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Review

Insights into the modeling of adsorption isotherm systems

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ABSTRACT

Concern about environmental protection has increased over the years from a global viewpoint. To date, the prevalence of adsorption separation in the environmental chemistry remains an aesthetic attention and consideration abroad the nations, owning to its low initial cost, simplicity of design, ease of operation, insensitivity to toxic substances and complete removal of pollutants even from dilute solutions. With the renaissance of isotherms modeling, there has been a steadily growing interest in this research field. Confirming the assertion, this paper presents a state of art review of adsorption isotherms modeling, its fundamental characteristics and mathematical derivations. Moreover, the key advance of the error functions, its utilization principles together with the comparisons of linearized and non-linearized isotherm models have been highlighted and discussed. Conclusively, the expanding of the nonlinear isotherms represents a potentially viable and powerful tool, leading to the superior improvement in the area of adsorption science.

1. Introduction

Over the past several decades, the exponential population and social civilization expansion, change affluent lifestyles and resources use, and continuing progress of the industrial and technologies has been accompanied by a sharp modernization and metropolitan growth [1]. With the rising awareness of the occurrences of industrial activities which has intensified numerous deteriorations on several ecosystems and seriously threatens the human health and environment, the enforcement of stringent rules and regulations concerning the emission of contaminants from industrial waste streams by various regulatory agencies has been promulgated [2].

Simultaneously, a developing research by the invention of a wide range of treatment technologies (precipitation, coagulation–flocculation, sedimentation, flotation, filtration, membrane processes, electrochemical techniques, biological process, chemical reactions, adsorption and ion exchange) with varying levels of successes has accelerated a dramatic progress in the scientific community [3–13]. Of major interest, adsorption process, a surface phenomenon by which a multi-component fluid (gas or liquid) mixture is attracted to the surface of a solid adsorbent and forms attachments via physical or chemical bonds, is recognized as the most efficient, promising and widely used fundamental approach in wastewater treatment processes [14], mainly hinges on its simplicity, economically viable, technically feasible and socially acceptable [15].

A notable trend in the development of activated carbon (AC), an adsorbent with its large porous surface area, controllable pore structure, thermo-stability and low acid/base reactivity has been witnesses [16], in terms its versatility for removal of a broad type of organic and inorganic pollutants dissolved in aqueous media, even from gaseous environment [17]. Despite its prolific use in adsorption processes, the biggest barrier of its application by the industries is the cost-prohibitive adsorbent and difficulties associated with regeneration [18]. Realizing the complication, a growing exploitation to evaluate the feasibility and suitability of natural, renewable and low-cost materials (bamboo dust, peat, chitosan, lignite, fungi, moss, bark husk, chitin, coir pith, maize cob, pinewood sawdust, rice husk, sugar cane bagasse, tea leaves, and sago waste) as alternative adsorbents in water pollution control, remediation and decontamination processes has been exerted [19,20].

In the endeavor to explore novel adsorbents in accessing an ideal adsorption system, it is essential to establish the most appropriate adsorption equilibrium correlation [21], which is indispensable for reliable prediction of adsorption parameters and quantitative comparison of adsorbent behavior for different adsorbent systems (or for varied experimental conditions) [22,23]. In the perspective, equilibrium relationships, generally known as adsorption isotherms, describe how pollutants interact with the adsorbent materials, and thus are critical for optimization of the adsorption mechanism pathways, expression of the surface properties and capacities of adsorbents, and effective design of the adsorption systems [24,25].

