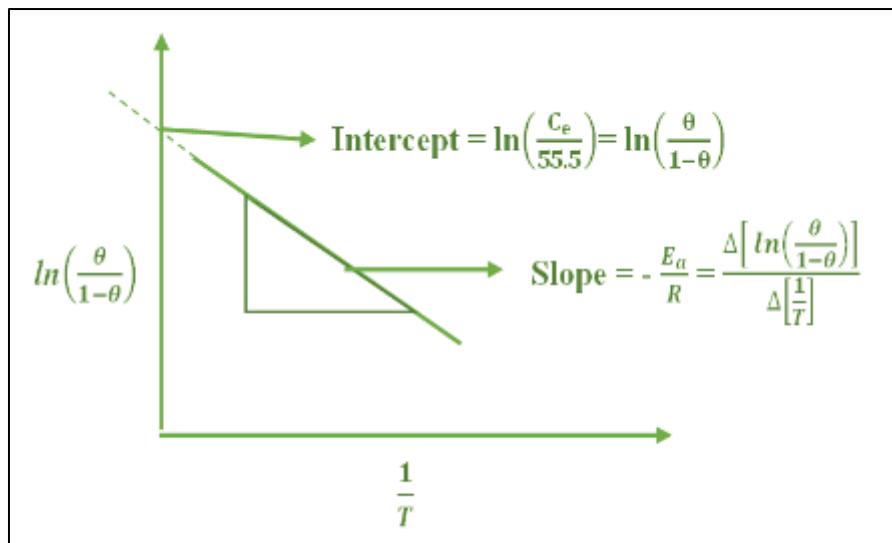
where  $K_{ads}$  is the rate constant for the adsorption reaction at  $T$ ;  $A$  = frequency factor for the reaction [11].

Compare equations 14.1 and 16.1, the Stern-Grahame equation can be re-written as:

$$\frac{\theta}{1-\theta} = \frac{C_e}{55.5} e^{-\frac{E_a}{RT}} \quad \dots \quad 16.2$$

$$\ln \left( \frac{\theta}{1-\theta} \right) = \ln \left( \frac{C_e}{55.5} \right) - \frac{E_a}{RT} \quad \text{at } T_1, T_2, T_3, \dots, T_n \quad \dots \quad 16.3$$

where  $\left( \frac{\theta}{1-\theta} \right)$  = Rate constant ( $K_{ads}$ ),  $\left( \frac{C_e}{55.5} \right)$  = Frequency factor (collision frequency). From the graph of  $\ln \left( \frac{\theta}{1-\theta} \right)$  against  $\frac{1}{T}$ ,  $\frac{E_a}{R}$  will be the slope/gradient and  $\ln \left( \frac{C_e}{55.5} \right)$  will be the intercept as represented in the hypothetical plot below;



**Figure 29** Hypothetical plot for determining  $\Delta E_{ads}$  from Stern-Grahame's equation

#### 10.2.1. Activation energy ( $E_a$ )

Activation energy is the minimum energy required for a chemical reaction to occur. In adsorption, it is the energy barrier that must be overcome for adsorbate molecules to bind to the adsorbent surface. It also influences the rate of adsorption [37]. Lower activation energy means faster adsorption rates, while higher activation energy slows down the process. This further means that higher activation energy causes some adsorbate molecules to lack enough energy to overcome the barrier, reducing adsorption efficiency [38].

#### 10.2.2. Rate constant ( $K_{ads}$ )

The rate constant is a measure of the rate at which adsorption occurs. It relates the rate of adsorption to concentration of adsorbate and adsorbent. A higher rate constant indicates faster adsorption and vice versa [38].

#### 10.2.3. Frequency factor ( $A$ )

The frequency factor, also known as the pre-exponential factor represents the frequency of collisions between adsorbate molecules and the adsorbent surface, influencing the rate of adsorption [39]. A higher frequency factor indicates more frequent collisions, increasing the likelihood of successful adsorption.

### 10.3. Nexus between Henry and Arrhenius law (Activation Energy)

Henry's law which is valid only at low surface coverages can be expressed as:

$$\Gamma_s = 2rC_e e^{-\frac{\Delta G_{ads}^0}{RT}} \dots\dots\dots 17$$

where  $\Gamma_s$  is adsorption density ( $\text{mol}/\text{m}^2$  or  $\text{mg}/\text{m}^2$ ) or surface excess in the Stern plane,  $r$  is the effective radius of the adsorbed species.  $C_e$  is the equilibrium bulk concentration of the adsorbate.  $R$  is the gas constant.  $T$  is the absolute temperature. And  $\Delta G_{ads}^0$  is the standard free energy of adsorption.

