[1.]Precious EHIOMOGUE, [2.]Israel I. AHUCHAOGU, [1.]Isiguzo Edwin AHANEKU

REVIEW OF ADSORPTION ISOTHERMS MODELS

[1.]Department of Agricultural and Bioresources Engineering, Michael Okpara University of Agriculture, Umudike, NIGERIA
[2.]Department of Agricultural and Food Engineering, Faculty of Engineering, University of Uyo, NIGERIA

Abstract: Adsorption phenomenon is a popular separation process in environmental remediation and wastewater treatment due to its simplicity, low cost, efficiency, and environmentally friendliness. The amount of material absorbed by a substrate is often expressed as a function of the equilibrium concentration at a constant temperature in a process known as Adsorption Isotherm. The study of adsorption isotherms is essential to gain insight into the design and operation of adsorption systems. In this review paper, the general knowledge and application of the isotherm model to date have been highlighted for an insight into the concept and application of adsorption isotherm models. The classification of the isotherm model has also been highlighted. In addition, various types of isotherm models in terms of the number of parameters have been extensively discussed. The criteria for selecting the appropriate model as well as the modern trend in the modelling approach have also been discussed. This review will enable researcher make informed choices in selecting adsorption isotherm models.
Keywords: Adsorption, Isotherms, sorption, Chemisorption, Physiosorption

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'ana, 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-Khaiary, 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 ISOTHERM MODEL

In environmental and bioremediation, molecules are absolved 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

is often expressed as a function of the equilibrium concentration after adsorption at a constant temperature. The process of representing this function is known as Adsorption Isotherms (Tadros, 2013). In other words, adsorption isotherm models 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 Quinton, 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).
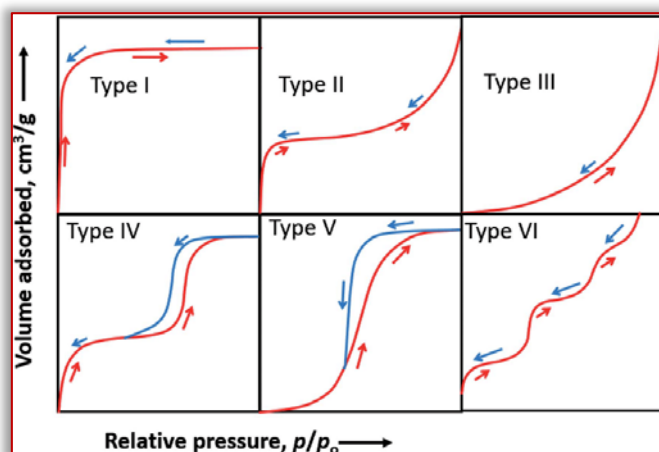

Figure 1: The IUPAC Classification of Adsorption Isotherms (Sing, 1982)

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, Ebelegi 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.

$$Q_e = K_H C_e \qquad (1)$$

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 absorbates 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.

$$Q_e = K_F C_e^{1/n} \qquad (2)$$
$$\ln Q_e = \ln K_F + \frac{1}{n}\ln C_e \qquad (3)$$

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 periphylic 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 when plotted in terms of relative pressure and is completely described by the Hill-de Boer equation (Tornquist et al., 1978). The linear form of the Hill Deboer Model is as shown in equation 4 (Kumara et al., 2010).

$$\ln\left[\frac{C_e(1-\theta)}{\theta}\right] - \frac{\theta}{1-\theta} = \ln K_1 - \frac{K_2\theta}{RT} \qquad (4)$$

where K_1, K_2 are the Hill-Deboer constant (Lmg⁻¹) and the energetic constant of the interaction between adsorbed molecules, respectively. A positive K_2 mean 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. θ is the fractional coverage, R is the universal gas constant (KJmol⁻¹K⁻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 θ 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

$$Q_e = \frac{Q_0 K_L C_e \theta}{(1+K_L C_e)} \qquad (5)$$

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

$$\frac{C_e}{Q_e} = \frac{1}{(K_L Q_0)} + \frac{C_e}{K_L} \qquad (6)$$

where Q_e 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).

$$R_l = \frac{1}{(1+K_L C_0)} \qquad (6)$$

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).

$$Q_e = \frac{RT}{b}\ln K_T + \left(\frac{RT}{b}\right)\ln C_e \qquad (7)$$

where K_T is the maximum binding energy or the Temkin isotherm equilibrium-biding constant (Lmol⁻¹), b is the Tempkin 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

