

## Review Article

# Modelling and Interpretation of Adsorption Isotherms

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The need to design low-cost adsorbents for the detoxification of industrial effluents has been a growing concern for most environmental researchers. So modelling of experimental data from adsorption processes is a very important means of predicting the mechanisms of various adsorption systems. Therefore, this paper presents an overall review of the applications of adsorption isotherms, the use of linear regression analysis, nonlinear regression analysis, and error functions for optimum adsorption data analysis.

## 1. Introduction

The migration of pollutant(s) in aqueous media and subsequent development of containment measures have resulted in the use of adsorption among other techniques [1, 2]. Adsorption equilibrium information is the most important piece of information needed for a proper understanding of an adsorption process.

A proper understanding and interpretation of adsorption isotherms is critical for the overall improvement of adsorption mechanism pathways and effective design of adsorption system [3].

In recent times, linear regression analysis has been one of the most applied tools for defining the best fitting adsorption models because it quantifies the distribution of adsorbates, analyzes the adsorption system, and verifies the consistency of theoretical assumptions of adsorption isotherm model [4].

Because of the inherent bias created by linearization, several error functions have been used to address this shortfall. Concomitant with the evolution of computer technology, the use of nonlinear isotherm modelling has been extensively used.

## 2. One-Parameter Isotherm

*2.1. Henry's Isotherms.* This is the simplest adsorption isotherm in which the amount of surface adsorbate is proportional to the partial pressure of the adsorptive gas [4].

This isotherm model describes an appropriate fit to the adsorption of adsorbate at relatively low concentrations such that all adsorbate molecules are secluded from their nearest neighbours [5].

Thus, the equilibrium adsorbate concentrations in the liquid and adsorbed phases are related to the linear expression:

$$q_e = K_{HE}C_e, \quad (1)$$

where  $q_e$  is amount of the adsorbate at equilibrium (mg/g),  $K_{HE}$  is Henry's adsorption constant, and  $C_e$  is equilibrium concentration of the adsorbate on the adsorbent.

## 3. Two-Parameter Isotherm

*3.1. Hill-Deboer Model.* The Hill-Deboer isotherm model describes a case where there is mobile adsorption as well as lateral interaction among adsorbed molecules [6, 7].

The linearized form of this isotherm equation is as follows [8]:

$$\ln \left[ \frac{C_e(1-\theta)}{\theta} \right] - \frac{\theta}{1-\theta} = -\ln K_1 - \frac{K_2\theta}{RT}, \quad (2)$$

where  $K_1$  is Hill-Deboer constant ( $\text{Lmg}^{-1}$ ) and  $K_2$  is the energetic constant of the interaction between adsorbed molecules ( $\text{KJmol}^{-1}$ ). Equilibrium data from adsorption experiments can be analyzed by plotting  $\ln[C_e(1-\theta)/\theta] - \theta/(1-\theta)$  versus  $\theta$  [8–10].

3.2. *Fowler-Guggenheim Model.* Fowler-Guggenheim proposed this isotherm equation which takes into consideration the lateral interaction of the adsorbed molecules [11]. The linear form of this isotherm model is as follows [8]:

$$\ln \left[ \frac{C_e(1-\theta)}{\theta} \right] = -\ln K_{FG} + \frac{2w\theta}{RT}, \quad (3)$$

where  $K_{FG}$  is Fowler-Guggenheim equilibrium constant ( $\text{Lmg}^{-1}$ ),  $\theta$  is fractional coverage,  $R$  is universal gas constant ( $\text{KJmol}^{-1} \text{K}^{-1}$ ),  $T$  is temperature (k), and  $w$  is interaction energy between adsorbed molecules ( $\text{KJmol}^{-1}$ ).

This isotherm model is predicated on the fact that the heat of adsorption varies linearly with loading. Therefore, if the interaction between adsorbed molecules is attractive, then the heat of adsorption will increase with loading because of increased interaction between adsorbed molecules as loading increases (i.e.,  $w =$  positive). However, if the interaction among adsorbed molecules is repulsive, then the heat of adsorption decreases with loading (i.e.,  $w =$  negative). But when  $w = 0$  then there is no interaction between adsorbed molecules, and the Fowler-Guggenheim isotherm reduces to the Langmuir equation.

A plot of  $\ln[C_e(1-\theta)/\theta]$  versus  $\theta$  is used to obtain the values for  $K_{FG}$  and  $w$ .

It is important to note that this model is only applicable when surface coverage is less than 0.6 ( $\theta < 0.6$ ).

Kumara et al. analyzed the adsorption data for the phenolic compounds onto granular activated carbon with the Fowler-Guggenheim isotherm and reported that the interaction energy ( $w$ ) was positive which indicates that there is attraction between the adsorbed molecules [8].