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Nomenclature

a_K	Khan isotherm model exponent
a_R	Redlich–Peterson isotherm constant (1/mg)
a_{RP}	Radke–Prausnitz isotherm model constant
a_S	Sips isotherm model constant (L/mg)
a_T	Toth isotherm constant (L/mg)
A	Koble–Corrigan isotherm constant ($\mathrm{L}^n\mathrm{mg}^{1-n}$/g)
A_T	Tempkin isotherm equilibrium binding constant (L/g)
b	Langmuir isotherm constant (dm^3/mg)
b_K	Khan isotherm model constant
b_T	Tempkin isotherm constant
B	Koble–Corrigan isotherm constant $(\mathrm{L/mg})^n$
B_{DR}	Dubinin–Radushkevich isotherm constant
C_e	equilibrium concentration (mg/L)
C_o	adsorbate initial concentration (mg/L)
C_s	adsorbate monolayer saturation concentration (mg/L)
C_{BET}	BET adsorption isotherm relating to the energy of surface interaction (L/mg)
d	Interlayer spacing (m)
ε	Dubinin–Radushkevich isotherm constant
E	mean free energy (kJ/mol)
g	Redlich–Peterson isotherm exponent
ΔG°	Gibbs energy change (kJ/mol)
k	MacMillan–Teller (MET) isotherm constant
K_{ad}	Dubinin–Radushkevich isotherm constant ($\mathrm{mol}^2/\mathrm{kJ}^2$)
K_D	Hill constant
K_F	Freundlich isotherm constant (mg/g) $(\mathrm{dm}^3/\mathrm{g})^n$ related to adsorption capacity
K_{FH}	Flory–Huggins isotherm equilibrium constant (L/g)
K_L	Langmuir isotherm constant (L/mg)
K_R	Redlich–Peterson isotherm constant (L/g)
K_s	Sips isotherm model constant (L/g)
K_T	Toth isotherm constant (mg/g)
n	adsorption intensity
n_{FH}	Flory–Huggins isotherm model exponent
n_H	Hill cooperativity coefficient of the binding interaction
p	number of parameter
q_e	amount of adsorbate in the adsorbent at equilibrium (mg/g)
$q_{e,calc}$	calculated adsorbate concentration at equilibrium (mg/g)
$q_{e,meas}$	measured adsorbate concentration at equilibrium (mg/g)
q_s	theoretical isotherm saturation capacity (mg/g)
q_{s_H}	Hill isotherm maximum uptake saturation (mg/L)
Q_o	maximum monolayer coverage capacities (mg/g)
r	inverse power of distance from the surface
r_R	Radke–Prausnitz isotherm model constant
R	universal gas constant (8.314 J/mol K)
R^2	correlation coefficient
R_L	separation factor
t	Toth isotherm constant
T	temperature (K)
θ	degree of surface coverage
α	Frenkel–Halsey–Hill isotherm constant ($\mathrm{J\,m}^r$/mole) with r is the sign of inverse power of distance from the surface
β_R	Radke–Prausnitz isotherm model exponent
β_S	Sips isotherm model exponent

Meanwhile, linear least-squares method is a traditional linearly transformed approach widely adopted to determine the isotherm parameters or the most fitted model, primarily subjected to its goodness fit to the experimental data, with the magnitude regression correlation coefficients that close to unity [26]. Nevertheless, a substantial constriction related to the linearized isotherm expressions has recently been pointed out, which produce a vast amount of different outcomes, implicitly alter the error structure, violate the error variance and normality assumptions of standard least squares, leading to the bias of the adsorption data [27,28]. Depending on the way the adsorptive equation is linearized, the error distribution changes worse. This has attested the utilization of non-linearized models in conjunction with a number of error analysis techniques [29–31]. With the aforementioned, this bibliographic review attempts to postulate a platform in describing the distinct properties, development and potential applications of adsorption isotherm systems. The present work is aimed at evaluating their accuracy and consistency in parameters prediction or estimation. The extent of the error functions together with its comprehensive literature comparisons has been highlighted and outlined, to familiarize the knowledge deficiencies regarding non-linearized adsorption isotherms.

