Interpretation of Adsorption Thermodynamics and Kinetics

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Abstract
A complete study of adsorption processes will be less complete if the structure and dynamics of its different elements and how they interact is not well captured. Therefore, the extensive study of adsorption thermodynamics in conjunction with adsorption kinetics is inevitable. Measurable thermodynamic properties such as temperature equilibrium constant and their non-measurable counterparts such as Gibbs free energy change, enthalpy, entropy etc. are very important design variables usually deployed for the evaluation and prediction of the mechanism of adsorption processes.

Keywords
Gibbs Free Energy, Entropy Change, Adsorption Density, Sticking Probability, Activation Energy, Pseudo-Second-Order Kinetic Model, Elovich Model, Brouers-Sotolongo Fractal Kinetic Model

1. Introduction
Although adsorption theory proposes a reduction in adsorption as temperature increases because adsorbates that were initially adsorbed on the surface of the adsorbent desorb at high temperatures [1], research reports have shown that different trends have been observed for porous, microporous and mesoporous adsorbents since higher temperatures facilitate the uptake of adsorbates into their pores and cavities [2] [3]. The effect of heat and time on the interaction between adsorbates and adsorbent surfaces during sorption processes is very important, because these interactions have been found to be temperature and time dependent [4] [5]. The experimental data obtained from adsorption processes monitored at different temperatures can be used to determine thermodynamic parameters such as free-energy change [6], enthalpy change [7], en-
tropy change [8], activation energy [9], sticking probability [10], etc. Similarly, information obtained from adsorption experiments at different contact time(s) defines the kinetic behavior of adsorbates on adsorbents [11]. This paper is intended to give further insights to scholars, academics and students alike, easy tools that will facilitate a better understanding on interpretation and applications of experimental data using kinetic and thermodynamic models.

2. Adsorption Thermodynamics

Thermodynamic parameters of adsorption processes are easily evaluated because adsorption is a temperature dependent process [8]. Thermodynamic considerations for adsorption experiments are required in order to establish the spontaneity and feasibility of such processes. Therefore, experimental data obtained from adsorption procedures are employed to determine thermodynamic parameters such as Gibbs free energy change ($\Delta G^0$), change in enthalpy ($\Delta H^0$), change in entropy ($\Delta S^0$), Isosteric heat of adsorption ($\Delta H_X$), adsorption potential ($A$), hopping number ($n$), sticking probability ($S^*$), adsorption density ($\rho$) and activation energy ($E_a$).

2.1. Gibbs Free Energy of Change ($\Delta G^0$)

Gibbs free energy of change is used to evaluate the spontaneity and feasibility of adsorption processes. A negative $\Delta G^0$ value validates a spontaneous process while a positive $\Delta G^0$ value is indicative of a non-spontaneous process as shown in Table 1.

The free energy change in an adsorption process is usually related to the equilibrium constant by the Gibbs fundamental equation [9].

| Thermodynamic parameter | Adsorbent | Adsorbate       | Value     | Remark      | Reference |
|-------------------------|-----------|-----------------|-----------|-------------|-----------|
| Gibbs free energy ($\Delta G^0$) kJ·mol⁻¹·K⁻¹ | Bakers yeast | Nickel          | −23.519   | Spontaneous | 10        |
|                         | Pleurotus eryngii | Malachite green | −10,388.3 | Spontaneous | 11        |
|                         | Coconut copra meal | Cadmium        | −7.4      | Spontaneous | 12        |
| Enthalpy change ($\Delta H^0$) kJ·mol⁻¹ | Chemically modified rice husk | Malachite green | 63.76   | Endothermic | 13        |
|                         | Mansonia wood | Basic dye      | 67.1      | Endothermic | 14        |
|                         | Wheat shell   | Basic dye      | 33.4      | Endothermic | 15        |
|                         | Hematite      | Cadmium        | −13.09    | Exothermic  | 16        |
| Entropy change ($\Delta S^0$) J·mol⁻¹ | Lateritic nickel Ore | Lead          | 28.56     | chemisorption | 17        |
|                         | Bentonite     | Copper         | 0.108     | chemisorption | 18        |
|                         | Modified oak sawdust | Copper      | 240       | chemisorption | 19        |

Table 1. Thermodynamic parameters for adsorption of different pollutants onto some low cost adsorbents.
\[ \Delta G^0 = -RT \ln K_C \]  

(1)

where \( R \) = Universal gas constant (Jmol\(^{-1}\)Kg\(^{-1}\)K\(^{-1}\))  
\( T \) = Temperature (K)  
\( K_C \) = Equilibrium constant.