3.3. *Langmuir Isotherm.* Langmuir adsorption which was primarily designed to describe gas-solid phase adsorption is also used to quantify and contrast the adsorptive capacity of various adsorbents [12]. Langmuir isotherm accounts for the surface coverage by balancing the relative rates of adsorption and desorption (dynamic equilibrium). Adsorption is proportional to the fraction of the surface of the adsorbent that is open while desorption is proportional to the fraction of the adsorbent surface that is covered [13].

The Langmuir equation can be written in the following linear form [14]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_e} + \frac{C_e}{q_m}, \quad (4)$$

where  $C_e$  is concentration of adsorbate at equilibrium ( $\text{mg g}^{-1}$ ).

$K_L$  is Langmuir constant related to adsorption capacity ( $\text{mg g}^{-1}$ ), which can be correlated with the variation of the suitable area and porosity of the adsorbent which implies that large surface area and pore volume will result in higher adsorption capacity.

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called the separation factor  $R_L$  [15].

$$R_L = \frac{1}{1 + K_L C_o}, \quad (5)$$

where  $K_L$  is Langmuir constant ( $\text{mg g}^{-1}$ ) and  $C_o$  is initial concentration of adsorbate ( $\text{mg g}^{-1}$ ).

$R_L$  values indicate the adsorption to be unfavourable when  $R_L > 1$ , linear when  $R_L = 1$ , favourable when  $0 < R_L < 1$ , and irreversible when  $R_L = 0$ .

Dąbrowski studied the adsorption of direct dye onto a Novel Green Adsorbate developed from *Uncaria Gambir* extract; their equilibrium data were well described by the Langmuir isotherm model [14].

3.4. *Freundlich Isotherm.* Freundlich isotherm is applicable to adsorption processes that occur on heterogenous surfaces [15]. This isotherm gives an expression which defines the surface heterogeneity and the exponential distribution of active sites and their energies [16].

The linear form of the Freundlich isotherm is as follows [17]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e, \quad (6)$$

where  $K_F$  is adsorption capacity ( $\text{L/mg}$ ) and  $1/n$  is adsorption intensity; it also indicates the relative distribution of the energy and the heterogeneity of the adsorbate sites.

Boparai et al. investigate the adsorption of lead (II) ions [17] from aqueous solutions using coir dust and its modified extract resins. Although several isotherm models were applied, the equilibrium data was best represented by Freundlich and Flory-Huggins isotherms due to high correlation coefficients [18].

3.5. *Dubinin-Radushkevich Isotherm.* Dubinin-Radushkevich isotherm model [19] is an empirical adsorption model that is generally applied to express adsorption mechanism with Gaussian energy distribution onto heterogeneous surfaces [20].

This isotherm is only suitable for intermediate range of adsorbate concentrations because it exhibits unrealistic asymptotic behavior and does not predict Henry's laws at low pressure [21].

The model is a semiempirical equation in which adsorption follows a pore filling mechanism [22]. It presumes a multilayer character involving Van Der Waal's forces, applicable for physical adsorption processes, and is a fundamental equation that qualitatively describes the adsorption of gases and vapours on microporous sorbents [23].

It is usually applied to differentiate between physical and chemical adsorption of metal ions [22]. A distinguishing feature of the Dubinin-Radushkevich isotherm is the fact that it is temperature dependent; hence when adsorption data at different temperatures are plotted as a function of logarithm of amount adsorbed versus the square of potential energy, all suitable data can be obtained [13].

Dubinin-Radushkevich isotherm is expressed as follows [16]:

$$\ln q_e = \ln q_m - \beta E^2$$

$$\epsilon = RT \ln \left( 1 + \frac{1}{C_e} \right)$$

$$E = \frac{1}{\sqrt{2B}}, \quad (7)$$

where  $\epsilon$  is Polanyi potential,  $\beta$  is Dubinin-Radushkevich constant,  $R$  is gas constant ( $8.31 \text{ Jmol}^{-1} \text{ K}^{-1}$ ),  $T$  is absolute temperature, and  $E$  is mean adsorption energy.

Ayawei et al. and Vijayaraghavan et al. applied the Dubinin-Radushkevich isotherm in their investigation of Congo red adsorption behavior on Ni/Al- $\text{CO}_3$  and sorption behavior of cadmium on nanozero-valent iron particles, respectively [16, 22].

**3.6. Temkin Isotherm.** Temkin isotherm model takes into account the effects of indirect adsorbate/adsorbate interactions on the adsorption process; it is also assumed that the heat of adsorption ( $\Delta H_{\text{ads}}$ ) of all molecules in the layer decreases linearly as a result of increase surface coverage [24]. The Temkin isotherm is valid only for an intermediate range of ion concentrations [25]. The linear form of Temkin isotherm model is given by the following [22]:

$$q_e = \frac{Rt}{b} \ln K_T + \frac{RT}{b} \ln C_e, \quad (8)$$

where  $b$  is Temkin constant which is related to the heat of sorption ( $\text{Jmol}^{-1}$ ) and  $K_T$  is Temkin isotherm constant ( $\text{Lg}^{-1}$ ) [26].

