

Monolayer and multilayer adsorption isotherm models for sorption from aqueous media

Reyhaneh Saadi^{*,‡}, Zahra Saadi^{*,‡}, Reza Fazaeli^{*,†}, and Narges Elmi Fard^{**}

^{*}Department of Chemical Engineering, Faculty of Engineering, South Tehran Branch, Islamic Azad University, Tehran, Iran

^{**}Department of Chemistry, Faculty of Science, East Tehran Branch, Islamic Azad University, Tehran, Iran

(Received 21 January 2015 • accepted 10 March 2015)

Abstract—Industrial wastewater polluted with various contaminants, including heavy metals, dyes, etc., endangers human health and the environment. Various separation techniques have been developed for the removal of pollutants from aqueous solutions. Adsorption process has drawn considerable attention due to its simplicity of design, high removal efficiency, even at dilute concentration, and economical aspect. We reviewed the most common two, three, four, and five parameter adsorption isotherm models corresponding to monolayer and multilayer adsorption on the basis of parameters that can be used for exploring novel adsorbents. Thermodynamic assumptions of the models give information about the surface properties, capacity of the adsorbent and adsorption mechanism. Seven error functions were investigated to evaluate the fitness quality of isotherm models with the experimental equilibrium data.

Keywords: Adsorption, Isotherm, Monolayer, Multilayer, Error

INTRODUCTION

The rapid progress of different industries and technologies has resulted in a huge amount of wastewater being produced from industrial processes that needs to be removed before discharge into the environment [1]. Inorganic and organic pollutants dissolved in aqueous solutions are considered to be hazardous because of their toxicity, even at low concentrations [2]. The global increase of polluted waters seriously threatens human health and the environment. Various regulatory agencies have determined maximum allowable concentration of the contaminants in drinking water to overcome the problem [3].

Various conventional methods for the removal of wastewater pollutants have been developed containing ion exchange, reverse osmosis, membrane, filtration, solvent extraction, floatation, electrodialysis, electrochemical operations, biological treatment, coagulation, oxidation, and chemical precipitation. Among these, adsorption is considered to be relatively superior because it is versatile and widely used, very efficient because of its high removal capacity, inexpensive, simple for design, and applicable at very low concentrations [4-13]. Different materials such as activated carbon, silica, titanium dioxide, alumina, and various nanomaterials such as nanometal oxides, carbon nanotubes and nanozeolite composites are applied as adsorbent for removal of contaminants from aqueous solutions [14-18]. These adsorbents have large porous surface area, good adsorption capacity, high thermal stability, good mechanical strength, fast kinetics and versatility for removal of a broad type

of inorganic and organic pollutants dissolved in aqueous media [19-21]. However, the materials have restrictions in the case of their applications on a large industrial scale because of their high cost and difficulties related to regeneration [22]. Cost-effective, natural and renewable materials are needed such as chitosan, tea leaves, lignite, waste activated sludge, agricultural waste and biomass [23-26]. The adsorption isotherm is a fundamental source of information on the adsorption process. The analytical forms of adsorption isotherm equations depend on the type of the surface phase that can be considered as a monolayer or multilayer, and as localized, mobile. These models are complex due to structural and energetic heterogeneity of the adsorbent surfaces, which is characteristic of a great number of adsorbents used at industrial or experimental scale [27-29]. Most adsorption isotherms are applied in both gas-solid and liquid-solid equilibrium systems. Several isotherm equations for adsorption at the solid-liquid interface, especially equations related to adsorption of diluted solutions, are derived from the theoretical description of single gases and their mixtures on solid surfaces. Isotherm equations that deal with physical adsorption of gases give the most important properties of adsorbents, including pore volume, pore size or energy distribution, specific surface area and capacities of adsorbents [30]. The specific curves of isotherms can be interpreted to obtain information associated with interactions between adsorbent materials and pollutants, optimization of the adsorption mechanism, and effective design of the adsorption systems [31,32].

Hossain et al. [33] studied the removal of copper from water and wastewater using palm oil fruit shells as a biosorbent. Nonlinear regression analyses for isotherm models revealed that three-parameter isotherms (Sips, Koble-Corrigan, Radke-Prausnitz, Redlich-Peterson, Toth, Hill) had a better fit to the experimental data than two-parameter isotherms (Langmuir, Temkin, Jovanovich, Flory - Huggins).

Subramanyam and Das [34] investigated the adsorption of phe-

[†]To whom correspondence should be addressed.

E-mail: r_fazaeli@azad.ac.ir

[‡]The first and second authors have identical collaboration in this review paper.

Copyright by The Korean Institute of Chemical Engineers.

nol onto natural soil. The experimental data were analyzed using three equilibrium isotherm correlations, namely, Langmuir, Freundlich and Redlich-Peterson equations, and results showed that the Langmuir and Redlich-Peterson isotherms provided better fit than the Freundlich isotherm model. In addition, error functions such as sum square error (ERRSQ), average relative error (ARE), hybrid fractional error (HYBRID), Marquardt's percent standard deviation error (MPSD), and sum of the absolute error (EABS) were discussed to evaluate the fitness quality of isotherm models with the experimental equilibrium data.

More previous research studies regarding the studies of adsorption isotherm models for various adsorbate-adsorbent systems are presented in Table 1.

The objective of this review was description of the distinct properties and application of monolayer and multilayer adsorption isotherm systems. The optimization procedure of nonlinear isotherm requires the selection of an error function in order to evaluate the agreement of the isotherm with the experimental equilibrium data. The choice of error function can affect the parameters derived. So that, in this study, evaluation of accuracy of the parameter values

was investigated based on seven non-linear error functions.

ADSORPTION ISOTHERM

Different adsorption isotherm models can be derived by assuming a thermodynamic equilibrium relationship between the quantity of the adsorbed molecule by a unit mass of adsorbent and the amount of adsorbate remaining in the bulk fluid phase at a constant temperature and pH [30]. It gives information about the distribution of adsorbable solute between the liquid and solid phases at different equilibrium concentrations. The parameters obtained from adsorption isotherm models are specific for each system [35]. The two, three, four and five parameter equilibrium adsorption isotherm models related to mono and multi-layer adsorption (Langmuir, Freundlich, Temkin, Flory-Huggins, Volmer, Dubinin-Radushkevich, Jovanovich, Elovich, Hill, Redlich-Peterson, Sips, Toth, Koble-Corrigan, Khan, Radke-Prausnitz, Kiselev, Jossens, Hill-de Boer, Unilan, Frumkin, Fowler-Guggenheim, Fritz-Schlunder (III), Fritz-Schlunder (IV), Dubinin-Astakhov (DA), Baudu, Weber-van Vliet, Fritz-Schlunder (V), Halsey, Brunauer-Emmett-Teller (BET),

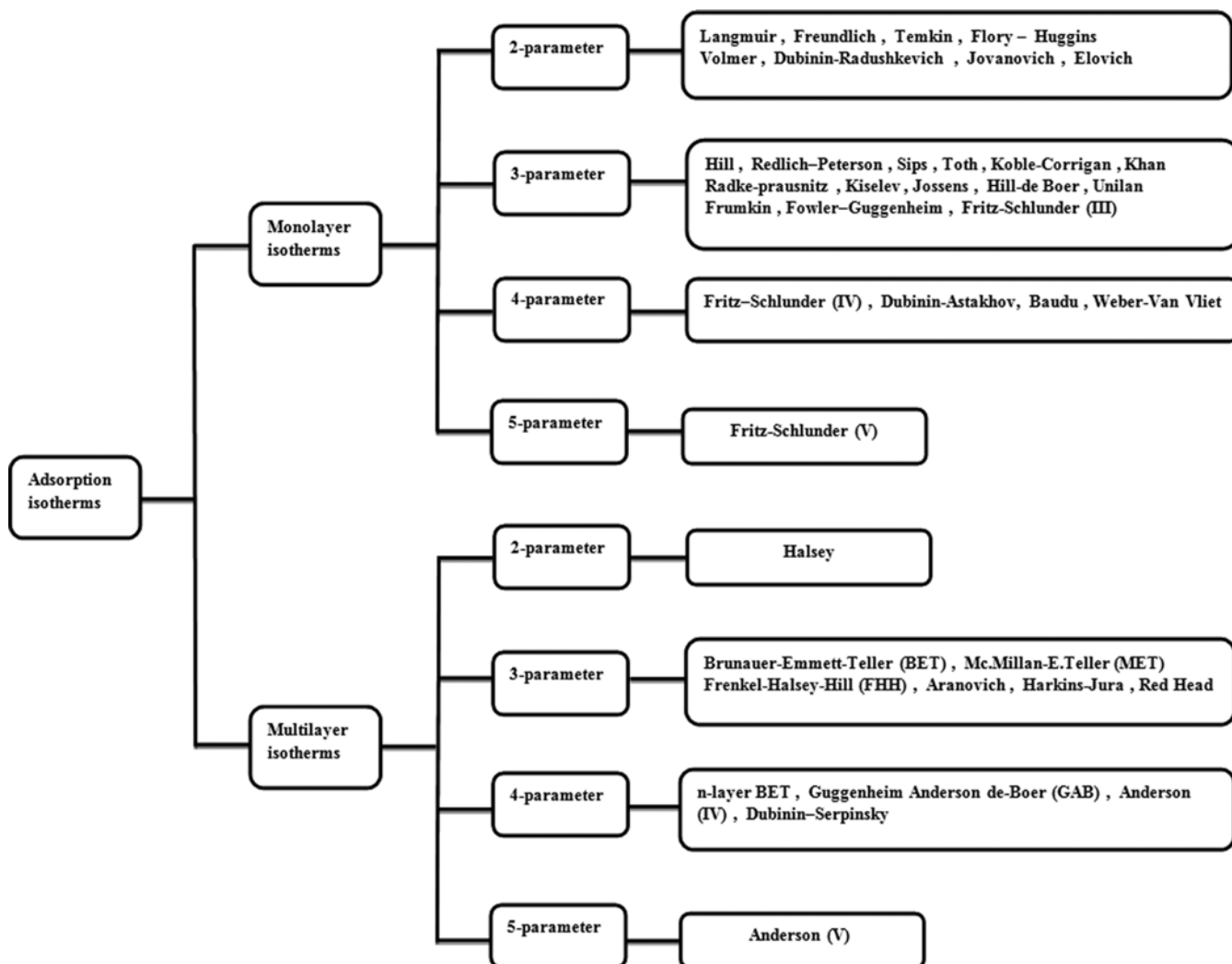


Fig. 1. Monolayer and multilayer adsorption isotherm models.