The adsorption density which is usually normalized in terms of unit surface area of solids

$$\Gamma_s = (C_i - C_f)VmS_m \dots\dots\dots 17.1$$

Where  $C_i$  is the initial concentration,  $C_f$  is the final or the equilibrium concentration of adsorbate,  $V$  is the volume of the solution used,  $m$  is the weight of adsorbent and  $S_m$  is the specific surface area of the solid per unit weight of solid.

Comparing equations 14.1, 16.1 and 17 we will have:

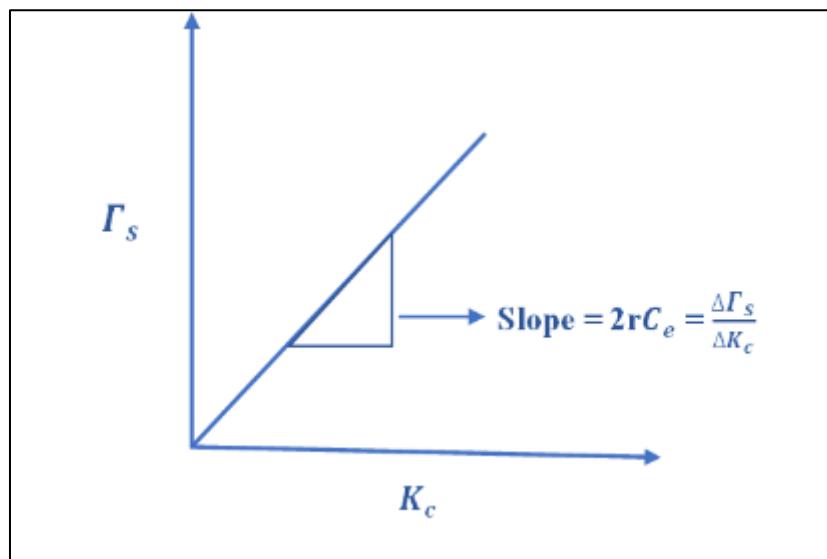
$$\Gamma_s = 2rC_e e^{-\frac{E_a}{RT}} \dots\dots\dots 17.2$$

$$\ln \Gamma_s = 2r \ln C_e - \frac{E_a}{RT} \quad \dots \dots \dots \quad 17.3$$

$$\Gamma_s = 2rC_e e^{\ln K_c} \quad \dots \quad 17.5$$

$$\Gamma_s = 2rC_e K_c \quad [e^{\ln K_c} = K_c] \quad \dots \quad 17.6$$

A plot of  $\Gamma_s$  against  $K_c$  will give a slope of  $2rC_e$  as represented hypothetically in figure 30.



**Figure 30** Hypothetical plot for determining equilibrium concentration from Henry and Arrhenius' laws

### 10.3.1. Adsorption density ( $\Gamma_s$ )

The adsorption density (denoted as  $\Gamma$ , Greek gamma) is a key parameter in surface chemistry that quantifies the amount of adsorbate per unit surface area of an adsorbent. It plays a central role in understanding the efficiency, mechanism, and capacity of adsorption at interfaces, especially solid-liquid or gas-solid [40].

### 10.3.2. Radius of the adsorbed species ( $r$ )

The size of adsorbed species can influence adsorption due to steric effects. Larger molecules may experience reduced adsorption due to spatial constraints, while smaller molecules can more easily fit onto the surface. The radius of adsorbed species affects surface coverage. Larger molecules may occupy more surface area, reducing the amount adsorbed, while smaller molecules can pack more densely [41].

#### 10.4. Nexus between Langmuir isotherm and Standard Gibbs free energy, Standard Enthalpy and Standard Entropy

The Langmuir model can be presented by the equation

Where  $q_{max}$  is the monolayer adsorption capacity of the adsorbent, i.e. the maximum amount adsorbed;  $K_L$  (L/mg or L/mol) is the Langmuir adsorption constant;  $C_e$  is the equilibrium adsorbate concentration in the solution.