Hutson and Yang applied Temkin isotherm model to confirm that the adsorption of cadmium ion onto nanozero-valent iron particles follows a chemisorption process. Similarly, Elmersi et al. used the Temkin isotherm model in their investigation of the adsorption of methylene blue onto miswak leaves [18].

**3.7. Flory-Huggins Isotherm.** Flory-Huggins isotherm describes the degree of surface coverage characteristics of the adsorbate on the adsorbent [27].

The linear form of the Flory-Huggins equation is expressed as

$$\ln \left( \frac{\theta}{C_o} \right) = \ln K_{\text{FH}} + n \ln (1 - \theta), \quad (9)$$

where  $\theta$  is degree of surface coverage,  $n$  is number of adsorbates occupying adsorption sites, and  $K_{\text{FH}}$  is Flory-Huggins equilibrium constant ( $\text{Lmol}^{-1}$ ).

This isotherm model can express the feasibility and spontaneity of an adsorption process.

The equilibrium constant  $K_{\text{FH}}$  is used to calculate spontaneity Gibbs free energy as shown in the following expression [28]:

$$\Delta G^\circ = RT \ln (K_{\text{FH}}), \quad (10)$$

where  $\Delta G^\circ$  is standard free energy change,  $R$  is universal gas constant  $8.314 \text{ Jmol}^{-1} \text{ K}^{-1}$ , and  $T$  is absolute temperature.

Hamdaoui and Naffrechoux used the Flory-Huggins isotherm model in their study of the biosorption of Zinc from aqueous solution using coconut coir dust [29].

**3.8. Hill Isotherm.** The Hill isotherm equation describes the binding of different species onto homogeneous substrates. This model assumes that adsorption is a cooperative phenomenon with adsorbates at one site of the adsorbent influencing different binding sites on the same adsorbent [30].

The linear form of this isotherm is expressed as follows [29]:

$$\log \frac{q_e}{q_H - q_e} = n_H \log (C_e) - \log (K_D), \quad (11)$$

where  $K_D$ ,  $n_H$ , and  $q_H$  are constants.

Hamdaoui and Naffrechoux investigated the equilibrium adsorption of aniline, benzaldehyde, and benzoic acid on granular activated carbon (GAC) using the Hill isotherm model; according to their report, the Hill model was very good in comparison with previous models with  $R^2 = 0.99$  for all adsorbates [29].

**3.9. Halsey Isotherm.** The Halsey isotherm is used to evaluate multilayer adsorption at a relatively large distance from the surface [16]. The adsorption isotherm can be given as follows [31]:

$$q_e = \frac{1}{n_H} I_n K_H - \frac{1}{n_H} \ln C_{qe}, \quad (12)$$

where  $K_H$  and  $n$  are Halsey isotherm constant and they can be obtained from the slope and intercept of the plot of  $\ln q_e$  versus  $\ln C_e$ .

Fowler and Guggenheim reported the use of Halsey isotherm in their equilibrium studies of methyl orange sorption by pinecone derived activated carbon. The fitting of their experimental data to the Halsey isotherm model attests to the heteroporous nature of the adsorbent [31]. Similarly, Song et al. applied the Halsey isotherm for the study of coconut shell carbon prepared by KOH activation for the removal of  $\text{pb}^{2+}$  ions from aqueous solutions. The Halsey isotherm fits the experimental data well due to high correlation coefficient ( $R^2$ ), which may be attributed to the heterogeneous distribution of activate sites and multilayer adsorption on coconut shell carbons [16].

**3.10. Harkin-Jura Isotherm.** Harkin-Jura isotherm model assumes the possibility of multilayer adsorption on the surface of adsorbents having heterogeneous pore distribution [32]. This model is expressed as follows:

$$\frac{1}{q_e^2} = \frac{B}{A} - \left( \frac{1}{A} \right) \log C_e, \quad (13)$$

where  $B$  and  $A$  are Harkin-Jura constants that can be obtained from plotting  $1/q_e^2$  versus  $\log C_e$ .

Foo and Hameed reported that the Harkin-Jura isotherm model showed a better fit to the adsorption data than Freundlich, Halsey, and Temkin isotherm models in their investigation of the adsorptive removal of reactive black 5 from wastewater using Bentonite clay [32].

**3.11. Jovanovic Isotherm.** The Jovanovic model is predicated on the assumptions contained in the Langmuir model, but in

addition the possibility of some mechanical contacts between the adsorbate and adsorbent [33].

The linear form of the Jovanovic isotherm is expressed as follows [34]:

$$\ln q_e = \ln q_{\max} - K_J C_e, \quad (14)$$

where  $q_e$  is amount of adsorbate in the adsorbent at equilibrium ( $\text{mg g}^{-1}$ ),  $q_{\max}$  is maximum uptake of adsorbate obtained from the plot of  $\ln q_e$  versus  $C_e$ , and  $K_J$  is Jovanovic constant.