McMillan-Teller (MET), Frenkel-Halsey-Hill (FHH), Aranovich, Harkins-Jura, Red Head, n-layer BET, Guggenheim Anderson de-Boer (GAB), Anderson (IV), Dubinin-Serpinsky (DS), Anderson (V)) were discussed. The diagram of all the studied adsorption isotherm models in this review is in Fig. 1. The amount of molecule adsorbed per unit mass of adsorbent, that is, the equilibrium adsorption capacity of adsorption is calculated as Eq. (1) [36]:

$$q_e = \frac{V(C_o - C_e)}{W} \quad (1)$$

1. Monolayer Adsorption Isotherm Models

1-1. Two Parameter Isotherm Models

1-1-1. Langmuir

The simplest and still the most useful isotherm, for both physical and chemical adsorption, is the Langmuir isotherm. This model assumes that adsorption is limited to a monolayer: only a single layer of molecules on the adsorbent surface are absorbed, adsorbent surface is homogeneous and adsorption energy is uniform for all sites and there is no transmigration of adsorbate in the plane of the surface. Once a pollutant occupies a site, no further adsorption can take place in that site; the intermolecular attractive forces rapidly decrease as distance rises. There is no interaction between molecules adsorbed on neighboring sites, adsorption on surface is localized, which means that adsorbed atoms or molecules are adsorbed at definite and localized sites [37]. Based upon these assumptions, the Langmuir isotherm is written as Eq. (2) [37,38]:

$$q_e = \frac{q_{mL} b C_e}{1 + b C_e} \quad (2)$$

b is the equilibrium constant (L/mg), which is a criterion of the tendency of the adsorbate to adsorb onto the active sites of the adsorbent surface. A larger b value represents higher adsorption energy. The dimensionless constant of the separation factor or equilibrium parameter to predict the adsorption efficiency and usability of the Langmuir equation is determined as Eq. (3) [39]:

$$R_L = \frac{1}{1 + b C_o} \quad (3)$$

R_L values between 0 and 1 indicate favorable adsorption, while $R_L > 1$, $R_L = 1$, and $R_L = 0$ indicate unfavorable, linear, and irreversible adsorption processes, respectively.

Based on previous research studies [34,40-46], the Langmuir model has the best fitness quality with experimental data among two parameter monolayer adsorption isotherm models.

1-1-2. Freundlich

The Freundlich isotherm model is an empirical equation and another form of Langmuir that can be applied to multilayer adsorption. This model assumes that the surface of the adsorbent is heterogeneous and active sites and their energies distribute exponentially [47]. The stronger binding sites are occupied first, until adsorption energy is exponentially decreased upon the completion of adsorption process [48]. The Freundlich isotherm is expressed as Eq. (4) [47]:

$$q_e = k_f \cdot C_e^{1/n_f} \quad (4)$$

where k_f is the adsorption coefficient and represents the adhesion

ability of the adsorbate onto the adsorbent (relative adsorption capacity of the adsorbent). $1/n_f$ indicates the adsorption intensity of adsorbate onto the adsorbent or surface heterogeneity. The slope ($1/n_f$) between 0 and 1 indicates favorable adsorption isotherm. When this value gets closer to zero, the surface of the adsorbent becomes more heterogeneous and the adsorption isotherm becomes more nonlinear; while, $1/n_f$ above one is indicative of unfavorable adsorption isotherms [49,50]. As $1/n_f$ gets smaller than about 0.1 the adsorption isotherm approaches irreversible isotherm [51]. Because such an equation does not approach Henry's law at low concentrations, it is not able to provide a good fit for adsorption data [52].

According to previous research [36,43,45,53-56], for two parameter monolayer adsorption isotherm models, the Freundlich model was found to be the most appropriate to describe the adsorption of different adsorbates from aqueous solutions.

1-1-3. Temkin

Another empirical equation, the Temkin equation, describes the adsorption of hydrogen onto platinum electrodes within the acidic solutions [51]. The model is given by Eq. (5) [57]:

$$q_e = B_T \ln(A_T C_e) \quad (5)$$

$$B_T = \frac{RT}{b_T} \quad (6)$$

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in the layer decreases linearly rather than logarithmically as equilibrium adsorption capacity increases because the b_T factor is related to adsorbent-adsorbate interactions [58]. The adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy. The Temkin equation is better for predicting the gas phase equilibrium rather than liquid-phase equilibrium [59].

1-1-4. Flory - Huggins

Flory-Huggins isotherm model, which occasionally derives the degree of surface coverage characteristics of adsorbate onto adsorbent, can express the feasibility and spontaneous nature of the adsorption process. The equation of Flory-Huggins isotherm is presented as Eq. (7) [60]:

$$\frac{\theta}{C_o} = K_{FH} (1 - \theta)^{n_{FH}} \quad (7)$$

$$\theta = 1 - \frac{C_e}{C_o} \quad (8)$$

The n_{FH} parameter is the number of adsorbate ions occupying sorption sites. The equilibrium constant, K_{FH} used for the calculation of spontaneity free Gibbs energy is related to the Eq. (9) [61]:

$$\Delta G^0 = -RT \ln(K_{FH}) \quad (9)$$

1-1-5. Volmer

The Volmer isotherm model assumes that adsorbed molecules are allowed to be mobile on the surface of adsorbent but adsorbed molecules are not allowed to have interaction with each other. The Volmer equation is defined as Eq. (10) [51]:

$$C_e = \frac{\theta_V}{d(1 - \theta_V)} \exp\left(\frac{\theta_V}{1 - \theta_V}\right) \quad (10)$$

In which θ_v ($\theta_v = q_e/q_m$) is fractional coverage lied between zero and unity. d is the Volmer affinity constant which depends on temperature. The factor $\exp(\theta_v/1 - \theta_v)$ in above equation accounts for the mobility of the adsorbate molecules.

1-1-6. Dubinin-Radushkevich

The Dubinin-Radushkevich model was chosen to estimate the characteristic porosity and the apparent free energy of adsorption. The Dubinin-Radushkevich isotherm model can be computed by Eq. (11) [60]:

$$q_e = q_{sd} \exp(-K_{ad} \varepsilon^2) \quad (11)$$

It is generally used to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [30]. The intermediate range of concentrations data can be successfully fitted with this model; however, the model is not able to predict Henry's law at low concentration [62]. This isotherm model is usually applied to distinguish the physical and chemical adsorption of adsorbate ions. The Polanyi potential, ε , can be correlated as Eq. (12) [60]:

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

The Dubinin-Radushkevich isotherm model is temperature dependent; when the adsorption data at various temperatures are plotted as a function of logarithm of amount adsorbed versus the square of potential energy, all suitable data will lie on the same curve, known as the characteristic curve [63]. The constant, K_{ad} , is associated with the mean free energy of sorption per mole of the sorbate as it is transferred to the surface of the solid from infinite distance in the solution and this energy can be calculated as Eq. (13) [60]:

$$E = \frac{1}{\sqrt{2K_{ad}}} \quad (13)$$

1-1-7. Jovanovich

The model of an adsorption surface considered by Jovanovich is essentially the same as that considered by Langmuir. The Jovanovich model can be shown as Eq. (14) [64]:

$$q_e = q_{mj} (1 - e^{-K_j C_e}) \quad (14)$$

The Jovanovich equation can be used less in physical adsorption. It is applicable to mobile and monolayer localized adsorption without lateral interactions. This equation reduces to Henry's law at low concentration. At high concentration, it reaches the saturation limit. The Jovanovich equation has a slower approach toward the saturation than that of the Langmuir equation [51].

