REVIEW OF ADSORPTION ISOOTHERMS MODELS

INTRODUCTION

Increase in human activities leading to agricultural and industrial waste has a severe impact on soil contamination (Garbuio, Howard and dos Santos, 2012). An increase in population implies a proportionate increase in environmentally unfriendly activities. Roser, Ritchie, and Ortiz-Ospina (2013) reported an exponential population growth in recent times. Industrial activities have also increased in China, India, and other developing countries like Nigeria. This increase in population and industrial activities leads to an increase in the deterioration of the ecosystem with more threat to the human physical environment. Continuous release of pollutants into the environment by human activities calls for the integration of various methodologies in place to minimize or eliminate toxic material materials from the environment. Wide range of researches on the treatment process have been carried out and are still ongoing in areas such as sedimentation, precipitation, coagulation, flocculation, flotation, filtration, membrane processes, electrochemical techniques, biological process, chemical reactions, ion exchange and adsorption (Food and Hameed, 2010). Of the technologies applied to environmental remediation, adsorption is of major interest due to its high efficiency and wider use. It is one of the most popular separation and purification/remediation processes (Al-Ghouti and Da'an, 2020).

The study of adsorption isotherms is essential to gain insight into the design and operation of adsorption systems and process, especially for the sake of environmental remediation and wastewater treatment plants. The study of adsorption chemical kinematics is an important subject matter in environmental analysis (Gautam and Chattopadhyaya, 2016). A proper understanding of adsorption isotherm models is useful to gain an understanding of the adsorption process of pollutants on adsorbents (El-Khiairy, 2008). In addition, adsorption isotherms show the equilibrium of the sorption of adsorbate on the surface of adsorbents and are useful knowledge in the optimization of adsorbent for the removal of pollutants from the environment.

The use of linear regression techniques to model adsorption isotherms has been popularly used in recent times to analyse adsorption systems due to their simplicity (Fost and Aly, 1981). Linear regression is capable of verifying the consistency of the models based on the assumptions made while quantifying the distribution of the adsorbate. The evolution and increase in computer technology have increased the use of nonlinear regression techniques in the analysis of adsorption isotherm as well (Ayawei, Ebelegi and Wankasi, 2017). The nonlinear regression approach has the advantage of minimizing errors due to linearization.

ADSORPTION AND ADSORPTION ISOOTHERM MODEL

In environmental and bioremediation, molecules are adsorbed from the bioavailable water-dissolved state through sorption to soil constituent (Harms, 2011). Sorption, in general, involves gas or liquid accumulation in another phase and includes absorption and adsorption. In other words, chemical and physical processes, which enable a gas or a liquid accumulate within another phase or phase boundary of two phases are popularly known as sorption. Sorption to natural solids is an underlying activity that affects the degradation, transport, and biological activities of organic compounds in the surroundings (Pignatello and Xing, 1995). When the liquid or gas accumulates on the boundary of two other phases, it is known as adsorption. Absorption, on the other hand, is the accumulation of two phases within another phase. While the molecules penetrate a three-dimensional matrix in absorption, the molecules attach to a two-dimensional matrix usually between phase boundaries in adsorption (Prasad and Srivastava, 2009; Qi et al., 2017). The adsorption phenomenon is a widely used separation process in environmental remediation and wastewater treatment due to its simplicity, low cost, efficiency, and environmentally friendliness (Wang and Guo, 2020). The amount of material absorbed by a substrate
Adsorption isotherms are curves describing the variation of gas absorbed with pressure. Adsorption isotherms profile equilibrium behaviour of adsorbents at constant temperature (Al-Ghouti and Da’ana, 2020a). Depending on the interaction between the adsorbate and the absorbent, the adsorption processes can be physisorption or chemisorption (Sims, Harmer and Quinto, 2019). Physisorption is a phenomenon, which occurs whenever an adsorptive (the substance in the fluid phase which is capable of being absorbed) is brought into contact with the surface of the adsorbent by intermolecular forces involving the same kind as those responsible for the imperfection of real gases and the condensation of vapours (Sing, 1982). However, when the processes involve forming transient chemical bonds to the surface, it is known as chemisorption (Jiang et al., 2019). An effective design of adsorption systems through the general improvement of adsorption pathways requires good knowledge and understanding of adsorption isotherms (El-Khaiary, 2008).