This equation measures the changes in equilibrium constant with variations of temperature. Padmavathy reported the Biosorption of nickel (II) ions onto baker’s yeast was a spontaneous and exothermic process [10]. Wu et al., also proved that the uptake of malachite green by a bio-sorbent *Pleurotuseryngii* was spontaneous [11]. In another report Y-S. Ho and A. E. Ofomaja showed that the biosorption of Cd\(^{2+}\) on coconut copra meal was feasible and spontaneous due to negative \( \Delta G^0 \) [12].

### 2.2. Enthalpy Change (\( \Delta H^0 \))

Change in enthalpy (\( \Delta H^0 \)) can be described as the energy supplied as heat at constant pressure when the system does no extra work. Enthalpy change is typically measured with a calorimeter by monitoring the temperature change that happens at constant pressure [12]. In adsorption study enthalpy change gives an insight into the nature and mechanism of adsorption processes and it is usually determined from the Van’t Hoff equation [13].

\[ \log K_C = \frac{\Delta S^0}{2.303R} - \frac{\Delta H}{2.303RT} \]  

(2)

where \( R \) = Universal gas constant (J∙mol\(^{-1}\)K\(^{-1}\)), \( T \) = Temperature (K)  
\( K_C \) = Distribution coefficient

\[ K_C (\text{Distribution coefficient}) = \frac{C_a}{C_e} \]  

(3)

\( C_a \) = Amount of adsorbate adsorbed at equilibrium (mg∙L\(^{-1}\))  
\( C_e \) = Equilibrium concentration of adsorbate in solution (mg∙L\(^{-1}\)).

A negative value of \( \Delta H^0 \) implies an exothermic adsorption process while a positive \( \Delta H^0 \) value is indicative of an endothermic process (see Table 1). In their report Chowdhury *et al.* showed that the positive value of \( \Delta H^0 \) (89.13 KJ∙mol\(^{-1}\)) confirmed that the adsorption of malachite green onto chemically modified rice husk was endothermic [14]. Endothermic adsorption have also been reported for basic dye on mansonia wood (67.1 KJ∙mol\(^{-1}\)) [15] and wheat shell (33.41 KJ∙mol\(^{-1}\)) [16].

### 2.3. Entropy Change (\( \Delta S^0 \))

A change in entropy during an adsorption process can be determined from the Vant’ Hoff equation, where a positive \( \Delta S^0 \) shows the affinity of the adsorbent towards the adsorbate, it also suggests increased randomness at the solid/liquid interface with some structural changes in the adsorbent and adsorbate. Mohapatra *et al.* showed that \( \Delta S^0 \) was positive in their study on the kinetics and thermodynamics of Pb\(^{2+}\) adsorption onto lateritic nickel ores of Indian origin. This is typical of chemisorption [17]. In another research report Gupta, V. K. revealed a
positive $\Delta S$ (0.108 kJ·K$^{-1}$·mol$^{-1}$) which reflects the affinity of Bentonite for copper (II) ions [18].

### 2.4. Isosteric Heat of Adsorption ($\Delta H_X$)

The Isosteric heat of adsorption is the ratio of the infinitesimal change in the adsorbate enthalpy to the infinitesimal change in the quantity adsorbed under constant temperature and pressure [16] heat of adsorption established at constant amount of adsorbate adsorbed. This parameter is essential in the characterization of adsorption processes and it is usually calculated using the Clausius-Clapeyron Equation (4) [17].

$$\frac{d}{dT} \ln C_s = -\frac{\Delta H_X}{RT^2} \quad (4)$$

Chowdhury et al. observed that the Isosteric heat of adsorption ($\Delta H_X$) for the adsorption of malachite green onto treated ice husk was chemisorption because Isosteric heat of adsorption ($\Delta H_X$) obtained in their investigation was between 78 and 89 KJ·mol$^{-1}$ [19]. Isosteric heat of adsorption could also be used as a means of characterizing the surface of adsorbents since it has been proven that an adsorbent is homogeneous if its Isosteric heat of adsorption is independent of the amount of adsorbate it adsorbs and heterogeneous if it varies with the amount of adsorbate adsorbed [16]. This parameter also has a direct influence on hydrogen storage capacity of Metal Organic Frameworks (MOFs). Bae, -S and Snurr, R. Q. reported the optimal Isosteric heat of adsorption for hydrogen storage and delivery using MOFs. Their investigation showed that increasing Isosteric heat of adsorption for MOFs with large surface area results in higher hydrogen storage capacity [18].