Kiseler reported the use of Jovanovic isotherm model while determining adsorption isotherms for L-Lysine imprinted polymer. Their report showed that the best prediction of retention capacity was obtained by applying the Jovanovic isotherm model [33].

**3.12. Elovich Isotherm.** The equation that defines this model is based on a kinetic principle which assumes that adsorption sites increase exponentially with adsorption; this implies a multilayer adsorption [35]. The equation was first developed to describe the kinetics of chemisorption of gas onto solids [36].

The linear forms of the Elovich model are expressed as follows [37]:

$$\frac{q_e}{q_m} = K_E C_e e^{\frac{q_e}{q_m}}, \quad (15)$$

but the linear form is expressed as follows [8]:

$$\ln \frac{q_e}{C_e} = \ln K_e q_m - \frac{q_e}{q_m}. \quad (16)$$

Elovich maximum adsorption capacity and Elovich constant can be calculated from the slope and intercept of the plot of  $\ln(q_e/C_e)$  versus  $q_e$ .

Rania et al. reported the use of Elovich isotherm model in their work titled "Equilibrium and Kinetic Studies of Adsorption of Copper (II) Ions on Natural Sorbent." Their investigation showed that the value of the regression coefficient ( $R^2$ ) for the Elovich model was 0.808 which is higher than that of Langmuir; therefore the adsorption of copper (II) onto Chitin was best described by the Elovich isotherm.

**3.13. Kiselev Isotherm.** The Kiselev adsorption isotherm equation also known as localized monomolecular layer model [38] is only valid for surface coverage  $\theta > 0.68$  and its linearized expression is as follows:

$$\frac{1}{C_e(1-\theta)} = \frac{K_1}{\theta} + K_i K_n, \quad (17)$$

where  $K_i$  is Kiselev equilibrium constant ( $\text{Lmg}^{-1}$ ) and  $K_n$  is equilibrium constant of the formation of complex between adsorbed molecules.

Equilibrium data from adsorption processes can be modelled by plotting  $1/C_e(1-\theta)$  versus  $1/\theta$  [8, 38–40].

## 4. Three-Parameter Isotherms

**4.1. Redlich-Peterson Isotherm.** The Redlich-Peterson isotherm is a mix of the Langmuir and Freundlich isotherms. The numerator is from the Langmuir isotherm and has the benefit of approaching the Henry region at infinite dilution [41].

This isotherm model is an empirical isotherm incorporating three parameters. It combines elements from both Langmuir and Freundlich equations; therefore the mechanism of adsorption is a mix and does not follow ideal monolayer adsorption [42].

This model is defined by the following expression:

$$q_e = \frac{AC_e}{1 + BC_e^\beta}, \quad (18)$$

where  $A$  is Redlich-Peterson isotherm constant ( $\text{Lg}^{-1}$ ),  $B$  is constant ( $\text{Lmg}^{-1}$ ),  $\beta$  is exponent that lies between 0 and 1,  $C_e$  is equilibrium liquid-phase concentration of the adsorbent ( $\text{mg l}^{-1}$ ), and  $q_e$  is equilibrium adsorbate loading on the adsorbent ( $\text{mg g}^{-1}$ ).

At high liquid-phase concentrations of the adsorbate, (16) reduces to the Freundlich equation:

$$q_e = \frac{A}{B} C_e^{1-\beta}, \quad (19)$$

where  $A/B = K_F$  and  $(1-\beta) = 1/n$  of the Freundlich isotherm model.

When  $\beta = 1$ , (18) reduces to Langmuir equation with  $b = B$  (Langmuir adsorption constant ( $\text{Lmg}^{-1}$ ) which is related to the energy of adsorption).

$A = bq_{ml}$  where  $q_{ml}$  is Langmuir maximum adsorption capacity of the adsorbent ( $\text{mg g}^{-1}$ ); when  $\beta = 0$ , (18) reduces to Henry's equation with  $1/(1+b)$  representing Henry's constant.

The linear form of the Redlich-Peterson isotherm can be expressed as follows [34]:

$$\ln \frac{C_e}{q_e} = \beta \ln C_e - \ln A \quad (20)$$

A plot of  $\ln(C_e/q_e)$  versus  $\ln C_e$  enables the determination of Redlich-Peterson constants, where  $\beta$  is slope and  $A$  is intercept [30, 42–45].

This isotherm model has a linear dependence on concentration in the numerator and an exponential function in the denominator which altogether represent adsorption equilibrium over a wide range of concentration of adsorbate which is applicable in either homogenous or heterogeneous systems because of its versatility [46, 47].