Three things are considered in the design of the adsorption mechanism, the physical adsorption that has to do with van der Waals force, the chemical adsorption that is made by the chemical bond and ion exchange. Modelling of adsorption equilibrium data by isotherm models is the most widely used method of investigating adsorption mechanisms (Wang and Guo, 2020). Adsorption isotherms are determined by the adsorbate adsorbent, adsorbed species, and physical properties such as ionic strength, temperature and pH (Yan et al., 2017). In the physical environment, the presence of the mixture of solids leads to the sorbate-sorbent associations which are governed by several interactions with varieties of behaviours described by different types of adsorption isotherms. According to IUPAC (International Union of Pure and Applied Chemistry), there are six types of adsorption isotherm models (types I, II, III, IV, V, and VI) based on the shape of the isotherm models as shown in Figure 1 (Sing, 1982). The type I model is reversible and is concave on the relative pressure axis. A typical example of this model can be found in molecular zeolites and activated carbon (Hauchhum and Mahanta, 2014). The reversible type II isotherm model is the regular type, which can be derived from a non-porous adsorbent. An example is the adsorption of Nitrogen on silica gel (Zhou et al., 2002; Sultan, Miyazaki and Koyama, 2018). The reversible type III isotherm model is convex on the pressure axis and a typical example is water vapour adsorption of nonporous carbon (Carrott, 1992). The type IV isotherms are characterized by their hysteresis loops due to capillary condensation occurring in the mesopores and limiting uptake over the range of high pressure. An example of the type IV isotherm model is the adsorption of humid air or water on a specific type of activated carbon (Buttersack, 2019; Wang et al., 2020).

The type V isotherm model is related to the type III model by its weak adsorbent-adsorbate interaction. The model is uncommon but can be found in the certain porous adsorbent. A typical example is the adsorption of water on a carbon molecular sieve or activated carbon fibre (Inglezakis, Poulopoulos and Kazemian, 2018; Buttersack, 2019). The type VI isotherm model is a multilayer and stepwise adsorptions which occurs on a uniform nonporous surface. This type of model can be found in the adsorption of inert gases on the surface of planer graphite (Sultan, Miyazaki and Koyama, 2018; Al-Ghouti and Da’ana, 2020a).

### CLASSIFICATION OF ISOTHERM MODELS BASED ON THE NUMBER OF PARAMETERS

#### One-Parameter Isotherm Models

- **Henry’s Isotherm Model**

In Henry’s isotherm model, the partial pressure of the adsorptive fluid is directly proportional to the amount of adsorbate (Fost and Aly, 1981; Erbil, 2006; Al-Ghouti and Da’ana, 2020b). It is considered one of the simplest adsorption isotherms (Ayawei, Ebelezi and Wankasi, 2017). Henry’s adsorption isotherm derived its name from Henry’s adsorption constant, i.e., the constant appearing in the linear adsorption isotherms, which is similar to Henry’s gas law (Wikipedia, 2021). It is derived from Gibbs adsorption (Deocaris and Osio, 2020) and is used in the determination of the equilibrium state of adsorption for adsorbates that are secluded at a low and constant temperature. Thus, in Henry’s adsorption isotherm, the equilibrium amount of adsorbate in the fluid is related to the partial pressure of the adsorptive fluid by Equation 1.

\[
Q_e = K_H C_e
\]

where \(Q_e\) is the amount of adsorbate at equilibrium condition (mg/g), \(K_H\) is Henry’s adsorption constant, and \(C_e\) is the equilibrium concentration of the adsorbate on the adsorbent.