1-1-8. Elovich

The Elovich is model based on a kinetic principle with the assumption of adsorption sites increasing exponentially with adsorption, which represents multilayer adsorption. The Elovich isotherm model is expressed as Eq. (15) [65]:

$$C_e = \frac{q_e}{q_{mE} K_E \exp\left(\frac{-q_e}{q_{mE}}\right)} \quad (15)$$

1-2. Three Parameter Isotherm Models

1-2-1. Hill

The Hill equation was postulated to describe the binding of dif-

ferent species onto homogeneous substrates. The Hill isotherm model is calculated as Eq. (16) [36]:

$$q_e = \frac{q_{sH} C_e^{n_H}}{K_D + C_e^{n_H}} \quad (16)$$

This model assumes that adsorption is a cooperative phenomenon, with the ligand binding ability at one site on the macromolecule, which may influence different binding sites on the same macromolecule. In this model three possibilities can occur: $n_H > 1$, positive cooperativity in binding, $n_H = 1$, non-cooperative or hyperbolic binding, $n_H < 1$, negative cooperativity in binding.

1-2-2. Redlich-Peterson

The Redlich-Peterson isotherm contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms, and the mechanism of adsorption is a hybrid and does not follow ideal monolayer adsorption. This model can be applied either in homogeneous or heterogeneous systems. The Redlich-Peterson isotherm model can be described as Eq. (17) [66]:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^g} \quad (17)$$

The exponent, g lies between 0 and 1. At high liquid-phase concentrations of the adsorbate, the Freundlich equation can be concluded, i.e., it reduces to the Langmuir equation for $g=1$ and it approaches Henry's equation for $g=0$.

Regarding recently published papers [33,34,67,68], Redlich-Peterson model provides the best agreement with experimental data between three parameter monolayer adsorption isotherm models.

1-2-3. Sips

By identifying the problem of continuing increase in the adsorbed amount with an increase in concentration in the Freundlich equation, Sips proposed an equation that combines the Freundlich and Langmuir isotherms. This produces an expression that exhibits a finite limit at sufficiently high concentration. This model is valid for predicting the heterogeneous adsorption systems and localized adsorption without adsorbate-adsorbate interactions. The Sips isotherm model is given by Eq. (18) [69]:

$$q_e = \frac{q_{ms} a_s C_e^{B_s}}{1 + a_s C_e^{B_s}} \quad (18)$$

At low adsorbate concentrations the Sips isotherm model effectively reduces to the Freundlich isotherm. Therefore, it does not follow Henry's law. At the high adsorbate concentrations, this model predicts a monolayer sorption capacity characteristic of the Langmuir isotherm [70]. The constant B_s is often regarded as the heterogeneity factor and the system heterogeneity could stem from the solid or the adsorbate or a combination of both. The B_s parameter is usually greater than unity, and therefore the larger is this parameter the more heterogeneous is the system. Values close to (or exactly) 1 indicate a solid with relatively homogeneous binding sites. If B_s is unity, the Langmuir equation applicable for ideal surfaces is recovered [51].

Previous studies [33,67,71,72] indicate that Sips model can be used as the most applicable isotherm model among the three parameter monolayer adsorption isotherm models.

1-2-4. Toth

The Toth isotherm model is another empirical equation devel-

oped to improve Langmuir isotherm fittings with experimental data when applied to Type I isotherms for porous adsorbents [73].

The Toth correlation is presented as Eq. (19) [36]:

$$q_e = \frac{q_m T C_e}{(a_T + C_e^z)^{1/z}} \quad (19)$$

The significance of the equation is useful in describing heterogeneous adsorption systems and multilayer adsorption, which is a special type of Langmuir isotherm and has very restrictive validity. The Toth equation also has an advantage over the Sips equation in that it describes the behavior of the data at low and high concentrations [61]. Parameter z is said to characterize the system heterogeneity. The more the parameter z deviates from unity, the more heterogeneous is the system [51]. The parameter z is independent of temperature, whereas a_T increases rapidly with increasing temperature [73].

1-2-5. Koble-Corrigan

Similar to the Sips isotherm model, the Koble-Corrigan isotherm is a three-parameter equation which incorporates both Langmuir and Freundlich isotherms for representing the equilibrium adsorption data. The Koble-Corrigan equation is computed as Eq. (20) [74]:

$$q_e = \frac{AC_e^{n_K}}{1 + BC_e^{n_K}} \quad (20)$$

The model is generally applied for heterogeneous sorbent surface [75]. This model is valid only when $n_K > 1$. This means the model is able to describe the experimental data [74].

1-2-6. Khan

The Khan isotherm is a generalized model suggested for pure solutions, which can represent both extremes, Langmuir and Freundlich type. It was developed for both multicomponent and single component adsorption systems. The generalized equation for pure component adsorption isotherms is expressed as Eq. (21) [76]:

$$q_e = \frac{q_{SK} b_K C_e}{(1 + b_K C_e)^{a_K}} \quad (21)$$

when a_K is equal to unity, Eq. (21) reduces to the Langmuir isotherm. This equation at large value of C_e reduces to the Freundlich isotherm [77].

1-2-7. Radke-Prausnitz

Radke and Prausnitz [78] proposed a slight modification to the Langmuir equation, introducing another coefficient which improved the fit to their experimental data. The three isotherms of this model can be calculated as Eqs. (22)-(24):

$$q_e = \frac{q_{mRPI} K_{RPI} C_e}{(1 + K_{RPI} C_e)^{m_{RPI}}} \quad (22)$$

$$q_e = \frac{q_{mRPII} K_{RPII} C_e}{1 + K_{RPII} C_e^{m_{RPII}}} \quad (23)$$

$$q_e = \frac{q_{mRPIII} K_{RPIII} C_e}{1 + K_{RPIII} C_e^{m_{RPIII}^{-1}}} \quad (24)$$

1-2-8. Kiselev

The Kiselev adsorption isotherm applied in localized monomo-

lecular layer is introduced by Eq. (25) [79]:

$$C_e = \frac{\theta_K}{K_K(1 - \theta_K)} \cdot \frac{1}{(1 + K_n \theta_K)} \quad (25)$$

1-2-9. Jossens

The Jossens isotherm model is based on a distribution of the energy of interactions adsorbate-adsorbent on adsorption sites. Regarding the interactions between adsorbate and adsorbent, the model assumes that the adsorbent surface is heterogeneous. The Jossens model is written as Eq. (26) [80]:

$$C_e = \frac{q_e}{H} \exp(Fq_e^u) \quad (26)$$

F and H are only temperature dependent. This equation can be reduced to Henry's law at low capacities.

1-2-10. Hill-de Boer

Hill and De Boer [81,82] represented an equation of the isotherm that takes account of lateral interactions among adsorbed molecules and the mobility of the adsorbed phase. The Hill-de Boer equation can be expressed as Eq. (27):

$$C_e = \frac{\theta_H}{K_{1H}(1 - \theta_H)} \exp\left(\frac{\theta_H}{1 - \theta_H} - \frac{K_{2H}\theta_H}{RT}\right) \quad (27)$$

where K_{1H} and K_{2H} represent, respectively, the adsorbate-adsorbent and the adsorbate-adsorbate interactions. A positive K_{2H} value indicates attraction between adsorbed species and a negative value means repulsion. The apparent affinity rises with loading when there is attraction between adsorbed species, and it is reduced with loading when there is repulsion among the adsorbed species. When there is no interaction between adsorbed molecules (i.e., $K_{2H}=0$), the Hill-de Boer equation reduces to the Volmer equation [51].

1-2-11. Unilan

The Unilan isotherm model is another empirical equation obtained by assuming uniform distribution of energy. The term "Unilan" comes from uniform distribution and Langmuir local isotherm. The Unilan equation has good fit with experimental data at low and high concentrations. The Unilan isotherm model is depicted in Eq. (28) [51]:

$$q_e = \frac{q_{mU}}{2s} \ln\left(\frac{1 + re^s C_e}{1 + re^{-s} C_e}\right) \quad (28)$$

The parameter s characterizes the heterogeneity of the system. The larger this parameter is, the more heterogeneous is the system. If the value of s reaches to around 10, the isotherm closes to irreversible behavior. If $s=0$, the Unilan equation reduces to the classical Langmuir equation as in this limit the range of energy distribution is zero.

1-2-12. Frumkin

The Frumkin isotherm equation was developed to describe the interaction between the adsorbed species. The Frumkin correlation is presented in Eq. (29) [83]

$$C_e = \frac{\theta}{K_F(1 - \theta)} \exp(-f\theta) \quad (29)$$

If $f=0$, i.e., there is no interaction between adsorbate species, above equation reduces to the Langmuir isotherm.

1-2-13. Fowler-Guggenheim

The Fowler-Guggenheim isotherm is the simplest equation developed by considering lateral interaction of the adsorbed molecules. The Fowler-Guggenheim model is defined by Eq. (30) [84]:

$$C_e = \frac{\theta_{FG}}{K_{FG}(1-\theta_{FG})} \exp\left(\frac{2\theta_{FG}w}{RT}\right) \quad (30)$$

The heat of adsorption varies linearly with loading. If the interaction between the adsorbed molecules is attractive (i.e., w is positive), the heat of adsorption will increase with loading. That is why there is increased interaction between adsorbed molecules as the loading rises. This means that if the measured heat of adsorption shows an upward trend with respect to loading, it indicates the positive lateral interaction between adsorbed molecules. Contrarily, if the interaction among adsorbed molecules is repulsive (i.e., w is negative), the heat of adsorption shows a decline with loading. When there is no interaction between adsorbed molecules ($w=0$), the Fowler-Guggenheim equation will reduce to the Langmuir equation.