### 2.5. Hopping Number ($n$)

The Hopping number describes the number of hopping done by the adsorbate molecule while finding a vacant site on the adsorbent surface during sorption processes [20]. The expression relating the hopping number ($n$) to the surface coverage is given as;

$$n = \frac{1}{(1 - \theta)\theta} \quad (5)$$

The hopping number ($n$) can be used to describe how fast an adsorption process happens, thus the smaller the hopping number ($n$) the faster the sorption process [20]. In their report Menkiti et al., observed that acid treated chrysophyllumalbidium biomass exhibited faster uptake of Solid and Dissolved Particles (SDP) than the salt treated chrysophyllumalbidium biomass because the former had a smaller hopping number than the latter [21].

### 2.6. Adsorption Potential ($A$)

Adsorption potential can be described as the chemical potential that occurs as an
adsorbate molecule moves from solution to the surface of an adsorbent during an adsorption process [18]. This parameter can be used to calculate the capability of an adsorbent to adsorb adsorbate molecules at a fixed temperature. Adsorption potential (A) can be evaluated by using the following expression

\[ A = -RT \ln \frac{C_i}{C_f} \]  

(6)

\( C_i \) and \( C_f \) are initial and final concentration of the adsorbate solution (mol∙mg⁻¹), \( R \) = universal gas constant (KJ∙mol⁻¹∙K⁻¹) and \( T \) = absolute temperature at which the sorption occurred. This parameter has been utilized to add value to data obtained from adsorption experiments using modified biomass as adsorbent [21] [22] [23]

2.7. Adsorption Density (ρ)

Adsorption density is a parameter used for the evaluation of the packing of adsorbates on the surface of an adsorbent. It is usually analyzed at a fixed temperature [19]. The value of adsorption density (ρ) of an adsorption process can be obtained using the following expression;

\[ \rho = ZC_i \exp \left[ \frac{\Delta G^0}{RT} \right] \]  

(7)

where;

\( \rho \) = adsorption density
\( Z \) = valency of adsorbed ion
\( R \) = effective radius of adsorbed ion
\( C_i \) = equilibrium concentration of adsorbate solution (mol∙mg⁻¹)
\( R \) = universal gas constant (KJ∙mol⁻¹∙K⁻¹)
\( T \) = absolute temperature (K)

Benjamin, M. M, used this parameter as the basis for comparing the multiple-site adsorption of Cd, Cu, Zn and Pb ions on amorphous iron Oxyhydroxide [24].

2.8. Sticking Probability (S*)

Sticking probability (sorption probability) is a parameter that shows the potential of an adsorbate to remain on an adsorbent indefinitely. It is a function of the adsorbate/adsorbent system and it serves the best purpose when its value lie between zero and unity (0 < S* < 1) and it is independent of the system’s operating temperature [25]. Sticking probability can be evaluated from the following equation:

\[ \ln(1 - \theta) = \ln S^* + \frac{E_a}{RT} \]  

(8)

where; \( \theta \) = surface coverage and \( E_a \) = activation energy.

In their report Horsfall and Spiff showed how acid treatment enhanced the sticking probability of nickel ions on fluted pumpkin waste [20].
2.9. Activation Energy ($E_a$)

Activation energy is the minimum energy required to cause a chemical reaction. For sorption processes, a negative $E_a$ suggests a low temperature favours the process in which case the sorption process is termed to be exothermic [26] [27]. Conversely, a positive $E_a$ is an indication of the presence of an energy barrier in the sorption process which means the system requires energy (increased temperature) to drive the sorption process therefore such a sorption process is termed endothermic [23] [28]. The activation energy of adsorption processes can be estimated by the Arrhenius Equation (9) [23].

$$\ln k_2 = -\frac{E_a}{RT} + \ln k_0$$  

(9)

where $k_0 = \text{Arrhenius factor}$

A plot of $\ln k_2$ against $1/T$ gives a straight line from which the activation energy ($E_a$) can be evaluated (slope of the linear graph). Chowdhury et al. showed that the activation energy of the adsorption of malachite green on chemically modified rice husk was 68.1 kJ∙mol$^{-1}$ [19]. In another report Podder and Majumder reported the activation energy of As(III) and As(V) biosorption onto TW/MnFe$_2$O$_4$ composite were 11.6 and 10.71 kJ∙mol$^{-1}$ [29]. These reports actually confirm the sorption processes to be endothermic.