It is important to note that Henry’s isotherm is not advisable for high temperature and pressure experimentation due to violent molecular motion caused by large interaction force and potential energy (Wang et al., 2016).
Two-Parameter Isotherm

**Freundlich Isotherm Model**

Freundlich adsorption isotherm model is a type of isotherm model in which the adsorbates form a monomolecular layer on the surface of the absorbent (Singh, 2016), but unlike the Langmuir model, application to multilayer adsorption is also possible (Al-Ghouti and Da’ana, 2020b). The Freundlich model expression shows the heterogeneity of the surface of the molecules (Gast and Adamson, 1997) as well as the exponential distribution of active sites and their energies. The non-linearized form of Freundlich isotherm model expression is shown in Equation 2, while the linearized form is shown in Equation 3.

\[ Q_e = K_F C_e^{1/n} \]
\[ \ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \]

where \( K_F \) is the Freundlich constant or maximum absorption capacity (L/mg), \( n \) is the adsorption intensity or surface heterogeneity, which indicates the energy distribution and the absorbate site’s heterogeneity. Freundlich isotherm is a power function and isotherms of this form have been observed for wide varieties of heterogeneous surfaces such as silica, clays, metals, activated carbon, and polymers (Fabrizius-Homan and Cooper, 1992; Keyes and Silcox, 1994; Murai et al., 1998). Umpleby et al. (2001) tested the generality of the Freundlich isotherm concerning molecularly imprinted polymers (MIPs) using a survey of systems from the literature. The results show that the Freundlich isotherm model gives a good mathematical approximation of the binding characteristics for non-covalently imprinted polymers. It has also been used in the fitting of the isotherm model for the removal of methyl orange by periphytic biofilms (Wu, 2017).

**Hill Deboer Model**

Hill Deboer Model (Deboer, 1953) applies to cases of lateral interaction between adsorbed molecules and mobile adsorption (Hill, 1946). When water adsorbed on pure and methylated quartz, there is an adsorption isotherm in which the amount adsorbed increases with increasing temperature (Hill, 1946). When water adsorbed on pure and methylated quartz, there is an adsorption isotherm in which the amount adsorbed increases with increasing temperature (Hill, 1946). The linear form of the Hill Deboer Model (Deboer, 1953) applies to cases of lateral interaction between adsorbed molecules, respectively. A positive \( k_2 \) means attraction while a negative \( k_2 \) means repulsion between the adsorbed species while zero value of \( k_2 \) means lack of attraction between the adsorbed species. \( \theta \) is the fractional coverage, \( R \) is the universal gas constant (KJmol\(^{-1}\)K\(^{-1}\)) and \( T \) is the temperature (K). To analyse the equilibrium data from adsorption experiments, a graph of \( \ln(C_e(1-\theta)/\theta) - (\theta/1-\theta) \) against \( \theta \) is usually plotted (Redlich and Peterson, 1959).

Hill Deboer isotherm model proved to be effective in the modelling of adsorption equilibrium isotherms of phenolic compounds from aqueous solutions onto granular activated carbon (Hamdaoui and Naffrechoux, 2007).

**Langmuir Isotherm**

The Langmuir isotherm model assumes that the distribution of the reactive groups over the surface of the particles are homogeneous and there is no lateral interaction between the particles (Miedaner, Weerasooriya and Tobschall, 2006). The Langmuir equation, which was developed based on the theory of gases, is used extensively to describe gas adsorption on solids (Olsen and Watanabe, 1957). The Langmuir sorption isotherm is valid when the adsorption of a solute from the solution is monolayer, the adsorption on a surface contains a definite number of identical sites with uniform strategy of adsorption, and there is no transmigration of adsorbate in the plane of surface (Gautam et al., 2014). The non-linearized form of the Langmuir isotherm model Langmuir (1918) is shown in equation 5

\[ Q_e = \frac{Q_0 K_L C_e}{(1+K_L C_e)} \]

The linearized form of the Langmuir model is given by Equation 6

\[ \frac{C_e}{Q_e} = \frac{1}{(K_L Q_0)} + \frac{C_e}{Q_L} \]

where \( Q_0 \) is the maximum adsorption capacity on a monolayer (mg/g) and \( K_L \) is the Langmuir adsorption constant (L/mg) that is related to the apparent energy of sorption. When a graph of \( C_e/Q_e \) against \( C_e \) will give a straight line of slope \( 1/(K_L Q_0) \).