1-2-14. Fritz-Schlunder (III)

Fritz and Schlunder [85] proposed an empirical relation with three parameter isotherm models to describe the equilibrium data. Fritz-Schlunder model is presented as Eq. (31):

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

1-3. Four Parameter Isotherm Model

1-3-1. Fritz-Schlunder (IV)

Four-parameter isotherm model of another form of Langmuir-Freundlich type was extended empirically by Fritz and Schlunder. The equation of this model is calculated as Eq. (32) [85]:

$$q_e = \frac{CC_e^\alpha}{1 + DC_e^\beta} \quad (32)$$

This equation is valid when α and $\beta \leq 1$. At high liquid-phase concentrations of the adsorbate, this model reduces to the Freundlich equation. For $\alpha = \beta = 1$, the model reduces to the Langmuir equation.

1-3-2. Dubinin-Astakhov

The Dubinin-Astakhov isotherm model describes surface heterogeneity of adsorbent. However, some empirical data confirm that this model can describe adsorption in an almost homogeneous microporous system. Dubinin-Astakhov equation is given by Eq. (33) [51]:

$$\theta_{DA} = \exp\left(\frac{-A_D}{E_A}\right)^{n_D} \quad (33)$$

$$A_D = RT \ln\left(\frac{C_s}{C_e}\right) \quad (34)$$

where n_D describes the surface heterogeneity.

1-3-3. Baudu

The calculation of the Langmuir coefficients, q_{mL} and b , carried out by the measurement of tangents at the different equilibrium concentrations indicates that they are not constants in a wide concentration range. Their variations with concentration are written as Eqs. (35, 36).

$$b = b_0 C_e^x \quad (35)$$

$$q_{mL} = q_{mB} C_e^y \quad (36)$$

Drawing plots of $\ln(q_{mL})$ and $\ln(b)$ versus $\ln C_e$ gives the parameters of model, b_0 , q_{mB} , x , and y . The Langmuir equation has been transformed to Eq. (37), which is known as Baudu isotherm model [86]:

$$q_e = \frac{q_{mB} b_0 C_e^{(1+x+y)}}{1 + b_0 C_e^{(1+x)}} \quad (37)$$

This equation is valid when $(1+x+y)$ and $(1+x) \geq 1$. For lower surface coverage, the model reduces to the Freundlich equation.

From previous studies [87-89], Baudu provides the best agreement with experimental data regarding four parameter monolayer isotherm models.

1-3-4. Weber-van Vliet

Weber-van Vliet equation was proposed as a four parameter isotherm model to predict the behavior of this model with the equilibrium data. This equation is Eq. (38) [90]:

$$C_e = P_1 q_e^{(P_2 q_e^{P_3} + P_4)} \quad (38)$$

1-4. Five Parameter Isotherm Model

1-4-1. Fritz-Schlunder (V)

A broad field of experimental equilibrium data can be analyzed by using a five-parameter model, named Fritz-Schlunder isotherm model. This model requires nonlinear regression techniques with higher complexities for its solution. The Fritz-Schlunder equation is expressed as Eq. (39) [85]:

$$q_e = \frac{q_{mFS5} K_1 C_e^{m_1}}{1 + K_2 C_e^{m_2}} \quad (39)$$

The isotherm model is valid when m_1 and $m_2 \leq 1$.

2. Multilayer Adsorption Isotherm Models

2-1. Two Parameter Isotherm Model

2-1-1. Halsey

This equation is suitable for evaluation of the multilayer adsorption system for adsorbate ions adsorption at a relatively large distance from the surface. The Halsey adsorption isotherm can be given as Eq. (40) [91]:

$$q_e = \exp\left(\frac{\ln K_H - \ln C_e}{m_H}\right) \quad (40)$$

The agreement of the experimental data with this equation especially at high concentrations confirms the nature of heterogeneous pore distribution of the adsorbent. This equation is a good representation of adsorption data regarding isotherms similar to type II which appear in heteroporous solids [92].

With respect to the literature [46,54,56], the Halsey model has the best fit with experimental data compared to multilayer adsorption isotherm models.

2-2. Three Parameter Isotherm Models

2-2-1. BET

The Brunauer-Emmett-Teller (BET) isotherm is a theoretical model, most extensively used in gas-solid equilibrium systems. BET is a special form of Langmuir isotherm extended to derive multilayer adsorption systems. BET model is commonly applied to deter-

mine the surface area of an adsorbent from nitrogen adsorption data [51]. The extension of this model to liquid-solid interface is described by Eq. (41) [51,93]:

$$q_e = \frac{q_{mBET} C_{BET} C_e}{(C_e - C_s) \left[1 + (C_{BET} - 1) \frac{C_e}{C_s} \right]} \quad (41)$$

The C_{BET} parameter is related to the energy of interaction with the surface. Validity of this theory is in the relative concentration range of 0.02 to 0.4. This isotherm uses the same assumptions applied in Langmuir isotherm: surface and distribution of sites is uniform and surface is energetically homogeneous (adsorption energy does not change with the progress of adsorption in the same layer), and there is no interaction among adsorbed molecules. Besides, the rate of adsorption on any layer is equal to the rate of desorption from that layer. According to multilayer adsorption of the BET model, other simplifying assumptions were added to this model: the second, third, and higher layers have the same energy of adsorption which equals heat of fusion, and are not influenced directly by adsorbent-adsorbate interactions. However, the energy for the first layer is different from that for the second or other layers. Furthermore, the number of layers as the concentration approaches the saturation concentration tends to infinity [51,94].

2-2-2. McMillan-Teller (MET)

The MacMillan-Teller (MET) isotherm model extended based on consideration of surface tension effects in the BET isotherm. The MET equation is defined by Eq. (42) [95]:

$$q_e = q_{SM} \left(\frac{k}{\ln \left(\frac{C_s}{C_e} \right)} \right)^{1/3} \quad (42)$$

When C_s/C_e is approaching unity, the logarithmic term can be approximated as:

$$q_e = q_{SM} \left(\frac{k C_e}{C_s - C_e} \right)^{1/3} \quad (43)$$

This empirical isotherm can be fitted with experimental data at relative concentrations higher than 0.8. However, the BET isotherm is valid for relative concentrations lower than 0.4.

2-2-3. FHH

The Frenkel-Halsey-Hill (FHH) adsorption isotherm describes multilayer adsorption, assuming variation of adsorption potential based on distance from the adsorbed molecule layer from the surface of the adsorbent [96]. The BET model for the case of heterogeneous surfaces neglects the effects of surface heterogeneity on the adsorption of the molecules in the second and the higher adsorbed layers. The FHH model, however, assumes that surface heterogeneity affects the adsorption in all the adsorbed layers [73]. The FHH adsorption isotherm is given by Eq. (44):

$$q_e = \left[\frac{-1}{A_{FHH}} \ln \left(\frac{C_e}{C_s} \right) \right]^{-\frac{1}{B_{FHH}}} \quad (44)$$

A_{FHH} specifies long-range van der Waals interactions between the surface and first adsorbed molecule layer and interactions between

neighboring adsorbate molecules containing information about the capacity of the surface for adsorption. (i.e., higher A_{FHH} values indicate that more adsorbate may be adsorbed). B_{FHH} describes the interactions between the surface and subsequent adsorbate layers [97]. This parameter increases from the value 2.55 for the most heterogeneous sample, through 2.69 for the less heterogeneous sample, up to 2.95 for the most homogeneous sample [73]. For van der Waals forces, B_{FHH} is equal to 3. A value of about 2.7 is commonly observed in adsorbent [51]. Smaller B_{FHH} values or larger degree of surface heterogeneity indicate that the adsorbent extends its influence on adsorbed molecules at further and further distances from the surface [73,97].

2-2-4. Aranovich

The Aranovich isotherm is a modified version of the BET isotherm which has similarity to this equation. The Aranovich equation is calculated as Eq. (45) [51]:

$$q_e = \frac{q_{mAr} C_{Ar} \frac{C_e}{C_s}}{\left(1 - \frac{C_e}{C_s} \right)^{1/2} \left(1 + C_{Ar} \frac{C_e}{C_s} \right)} \quad (45)$$

The difference between these two equations is the exponent of the term $(1 - C_e/C_s)$. In the BET isotherm model, the exponent is one while in the Aranovich isotherm model the exponent is one-half. This isotherm describes a broad concentration range; however, the range of validity of the BET equation is narrow (relative concentration of 0.02 to 0.4).

The Aranovich model is based on the following hypotheses: (1) The adsorbent surface is flat and uniform. (2) The phase in contact with the adsorbent is a vacancy solution to which a lattice model can be applied. (3) The energy change accompanying the evaporation of a molecule depends on the number of layers. (4) Only the configurational components of the free energy are considered.