2. Adsorption isotherms models

In general, an adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH [32,33]. Adsorption equilibrium (the ratio between the adsorbed amount with the remaining in the solution) is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration [30,34]. Typically, the mathematical correlation, which constitutes an important role towards the modeling analysis, operational design and applicable practice of the adsorption systems, is usually depicted by graphically expressing the solid-phase against its residual concentration [35].

Its physicochemical parameters together with the underlying thermodynamic assumptions provide an insight into the adsorption mechanism, surface properties as well as the degree of affinity of the adsorbents [36].

Over the years, a wide variety of equilibrium isotherm models (Langmuir, Freundlich, Brunauer–Emmett–Teller, Redlich–Peterson, Dubinin–Radushkevich, Temkin, Toth, Koble–Corrigan, Sips, Khan, Hill, Flory–Huggins and Radke–Prausnitz isotherm), have been formulated in terms of three fundamental approaches [37]. Kinetic consideration is the first approach to be referred. Hereby, adsorption equilibrium is defined being a state of dynamic equilibrium, with both adsorption and desorption rates are equal [38]. Whereas, thermodynamics, being a base of the second approach, can provide a framework of deriving numerous forms of adsorption isotherm models [39,40], and potential theory, as the third approach, usually conveys the main idea in the generation of characteristic curve [41]. However, an interesting trend in the isotherm modeling is the derivation in more than one approach, thus directing to the difference in the physical interpretation of the model parameters [42].

2.1. Two parameter isotherms

2.1.1. Langmuir isotherm model

Langmuir adsorption isotherm, originally developed to describe gas–solid-phase adsorption onto activated carbon, has traditionally been used to quantify and contrast the performance of different bio-sorbents [38]. In its formulation, this empirical model assumes monolayer adsorption (the adsorbed layer is one molecule in thickness), with adsorption can only occur at a finite (fixed) number of definite localized sites, that are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites [43]. In its derivation, Langmuir isotherm refers to homogeneous adsorption, which each molecule possess constant enthalpies and sorption activation energy (all sites possess equal affinity for the adsorbate) [44], with no transmigration of the adsorbate in the plane of the surface [45].

Graphically, it is characterized by a plateau, an equilibrium saturation point where once a molecule occupies a site, no further adsorption can take place [33,46]. Moreover, Langmuir theory has related rapid decrease of the intermolecular attractive forces to the rise of distance. The mathematical expression of Langmuir isotherm models are illustrated in Table 1. Hereby, a dimensionless constant, commonly known as separation factor (R_L) defined by Webber and Chakkravorti [47] can be represented as:

$$R_L = \frac{1}{1 + K_L C_o} \tag{1}$$

where K_L (L/mg) refers to the Langmuir constant and C_o is denoted to the adsorbate initial concentration (mg/L). In this context, lower R_L value reflects that adsorption is more favourable. In a deeper explanation, R_L value indicates the adsorption nature to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

2.1.2. *Freundlich isotherm model*

Freundlich isotherm [48] is the earliest known relationship describing the non-ideal and reversible adsorption, not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface [49]. Historically, it is developed for the adsorption of animal charcoal, demonstrating that the ratio of the adsorbate onto a given mass of adsorbent to the solute was not a constant at different solution concentrations [19]. In this perspective, the amount adsorbed is the summation of adsorption on all sites (each having bond energy), with the stronger binding sites are occupied first, until adsorption energy are exponentially decreased upon the completion of adsorption process [50].

At present, Freundlich isotherm is widely applied in heterogeneous systems especially for organic compounds or highly interactive species on activated carbon and molecular sieves. The slope ranges between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. Whereas, a value below unity implies chemisorptions process where $1/n$ above one is an indicative of cooperative adsorption [51]. Its linearized and non-linearized equations are listed in Table 1. Recently, Freundlich isotherm is criticized for its limitation of lacking a fundamental thermodynamic basis, not approaching the Henry's law at vanishing concentrations [23].