The separation factor (\( R_L \)) is another key parameter that is often used to determine the nature of the adsorption process described in the Langmuir model. The separation factor is defined by equation 7 (Karagöz et al., 2008).

\[ R_L = \frac{1}{(1+K_L Q_0)} \]

where \( C_0 \) is the starting concentration of the absorbate (mg/L).

Langmuir model was used by Kausar, Bhatti and MacKinnon (2013) in the equilibrium kinetic studies on the removal of uranium from low-cost agricultural waste such as rice husk. The results showed that the model correlated best with the uranium biosorption equilibrium data at 10-100mgL\(^{-1}\) concentration range.

**Temkin Isotherm Model**

Temkin isotherm ignores the extremely low and high values of the concentrations and assumes that the heat of adsorption of all molecules in the layer would not decrease logarithmically but linearly (Aharoni and Tompkins, 1970; Piccin). The Temkin isotherm (Piccin, Dotto and Pinto, 2011) can be described by the following equation (equation 7).

\[ Q_e = \frac{RT}{b} \ln K_T + \left(\frac{RT}{b}\right) \ln C_e \]

where \( K_T \) is the maximum binding energy or the Temkin isotherm equilibrium-biding constant (Lmol\(^{-1}\)), \( b \) is the Temkin isotherm constant related to the adsorption heat.

**Kiselev Isotherm**

The Kiselev adsorption isotherm is a localized single-molecular layer model (Song et al., 2014). Like other isotherm models, it is only valid for surface coverage
The linearized Kiselev isotherm model is shown below (Ojediran et al., 2019):

$$\ln\left(\frac{1}{C_0(1-\theta)}\right) = \frac{K_1}{\theta} + K_n$$  \hspace{0.5cm} (8)

where $K_1$ is the Kiselev equilibrium constant (Lmg$^{-1}$), $K_n$ is the equilibrium constant of the formation of complexes between adsorbed molecules.

**Flory-Huggins Isotherm**

Flory-Huggins isotherm model considers the characteristics of surface coverage of the fluid on the adsorbent (Nechifor et al., 2015). The equation deals with similar chemical molecules, which differs in physical properties such as length. The linearized form of the equation is expressed as:

$$\ln\left(\frac{\theta}{C_0}\right) = \ln K_{FH} + n \ln(1 - \theta)$$  \hspace{0.5cm} (9)

where $n$ is the ion number occupying adsorption sites on two membranes, $K_{FH}$ is the Flory-Huggins equilibrium constant, $C_0$ is the initial concentration of the adsorbate ions (mEq/L), $C_0 = (1 - C_a/C_0)$ is the degree of membrane surface coverage, $C_a$ is the equilibrium concentration of the adsorbate.

Flory-Huggins isotherm model has been applied in the study of the adsorption of phosphate in drinking water (Nechifor et al., 2015). Flory-Huggins isotherm model can express the spontaneity of an adsorption process. The relationship between the Flory-Huggins equilibrium constant and Gibbs free energy is shown in the following expression (Ayawei, Ebelegi and Wankasi, 2017):

$$\Delta G^o = RT \ln K_{FH}$$  \hspace{0.5cm} (10)

where $\Delta G^o$ is standard free energy change, $R$ is the universal gas constant, and $T$ is the absolute temperature.

**Dubinin-Kaganer-Radushkevich Isotherm Model**

Dubinin–Kaganer–Radushkevich isotherm is mostly used for cases where the Gaussian energy spread onto a heterogeneous surface (Celebi et al., 2007). The model is a semiempirical equation and follows a pore-filling mechanism with unrealistic asymptotic behaviour which is unable to predict Henry's law at low pressure (Vijayaraghavan et al., 2006; Theivarasu and Myslami, 2011). The model is used to distinguish between physio sorption and chemisorption of metal iron, Vijayaraghavan et al., 2006). The Dubinin–Kaganer–Radushkevich isotherm model is shown below (Kadhim, 2016):

$$\ln Q_a = \ln Q_m - K_a \varepsilon^2$$  \hspace{0.5cm} (11)

where $Q_a$ is the number of metal ions adsorbed per unit weight of adsorbent (mol/g), $Q_m$ is the maximum sorption capacity (mol/g), $K_a$ is the activity coefficient related to mean sorption energy (mol$^2$/J$^2$) and $\varepsilon$ is Dubinin–Kaganer–Radushkevich isotherm constant which can be determined using the equation below:

$$\varepsilon = RT \ln \left(1 - \frac{1}{e^2}\right)$$  \hspace{0.5cm} (12)