(Ayawei, Ebelegi and Wankasi, 2017). The linearized Kiselev isotherm model is shown below (Ojediran et al., 2019)

$$\ln\left[\frac{1}{C_e(1-\theta)}\right] = \frac{K_1}{\theta} + K_1 K_n \quad (8)$$

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:

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

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). $C_0 = (1 - C_e/C_0)$ is the degree of membrane surface coverage, C_e 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):

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

where ΔG^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 Mylsamy, 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):

$$\ln Q_e = \ln Q_m - K\varepsilon^2 \quad (11)$$

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

$$\varepsilon = RT\ln\left(1 - \frac{1}{C_0}\right) \quad (12)$$

R and T are gas constant and absolute temperature (K), respectively, while C0 is the initial concentration. The sorption energy is determined using equation 11 below:

$$E = \left(\frac{1}{\sqrt{2K_a}}\right) \quad (13)$$

≡ **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, Charnkeitkong 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).

$$\ln\left[\frac{C_e(1-\theta)}{\theta}\right] = \ln K_{FG} + \frac{2\omega\theta}{RT} \quad (14)$$

where K_{FG} is the Fowler-Guggenheim equilibrium constant (Lmg^{-1}), and θ 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 (Rudzinkski and Wojciechowski, 1977). The general Jovanovic equation for the homogeneous surface is given by the expression (Jovanovic, 1969; Hines, Kuo and Dural, 1990):

$$Q_e(P, T, e) = A[1 - \exp(-bP)] \quad (15)$$

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

$$b = b_0\exp(q/RT) \quad (16)$$

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):

$$\ln Q_e = \ln Q_{max} - K_J C_e \quad (17)$$

where Q_e is the amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}), Q_{max} is the maximum uptake of adsorbate obtainable when $\ln Q_e$ is plotted against C_e, K_J 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; Singha and Das, 2013). This model is expressed as follows (Liu and Wang, 2013):

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

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):

$$\frac{1}{Q_e{}^2} = \frac{B}{A} - \left(\frac{1}{A}\right) \log C_e \qquad (19)$$

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 (Tóth, Berger and Dékány, 1999). The Langmuir model was modified to minimize the error between the predicted value and the experimental data (Behbahani and Behbahani, 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).

$$\frac{Q_e}{Q_m} = \frac{K_L C_e}{[1+(K_L C_e)^n]^{1/n}} \qquad (20)$$

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

$$\ln\frac{Q_e{}^n}{Q_m{}^n - Q_e{}^n} = n \ln K_L + n \ln C_e \qquad (21)$$

≡ **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 for 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 and is capable of approaching Henry's region when the dilution is infinite (Davoudinejad and Ghorbanian, 2013; Ayawei, Ebelegi and Wankasi, 2017)

$$Q_e = \frac{K_R C_e}{1+BC_e{}^\beta} \qquad (22)$$

$$\ln\left(K_R \frac{C_e}{Q_e} - 1\right) = \ln(B) + \beta \ln(C_e) \qquad (23)$$

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

Due to the presence of three additional unknown, KR, B, and β, plotting the left-hand side of Equation 9 against ln Ce 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]:

$$Q_e = \frac{A_k{}^p}{1+B_k C_e{}^p} \qquad (24)$$

where A_k, B_k, and p 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).

$$\frac{1}{Q_e} = \frac{1}{A_k} * \frac{1}{C_e{}^p} + \frac{B_k}{A_k} \qquad (25)$$

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-Prausniiz 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):

$$Q_e = \frac{Q_M K_R C_e}{1+K_R C_e{}^p} \qquad (26)$$

Where Q_M and K_R are the Radke-Prausnitz equilibrium constant, and p 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):

$$Q_e = \frac{Q_M (K_{LF} C_e)^n}{(K_{LF} C_e)^n + 1} \qquad (27)$$

where Q_M is the adsorption capacity of the system (mg of sorbate/g sorbent), K_{LF} is the affinity constant for adsorption (L/mg), and n is the index of heterogeneity

≡ **Jossens Isotherm**

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 Jossen 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:

$$C_e = \frac{Q_e}{H}\exp(FQ_e{}^p) \qquad (28)$$

$$\ln\left(\frac{C_e}{Q_e}\right) = -\ln(H) + FQ_e{}^p \qquad (29)$$

The linearized form of the Jossen equation is shown in equation 29, where H, F and p are the Jossens isotherms constant.