2-2-5. Harkins-Jura

The Harkins-Jura isotherm equation accounts for multilayer adsorption and can describe isotherm of type II that can appear in heteroporous solids. The Harkins-Jura adsorption isotherm is presented as Eq. (46) [51,98]:

$$q_e = \left[\frac{B_{HJ}}{A_{HJ} - \ln \left(\frac{C_e}{C_s} \right)} \right]^{1/2} \quad (46)$$

At high concentrations, the high fit of adsorption data with Harkins-Jura similar to Halsey equation can be explained with the existence of a heterogeneous pore distribution [92]. Although the BET theory is applied for evaluation of the surface area of an adsorbent as a convenient method, the Harkins-Jura isotherm can also be used to determine the surface area [51].

With regard to previous studies [46,99], Harkins-Jura gives the best agreement with equilibrium data in case of three parameter multilayer adsorption isotherm models.

2-2-6. Red Head

The Redhead isotherm covers the multilayer adsorption region. The purpose of the Redhead isotherm is to expand the range of validity of this model to higher concentration range. The Redhead

isotherm equation is written as Eq. (47) [51]:

$$q_e = q_{mR} \cdot \left[\frac{(2n_R - 1) \cdot C_e}{C_s - C_e} \right]^{1/n_R} \quad (47)$$

where n_R is the empirical parameter and it was found to be in the range of 2.5 and 4.5 for most cases. Similar to the Aranovich equation, the Redhead equation lies below the BET equation in the high range of the reduced concentration.

2-3. Four Parameter Isotherm Models

2-3-1. n-Layer BET Isotherm Model

The n-layer BET isotherm assumes there are a maximum n layers that can be adsorbed onto the internal surface. When the adsorption space is finite in the case of the finite size of pores that is when the adsorption layer is limited by n layers. The n-layer BET model is taken as Eq. (48) [51,100]

$$q_e = \frac{q_{m,nBET} C_{nBET} C_e}{C_s - C_e} \cdot \frac{1 - (n_{BET} + 1) \left(\frac{C_e}{C_s} \right)^n + n_{BET} \left(\frac{C_e}{C_s} \right)^{n_{BET} + 1}}{1 + (C_{nBET} - 1) \left(\frac{C_e}{C_s} \right) - c_{nBET} \left(\frac{C_e}{C_s} \right)^{n_{BET} + 1}} \quad (48)$$

where C_{nBET} is BET adsorption constant relating to the energy of interaction with the surface.

When n approaches infinity, Eq. (48) reduces to the standard BET equation. When $n_{BET}=1$, the equation is transformed to the Langmuir equation. The parameter C_{nBET} is commonly greater than 1 because the heat of adsorption of the first layer is greater than the heat of fusion, i.e., the attractive forces between the adsorbed molecule and the adsorbent are greater than the attractive forces between molecules in the liquid state [51].

2-3-2. GAB

The Guggenheim Anderson de-Boer (GAB) isotherm is a modification of the Langmuir and BET physical adsorption isotherms. This isotherm necessarily includes an additional parameter, K_G , which is the criterion for the difference of the standard chemical potential between the molecules of the second and subsequent adsorption layers and those of molecules in liquid state. The GAB equation is determined as Eq. (49) [101,102]:

$$q_e = \frac{q_{mG} C_{GAB} K_G C_e}{(C_s - K_G C_e) \left[1 + (C_{GAB} - 1) K_G \frac{C_e}{C_s} \right]} \quad (49)$$

where C_{GAB} and K_G are the GAB constants, which are related to the energies of interaction between the first and the further sorbed molecules at the individual sorption sites [101]. A K_G parameter of normally less than unity means that the heat of adsorption of the second layer is identical to the higher layers, but heat of adsorption of the second layer and subsequent layers is less than the heat of fusion [51,101]. Following equation is valid when:

$$q_{mBET} < q_{mG} \quad C_{BET} > C_{GAB}$$

However, if $K_G=1$, Eq. (49) is transformed into the BET equation; therefore:

$$q_{mBET} = q_{mG} \quad C_{BET} = C_{GAB}$$

Based on BET isotherm, the heat of adsorption of the second and higher layers equals the heat of fusion [102].

2-3-3. Anderson (IV)

Anderson (IV) adsorption isotherm is another modification of the BET equation that assumes the structure of adsorbent is such that only finite number of layers is allowed to adsorb adsorbate, so the surface area available for adsorption is smaller in each subsequent layer. The isotherm can be expressed as Eq. (50) [51]:

$$q_e = \frac{q_{mAn,4} C_{An,4} C_e}{(C_s - j C_e) \left[1 + (C_{An,4} - 1) \frac{C_e}{C_s} \right]} \quad (50)$$

where j is the fraction available in the subsequent layer. This fraction is assumed constant in each layer. When $j=0$, this equation reduces to the Langmuir equation, and when $j=1$, the famous BET equation is obtained.

2-3-4. Dubinin-Serpinsky

An equation describing the adsorption of water by active carbons was proposed by Dubinin and Serpinsky [103,104]. It assumes that adsorption initially occurs at so-called primary sites and that further adsorption takes place at these hydrated sites by the formation of hydrogen bonds. This equation is the improved version of an earlier description [105], and it can be presented as Eq. (51):

$$C_e = \frac{C_s q_e}{C_{DS}(q_0 + q_e)(1 - k_{DS} q_e)} \quad (51)$$

The term $(1 - k_{DS} q_e)$ takes into account the decrease in acting adsorption centers with increasing micropore filling. The value of the parameter k_{DS} is determined by the condition that, at the saturated concentration, the quantity adsorbed will be equal to the maximum adsorption capacity [106].

2-4. Five Parameter Isotherm Model

2-4-1. Anderson (V)

The Anderson (V) equation is a five parameter isotherm model that is another modified version of the BET adsorption isotherm. It extends the relative concentration range of the BET model by combination of the GAB and the Anderson (IV) isotherm models, which is when the heat of adsorption of second layer and above is less than the heat of fusion and the surface area of a layer available for adsorption is smaller than the preceding layer. By combination of Eqs. (49, 50) the following is obtained [51]:

$$q_e = \frac{q_{mAn,5} C_{An,5} K_A C_e}{(C_s - j K_A C_e) \left[1 + (C_{An,5} - 1) K_A \frac{C_e}{C_s} \right]} \quad (52)$$

ERROR FUNCTIONS

Isotherm parameters can be determined by non-linear regression method involving the original form of the isotherm equations. Nonlinear regression of isotherm models usually contains error between the experimental data and the predicted isotherm. Therefore, several mathematically rigorous error functions, including sum square error (ERRSQ), hybrid fractional error function (HYBRID), sum of absolute error (EABS), average relative error (ARE), Marquardt's percent standard deviation (MPSD), nonlinear chi square error and residual root mean square error (RMSE) were investigated. If data from a model are similar to the experimental data,

the error value will be a small number, and if they differ, it will be a large number. The error values can be minimized by various methods like shuffled complex evolution (SCE) in order to determine the optimum values of isotherm parameters.

1. Sum Square Error (ERRSQ)

The sum square error function can be represented as Eq. (53) [107]:

$$\sum_{i=1}^n (q_{e,cal} - q_{e,exp})_i^2 \quad (53)$$

Despite extensive application of ERRSQ error function, it has a signif-

icant imperfection: isotherm parameters calculated from such error function provide a better fit at higher adsorbate concentration range. The main reason for this is that as concentration increases, the magnitude of the error and therefore square of the error also increases.

2. Sum of the Absolute Error (EABS)

The sum of the absolute error equation is given by Eq. (54) [108]:

$$\sum_{i=1}^n |q_{e,cal} - q_{e,exp}|_i \quad (54)$$

This approach is analogous to ERRSQ error function. Isotherm parameters derived from the EABS error function provide a bet-

Table 1. Applicable isotherm models in previous research studies

Adsorbent	Adsorbate	Best fitted isotherm	Error	Reference
Copper nanowires loaded on activated carbon	Malachite green	Langmuir	-	[41]
Nanostructured γ -alumina	Ni (II)	Langmuir	-	[42]
Activated carbon	Pb(II), Ni(II) and Cd(II)	Langmuir, Freundlich, Dubinin-Radushkevich	-	[43]
Natural soil	Phenol	Langmuir, Redlich Peterson	ARE, MPSD, HYBRID, ERRSQ, EABS	[34]
Activated carbon and bio-polymer modified activated carbon	Palladium and platinum	Langmuir, Freundlich	ERRSQ	[45]
Magnetic vinylphenyl boronic acid microparticles	Cr(VI)	Langmuir, Dubinin-Radushkevich	-	[40]
Clay	Methylene blue	Langmuir, Halsey, Harkins-Jura	-	[46]
Novel Silica Based Hybrid	Pb(II)	Freundlich, Halsey, Dubinin-Radushkevich	-	[56]
Neem leaves, hyacinth roots, coconut shell, rice bran, rice husk, rice straw	Cu(II)	Halsey, Freundlich	-	[54]
Activated charcoal from toluene and titanium dioxide from toluene	Aniline	Harkins-Jura	-	[99]
Natural zeolite modified with hexamethylenediamine	Reactive red 239 and Reactive blue 250	Freundlich	-	[55]
Acacia nilotica leaf carbon	Co (II)	Freundlich	-	[53]
Yeast biomass	Ochratoxin A	Freundlich, Hill, BET	ERRSQ, ARE, HYBRID, MPSD, EABS	[36]
H ₂ SO ₄ activated immature Gossypium hirsutum seeds	Basic Magenta II	Sips, Hill	ERRSQ, ARE, HYBRID, MPSD, EABS, RMSE	[71]
Palm oil fruit shells	Cu(II)	Sips, Redlich-Peterson, Hill, Radke-Prausnitz, Toth, Koble Corrigan	ARE, Chi-square, RMSE, NSD	[33]
Cashew nut shell	Congo red	Sips, Redlich-Peterson, Koble Corrigan, Toth	-	[67]
TiO ₂ nanoparticles	Natural pigment	Sips	-	[72]
Clinoptilolite	Ammonium	Dubinin-Radushkevich, Redlich-Peterson	ARE, HYBRID	[68]
Anionic exchange resin	α -Lactalbumin	Jovanovich, Langmuir	Chi-square	[44]
Granular activated carbon	Phenol and chlorophenols	Baudu, Fowler-Guggenheim	ARE	[87,88]
Kalathur soil and adhanur soil	Phenol	Baudu	ARE	[89]
Diethylenetriamine cotton fibers	Pesticide	Jossens	-	[113]

ter fit as extent of the error increases, biasing the fit towards the higher concentration data.