R and T are gas constant and absolute temperature (K), respectively, while $C_0$ is the initial concentration. The sorption energy is determined using equation II below:

$$E = \frac{1}{\sqrt{2K_a}}$$  \hspace{0.5cm} (13)

**Fowler-Guggenheim Model**

The Fowler–Guggenheim isotherm model (Febrianto et al., 2009; Foo and Hameed, 2010) includes the study of the lateral interaction of the adsorbate in the absorbent (Sampranpiboon, Charnkeitong and Feng, 2014; Ojediran et al., 2019). The heat of adsorption varies linearly as the loading in the Fowler–Guggenheim isotherm model and is applicable only when the surface coverage is less than 0.6 (Ayawei, Ebelegi and Wankasi, 2017). The linearized form of the Fowler–Guggenheim isotherm model is stated as follows (Ojediran et al., 2019):

$$\ln\left(\frac{C_a(1-\theta)}{\theta}\right) = \ln K_{FG} + \frac{2n\theta}{RT}$$  \hspace{0.5cm} (14)

where $K_{FG}$ is the Fowler–Guggenheim equilibrium constant (Lmg$^{-1}$), and $\theta$ is the fractional.

**Jovanovic Isotherm**

The Jovanovic isotherm model shares a similar assumption as the Langmuir. In addition to the Langmuir model, however, it considers the possibility of mechanical contacts between the adsorbing molecules (Panahi, Vasheghani-Farahani and Shojosadati, 2008). Furthermore, unlike the Langmuir model which is valid for mobile adsorption, the Jovanovic model is valid for localized adsorption (Rudzinski and Wojciechowski, 1977). The general Jovanovic equation for the homogeneous surface is given by the expression (Jovanovic, 1969; Hines, Kuo and Dural, 1990):

$$Q_a(P, T, e) = A[1 - \exp(-bP)]$$  \hspace{0.5cm} (15)

where $A$ is the adsorption capacity at equilibrium and $b$ is the Jovanovic parameter defined by:

$$b = b_0\exp(q/RT)$$  \hspace{0.5cm} (16)

$b_0$ is the corresponding limiting value of $b$ as the temperature approaches infinity, $q$ is the isosteric heat of adsorption. The linearized form of the Jovanovic isotherm model is shown below (Ayawei, Ebelegi and Wankasi, 2017):

$$\ln Q_a = \ln Q_{max} - K_f C_a$$  \hspace{0.5cm} (17)

where $Q_a$ is the amount of adsorbate in the adsorbent at equilibrium (mg g$^{-1}$), $Q_{max}$ is the maximum uptake of adsorbate obtainable when $\ln Q_a$ is plotted against $C_a$. $K_f$ is the Jovanovic constant.

A modified form of the Jovanovic isotherm model known as the Jovanovic-Freundlich isotherm model has proven to better fit the optimization model for L-Lysine imprinted Polymer (Panahi, Vasheghani-Farahani and Shojosadati, 2008).

**Halsey Isotherm**

Halsey Isotherm (Halsey, 1948) is applied to a multilayer adsorption system with distance from the surface especially for metal ions (Kausar, Bhatti and MacKinnon, 2013; Liu and Wang, 2013; Singh and Das, 2013). This model is expressed as follows (Liu and Wang, 2013):

$$\ln Q_e = \frac{1}{n_H} \ln K_H - \frac{1}{n_H} \ln C_{qe}$$  \hspace{0.5cm} (18)

where $K_H$ and $n_H$ are the Halsey constants.