≡ **Sips Isotherm**

The sips isotherm model was developed to recognize and solve the problem of continuous increase in the adsorbed amount when the concentration increases which is usually experienced in the Freundlich isotherms model (Sips, 1948). Sips Isotherm model is mathematically represented by the following equation (El Nemr, El-Sikaily and Khaled, 2010):

$$Q_e = \frac{Q_{ms}K_S C_e{}^{ms}}{1+K_S C_e{}^{ms}} \qquad (30)$$

where Q_{ms} is the Sips maximum adsorption capacity (mg/g), K_S is the Sips constant (L/mg)^{ms}, and ms is the Sips model exponent. The sip model is also sometimes called the Langmuir

— **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).

$$Q_e = \frac{Q_{m0}b_0 C_e{}^{(1+x+y)}}{1+b_0 C_e{}^{(1+x)}} \qquad (31)$$

where Q_{m0} is the Baudu maximum adsorption capacity (mg/g), b_0 is the equilibrium 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-Freundlich to cater for the case of low liquid phase concentration of the adsorbate (Fritz and Schluender, 1974). The mathematical expression of the model is shown below (Yaneva, Koumanova and Georgieva, 2013).

$$Q_e = \frac{A \cdot C_e{}^{\alpha}}{1+B \cdot C_e{}^{\beta}} \qquad (32)$$

A and B are the Fritz-Schlunder maximum equilibrium constants, α and β are the Fritz-Schlunder equilibrium exponents.

≡ **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 (Hamdaoui 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 (Hamdaoui and Naffrechoux, 2007).

$$C_e = P_1 Q_e{}^{(P_2 (Q_e)^{P_3}+P_4)} \qquad (33)$$

P_1, P_2, P_3 and P_4 are the Weber-Van Vliet isotherms parameters.

— **Five-Parameter Isotherms**

≡ **Fritz–Schlunder isotherm model**

Fritz and Schluender (1974) proposed an additional five parameter empirical model known as the Fritz–Schlunder isotherm model, which can be used for a broad field of equilibrium data. The expression of the model is shown below (Hamdaoui and Naffrechoux, 2007).

$$Q_e = \frac{Q_{mFS}K_1 C_e{}^{m_1}}{1+K_2 C_e{}^{m_2}} \qquad (34)$$

$$(m_1 \text{ and } m_2 \leq 1)$$

where Q_{mFS} 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 (Marković 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 feasible thermodynamically 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 be 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

[1] Aharoni, C. and Tompkins, F. C. (1970) 'Kinetics of adsorption and desorption and the Elovich equation, in Advances in catalysis. Elsevier, pp. 1–49.

[2] Al-Ghouti, M. A. and Da'ana, D. A. (2020a) 'Guidelines for the use and interpretation of adsorption isotherm models: A review, Journal of Hazardous Materials, 393, p. 122383

[3] Al-Ghouti, M. A. and Da'ana, D. A. (2020b) 'Guidelines for the use and interpretation of adsorption isotherm models: A review', Journal of hazardous materials, 393, p. 122383.

[4] Allen, S. J. et al. (2003) 'Comparison of optimised isotherm models for basic dye adsorption by kudzu', Bioresource technology, 88(2), pp. 143–152.

[5] Ayawei, N., Ebelegi, A. N. and Wankasi, D. (2017) 'Modelling and Interpretation of Adsorption Isotherms', Journal of Chemistry, 2017, p. e3039817

[6] Behbahani, T. J. and Behbahani, Z. J. (2014) 'A New study on Asphaltene Adsorption in Porous Media.', Petroleum & Coal, 56(5).

[7] Buttersack, C. (2019) 'Modeling of type IV and V sigmoidal adsorption isotherms', Physical Chemistry Chemical Physics, 21.

[8] Carrott, P. J. M. (1992) 'Adsorption of water vapour by non-porous carbons', Carbon, 30(2), pp. 201–205

[9] Celebi, O. et al. (2007) 'A radiotracer study of the adsorption behaviour of aqueous Ba^{2+} ions on nanoparticles of zero-valent iron, Journal of Hazardous Materials, 148(3), pp. 761–767.