3. Adsorption Kinetics

The kinetic behaviour of adsorbates on adsorbents has been studied using the effect of time on sorption. Due to the large collection of kinetic models the selection of suitable models for the analysis of sorption data is quite challenging. Scientific reports have shown how mathematical models were proposed and used to describe adsorption experiments [30] [31] [32] [33] [34]. Thus, adsorption kinetic models have been classified into two groups namely; adsorption reaction models and adsorption diffusion models. Adsorption reaction models reveal the rate of adsorbate uptake by adsorbents but they do not show the actual cause of adsorption. On the contrary adsorption diffusion models take into cognizance external diffusion, internal (pore) diffusion and effect of mass action (i.e. adsorption/desorption between adsorbates and active sites of adsorbents [35].

Pursuant to the aforementioned adsorption reaction models should be consistent with proposed mechanisms defined by fitting adsorption diffusion models.

4. Adsorption Reaction Models

4.1. Pseudo-First-Order (Lagergren) Model

The pseudo-first-order model is mostly used to analyze adsorption data obtained from the adsorption of adsorbates from aqueous solutions. It describes the rate of adsorption which is proportional to number of unoccupied binding sites on adsorbents [36]. This kinetic model is usually represented in the following equation [37].
\[
\log(q_e - e) = \log q_e \left( \frac{K_1}{2.303} \right) k
\]

Several researchers have employed this model to evaluate the rate of uptake of different adsorbates by specific adsorbents in aqueous media. Kazeem et al. reported a high correlation coefficient \( (r^2 = 0.9778) \) using this model while investigating the removal of cationic dye from wastewater using aluminum activated carbon adsorbent [38]. In like manner Tran et al. investigated the uptake of Methylene green 5 by activated carbon using the pseudo-first-order kinetic model \( (r^2 = 0.37) \). The low correlation coefficient obtained is an indication that this model is not the best fit [39]. A high correlation coefficient \( (r^2 = 0.989) \) was obtained by Fungaro et al. in their study of the removal of reactive orange 16 from wastewater using zeolite from cyclone ash [40]. Although the correlation coefficient was high, experimental data was best described by the pseudo-second-order kinetic model due to higher correlation coefficient.

4.2. Pseudo-Second-Order Model

The pseudo-second-order kinetic model describes the adsorption of adsorbates onto adsorbents where the chemical bonding (interaction) between adsorbates and functional groups on the surface of adsorbents are responsible for the adsorption capacity of adsorbent. It is based on equilibrium adsorption, which is dependent on the amount of adsorbate adsorbed onto the surface of an adsorbent and the amount of adsorbate adsorbed at equilibrium [41]. This model is used to predict the order of the sorption process, it also facilitates the evaluation of sorption capacity [42] [43]. The pseudo-second-order kinetic rate expression in the linearized form is shown in Equation (10).

\[
\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}
\]

For this model to emerge the best fit for sorption data a plot of \( tl/q_t \) against \( t \) should show a linear connection, from which the amount of adsorbate adsorbed at equilibrium \( (q_e, \text{mg/g}) \) and the equilibrium rate constant of pseudo-second-order sorption \( (K_2, \text{g/mg min}) \) can be evaluated from the slope and intercept respectively [44]. The pseudo-second-order kinetic model has been applied successfully to determine chemisorption in several sorption systems. Crini et al. proved the removal of malachite green from aqueous media with a cyclodextrin-based adsorbent followed the pseudo-second-order kinetic model \( (r^2 = 0.9998) \) [45]. In another research Gong et al. reported the sorption of basic dye onto phosphoric acid esterified soya bean hull was best described by this model \( (r^2 = 0.999) \) [46]. Similar reports have been published by Tsai et al. [47] and Santhi et al. [48].

4.3. Elovich Model

This model is used to describe adsorption processes that follow second-order kinetics with the assumption that the surface of the adsorbent is energetically
heterogeneous in nature as such they show evidence of different activation ener-
gies [49] [50]. It has been extensively applied in the elucidation of chemisorption
processes [51].