The Halsey Isotherm model fitted well for the analysis of Novel Silica-Based Hybrid adsorbents using lead (II) as presented by Liu and Wang (2013).
The model has also been applied in fitting the adsorption removal of copper from aqueous solution and industrial effluent using agricultural wastes (Singha and Das, 2013).

≡ Harkin-Jura Isotherm

Harkin-Jura isotherm model applies to solid-gas systems (Iyer and Kunju, 1992) and it is based on the assumption that there is a possibility of multilayer adsorption occurring on the surface of absorbents with heterogeneous pore distribution (Foo and Hameed, 2010; Ayawei, Ebelegi and Wankasi, 2017). This Harkin-Jura isotherm model is expressed as follows (Nworie et al., 2019):

\[ \frac{1}{Q_e} = \frac{B}{A} - \left( \frac{1}{A} \right) \log C_e \]  (19)

where A and B are Harkin-Jura constants.

The Harkin-Jura isotherm model has been used in the study of adsorption isotherms, kinetics and error analysis of the removal of methylene blue from aqueous solution using activated rice husk biochar (Nworie et al., 2019).

— Three-Parameter Isotherms

≡ Toth Isotherm

Another useful modification of the Langmuir isotherm model is the Toth isotherm model (Toth, Berger and Dekany, 1999). The Langmuir model was modified to minimize the error between the predicted value and the experimental data (Abbehahani and Abbehahani, 2014). The model is applied in the description of the high and low-end boundary of adsorbate concentration that is heterogeneous in nature (Ayawei, Ebelegi and Wankasi, 2017). The Toth isotherm model is expressed as shown below (Ayawei, Ebelegi and Wankasi, 2017).

\[ Q_e = \frac{K_L C_e}{1 + (K_L C_e)\beta} \]  (20)

where \(K_L\), \(Q_m\), and \(\beta\) are Toth isotherm constants (mg g\(^{-1}\)). The Toth isotherm may be rearranged to a linearized form as follows.

\[ \ln \left( \frac{Q_m}{Q_m - Q_e} \right) = n \ln K_L + n \ln C_e \]  (21)

≡ Redlich-Peterson Isotherm

The Redlich-Peterson isotherm model (Redlich and Peterson, 1959) is shown in equation 8 below (Ayawei, Ebelegi and Wankasi, 2017). While the linearized form is shown in equation 9 (Piccin, Dotto and Pinto, 2011). The model is used in a situation where there is a wide range of adsorbent concentrations in equilibrium. It can also be used in either homogeneous or heterogeneous systems (Piccin, Dotto and Pinto, 2011). The model combines the Langmuir and Freundlich isotherms with the numerator of Langmuir in either homogeneous or heterogeneous systems (Piccin, Dotto and Pinto, 2011). The model has also been applied in fitting the adsorption removal of copper from aqueous solution and industrial effluent using agricultural wastes (Singha and Das, 2013).

\[ Q_e = \frac{K_R C_e}{1 + B C_e\beta} \]  (22)

where \(K_R\) is the Redlich-Peterson isotherms constant (Lg\(^{-1}\)), B is the Redlich-Peterson constant (L mg\(^{-1}\)), \(\beta\) is an exponent which lies between 1 and 0 (Mane, Mall and Srivastava, 2007).

Due to the presence of three additional unknown, \(K_R\), B, and \(\beta\), plotting the left-hand side of Equation 9 against \(\ln C_e\) for obtaining the isotherm constants is not applicable. Therefore, a maximization procedure of the coefficient of correlation is usually adopted for solving the equation (Piccin, Dotto and Pinto, 2011).

≡ Koble-Carrigan Isotherm

Koble-Carrigan isotherm model combines the Langmuir and Freundlich isotherms with other modifications for representing equilibrium adsorption data (Han et al., 2005). The linear form of this module is represented by the following equation [56]:

\[ Q_e = \frac{A_k}{1 + B_k C_e \beta} \]  (24)

where \(A_k\), \(B_k\), and \(\beta\) are Koble-Carrigan’s parameters. The three Koble-Carrigan isotherm parameters are usually evaluated using Microsoft Excel or manually using trial and error on equation 25 (Han et al., 2005; Ayawei, Ebelegi and Wankasi, 2017).

\[ \frac{1}{Q_e} = \frac{1}{A_k} + \frac{1}{C_e \beta} + \frac{B_k}{A_k} \]  (25)

Koble-Carrigan isotherm has proven to best fit the data for the use of cereal chaff in the removal of lead ions from aqueous solutions as described by (Han et al., 2005).