[10] Davoudinejad, M. and Ghorbanian, S. A. (2013) 'Modeling of adsorption isotherm of benzoic compounds onto GAC and introducing three new isotherm models using the new concept of Adsorption Effective Surface (AES)', Scientific Research and Essays, 8(46), pp. 2263–2275.

[11] Deboer, J. H. (1953) The dynamical character of adsorption. LWW.

[12] Deocaris, C. and Osio, L. (2020) 'Fitting Henry's Adsorption Isotherm model in R using PUPAIM package'.

[13] El Nemr, A., El-Sikaily, A. and Khaled, A. (2010) 'Modeling of adsorption isotherms of Methylene Blue onto rice husk activated carbon', Egyptian Journal of Aquatic Research, 36, pp. 403–425.

[14] El-Khaiary, M. I. (2008) 'Least-squares regression of adsorption equilibrium data: comparing the options', Journal of Hazardous Materials, 158(1), pp. 73–87.

[15] Erbil, H. Y. (2006) Surface Chemistry of Solid and Liquid Interfaces. Wiley

[16] Fabrizius-Homan, D. J. and Cooper, S. L. (1992) 'A comparison of the adsorption of three adhesive proteins to biomaterial surfaces, Journal of Biomaterials Science, Polymer Edition, 3(1), pp. 27–47.

[17] Febrianto, J. et al. (2009) 'Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: a summary of recent studies, Journal of hazardous materials, 162(2–3), pp. 616–645.

[18] Foo, K. Y. and Hameed, B. H. (2010) 'Insights into the modelling of adsorption isotherm systems, Chemical Engineering Journal, 156(1), pp. 2–10

[19] Fost, S. D. and Aly, M. O. (1981) Adsorption Processes for Water Treatment. Betterworth Publications, Stoneharm, Massachusetts, Mass, USA.

[20] Fritz, W. and Schluender, E.-U. (1974) 'Simultaneous adsorption equilibria of organic solutes in dilute aqueous solutions on activated carbon', Chemical Engineering Science, 29(5), pp. 1279–1282.

[21] Garbuio, F. J., Howard, J. L. and dos Santos, L. M. (2012) 'Impact of Human Activities on Soil Contamination', Applied and Environmental Soil Science, 2012, p. e619548

[22] Gast, A. P. and Adamson, A. W. (1997) Physical Chemistry of Surfaces, 6th Edition | Wiley, Wiley.com. Available at: https://www.wiley.com/en-us/Physical+Chemistry+of+Surfaces%2C+6th+Edition-p-9780471148739 (Accessed: 28 May 2021).

[23] Gautam, R. K. et al. (2014) 'Biomass-derived biosorbents for metal ions sequestration: Adsorbent modification and activation methods and adsorbent regeneration, Journal of environmental chemical engineering, 2(1), pp. 239–259.

[24] Gautam, R. K. and Chattopadhyaya, M. C. (2016) 'Chapter 5 - Kinetics and Equilibrium Isotherm Modeling: Graphene-Based Nanomaterials for the Removal of Heavy Metals From Water', in Gautam, R. K. and Chattopadhyaya, M. C. (eds) Nanomaterials for Wastewater Remediation. Boston: Butterworth-Heinemann, pp. 79–109

[25] Halsey, G. (1948) 'Physical Adsorption on Non-Uniform Surfaces', The Journal of Chemical Physics, 16(10), pp. 931–937

[26] Hamdaoui, O. and Naffrechoux, E. (2007) 'Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon: Part I. Two-parameter models and equations allowing determination of thermodynamic parameters', Journal of hazardous materials, 147(1–2), pp. 381–394.

[27] Han, R. et al. (2005) 'Equilibrium biosorption isotherm for lead ion on chaff', Journal of Hazardous Materials, 125(1–3), pp. 266–271. DOI: 10.1016/j.jhazmat.2005.05.031.

[28] Harms, H. (2011) '6.09 - Bioavailability and Bioaccessibility as Key Factors in Bioremediation', in Moo-Young, M. (ed.) Comprehensive Biotechnology (Second Edition). Burlington: Academic Press, pp. 83–94

[29] Hauchhum, S. and Mahanta, P. (2014) 'Carbon dioxide adsorption on zeolites and activated carbon by pressure swing adsorption in a fixed bed', International Journal of Energy and Environmental Engineering, 5, pp. 349–356

[30] Hill, T. L. (1946) 'Statistical mechanics of multimolecular adsorption II. Localized and mobile adsorption and absorption', The Journal of Chemical Physics, 14(7), pp. 441–453.