The Elovich model is represented by the following expression

\[
q_t = \ln\left(\frac{\alpha \beta}{\beta} + \frac{\ln t}{\beta}\right)
\]

where;

- \(q_t\) = adsorption capacity at time \(t\) (mg\cdot g^{-1})
- \(\alpha\) = Initial adsorbate adsorption rate (mg\cdot g^{-1}\cdot min^{-1})
- \(\beta\) = Adsorption constant (mg\cdot g^{-1}\cdot min^{-1})

Initial adsorption rate \((\alpha)\) and adsorption constant \((\beta)\) can be evaluated from a
linear plot of \(q_t\) versus \(\ln t\).

Hussien et al. utilized this model to analyze adsorption data obtained from the
of adsorption process using spent-FCC catalyst and their report confirmed that
the adsorption process is chemisorption [52]. Wu et al. showed the Elovich ki-
etic model was the most suitable kinetic model for describing the adsorption
kinetics in dye-Chitosan systems [53]. Juan and Chen also established that the
sorption of Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} by solvent-impregnated resins as best
described by the Elovich equation [54]. Other similar investigations have been
reported [55] [56] [57] [58] [59].

4.4. Brouers-Sotolongo Fractal Kinetic Model

This model was developed specially to address sorption processes that occur at
the solid-liquid interface of nanomaterials which usually present unique envi-
ronments such as heterogeneous surfaces and complex reactions [60]. Reports
have it that adsorbents made of nanomaterials have boundaries that separate
mass and pore spaces (fractal surfaces) [61]. The fractality of nanomaterials
could have arisen from the well defined pore network built up during synthesis
and post synthesis processes, thus fractality is a foreseeable feature that can in-
fluence the adsorptive properties of adsorbents. The complex nature of adsor-
pition on nanomaterials and its effects on kinetics are not often taken into account
as such they are mostly illustrated using classical kinetic equations [62].

The fractal differential equation is given as;

\[
-\frac{dq_{(i)}}{dr^n} = k_{w,a}q_{(i)}^n
\]

where

- \(q_{(i)}\) = mass of adsorbate adsorbed per mass of adsorbent at time \(t\),
- \(n\) = apparent reaction order
- \(a\) = global fractal time index due to supposed fractal diffusion and sorption
  kinetics arising from geometric and energetic heterogeneity of adsorbent.

If particular values are assigned to the apparent reaction order \((n)\) and global
fractal time index \((a)\) Equation (13) then corresponds to pseudo-first-order ki-
etics \((n = 1, a = 1)\), pseudo-second-order kinetics \((n = 2, a = 1)\), Weibull kinet-
ics or Avrami kinetics \((n \neq 1, a = 1)\) and Hill kinetics or fractal second-order-kinetics \((n = 2, a \neq 1)\) [63].

Pseudo-first-order kinetic and pseudo-second-order kinetic models have been previously discussed (sections 3.1 and 3.2), thus the Weibull kinetic model can be represented with the following expression;

\[
q(t) = q_m \left(1 - \exp\left(\frac{t}{\tau}\right)^a\right)
\]

(14)

where,

\[
\tau_{50\%} = \tau \left(\ln 2\right)^{\frac{1}{a}}
\]

(15)

\(\tau_{50\%}\) represents the time required to adsorb one-half of the maximum adsorbed quantity.

The Hill kinetics model is expressed as follows;

\[
q_t = q_m \left(\frac{t/\tau}{1 + (t/\tau)^a}\right)
\]

(16)

where, \(\tau = (k_2, aq_m)^{-\frac{1}{a}}\) and \(\tau_{50\%} = \tau\)

Hamissa et al., reported the modeling of Methylene blue sorption onto Agave Americana fibre using fractal kinetics, the study showed that Methylene blue sorption were satisfactorily fitted by the Brouers-Sotolongo kinetic model with no systematic variation of the global fractal time index \(a\) which varies in the limits 0.6 - 0.9 [64]. In another study Al-Musawi et al., reported the modeling of kinetic data obtained from the adsorption of two antibiotics onto three nanoadsorbents using the Brouers-Sotolongo fractal equation [60].

5. Adsorption Diffusion Models

5.1. Boyd Model

This model predicts the rate determining step (slow step) involved in the adsorption process. The Boyd kinetic model is represented by the following expression [65];

\[
B_t = -0.4978 - \ln \left(1 - \frac{q}{q_\infty}\right)
\]

(17)

where;

- \(q\) = Amount of adsorbate adsorbed at time \(t\) (mg·g⁻¹)
- \(q_\infty\) = Amount of adsorbate adsorbed (mg·g⁻¹)

Meng, F. W., applied this model for the study of phenol adsorption by a polymeric adsorbent (NDA-100) [66]. Nethaji et al., used this model to prove that external mass transfer is the rate determining step for the adsorption of cationic and anionic dyes onto carbonaceous particles prepared from Juglansregia shell biomass [44].