**4.2. Sips Isotherm.** Sips isotherm is a combination of the Langmuir and Freundlich isotherms and it is given the following general expression [48]:

$$q_e = \frac{K_s C_e^{\beta_s}}{1 + a_s C_e^{\beta_s}}, \quad (21)$$

where  $K_s$  is Sips isotherm model constant ( $\text{Lg}^{-1}$ ),  $\beta_s$  is Sips isotherm exponent, and  $a_s$  is Sips isotherm model constant ( $\text{Lg}^{-1}$ ). The linearized form is given as follows [12]:

$$\beta_s \ln C_e = -\ln\left(\frac{K_s}{q_e}\right) + \ln(a_s). \quad (22)$$

This model is suitable for predicting adsorption on heterogeneous surfaces, thereby avoiding the limitation of increased adsorbate concentration normally associated with the Freundlich model [19]. Therefore at low adsorbate concentration this model reduces to the Freundlich model, but at high concentration of adsorbate, it predicts the Langmuir model (monolayer adsorption). The parameters of the Sips isotherm model are  $p^H$ , temperature, and concentration dependent [12, 49] and isotherm constants differ by linearization and nonlinear regression [50].

**4.3. Toth Isotherm.** The Toth isotherm is another empirical modification of the Langmuir equation with the aim of reducing the error between experimental data and predicted value of equilibrium data [51]. This model is most useful in describing heterogeneous adsorption systems which satisfy both low and high end boundary of adsorbate concentration [52]. The Toth isotherm model is expressed as follows [52]:

$$\frac{q_e}{q_m} = \theta = \frac{K_e C_e}{[1 + (K_L C_e)^n]^{1/n}}, \quad (23)$$

where  $K_L$  is Toth isotherm constant ( $\text{mg g}^{-1}$ ) and  $n$  is Toth isotherm constant ( $\text{mg g}^{-1}$ ).

It is clear that when  $n = 1$ , this equation reduces to Langmuir isotherm equation. Therefore the parameter  $n$  characterizes the heterogeneity of the adsorption system [51] and if it deviates further away from unity (1), then the system is said to be heterogeneous. The Toth isotherm may be rearranged to give a linear form as follows:

$$\ln \frac{q_e^n}{q_m^n - q_e^n} = n \ln K_L + n \ln C_e. \quad (24)$$

The values of parameters of the Toth model can be evaluated by nonlinear curve fitting method using sigma plot software [53].

This isotherm model has been applied for the modelling of several multilayer and heterogeneous adsorption systems [53, 54].

**4.4. Koble-Carrigan Isotherm.** Koble-Carrigan isotherm model is a three-parameter equation which incorporates both Langmuir and Freundlich isotherms for representing equilibrium adsorption data [55]. The linear form of this module is represented by the following equation [56]:

$$\frac{1}{q_e} = \left(\frac{1}{A_k C_e^p}\right) + \frac{B_k}{A_k}, \quad (25)$$

where  $A_k$  is Koble-Carrigan's isotherm constant,  $B_k$  is Koble-Carrigan's isotherm constant, and  $p$  is Koble-Carrigan's isotherm constant.

All three Koble-Carrigan isotherm constants can be evaluated with the use of a solver add-in function of the Microsoft Excel [56]. At high adsorbate concentrations, this model reduces to Freundlich isotherm. It is only valid when the constant " $p$ " is greater than or equal to 1. When " $p$ " is less than unity (1), it signifies that the model is incapable of defining the experimental data despite high concentration coefficient or low error value [54].

**4.5. Kahn Isotherm.** The Kahn isotherm model is a general model for adsorption of biadsorbate from pure dilute equations solutions [57].

This isotherm model is expressed as follows [58]:

$$Q_e = \frac{Q_{\max} b_k C_e}{(1 + b_k C_e) a_k}, \quad (26)$$

where  $a_k$  is Kahn isotherm model exponent,  $b_k$  is Khan isotherm model constant, and  $Q_{\max}$  is Khan isotherm maximum adsorption capacity ( $\text{mg g}^{-1}$ ).

Nonlinear methods have been applied by several researchers to obtain the Khan isotherm model parameters [59, 60].

**4.6. Radke-Prausnitz Isotherm.** The Radke-Prausnitz isotherm model has several important properties which makes it more preferred in most adsorption systems at low adsorbate concentration [61].

The isotherm is given by the following expression:

$$q_e = \frac{q_{\text{MRP}} K_{\text{RP}} C_e}{(1 + K_{\text{RP}} C_e)^{\text{MRP}}}, \quad (27)$$

where  $q_{\text{MRP}}$  is Radke-Prausnitz maximum adsorption capacity ( $\text{mg g}^{-1}$ ),  $K_{\text{RP}}$  is Radke-Prausnitz equilibrium constant, and MRP is Radke-Prausnitz model exponent.

At low adsorbate concentration, this isotherm model reduces to a linear isotherm, while at high adsorbate concentration it becomes the Freundlich isotherm and when  $M_{\text{RP}} = 0$ , it becomes the Langmuir isotherm. Another important characteristic of this isotherm is that it gives a good fit over a wide range of adsorbate concentration. The Radke-Prausnitz model parameters are obtained by nonlinear statistical fit of experimental data [61, 62].