[31] Hines, A. L., Kuo, S.-L. and Dural, N. H. (1990) 'A New Analytical Isotherm Equation for Adsorption on Heterogeneous Adsorbents', Separation Science and Technology, 25(7–8), pp. 869–888

[32] Ho, Y. S., Porter, J. F. and McKay, G. (2002) 'Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems', Water, air, and soil pollution, 141(1), pp. 1–33.

[33] Ho, Y.-S. (2004) 'Selection of optimum sorption isotherm', Carbon, 42(10), pp. 2115–2116

[34] Inglezakis, V. J., Poulopoulos, S. G. and Kazemian, H. (2018) 'Insights into the S-shaped sorption isotherms and their dimensionless forms', Microporous and Mesoporous Materials, 272, pp. 166–176.

[35] Iyer, K. P. D. and Kunju, A. S. (1992) 'Extension of Harkins—Jura adsorption isotherm to solute adsorption', Colloids and Surfaces, 63(3), pp. 235–240

[36] Jeppu, G. and Clement, P. (2012) 'A modified Langmuir-Freundlich isotherm model for simulating pH-dependent adsorption effects', Journal of contaminant hydrology, 129–130, pp. 46–53

[37] Jiang, H. et al. (2019) 'Imaging covalent bond formation by H atom scattering from graphene', Science, 364(6438), pp. 379–382.

[38] Jossens, L. et al. (1978) 'Thermodynamics of multi-solute adsorption from dilute aqueous solutions, Chemical Engineering Science, 33(8), pp. 1097–1106.

[39] Jovanovic, D. S. (1969) 'Physical adsorption of gases. I. Isotherms for monolayer and multilayer adsorption', Kolloid-Zeitschrift and Zeitschrift Fur Polymere, 235(1), pp. 1203-+.

[40] Kadhim, Z. N. (2016) 'Using of Isolated Hydroxyapatite from Sheep Bones to Remove Lead (II) from Aqueous Solution and Studying the Thermodynamics and Adsorption Isotherm', 4, pp. 149–160.

[41] Karagöz, S. et al. (2008) 'Activated carbons from waste biomass by sulfuric acid activation and their use on methylene blue adsorption, Bioresource technology, 99(14), pp. 6214–6222.

[42] Kausar, A., Bhatti, H. N. and MacKinnon, G. (2013) 'Equilibrium, kinetic and thermodynamic studies on the removal of U (VI) by low-cost agricultural waste', Colloids and Surfaces B: Biointerfaces, 111, pp. 124–133.

[43] Keyes, B. R. and Silcox, G. D. (1994) 'Fundamental study of the thermal desorption of toluene from montmorillonite clay particles', Environmental science & technology, 28(5), pp. 840–849.

[44] Khalid, A. et al. (2015) 'Kinetic & Equilibrium Modelling of Copper Biosorption', Journal of Faculty of Engineering and Technology, 22(1), pp. 131–145.

[45] Kumara, P. S. et al. (2010) 'Adsorption behaviour of Nickel (II) onto cashew nut shell', Equilibrium, Thermodynamics, Kinetics, Mechanism and Process design. Chemical Engineering Journal, 1169, pp. 122–131.

[46] Langmuir, I. (1918) 'The adsorption of gases on plane surfaces of glass, mica and platinum.', Journal of the American Chemical Society, 40(9), pp. 1361–1403.

[47] Liu, J. and Wang, X. (2013) 'Novel Silica-Based Hybrid Adsorbents: Lead(II) Adsorption Isotherms', TheScientificWorldJournal, 2013, p. 897159

[48] Mane, V. S., Mall, I. D. and Srivastava, V. C. (2007) 'Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green dye from aqueous solution by rice husk ash, Journal of environmental management, 84(4), pp. 390–400.

[49] Marković, D. D. et al. (2014) 'A New Approach in Regression Analysis for Modeling Adsorption Isotherms', The Scientific World Journal, 2014, p. e930879

[50] Miedaner, M. M., Weerasooriya, R. and Tobschall, H. J. (2006) 'Chapter 17 - 1-pK modeling strategies for the adsorption of some trace elements onto gibbsite', in Lützenkirchen, J. (ed.) Interface Science and Technology. Elsevier (Surface Complexation Modelling), pp. 469–490

[51] Murai, S. et al. (1998) 'Removal of phthalic acid esters from aqueous solution by inclusion and adsorption on β-cyclodextrin', Environmental science & technology, 32(6), pp. 782–787.