The Langmuir adsorption constant (typically denoted as  $K_L$  or  $b$ ) is directly related to the thermodynamic equilibrium constant for the adsorption process ( $K_{eq}$ ). It represents the affinity of the adsorbate for the adsorbent surface and can be interpreted as an equilibrium constant under specific assumptions [42-44] that:

$$K_{eq} = K_L C^o \quad \dots \quad 18.1$$

$C^o$  is the standard concentration (usually 1 mol/L or 1 mg/mL) so that

$$K_{eq} = K_L \quad \dots \quad 18.2$$

Hence standard Gibbs' free energy can be expressed as

$$\Delta G^o = -RT \ln K_L \quad \dots \quad 18.3$$

such that

$$\ln K_L = -\frac{\Delta G^o}{RT} = -\frac{(\Delta H^o - T\Delta S^o)}{RT} \quad \dots \quad 18.4$$

$$\ln K_L = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad \text{at } T_1, T_2, T_3, \dots, T_n \quad \dots \quad 18.5$$

A graph of the natural log of the Langmuir equilibrium constant  $\ln K_L$  versus  $\frac{1}{T}$  will give a slope of  $-\frac{\Delta H^o}{R}$  and intercept of  $\frac{\Delta S^o}{R}$ .

### 10.5. Nexus between Langmuir isotherm equation and Stern-Grahame's equations

From the Stern-Grahame;

$$\frac{\theta}{1-\theta} = \frac{C_e}{55.5} e^{-\frac{\Delta G_{ads}^o}{RT}} \quad \dots \quad 14.1$$

$$\ln\left(\frac{\theta}{1-\theta}\right) = \ln\left(\frac{C_e}{55.5}\right) - \frac{\Delta G_{ads}^o}{RT} \quad \dots \quad 14.2$$

And considering equations 14.1 and 18.3 the Stern-Grahame's equation can be re-written as

$$\frac{\theta}{1-\theta} = \frac{C_e}{55.5} e^{\ln K_L} \quad [\ln K_L = -\frac{\Delta G^o}{RT}] \quad \dots \quad 19.1$$

$$\left(\frac{\theta}{1-\theta}\right) = \left(\frac{C_e}{55.5}\right) + K_L \quad \dots \quad 19.2$$

$$K_L = \left(\frac{\theta}{1-\theta}\right) - \left(\frac{C_e}{55.5}\right) \quad \dots \quad 19.3$$

### 10.6 Nexus between Pseudo-first order and Pseudo-second Order

The PFO and PSO equations are based on the assumption that the rate of adsorption is a directly proportional or quadratic function of the difference between adsorption capacities at equilibrium and at time  $t$ , which are given as [45]

$$\frac{dq_t}{dt} = K_1 (q_e - q_t) \quad \dots \quad 20.0$$

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 \quad \dots \quad 20.1$$

In order to facilely analyze mathematical characteristics of the PFO and PSO equations, we rewrite Eq. (19) and Eq. (19.1) as the following forms [46]:

$$q_t = q_e \left(1 - \frac{1}{\exp(K_1 t)}\right) \quad \dots \quad 20.2$$

$$q_t = q_e \left(1 - \frac{1}{1 + q_e K_2 t}\right) \quad \dots \quad 20.3$$

It is quite clear that  $q_t$  approaches to  $q_e$  when  $t \rightarrow \infty$  and that the PFO and PSO equations have identical mathematical structure, conforming to the following from:

$$q_t = q_e \left(1 - \frac{1}{\varphi(t)}\right) \quad \dots \dots \quad 20.4$$

Thus,  $\varphi(t)$  is an exponential function for PFO and a linear function for PSO, and both are increasing functions of time.

## 11. Conclusion

Adsorbates adsorption on adsorbent is a complex process. Although considerable advances have been made in understanding the isolated role played by various system properties. Theoretical developments have not been rigorous and they lag behind experimental and conceptual developments. Some of the experimental difficulties and theoretical complexities that are responsible for the slow development of a unifying adsorption model covering a range of adsorbates-adsorbent combinations have been analyzed critically from adsorption principle, methods of obtaining adsorption and adsorption kinetics parameters as well as the adsorption parameters analysis using different adsorption, kinetic and thermodynamic models. The nexus between existing adsorption models such as Stern-Grahame and Equilibrium Constant ( $K_c$ ), Henry and Arrhenius laws, Langmuir isotherm and thermodynamic variables ( $\ln K_{eq}$ ,  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ ) Langmuir and Stern-Grahame's isotherm equation and pseudo first and second kinetic models were analyzed. The major individual contributions to the overall energy of adsorption have been identified and discussed.

## Compliance with ethical standards

### Disclosure of conflict of interest

Authors declare no conflict of interest

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