**4.7. Langmuir-Freundlich Isotherm.** Langmuir-Freundlich isotherm includes the knowledge of adsorption heterogeneous surfaces. It describes the distribution of adsorption energy onto heterogeneous surface of the adsorbent [54]. At low adsorbate concentration this model becomes the Freundlich isotherm model, while at high adsorbate concentration it becomes the Langmuir isotherm. Langmuir-Freundlich isotherm can be expressed as follows:

$$q_e = \frac{q_{\text{MLF}} (K_{\text{LF}} C_e)^{\text{MLF}}}{1 + (K_{\text{LF}} C_e)^{\text{MLF}}}, \quad (28)$$

where  $q_{\text{MLF}}$  is Langmuir-Freundlich maximum adsorption capacity ( $\text{mg g}^{-1}$ ),  $K_{\text{LF}}$  is equilibrium constant for heterogeneous solid, and  $M_{\text{LF}}$  is heterogeneous parameter and it lies

between 0 and 1. These parameters can be obtained by using the nonlinear regression techniques [63].

**4.8. Jossens Isotherm.** The Jossens isotherm model predicts a simple equation based on the energy distribution of adsorbate-adsorbent interactions at adsorption sites [64]. This model assumes that the adsorbent has heterogeneous surface with respect to the interactions it has with the adsorbate. The Jossen isotherm can be represented as follows:

$$C_e = \frac{q_e}{H} \exp(Fq_e^p), \quad (29)$$

where  $H$  is Jossens isotherm constant (it corresponds to Henry's constant),  $p$  is Jossens isotherm constant and it is characteristic of the adsorbent irrespective of temperature and the nature of adsorbents, and  $F$  is Jossens isotherm constant.

The equation reduces to Henry's law at low capacities. However, upon rearranging (29) [65],

$$\ln\left(\frac{C_e}{q_e}\right) = -\ln(H) + Fq_e^p. \quad (30)$$

The values of  $H$  and  $F$  can be obtained from either a plot of  $\ln(C_e/Q_e)$  versus  $q_e$  or using a least square fitting procedure.

A good representation of equilibrium data using this equation was reported for phenolic compounds on activated carbon [66] and on amberlite XAD-4 and XAD-7 macroporous resins [67].

## 5. Four-Parameter Isotherms

**5.1. Fritz-Schlunder Isotherm.** Fritz and Schlunder derived an empirical equation which can fit a wide range of experimental results because of the large number of coefficients in the isotherm [68].

This isotherm model has the following equation:

$$q_e = \frac{q_{mFS} K_{FS} C_e}{1 + q_{mFS} C_e^{MFS}}, \quad (31)$$

where  $q_{mFS}$  is Fritz-Schlunder maximum adsorption capacity ( $\text{mg g}^{-1}$ ),  $K_{FS}$  is Fritz-Schlunder equilibrium constant ( $\text{mg g}^{-1}$ ), and  $MFS$  is Fritz-Schlunder model exponent.

If  $M_{FS} = 1$ , then the Fritz-Schlunder model becomes the Langmuir model, but, for high adsorbate concentrations, the model reduces to Freundlich model.

Fritz-Schlunder isotherm parameters can be determined by nonlinear regression analysis [69, 70].

**5.2. Baudu Isotherm.** Bauder observed that the estimation of the Langmuir coefficients,  $b$  and  $q_m$ , by measurement of tangents at different equilibrium concentrations shows that they are not constants in a broad range [71]; therefore the Langmuir isotherm has been reduced to the Bauder isotherm [62]:

$$q_e = \frac{q_m b o C_e^{1+x+y}}{1 + b o C_e^{1+x}}, \quad (32)$$

where  $q_m$  is Bauder maximum adsorption capacity ( $\text{mg g}^{-1}$ ),  $bo$  is equilibrium constant,  $x$  is Baudu parameter, and  $Y$  is Baudu parameter.

For lower surface coverage the Bauder isotherm model reduces to Freundlich model.

Due to the inherent bias resulting from linearization this isotherm parameters are determined by nonlinear regression analysis [72].

**5.3. Weber-Van Vliet Isotherm.** Weber and Van Vliet postulated an empirical relation with four parameters that provided excellent description of data patterns for a wide range of adsorption systems [73].

The isotherm developed by weber and Van Vliet has the following form:

$$C_e = p_1 q_e^{(p_2 q_e^{p_3} + p_4)}, \quad (33)$$

where  $C_e$  is equilibrium concentration of the adsorbate ( $\text{mg g}^{-1}$ ),  $q_e$  is adsorption capacity  $\text{mg g}^{-1}$ ,  $p_1$ ,  $p_2$ ,  $p_3$ , and  $p_4$  are Weber-Van Vliet isotherm parameters

The isotherm parameters ( $p_1$ ,  $p_2$ ,  $p_3$ , and  $p_4$ ) can be defined by multiple nonlinear curve fitting techniques which is predicated on the minimization of sum of square of residual [72–74].

**5.4. Marczewski-Jaroniec Isotherm.** The Marczewski-Jaroniec isotherm is also known as the four-parameter general Langmuir equation [75]. It is recommended on the basis of the supposition of local Langmuir isotherm and adsorption energies distribution in the active sites on adsorbent [76].