2.1.3. *Dubinin–Radushkevich isotherm model*

Dubinin–Radushkevich isotherm [52], is an empirical model initially conceived for the adsorption of subcritical vapors onto micropore solids following a pore filling mechanism. It is generally applied to express the adsorption mechanism [53] with a Gaussian energy distribution onto a heterogeneous surface [54]. The model has often successfully fitted high solute activities and the intermediate range of concentrations data well, but has unsatisfactory asymptotic properties and does not predict the Henry's law at low pressure [55]. The approach was usually applied to distinguish the physical and chemical adsorption of metal ions [41], with its mean free energy, E per molecule of adsorbate (for removing a molecule from its location in the sorption space to the infinity) can be computed by the relationship [56]:

$$E = \left[\frac{1}{\sqrt{2B_{DR}}}\right] \tag{2}$$

where B_{DR} is denoted as the isotherm constant. Meanwhile, the parameter ε can be correlated as:

$$\varepsilon = RT \ \ln \left[1 + \frac{1}{C_e}\right] \tag{3}$$

where R, T and C_e represent the gas constant (8.314 J/mol K), absolute temperature (K) and adsorbate equilibrium concentration (mg/L), respectively. One of the unique features of the Dubinin–Radushkevich isotherm model lies on the fact that it is temperature-dependent, which when adsorption data at different temperatures are plotted as a function of logarithm of amount adsorbed vs the square of potential energy, all suitable data will lie on the same curve, named as the characteristic curve.

2.1.4. *Temkin isotherm model*

Temkin isotherm is the early model describing the adsorption of hydrogen onto platinum electrodes within the acidic solutions. The isotherm [57] contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage [58]. As implied in the equation, its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy). Temkin equation is excellent for predicting the gas phase equilibrium (when organization in a tightly packed structure with identical orientation is not necessary), conversely complex adsorption systems including the liquid-phase adsorption isotherms are usually not appropriate to be represented [59].

2.1.5. *Flory–Huggins isotherm model*

Flory–Huggins isotherm model [60], which occasionally deriving the degree of surface coverage characteristics of adsorbate onto adsorbent, can express the feasibility and spontaneous nature of an adsorption process. In this respect, θ is the degree of surface coverage, where K_{FH} and n_{FH} are the indication of its equilibrium constant and model exponent. Its equilibrium constant, K_{FH} that used for the calculation of spontaneity free Gibbs energy, is related to the equation [43]:

$$\Delta G^{\circ} = -RT \ \ln(K_{FH}) \tag{4}$$

2.1.6. *Hill isotherm model*

Hill equation [61], that originated from the NICA [62] model, was postulated to describe the binding of different species onto homogeneous substrates. The model assumes that adsorption is a cooperative phenomenon, with the ligand binding ability at one site on the macromolecule, may influence different binding sites on the same macromolecule [63].

2.2. *Three parameter isotherms*

2.2.1. *Redlich–Peterson isotherm model*

Redlich–Peterson isotherm [64] is a hybrid isotherm featuring both Langmuir and Freundlich isotherms, which incorporate three parameters into an empirical equation [65]. The model has a linear dependence on concentration in the numerator and an exponential function in the denominator [66] to represent adsorption equilibria over a wide concentration range, that can be applied either

Table 1
Lists of adsorption isotherms models.