≡ Radke-Prausnitz Isotherm

The Radke-Prausnitz isotherm model is used mostly in adsorption systems at low adsorbate concentration. The Radke-Prausnitz isotherm model is mathematically represented by the following expression (Khalid et al., 2015; Ayawei, Ebelegi and Wankasi, 2017):

\[ Q_e = \frac{Q_m K_R C_e}{1 + K_R C_e \beta} \]  (26)

Where \(Q_m\) and \(K_R\) are the Radke-Prausnitz equilibrium constant, and \(\beta\) is Radke-Prausnitz model exponent.

The Radke-Prausnitz isotherm model fitted well for the modelling of surface diffusion in the adsorption of aromatic compounds on activated carbon (Ocampo et al., 2013). Khalid et al. (2015) also used it in the modelling of copper biosorption with good performance and representation.

≡ Langmuir-Freundlich Isotherm

Langmuir-Freundlich isotherm is a versatile model that is capable of simulating both the Freundlich and Langmuir behaviour of adsorbates and adsorbents (Jeppu and Clement, 2012). The Langmuir-Freundlich isotherm has shown to best fit arsenate adsorption on metal oxides using different types of adsorption isotherms (Rau et al., 2003). At low and high adsorbate concentration, the Langmuir-Freundlich isotherm model becomes the Freundlich isotherm model and Langmuir isotherms model respectively (Ayawei, Ebelegi and Wankasi, 2017). Langmuir-Freundlich isotherm model can be mathematically represented by the expressed (Jeppu and Clement, 2012):

\[ Q_e = \frac{Q_m (K_L C_e)^\beta}{(K_L C_e)^\beta + 1} \]  (27)

where \(Q_m\) is the adsorption capacity of the system (mg of sorbate/g sorbent), \(K_L\) is the affinity constant for adsorption (L/mg), and \(n\) is the index of heterogeneity.
The Jossens isotherm model (Jossens et al., 1978; El Nemr, El-Sikaily and Khaled, 2010) takes into account the distribution of interaction energy between the adsorbate adsorbent on the site of adsorption (El Nemr, El-Sikaily and Khaled, 2010; Ayawei, Ebelegi and Wankasi, 2017). This Jossens model accounts for the heterogeneous nature of the adsorbent surface due to the interaction within the adsorbate molecules. Equation 28 below shows the mathematical representation of the model:

$$ Q_e = \frac{Q_m K_s C_e^{m_s}}{1 + K_s C_e^{m_s}} $$

where \( Q_m \) is the Sips maximum adsorption capacity (mg/g), \( K_s \) is the Sips constant (L/mg)\(^{m_s} \), and \( m_s \) is the Sips model exponent. The sip model is also sometimes called the Langmuir isotherm model.

— Four-Parameter Isotherms

≡ Baudu Isotherm Model

Baudu isotherm model was developed to minimize the discrepancies in solving the Langmuir constant and coefficient from the gradient and tangent of the isotherm over a wider range of concentration (El Nemr, El-Sikaily and Khaled, 2010; Ramadoss and Subramaniam, 2018). The model is a modification of the Langmuir model and it is given by the expression below (El Nemr, El-Sikaily and Khaled, 2010):

$$ Q_e = \frac{Q_m K C_e^{m}}{1 + K C_e^{m}} $$

where \( Q_m \) is the Baudu maximum adsorption capacity (mg/g), \( K \) is the Baudu constant, \( x \) and \( y \) are the Baudu parameters.