5.2. Intra-Particle Diffusion Model

Webber-Morris observed that in most adsorption processes the uptake of ad-
sorbates varies proportionally with the square root of time \( t^{1/2} \) [66]. The linearized form of this model is given as [67];

\[
q_t = K_{IPD} t^{1/2} + C
\]

where;

\( K_{IPD} \) = Intra-particle diffusion constant (mg·g min\(^{-1/2}\))

\( C \) = Thickness of boundary layer (intercept).

When intra-particle diffusion alone is the rate determining step then a plot of \( q_t \) vs \( t^{1/2} \) appears as a linear graph that passes through the origin. However, if film diffusion also takes place simultaneously then the intercept “C” gives a clue on the thickness of the boundary layer [63]. Wang et al explored the kinetics of nitrate adsorption onto modified wheat residues and their results showed that the intra-particle diffusion model generated the best agreement with experimental data, which means intra-particle diffusion was the main rate determining step during the sorption process [64]. Similarly, Baduzzman et al. evaluated the removal of arsenic in aqueous solution using Granular Ferric Hydroxide (GFH) and their results showed that intra-particle diffusion in an important mass transport process in the removal of arsenic using packed-bed treatment systems [65]. Several researchers have used this model to show that sorption processes they investigated were not only controlled by intraparticle diffusion but that film diffusion also played a role [66]-[71].

5.3. Model Performance Indicators

The linear forms of kinetic models discussed here are usually employed to plot graphs from which associated parameters are determined (intercepts and slopes). Thus the 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.

5.4. Coefficient of Determination \( (R^2) \)

The coefficient of determination represents the variance about the mean, it is used to analyze the fitting degrees of kinetic models with experimental data [27] [39] [72] [73] [74]. The coefficient of determination \( (R^2) \) is defined by the following equation [75].

\[
R^2 = \frac{\sum (q_{cal} - q_{mexp})^2}{\sum (q_{cal} - q_{mexp})^2 + \sum (q_{cal} - q_{mexp})^2}
\]

where

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

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

\( q_{mexp} \) = average of \( q_{exp} \) (mg·g\(^{-1}\))

Moussavi et al., applied this model as a criteria of goodness of fit. Their
results showed that the coefficient of determination ($R^2$) for the pseudo-second-order kinetic (PSO) is higher than that for pseudo-first-order kinetic (PFO) for the adsorption of all tested concentrations of amoxicillin onto ammonium chloride induced activated carbon (NAC) and standard activated carbon (SAC) is an indication that the kinetic data were best described with the pseudo-second-order kinetic model [76]. Similarly, Velinov et al. used the coefficient of determination as the basis for evaluation the best fit kinetic model for the Biosorption of loperamide by lignocellulosic-$\text{Al}_2\text{O}_3$ hybrid. The obtained result showed that the pseudo-second-order fitted better than the pseudo-first-order model because of higher coefficient of correlation [77].

5.5. Chi-Square Test ($x^2$)

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 [78]. The value of this function can be evaluated from the following expression;

$$
\sum_{i=1}^{n} \frac{(q_{\text{eval}} - q_{\text{meas}})^2}{q_{\text{meas}}}
$$

Elbardiji et al., evaluated the predictive performance of the modified f-mexp equation for the modeling of adsorption kinetics of experimental systems using chi square ($x^2$), and results revealed that the f-mexp equation can fit the experimental data very well over the whole adsorption range [79]. Podder and Majumder also used this model to evaluate the goodness of fitness of adsorption kinetic data for As(III) and As(V) on MnFe$_2$O$_4$ composite [29].

6. Conclusion

In this review, we have discussed several thermodynamic and kinetic parameters with respect to how they impinge on adsorption processes. Thermodynamic parameters described herein are essential in determining the effect of heat on adsorption procedures and ultimately they help to define the spontaneity of adsorption processes. On the other hand, kinetic models were discussed under two basic categories namely: adsorption reaction models which in most instances define the rate at which adsorption takes place without providing exact insights into the mechanism of adsorption. Conversely, adsorption diffusion models describe basic steps that envisage mechanisms of adsorption processes.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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