Isotherm	Nonlinear form	Linear form	Plot	Reference
Langmuir	$q_e = \frac{Q_o b C_e}{1+bC_e}$	$\frac{C_e}{q_e} = \frac{1}{bQ_o} + \frac{C_e}{Q_o}$	$\frac{C_e}{q_e}$ vs C_e	[38]
		$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_o C_e}$	$\frac{1}{q_e}$ vs $\frac{1}{C_e}$	
		$q_e = Q_o - \frac{q_e}{bC_e}$	q_e vs $\frac{q_e}{bC_e}$	
		$\frac{q_e}{C_e} = bQ_o - bq_e$	$\frac{q_e}{C_e}$ vs q_e	
Freundlich	$q_e = K_F C_e^{1/n}$	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	$\log q_e$ vs $\log C_e$	[48]
Dubinin–Radushkevich	$q_e = (q_s) \exp(-k_{ad}\varepsilon^2)$	$\ln(q_e) = \ln(q_s) - k_{ad}\varepsilon^2$	In(q_e) vs ε^2	[52]
Tempkin	$q_e = \frac{RT}{b_T} \ln A_T C_e$	$q_e = \frac{RT}{b_T} \ln A_T + \left(\frac{RT}{b_T}\right) \ln C_e$	q_e vs $\ln C_e$	[57]
Flory–Huggins	$\frac{\theta}{C_o} = K_{FH}(1-\theta)^{n_{FH}}$	$\log\left(\frac{\theta}{C_o}\right) = \log(K_{FH}) + n_{FH}\log(1-\theta)$	$\log\left(\frac{\theta}{C_o}\right)$ vs $\log(1-\theta)$	[60]
Hill	$q_e = \frac{q_{s_H} C_e^{n_H}}{K_D + C_e^{n_H}}$	$\log\left(\frac{q_e}{q_{s_H} - q_e}\right) = n_H \log(C_e) - \log(K_D)$	$\log\left(\frac{q_e}{q_{s_H} - q_e}\right)$ vs $\log(C_e)$	[61]
Redlich–Peterson	$q_e = \frac{K_R C_e}{1 + a_R C_e^{g}}$	$\ln\left(K_R \frac{C_e}{q_e} - 1\right) = g\ln(C_e) + \ln(a_R)$	$\ln\left(K_R \frac{C_e}{q_e} - 1\right)$ vs $\ln(C_e)$	[64]
Sips	$q_e = \frac{K_s C_e^{\beta_S}}{1 + a_S C_e^{\beta_S}}$	$\beta_S \ln(C_e) = -\ln\left(\frac{K_s}{q_e}\right) + \ln(a_S)$	$\ln\left(\frac{K_s}{q_e}\right)$ vs $\ln(C_e)$	[68]
Toth	$q_e = \frac{K_T C_e}{(a_T + C_e)^{1/t}}$	$\ln\left(\frac{q_e}{K_T}\right) = \ln(C_e) - \frac{1}{t}\ln(a_T + C_e)$	$\ln\left(\frac{q_e}{K_T}\right)$ vs $\ln(C_e)$	[69]
Koble–Corrigan	$q_e = \frac{AC_e^n}{1 + BC_e^n}$	$\frac{1}{q_e} = \frac{1}{AC_e^n} + \frac{B}{A}$	–	[70]
Khan	$q_e = \frac{q_s b_K C_e}{(1 + b_K C_e)^{a_K}}$	–	–	[71]
Radke–Prausnitz	$q_e = \frac{a_{RP} r_R C_e^{\beta_R}}{a_{RP} + r_R C_e^{\beta_R - 1}}$	–	–	[43]
BET	$q_e = \frac{q_s C_{\mathrm{BET}} C_e}{(C_s - C_e)[1 + (C_{\mathrm{BET}} - 1)(C_e/C_s)]}$	$\frac{C_e}{q_e(C_s - C_e)} = \frac{1}{q_s C_{\mathrm{BET}}} + \frac{(C_{\mathrm{BET}} - 1)}{q_s C_{\mathrm{BET}}} \frac{C_e}{C_s}$	$\frac{C_e}{q_e(C_s - C_e)}$ vs $\frac{C_e}{C_s}$	[73]
FHH	$\ln\left(\frac{C_e}{C_s}\right) = -\frac{\alpha}{RT}\left(\frac{q_s}{q_e d}\right)^r$	–	–	[74]
MET	$q_e = q_s\left(\frac{k}{\ln(C_s/C_e)}\right)^{1/3}$	–	–	[75]

in homogeneous or heterogeneous systems due to its versatility [22]. Typically, a minimization procedure is adopted in solving the equations by maximizing the correlation coefficient between the experimental data points and theoretical model predictions with solver add-in function of the Microsoft excel [26]. In the limit, it approaches Freundlich isotherm model at high concentration (as the exponent β tends to zero) and is in accordance with the low concentration limit of the ideal Langmuir condition (as the β values are all close to one) [67].