[52] Nechifor, G. et al. (2015) 'Comparative study of Temkin and Flory-huggins isotherms for adsorption of phosphate anion on membranes', Sci Bull B [Internet], 77(2), pp. 63–72.

[53] Nworie, F. S. et al. (2019) 'Removal of Methylene Blue From Aqueous Solution Using Activated Rice Husk Biochar: Adsorption Isotherms, Kinetics and Error Analysis', Journal of the Chilean Chemical Society, 64(1), pp. 4365–4376

[54] Ocampo, R. et al. (2013) 'Role of pore volume and surface diffusion in the adsorption of aromatic compounds on activated carbon', Adsorption, 19.

[55] Ojediran, J. et al. (2019) 'Modeling of Biosorption of Pb(Ii) and Zn(Ii) Ions Onto Pamrh: Langmuir, Freundlich, Temkin, Dubinin-Raduskevich, Jovanovic, Flory-Huggins, Fowler-Guggenheim And Kiselev Comparative Isotherm Studies'.

[56] Olsen, S. R. and Watanabe, F. S. (1957) 'A method to determine a phosphorus adsorption maximum of soils as measured by the Langmuir isotherm', Soil Science Society of America Journal, 21(2), pp. 144–149.

[57] Panahi, R., Vasheghani-Farahani, E. and Shojosadati, S. A. (2008) 'Determination of adsorption isotherm for l-lysine imprinted polymer', Iranian Journal of Chemical Engineering, 5(4), pp. 49–55.

[58] Parker, G. R. (1995) 'Optimum isotherm equation and thermodynamic interpretation for aqueous 1, 1, 2-trichloroethene adsorption isotherms on three adsorbents', Adsorption, 1(2), pp. 113–132.

[59] Petrovic, M., Radjenovic, J. and Barcelo, D. (2011) 'Advanced oxidation processes (AOPs) applied for wastewater and drinking water treatment. Elimination of pharmaceuticals', The holistic approach to Environment, 1(2), pp. 63–74.

[60] Piccin, J. S., Dotto, G. L. and Pinto, L. A. A. (2011) 'Adsorption isotherms and thermochemical data of FD&C Red n° 40 bindings by Chitosan', Brazilian Journal of Chemical Engineering, 28(2), pp. 295–304

[61] Pignatello, J. J. and Xing, B. (1995) 'Mechanisms of slow sorption of organic chemicals to natural particles', Environmental science & technology, 30(1), pp. 1–11.

[62] Prasad, R. K. and Srivastava, S. N. (2009) 'Sorption of distillery spent wash onto fly ash: kinetics and mass transfer studies', Chemical Engineering Journal, 146(1), pp. 90–97.

[63] Qi, Y. et al. (2017) 'Sorption of Cu by humic acid from the decomposition of rice straw in the absence and presence of clay minerals, Journal of Environmental Management, 200, pp. 304–311

[64] Ramadoss, R. and Subramaniam, D. (2018) 'Adsorption of chromium using blue-green algae-Modeling and application of various isotherms', International Journal of Chemical Technology, 10, pp. 1–22.

[65] Ratkowsky, D. A. and Giles, D. E. (1990) Handbook of nonlinear regression models. M. Dekker New York.

[66] Rau, I. et al. (2003) 'Modelling the arsenic (V) and (III) adsorption, Czechoslovak Journal of Physics, 53(1), pp. A549–A556.

[67] Redlich, O. and Peterson, D. L. (1959) 'A useful adsorption isotherm', Journal of physical chemistry, 63(6), pp. 1024–1024.

[68] Rudzinkski, W. and Wojciechowski, B. W. (1977) 'On the Jovanovic model of adsorption', Colloid and Polymer Science, 255(11), pp. 1086–1097

[69] Sampranpiboon, P., Charnkeitkong, P. and Feng, X. (2014) 'Equilibrium isotherm models for the adsorption of zinc (II) ion from aqueous solution on pulp waste', WSEAS Transactions on Environment and Development, 10, pp. 35–47.

[70] Sims, R. A., Harmer, S. L. and Quinton, J. S. (2019) 'The Role of Physisorption and Chemisorption in the Oscillatory Adsorption of Organosilanes on Aluminium Oxide', Polymers, 11(3), p. 410

[71] Sing, K. S. W. (1982) 'Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Provisional)', Pure and applied chemistry, 54(11), pp. 2201–2218.