3. Hybrid Fractional Error Function (HYBRID)

The hybrid fractional error function is calculated as Eq. (55) [109]:

$$\frac{100}{n-p} \sum_{i=1}^n \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,exp}} \quad (55)$$

The HYBRID error function was developed to improve sum squares error at low concentrations by dividing it to the experimental solid-phase concentration. It also includes the number of degrees of freedom related to the system (the number of data points) and number of parameters of the isotherm equation as a divisor.

4. Average Relative Error Function (ARE)

Average relative error equation can be determined as Eq. (56) [110]:

$$\frac{100}{n} \sum_{i=1}^n \left| \frac{(q_{e,cal} - q_{e,exp})}{q_{e,exp}} \right|_i \quad (56)$$

The ARE error function attempts to decrease the fractional error distribution across the overall concentration range.

5. Marquardt's Percent Standard Deviation Error Function (MPSD)

Marquardt's percent standard deviation error function is defined by Eq. (57) [111]:

$$100 \sqrt{\frac{1}{n-p} \sum_{i=1}^n \left(\frac{q_{e,exp} - q_{e,cal}}{q_{e,exp}} \right)^2} \quad (57)$$

This error function is similar in some respect to geometric mean error distribution and has been modified according to number of degrees of freedom of the system.

6. Nonlinear Chi-square Error Function (X^2)

The chi-square error function is expressed as Eq. (58) [112]:

$$\sum_{i=1}^n \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,cal}} \quad (58)$$

Nonlinear chi-square error is a statistical tool necessary for the best fit of an adsorption system, derived by judging the sum squares differences between the experimental and the calculated data, with each squared difference is divided by its corresponding value (calculated from the models).

7. Residual Root Mean Square Error (RMSE)

RMSE is another error function calculated for validate the fitness of isotherm models to experimental data for understanding the adsorption process, which is defined as Eq. (59) [33]:

$$\sqrt{\frac{1}{n-1} \sum_{i=1}^n (q_{e,exp} - q_{e,cal})^2} \quad (59)$$

The various adsorbents and the best fitted adsorption isotherm models studied in previous researches are presented in Table 1. Based on the following table, in case of monolayer isotherm models, Langmuir and Freundlich models were found to be the most appropriate to describe the adsorption of different adsorbates from aqueous solutions, and in case of multilayer isotherm models, Halsey and Harkins-Jura models had the best agreement with the experimental data.

CONCLUSION

Different adsorption isotherm models have been discussed and categorized based on type of adsorption (monolayer and multilayer) and number of adjustable parameters (two, three, four, and five parameter isotherm models). Some isotherms were obtained to modify former isotherms. For instance, the GAB isotherm equation was developed to modify the Langmuir and BET models by adding other parameter. Furthermore, the Aranovich and MET multilayer isotherms expanded wider concentration range rather than the BET theory.

Better fit of isotherm models with experimental data is commonly concluded as the number of parameters of adsorption isotherms increased. The optimum isotherm parameters can be determined by minimizing the error function across the considered concentration range. For this purpose, seven non-linear error functions were evaluated. Parameters of some isotherm models including Freundlich, Toth, Unilan, and Dubinin-Astakhov determine surface heterogeneity. Some isotherm models give information about adsorbent properties. For example, BET and Harkins-Jura isotherms are applied for evaluation of the surface area of an adsorbent. The majority of published papers investigated two and three parameter isotherm models. According to previous research studies, Langmuir and Freundlich models have the best fitness quality with experimental data in case of two parameter isotherm models. Regarding three parameter isotherm models, Redlich-Peterson and Sips models provide the best agreement with experimental data. With respect to four parameter isotherm models, the Baudu model is found to be the most appropriate to describe equilibrium data.

NOMENCLATURE

a_K	: Khan model exponent
a_R	: Redlich-Peterson isotherm constant [L/mg]
a_S	: sips equilibrium constant [L/mg]
a_T	: toth equilibrium constant
A	: Koble-Corrigan constant ($L^n \text{mg}^{1-n} \text{g}^{-1}$)
A_D	: adsorption potential
A_{FHH}	: FHH constant
A_{HJ}	: Harkins-Jura constant
A_T	: Temkin equilibrium binding constant [L/mg]
b	: Langmuir equilibrium constant [L/mg]
b_K	: Khan constant
b_0	: Baudu equilibrium constant
b_T	: the constant related to heat of sorption [J/mol]
B	: Koble-Corrigan constant (L/mg) ⁿ
B_{FHH}	: FHH constant
B_{HJ}	: Harkins-Jura constant
B_S	: sips model exponent
B_T	: Temkin constant
C	: Fritz-Schlunder (IV) constant
$C_{An,4}$: anderson (IV) constant
$C_{An,5}$: anderson (V) constant
C_{Ar}	: aranovich constant
C_{BET}	: BET constant
C_{DS}	: ratio between the kinetic constants of adsorption and desorp-

tion reactions	mRPI
Ce : equilibrium concentration of adsorbate [mg/L]	mRPII : Radke-Prausnitz models exponents
C _{GAB} : GAB constant	mRPIII
C _{nBET} : n-layer BET constant	n : degree of freedom
C ₀ : adsorbate initial concentration [mg/L]	n _{BET} : maximum number of adsorption layers
C _s : adsorbate monolayer saturation concentration [mg/L]	n _D : Dubinin-Astakhov model exponent
d : volmer affinity constant	n _F : Freundlich constant
D : Fritz-Schlunder (IV) constant	n _{FH} : Flory-Huggins exponent
E : mean free energy [J/mol]	n _H : Hill cooperativity coefficient of the binding interaction
E _A : characteristic energy of adsorption	n _K : Koble-Corrigan model exponent
f : interaction coefficient of the Frumkin model	n _R : red head constant
F : Jossens constant	p : number of isotherm parameters
g : Redlich-Peterson isotherm exponent	P ₁ : Weber-van Vliet constant
H : Jossens constant	P ₂ : Weber-van Vliet model exponent
j : fraction available in the subsequent layer	P ₃ : Weber-van Vliet model exponent
r : unilan contant	P ₄ : Weber-van Vliet model exponent
R : universal gas constant [8.314 J/mol·K]	q ₀ : surface concentration of primary hydrophilic active centers
R _L : dimensionless constant of separation factor	q _e : equilibrium adsorption capacity of adsorbent [mg/g]
D : Fritz-Schlunder (IV) constant	q _{e, cal} : theoretical equilibrium adsorption capacity of adsorbent [mg/g]
E : mean free energy [J/mol]	q _{e, exp} : experimental equilibrium adsorption capacity of adsorbent [mg/g]
E _A : characteristic energy of adsorption	q _{mAn, 4} : anderson (IV) maximum adsorption capacity of adsorbent corresponding to monolayer saturation [mg/g]
f : interaction coefficient of the Frumkin model	q _{mAn, 5} : anderson (V) maximum adsorption capacity of adsorbent corresponding to monolayer saturation [mg/g]
F : Jossens constant	q _{mAr} : aranovich maximum adsorption capacity of adsorbent corresponding to saturation [mg/g]
g : Redlich-Peterson isotherm exponent	q _{mB} : Baudu maximum adsorption capacity [mg/g]
H : Jossens constant	q _{mBET} : BET maximum adsorption capacity of adsorbent corresponding to monolayer saturation [mg/g]
j : fraction available in the subsequent layer	q _{mE} : elovich maximum adsorption capacity [mg/g]
k _{DS} : loss of secondary sites in the course of adsorption	q _{mFS} : Fritz-Schlunder (III) maximum adsorption capacity [mg/g]
k _f : Freundlich constant [mg ¹⁻ⁿ L ⁿ g ⁻¹]	q _{mFS5} : Fritz-Schlunder (V) maximum adsorption capacity [mg/g]
K ₁ : Fritz-Schlunder (V) constant	q _{mG} : GAB maximum adsorption capacity of adsorbent corresponding to monolayer saturation [mg/g]
K ₂ : Fritz-Schlunder (V) constant	q _{mJ} : Jovanovich maximum adsorption capacity [mg/g]
K _{1H} : energetic constant of the interaction between adsorbate and adsorbent [J/mol]	q _{mL} : Langmuir maximum adsorption capacity of adsorbent [mg/g]
K _{2H} : energetic constant of the interaction between adsorbates [J/mol]	q _{m, nBET} : n-layer BET maximum adsorption capacity of adsorbent corresponding to monolayer saturation [mg/g]
K _{ad} : Dubinin-Radushkevich isotherm constant related to adsorption energy [mol ² /J ²]	q _{mR} : red head maximum adsorption capacity of adsorbent corresponding to saturation [mg/g]
K _A : anderson (V) constant	q _{mRPI} : Radke-Prausnitz maximum adsorption capacities [mg/g]
K _D : hill constant	q _{mRPII}
K _E : Elovich equilibrium constant [L/mg]	q _{mRPIII}
K _F : Frumkin equilibrium constant	q _{mS} : sips maximum adsorption capacity [mg/g]
K _{FG} : Fowler-Guggenheim equilibrium constant [L/mg]	q _{mT} : toth maximum adsorption capacity [mg/g]
K _{FH} : Flory-Huggins equilibrium constants [L/mg]	q _{mU} : unilan maximum adsorption capacities [mg/g]
K _{FS} : Fritz-Schlunder(III) equilibrium constant [L/mg]	q _{SD} : Dubinin-Radushkevich theoretical isotherm saturation capacity [mg/g]
K _G : GAB constant	q _{SH} : hill theoretical isotherm saturation capacity [mg/g]
K _H : Halsey constant	q _{SK} : Khan theoretical isotherm saturation capacity [mg/g]
K _J : Jovanovich constant [L/mg]	q _{SM} : MET theoretical isotherm saturation capacity [mg/g]
K _K : Kiselev equilibrium constant [L/mg]	s : unilan model exponent
K _n : constant of complex formation between adsorbed molecules	T : absolute temperature [K]
K _R : Redlich-Peterson isotherm constant [L/g]	
KRPI	
KRPII: Radke- Prausnitz equilibrium constants	
KRPIII	
m ₁ : Fritz-Schlunder (V) model exponent	
m ₂ : Fritz-Schlunder (V) model exponent	
m _{FS} : Fritz-Schlunder (III) model exponent	
m _H : Halsey equation exponent	