≡ Fritz–Schlunder model

The Fritz–Schlunder model empirically developed another four-parameter equation that follows the Langmuir-Freudlich to cater for the case of low liquid phase concentration of the adsorbate (Fritz and Schlunder, 1974). The mathematical expression of the model is shown below (Yaneva, Koumanova and Georgieva, 2013).

$$ Q_e = \frac{Q_m b_0 C_e^{x+y}}{1 + b_0 C_e^{x+y}} $$

where \( Q_m \) is the Fritz-Schlunder maximum adsorption capacity (mg/g), \( b_0 \) is the equilibrium constant, \( x \) and \( y \) are the Fritz-Schlunder parameters.

≡ Weber-Van Vliet Isotherms Model

The Weber-Van Vliet Isotherms Model (Weber Jr and Morris, 1963) has been used along with other isotherm models in fitting experimental data for the modelling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon (Hamaou and Naffrechoux, 2007). The model is an empirical relation with four parameters to which is proposed for describing equilibrium data and it is shown in the expression below (Hamaou and Naffrechoux, 2007).

$$ Q_e = P_1 \frac{Q_m C_e^{m_1}}{1 + K_2 C_e^{m_2}} \leq 1 $$

where \( Q_m \) is the Fritz-Schlunder maximum adsorption capacity (mg/g), \( K_1 \), \( K_2 \), \( m_1 \), and \( m_2 \) are the Fritz-Schlunder parameters.

CRITERIA FOR CHOOSING THE OPTIMUM ISOTHERM MODEL

The first and one of the most important conditions for selecting any isotherm model is that there should be a good fit between the experimental data and the isotherm function. Conventionally, the isotherm models are linearized and the parameters obtained from linear regression and the model with the coefficient of determination close to unity is the best fit (Markovic et al., 2014). Another common procedure for determining the best-fit model is by using the reduced chi-square statistics technique. The reduced chi-square statistics (< 1) is estimated by dividing the variance of the fit by the average variance of the experimental data. A larger value of the reduced chi-square implies a poor-fitting (Parker, 1995; Al-Ghouti and Da’ana, 2020b). The general procedures are to fit as many relevant models as possible to the experimental data and then selecting the one with the best fit using the methods highlighted above. Secondly, the selected isotherm model should be thermodynamically feasible and for this, Al-Ghouti and Da’ana (2020b) gave three conditions for an isotherm model to be thermodynamically feasible.

≡ The isotherm model should be linear when the concentration is zero
≡ There should be a finite capacity at maximum concentration and
≡ The gradient of the function should be positive for all concentrations.
RECENT ADVANCES IN THE SELECTION OF OPTIMUM ISOTHERM MODELS

The conventional method of determining the best fit isotherm model involves linearizing the model and then checking for fit using linear regression. The least-squares method has been frequently used for finding the parameters of the models. However, linearization of the isotherm model violates the least square assumptions and also capable of altering their error structure (Ratkowsky and Giles, 1990). Given the advancement in computer abilities, the nonlinear regression approach has gained popularity in recent time. In this approach, the parameters of the model are obtained through minimization of the quadratic error between experimental data and model outputs of the model (Marković et al., 2014). Coefficient of determination, some of the errors squared, sum of absolute errors, Marquardt’s per cent standard deviation, the average relative error and hybrid error function are some of the techniques used in recent times to determine the goodness of fit (Ho, Porter and McKay, 2002; Allen et al., 2003; Ho, 2004; Marković et al., 2014).

CONCLUSION

In this paper, the general concept of sorption, adsorption isotherms has been reviewed and presented. The various types, application and expression of most isotherm models have also been outlined. From the studies, it is clear that several studies have been carried out by researchers, giving rise to several isotherms models applicable in different specific areas. In selecting an appropriate isotherm model for a specific application, it is necessary to ensure that the model fits well and also thermodynamically feasible. Conventional method modelling isotherm systems involves using a linearized form of an isotherm model of interest to fit experimental data using linear regression techniques. To minimize error in fitting the regression models, nonlinear regression has been employed in recent times. Performance parameters used in most cases include coefficient of determination, sum of errors squared, and sum of absolute errors, Marquardt’s per cent standard deviation, the average relative error and hybrid error function.

References