[72] Singh, A. K. (2016) 'Chapter 8 - Nanoparticle Ecotoxicology', in Singh, A. K. (ed.) Engineered Nanoparticles. Boston: Academic Press, pp. 343–450

[73] Singha, B. and Das, S. K. (2013) 'Adsorptive removal of Cu (II) from aqueous solution and industrial effluent using natural/agricultural wastes', Colloids and Surfaces B: Biointerfaces, 107, pp. 97–106.

[74] Sips, R. (1948) 'On the structure of a catalyst surface', The journal of chemical physics, 16(5), pp. 490–495.

[75] Song, C. et al. (2014) 'Adsorption studies of coconut shell carbons prepared by KOH activation for removal of lead (II) from aqueous solutions, Sustainability, 6(1), pp. 86–98.

[76] Sultan, M., Miyazaki, T. and Koyama, S. (2018) 'Optimization of adsorption isotherm types for desiccant air-conditioning applications', Renewable Energy, 121, pp. 441–450

[77] Tadros, T. (2013) 'Adsorption Isotherm', Encyclopedia of Colloid and Interface Science. Edited by T. Tadros. Berlin, Heidelberg: Springer Berlin Heidelberg

[78] Theivarasu, C. and Mylsamy, S. (2011) 'Removal of malachite green from aqueous solution by activated carbon developed from cocoa (Theobroma Cacao) shell-A kinetic and equilibrium studies', E-Journal of Chemistry, 8(S1), pp. S363–S371.

[79] Tornquist, A. et al. (1978) 'The Hill-de Boer equation in the adsorption of water on quartz', Journal of Colloid and Interface Science, 66(3), pp. 415–420

[80] Tóth, J., Berger, F. and Dékány, I. (1999) 'Separation of the first adsorbed layer from others and calculation of the BET compatible surface area from Type II isotherms', Journal of colloid and interface science, 212(2), pp. 411–418.

[81] Umpleby, R. et al. (2001) 'Application of the Freundlich adsorption isotherm in the characterization of molecularly imprinted polymers', Analytica Chimica Acta, 435, pp. 35–42

[82] Vijayaraghavan, K. et al. (2006) 'Biosorption of nickel (II) ions onto Sargassum wightii: application of two-parameter and three-parameter isotherm models', Journal of hazardous materials, 133(1–3), pp. 304–308.

[83] Wang, G. et al. (2020) 'Gaseous adsorption of hexamethyldisiloxane on carbons: Isotherms, isosteric heats and kinetics', Chemosphere, 247, p. 125862.

[84] Wang, J. and Guo, X. (2020) 'Adsorption isotherm models: Classification, physical meaning, application and solving method', Chemosphere, 258, p. 127279

[85] Wang, Z. et al. (2016) 'Analyzing the adaption of different adsorption models for describing the shale gas adsorption law', Chemical Engineering & Technology, 39(10), pp. 1921–1932.

[86] Weber Jr, W. J. and Morris, J. C. (1963) 'Kinetics of adsorption on carbon from solution', Journal of the sanitary engineering division, 89(2), pp. 31–59.

[87] Wikipedia (2021) 'Henry adsorption constant', Wikipedia. Available at: https://en.wikipedia.org/w/index.php?title=Henry_adsorp

tion_constant&oldid=998548677 (Accessed: 28 May 2021).

[88] Wu, Y. (2017) 'Chapter 16 - The Removal of Methyl Orange by Periphytic Biofilms: Equilibrium and Kinetic Modeling', in Wu, Y. (ed.) Periphyton. Boston: Elsevier, pp. 367–387

[89] Yan, X.-F. et al. (2017) 'An adsorption isotherm model for adsorption performance of silver-loaded activated carbon', Thermal Science, 21(4), pp. 1645–1649.

[90] Yaneva, Z., Koumanova, B. and Georgieva, N. (2013) 'Linear and Nonlinear Regression Methods for Equilibrium Modelling of p-Nitrophenol Biosorption by Rhizopus Oryzae - Comparison of Error Analysis Criteria', E-Journal of Chemistry, 2013

[91] Zhou, L. et al. (2002) 'Adsorption of Nitrogen on Silica Gel Over a Large Range of Temperatures', Adsorption, 8, pp. 79–87.