- u : Jossens model exponent
 V : volume of adsorbate solution [L]
 w : interaction energy between adsorbed molecules [J/mol]
 W : mass of adsorbent [g]
 x : Baudu model exponent
 y : Baudu model exponent
 z : Toth model exponent

Greek Letters

- α : Fritz-Schlunder (IV) model exponent
 β : Fritz-Schlunder (IV) model exponent
 ΔG^0 : Gibbs free energy [J/mol]
 ε : Polanyi potential constant related to Dubinin-Radushkevich model
 θ : coverage degree of adsorbent surface
 θ_{DA} : degree of micropore filling
 θ_{FG} : fractional coverage related to Fowler-Guggenheim model
 θ_H : fractional coverage related to Hill-de Boer model
 θ_K : Fractional coverage related to Kiselev model
 θ_V : fractional coverage related to Volmer model

REFERENCES

1. M. Yang, *J. Environ. Sci. Health Part. C.*, **29**, 223 (2011).
2. K. Kadirvelu, K. Thamaraiselvi and C. Namasivayam, *Sep. Purif. Technol.*, **24**, 497 (2001).
3. K. Y. Foo and B. H. Hameed, *J. Hazard. Mater.*, **172**, 523 (2009).
4. L. Marder, G. O. Sulzbach, A. M. Bernardes and J. Z. Ferreira, *J. Braz. Chem. Soc.*, **14**, 610 (2003).
5. H. B. Bradl, *J. Colloid Interface Sci.*, **277**, 1 (2004).
6. A. M. Y. Chong, Y. S. Wong and N. F. Y. Tam, *Chemosphere*, **41**, 251 (2000).
7. S. Ricordel, S. Taha, I. Cisse and G. Dorange, *Sep. Purif. Technol.*, **24**, 389 (2001).
8. D. W. O'Connell, C. Birkinshaw and T. F. O'Dwyer, *J. Biores. Technol.*, **99**, 6709 (2008).
9. M. A. O. Badmus, T. O. K. Audu and B. U. Anyata, *Afr. J. Biotechnol.*, **6**, 238 (2007).
10. F. Fu and Q. Wang, *J. Environ. Manage.*, **92**, 407 (2010).
11. A. I. Zouboulis and K. A. Matis, *Crit. Rev. Sci. Technol.*, **27**, 195 (1997).
12. M. Arami, N. Y. Limaee, N. M. Mahmoodi and N. S. Tabrizi, *J. Hazard. Mater.*, **135**, 171 (2006).
13. K. Mohanty, D. Das and M. N. Biswas, *Adsorption*, **12**, 119 (2006).
14. D. Mohan and K. P. Singh, *J. Water Res.*, **36**, 2304 (2002).
15. M. S. Kim and J. G. Chung, *Environ. Eng. Res.*, **7**, 49 (2002).
16. L. Zhang, T. Huang, M. Zhang, X. Guo and Z. Yuan, *J. Hazard. Mater.*, **157**, 352 (2008).
17. M. Ahmedna, W. E. Marshall, A. A. Hussein, R. M. Rao and I. Goktepe, *Water Res.*, **38**, 1062 (2004).
18. A. F. Ngomsik, A. Bee, M. Draye, G. Cote and V. Cabuil, *CR Chimie*, **8**, 963 (2005).
19. P. Sathishkumar, M. Arulkumar and T. Palvannan, *J. Clean. Prod.*, **22**, 67 (2012).
20. A. Bhatnagar, W. Hogland, M. Marques and M. Sillanpaa, *Chem. Eng. J.*, **219**, 499 (2013).
21. D. Mohan and C. U. Pittman Jr., *J. Hazard. Mater.*, **137**, 762 (2006).
22. K. Y. Foo and B. H. Hameed, *Adv. Colloid Interface Sci.*, **149**, 19 (2009).
23. M. d. Ahmaruzzaman, *Adv. Colloid Interface Sci.*, **143**, 48 (2008).
24. D. Kalderis, D. Koutoulakis, P. Paraskeva, E. Diamadopoulos, E. Ota, J. O. del Valle and C. Fernández-Pereira, *Chem. Eng. J.*, **144**, 42 (2008).
25. V. S. Munagapati, V. Yarramuthi, S. K. Nadavala, S. R. Alla and K. Abburi, *Chem. Eng. J.*, **157**, 357 (2010).
26. W. Qiu and Y. Zheng, *Chem. Eng. J.*, **145**, 483 (2009).
27. M. Jaroniec and R. Madey, *Physical Adsorption on Heterogeneous Solids*, Elsevier, Amsterdam (1988).
28. A. Dabrowski, M. Jaroniec and J. Oscik, in: E. Matijevic Eds., *Surface and Colloid Science*, Plenum Press, New York, 83 (1987).
29. A. Dabrowski and M. Jaroniec, *Adv. Colloid Interface Sci.*, **27**, 211 (1987).
30. A. Dabrowski, *Adv. Colloid Interface Sci.*, **93**, 135 (2001).
31. M. I. El-Khaiary, *J. Hazard. Mater.*, **158**, 73 (2008).
32. G. Thompson, J. Swain, M. Kay and C. F. Forster, *Bioresour. Technol.*, **77**, 275 (2001).
33. M. A. Hossain, H. H. Ngo, W. S. Guo and T. V. Nguyen, *Bioresour. Technol.*, **113**, 97 (2012).
34. B. Subramanyam and A. Das, *J. Environ. Health Sci. Eng.*, **12**, 92 (2014).
35. N. Chilton, N. Jack, N. Losso, E. Wayne and R. Marshall, *Biore-sour. Technol.*, **85**, 131 (2002).
36. D. Ringot, B. Lerzy, K. Chaplain, J. P. Bonhoure, E. Auclair and Y. Larondelle, *Bioresour. Technol.*, **98**, 1812 (2007).
37. I. Langmuir, *J. Am. Chem. Soc.*, **38**, 2221 (1916).
38. W. Jianlong, Z. Xinmin, D. Decai and Z. Ding, *J. Biotechnol.*, **87**, 273 (2001).
39. G. McKay, H. S. Blair and J. R. Gardener, *J. Appl. Polym. Sci.*, **27**, 3043 (1982).
40. A. Kara, E. Demirbel, N. Tekin, B. Osman and N. Besirli, *J. Hazard. Mater.* (2014), DOI:10.1016/j.jhazmat.2014.12.011.
41. M. Ghaedi, E. Shojaeipour, A. M. Ghaedi and Reza Sahraei, *Spectrochim. Acta Mol. Biomol. Spectros.* (2015), DOI:10.1016/j.saa.2015.01.086.
42. R. Saadi, Z. Saadi and R. Fazaeli, *Desalin. Water Treat.* (2013), DOI:10.1080/19443994.2013.862869.
43. M. Kavand, M. Soleimani, T. Kaghazchi and N. Asasian, *Chem. Eng. Commun.* (2014), DOI:10.1080/00986445.2014.96269.
44. R. C. I. Fontan, L. A. Minim, R. C. F. Bonomo, L. H. M. da Silva and V. P. R. Minim, *Fluid Phase Equilib.*, **348**, 39 (2013).
45. H. Sharifard, M. Soleimani and F. Zokaei Ashtiani, *J. Taiwan Inst. Chem. Eng.*, **43**, 696 (2012).
46. A. Gurses, S. Karaca, C. Dogar, R. Bayrak, M. Acikyildiz and M. Yalcin, *J. Colloid Interface Sci.*, **269**, 310 (2004).
47. G. Garcia, A. Faz and M. Cunha, *Int. Biodeterior. Biodegrad.*, **54**, 245 (2004).
48. J. Zeldowitsch, *Acta Phys. Chim. URSS.*, **1**, 961 (1934).
49. F. Haghseresht and G. Lu, *Energy Fuels*, **12**, 1100 (1998).
50. M. M. Rao, D. K. Ramana, K. Seshiah, M. C. Wang and S. W. C. Chien, *J. Hazard. Mater.*, **166**, 1006 (2009).
51. D. D. Do, *Adsorption analysis: Equilibria and kinetics*, Imperial College Press, London (1998).