The isotherm equation is expressed as follows:

$$q_e = q_{MMJ} \left( \frac{(K_{MJ} C_e)^{n_{MJ}}}{1 + (K_{MJ} C_e)^{n_{MJ}}} \right)^{M_{MJ}/n_{MJ}}, \quad (34)$$

where  $n_{MJ}$  and  $M_{MJ}$  are parameters that characterize the heterogeneity of the adsorbent surface,  $M_{MJ}$  describes the spreading of distribution in the path of higher adsorption energy, and  $n_{MJ}$  describes the spreading in the path of lesser adsorption energies.

The isotherm reduces to Langmuir isotherm when  $n_{MJ}$  and  $M_{MJ} = 1$ , when  $n_{MJ} = M_{MJ}$ ; it reduces to Langmuir-Freundlich model.

## 6. Five-Parameter Isotherms

Fritz and Schlunder developed a five-parameter empirical model that is capable of simulating the model variations more precisely for application over a wide range of equilibrium data [74].

The isotherm equation is

$$q_e = \frac{1_m FS_s K_1 C_e^{\alpha_{FS}}}{1 + K_2 C_e^{\beta_{FS}}}, \quad (35)$$

where  $q_{mFS}$  is Fritz-Schlunder maximum adsorption capacity ( $\text{mg g}^{-1}$ ) and  $K_1$ ,  $K_2$ ,  $\alpha_{FS}$ , and  $\beta_{FS}$  are Fritz-Schlunder parameters.

This isotherm is valid only in the range of  $L_{FS}$  value less than or equal to 1.

This model approaches Langmuir model while the value of both exponents  $\alpha_{FS}$  and  $\beta_{FS}$  equals 1 and for higher adsorbate concentrations it reduces to Freundlich model.

## 7. Error Analysis

In recent times linear regression analysis has been among the most pronounced and viable tools frequently applied for analysis of experimental data obtained from adsorption process. It has been used to define the best fitting relationship that quantify the distribution of adsorbates and also in the verification of the consistency of adsorption models and the theoretical assumptions of adsorption models [77, 78].

Studies have shown that the error structure of experimental data is usually changed during the transformation of adsorption isotherms into their linearized forms [79]. It is against this backdrop that nonlinearized regression analysis became inevitable, since it provides a mathematically rigorous method for determining adsorption parameters using original form of isotherm equations [80, 81].

Unlike linear regression, nonlinear regression usually involved the minimization of error distribution between the experimental data and the predicted isotherm based on its convergence criteria [82]. This operation is no longer computationally difficult because of availability of computer algorithms [21].

**7.1. The Sum Square of Errors (ERRSQ).** The sum of square of errors (ERRSQ) is said to be the most widely used error function [83]. This method can be represented by the following expression [45]:

$$\sum_{i=1}^n (q_{e,i,calc} - q_{e,i,meas})^2, \quad (36)$$

where  $q_{e,i,calc}$  is the theoretical concentration of adsorbate on the adsorbent, which have been calculated from one of the isotherm models.

$q_{e,i,meas}$  is the experimentally measured adsorbed solid phase concentration of the adsorbate adsorbed on the adsorbent.

One major disadvantage of this error function is that at higher end of liquid-phase adsorbate concentration ranges the isotherm parameters derived using this error function will provide a better fit as the magnitude of the errors and therefore the square of errors tend to increase illustrating a better fit for experimental data obtained at the high end of concentration range [45, 84].

**7.2. Hybrid Fractional Error Function (HYBRID).** The hybrid fractional error function (HYBRID) was developed by Kapoor and Yang, to improve the fit of the sum square of errors (ERRSQ) [85] at low concentrations by dividing it by the measured value. This function includes the number of data points ( $n$ ), minus the number of parameters ( $p$ ) or isotherm equation as a divisor [85].

The equation for this error function is

$$\text{HYBRID} = \frac{100}{n-p} \sum_{i=1}^n \left[ \frac{(q_{e,i,meas} - q_{e,i,calc})^2}{q_{e,i,meas}} \right]. \quad (37)$$

**7.3. Average Relative Error (ARE).** The average relative error was developed by Marquardt [86] with the aim of minimizing the fractional error distribution across the entire concentration range. It is given by the following expression:

$$\text{ARE} = \frac{100}{n} \sum_{i=1}^n \left[ \frac{q_{e,i,calc} - q_{e,i,meas}}{q_{e,i,meas}} \right]. \quad (38)$$

**7.4. Marquardt's Percent Standard Deviation (MPSD).** The Marquardt's percent standard deviation error function is similar to a geometric mean error distribution modified according to the degree of freedom of the system [87]. It is given by the following expression:

$$\text{MPSD} = \sqrt{\frac{1}{n-p} \sum_{i=1}^n \left( \frac{(q_{e,i,exp} - q_{e,i,calc})}{q_{e,i,exp}} \right)^2}. \quad (39)$$