52. Y. S. Ho, J. F. Porter and G. McKay, *Water Air Soil Pollut.*, **141**, 1 (2002).
53. P. Thilagavathy and T. Santhi, *Chinese J. Chem. Eng.* (2014), DOI: 10.1016/j.cjche.2014.08.006.
54. B. Singha and S. Kumar Das, *Colloids Surf.*, **107**, 97 (2013).
55. E. Alver and A. U. Metin, *Chem. Eng. J.*, **200-202**, 59 (2012).
56. J. Liu and X. Wang, *Scientific. World J.* (2013), DOI:10.1155/2013/897159.
57. A. Seker, T. Shahwan, A. E. Erog lu, S. Yilmaz, Z. Demirel and M. Conk Dalay, *J. Hazard. Mater.*, **154**, 973 (2008).
58. C. Aharoni and M. Ungarish, *J. Chem. Soc., Faraday Trans.*, **73**, 456 (1977).
59. Y. Kim, C. Kim, I. Choi, S. Rengraj and J. Yi, *Environ. Sci. Technol.*, **38**, 924 (2004).
60. M. Horsfall and A. I. Spiff, *Acta Chim. Slovenica*, **52**, 174 (2005).
61. K. Vijayaraghavan, T. V. N. Padmesh, K. Palanivelu and M. Velan, *J. Hazard. Mater.*, **133**, 304 (2006).
62. O. Altin, H. O. Ozbelge and T. Dogu, *J. Colloid Interface Sci.*, **198**, 130 (1998).
63. A. Benhammou, A. Yaacoubi, L. Nibou and B. Tanouti, *J. Colloid Interface Sci.*, **282**, 320 (2005).
64. D. S. Jovanovic, *Colloid Polym. Sci.*, **235**, 1203 (1969).
65. S. Y. Elovich and O. G. Larinov, *Izv. Akad. Nauk. USSR, Otd. Khim. Nauk.*, **2**, 209 (1962).
66. O. Redlich and D. L. Peterson, *J. Phys. Chem.*, **63**, 1024 (1959).
67. P. Senthil Kumar, S. Ramalingam, C. Senthamarai, M. Niranjana, P. Vijayalakshmi and S. Sivanesan, *Desalination*, **261**, 52 (2010).
68. I. Tosun, *Int. J. Environ. Res. Public Health*, **9**, 970 (2012).
69. R. Sips, *J. Chem. Phys.*, **16**, 490 (1948).
70. A. B. Pérez-Marn, V. Meseguer Zapata, J. F. Ortuno, M. Aguilar, J. Saez and M. Llorens, *J. Hazard. Mater.*, **139**, 122 (2007).
71. N. Sivarajasekar and R. Baskar, *Arabian J. Chem.* (2014), DOI: 10.1016/j.arabjc.2014.10.040.
72. N. T. R. N. Kumara, N. Hamdan, M. Iskandar Petra, K. U. Tennakoon and P. Ekanayake, *J. Chem.* (2014), DOI:10.1155/2014/468975.
73. W. Rudzinski and D. H. Everett, *Adsorption of Gases on Heterogeneous Surfaces*, Academic Press Ltd., Bristol (1992).
74. O. Abdelwahab, *Egyptian. J. Aquatic. Res.*, **33**, 125 (2007).
75. R. Han, J. Zhang, P. Han, Y. Wang, Z. Zhao and M. Tang, *Chem. Eng. J.*, **145**, 496 (2009).
76. I. Quesada-Penate, C. Julcour-Lebiguea, U. J. Jáuregui-Hazac, A. M. Wilhelma and H. Delmas, *Chem. Eng. J.*, **152**, 183 (2009).
77. A. R. Khan, I. R. Al-Waheab and A. Al-Haddad, *Environ. Technol.*, **17**, 13 (1996).
78. C. J. Radke and J. M. Prausnitz, *Ind. Eng. Chem. Fundam.*, **11**, 445 (1972).
79. A. V. Kiselev, *Kolloid. Zhur.*, **20**, 338 (1958).
80. L. Jossens, J. M. Prausnitz, E. U. Fritz and A. L. Myers, *Chem. Eng. Sci.*, **33**, 1097 (1978).
81. T. L. Hill, *J. Chem. Phys.*, **14**, 441 (1946).
82. J. H. de Boer, *The Dynamical Character of Adsorption*, Oxford University Press, Oxford (1953).
83. T. Grchev, M. Cvetkovska, T. Stafilov and J. W. Schultze, *Electrochim. Acta*, **36**, 1315 (1991).
84. R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics*, Cambridge University Press, London (1939).
85. W. Fritz and E. U. Schlunder, *Chem. Eng. Sci.*, **29**, 1279 (1974).
86. M. Baudu, *Etude des interactions solute-fibres de charbon actif: Application et regeneration*, Ph.D. Thesis, Université de Rennes I (1990).
87. O. Hamdaoui and E. Naffrechoux, *J. Hazard. Mater.*, **147**, 401 (2007).
88. O. Hamdaoui and E. Naffrechoux, *J. Hazard. Mater.*, **147**, 381 (2007).
89. B. Subramanyam and D. Ashutosh, *Int. J. Environ. Res.*, **6**, 265 (2012).
90. B. M. Van Vliet, W. J. Weber and H. Hozumi, *Water Res.*, **14**, 1719 (1980).
91. H. A. Alegria, M. Y. Arica and J. L. Zhou, *Scientific. World Journal*, **2013**, 1 (2013).
92. M. J. Rosen, *Surfactants and Interfacial Phenomena*, Wiley, New York (2012).
93. A. R. Khan, R. Ataullah and A. Al-Haddad, *J. Colloid Interface Sci.*, **194**, 154 (1997).
94. S. J. Gregg and K. S. W. Sing, *Adsorption, surface area, and porosity*, Academic Press, London (1982).
95. W. G. McMillan and E. Teller, *J. Phys. Colloid. Chem.*, **55**, 17 (1951).
96. A. W. Adamson and A. P. Gast, *Physical Chemistry of Surfaces*, Wiley Interscience, New York (1997).
97. P. Kumar, A. Nenes and I. N. Sokolik, *Geophys. Res. Lett.*, **36**, (2009).
98. C. O. Aboluwoye, Y. B. Oladimeji and A. O. Ashogbon, *Turkish J. Eng. Env. Sci.*, **32**, 143 (2008).
99. S. Shanavas, A. Salahuddin Kunju, H. Tresa Varghese and C. Yohannan Panicker, *Orient. J. Chem.*, **27**, 245 (2011).
100. P. Zhang and L. Wang, *Sep. Purif. Technol.*, **70**, 367 (2010).
101. R. D. Andradep, R. Lemusm and C. E. Perezc, *Vitae. Columbia.*, **18**, 325 (2011).
102. O. A. Kamalyan, *Colloid J.*, **72**, 286 (2010).
103. M. M. Dubinin and V. V. Serpinsky, *Carbon*, **19**, 402 (1981).
104. M. M. Dubinin and V. V. Serpinsky, *Dokl. Akad. Nauk SSSR*, **285**, 1151 (1981).
105. M. M. Dubinin, E. D. Zaverina and V. V. Serpinsky, *J. Chem. Soc.*, 1760 (1955).
106. H. F. Stoeckli, F. Kraehenbuehl and D. Morel, *Carbon*, **21**, 589 (1983).
107. V. S. Mane, I. D. Mall and V. C. Srivastava, *J. Environ. Manage.*, **84**, 390 (2007).
108. J. C. Y. Ng, W. H. Cheung and G. McKay, *Chemosphere*, **52**, 1021 (2003).
109. J. C. Y. Ng, W. H. Cheung and G. McKay, *J. Colloid Interface Sci.*, **255**, 64 (2002).
110. A. Kapoor and R. T. Yang, *Gas. Sep. Purif.*, **3**, 187 (1989).
111. A. Seidel and D. Gelbin, *Chem. Eng. Sci.*, **43**, 79 (1988).
112. B. Boulinguez, P. Le Cloirec and D. Wolbert, *Langmuir*, **24**, 6420 (2008).
113. A. E. Ghali, M. H. V. Baouab and M. S. Roudesli, *Ind. Crop Prod.*, **39**, 139 (2012).