**7.5. Sum of Absolute Errors (EABS).** This model is similar to the sum square error (ERRSQ) function. In this case isotherm parameters determined using this error function would provide a better fit as the forward high concentration data [88]. It is represented by the following equation:

$$\text{EABS} = \sum_{i=1}^p [q_{e,i,meas} - q_{e,i,calc}]. \quad (40)$$

**7.6. Sum of Normalized Errors (SNE).** Since each of the error criteria is likely to produce a different set of parameters of the isotherm, a standard procedure known as sum of the normalized errors is adopted to normalize and to combine the error in order to make a more meaningful comparison between the parameters sets. It has been used by several researchers to determine the best fitting isotherm model [88–91].

Calculation procedure is as follows:

- (i) Selection of an isotherm model and error function and determination of the adjustable parameters which minimized the error function
- (ii) Determination of all other error functions by referring to the parameters set
- (iii) Computation of other parameter sets associated with their error function values
- (iv) Normalization and selection of maximum parameters sets with respect to the largest error measurement
- (v) Summation of all these normalized errors for each parameter set

**7.7. Coefficient of Determination ( $R^2$ ) Spearman's Correlation Coefficient ( $R_s$ ) and Standard Deviation of Relative Errors ( $S_{RE}$ ).** The coefficient of determination represents the

variance about the mean; it is used to analyze the fitting degrees of isotherms and kinetic models with experimental data [12, 92]. The coefficient of determination ( $R^2$ ) is defined by the following equation [93]:

$$R^2 = \frac{\sum (q_{ecal} - q_{mexp})^2}{\sum (q_{ecal} - q_{mexp})^2 + (q_{cal} - q_{mexp})^2}, \quad (41)$$

where  $q_{exp}$  is amount of adsorbate adsorbed by adsorbent during the experiment ( $\text{mg g}^{-1}$ ),  $q_{cal}$  is amount of adsorbate obtained by kinetic isotherm models ( $\text{mg g}^{-1}$ ), and  $q_{mexp}$  is average of  $q_{exp}$  ( $\text{mg g}^{-1}$ ).

**7.8. Nonlinear Chi-Square Test ( $X^2$ ).** This function is very important in the determination of the best fit of an adsorption system. It can be obtained by judging the sum square difference between experimental and calculated data, with each square difference divided by its corresponding values [90]. The value of this function can be obtained from the following equation:

$$\sum_{i=1}^n \frac{(q_{ecal} - q_{emeas})^2}{q_{emeas}}. \quad (42)$$

**7.9. Coefficient of Nondetermination.** This function is very valuable tool for describing the extent of relationship between the transformed experimental data and the predicted isotherms and minimization of error distribution [93].

$$\text{Coefficient of nondetermination} = 1.00 - R^2, \quad (43)$$

where  $R^2$  is coefficient of determination.

## 8. Conclusion

The level of accuracy obtained from adsorption processes is greatly dependent on the successful modelling and interpretation of adsorption isotherms.

While linear regression analysis has been frequently used in accessing the quality of fits and adsorption performance because of its wide applicability in a variety of adsorption data, nonlinear regression analysis has also been widely used by a number of researchers in a bid to close the gap between predicted and experimental data. Therefore, there is the need to identify and clarify the usefulness of both linear and nonlinear regression analysis in various adsorption systems.

## Conflicts of Interest

The authors (Ayawei Nimibofa, Ebelegi Newton Augustus, and Wankasi Donbebe) declare that there are no conflicts of interest regarding the publication of this paper.

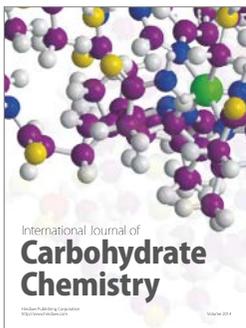
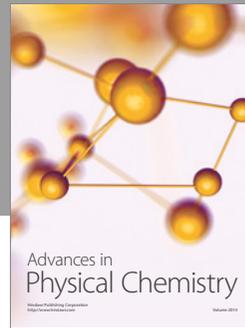
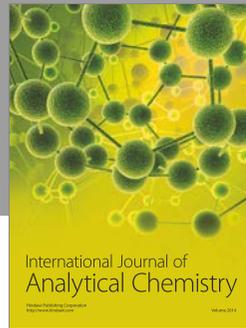
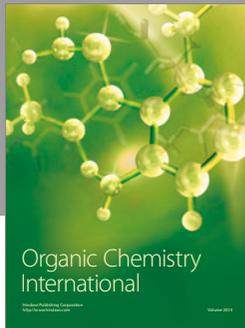
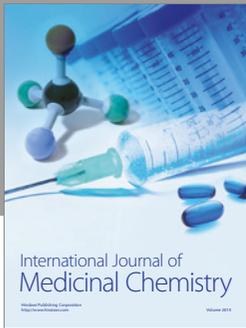
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