2.2.2. *Sips isotherm model*

Sips isotherm [68] is a combined form of Langmuir and Freundlich expressions deduced for predicting the heterogeneous adsorption systems [53] and circumventing the limitation of the rising adsorbate concentration associated with Freundlich isotherm model. At low adsorbate concentrations, it reduces to Freundlich isotherm; while at high concentrations, it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm. As a general rule, the equation parameters are governed mainly by the operating conditions such as the alteration of pH, temperature and concentration [45].

2.2.3. *Toth isotherm model*

Toth isotherm model [69], is another empirical equation developed to improve Langmuir isotherm fittings (experimental data), and useful in describing heterogeneous adsorption systems, which satisfying both low and high-end boundary of the concentration [43]. Its correlation presupposes an asymmetrical quasi-Gaussian energy distribution, with most of its sites has an adsorption energy lower than the peak (maximum) or mean value [23].

2.2.4. *Koble–Corrigan isotherm model*

Similar to the Sips isotherm model, Koble–Corrigan isotherm [70] is a three-parameter equation, which incorporated both Langmuir and Freundlich isotherm models for representing the equilibrium adsorption data. The isotherm constants, A, B and n are evaluated from the linear plot using a trial and error optimization.

2.2.5. *Khan isotherm model*

Khan isotherm [71] is a generalized model suggested for the pure solutions, with b_K and a_K are devoted to the model constant and model exponent. At relatively high correlation coefficients and minimum ERRSQ or chi-square values, its maximum uptake values can be well determined [72].

2.2.6. *Radke–Prausnitz isotherm model*

The correlation of Radke–Prausnitz isotherm is usually predicted well by the high RMSE and chi-square values. Its model exponent is represented by β_R, where a_R and r_R are referred to the model constants [43].

2.3. *Multilayer physisorption isotherms*

Brunauer–Emmett–Teller (BET) [73] isotherm is a theoretical equation, most widely applied in the gas–solid equilibrium systems. It was developed to derive multilayer adsorption systems

Table 2
Lists of error functions.

Error function	Abbreviation	Definition/expression	Reference
Sum squares errors	ERRSQ/SSE	$\sum_{i=1}^{n}(q_{e,calc}-q_{e,meas})_i^2$	[80]
Hybrid fractional error function	HYBRID	$\frac{100}{n-p}\sum_{i=1}^{n}\left[\frac{q_{e,meas}-q_{e,calc}}{q_{e,meas}}\right]_i$	[66]
Average relative error	ARE	$\frac{100}{n}\sum_{i=1}^{n}\left\lvert\frac{q_{e,meas}-q_{e,calc}}{q_{e,meas}}\right\rvert_i$	[82]
Sum of absolute error	EABS	$\sum_{i=1}^{n}\lvert q_{e,meas}-q_{e,calc}\rvert_i$	[83]
Marquardt's percent standard deviation	MPSD	$100\sqrt{\frac{1}{n-p}\sum_{i=1}^{n}\left(\frac{q_{e,meas}-q_{e,calc}}{q_{e,meas}}\right)_i^2}$	[84]
The coefficient of determination	R^2	$r^2=\frac{(q_{e,meas}-\overline{q_{e,calc}})^2}{\sum(q_{e,meas}-\overline{q_{e,calc}})^2+(q_{e,meas}-q_{e,calc})^2}$	[78]
Spearman's correlation coefficient	r_s	$1-\frac{6\sum_{i=1}^{n}(q_{e,meas}-q_{e,calc})_i^2}{n(n-1)^2}$	[78]
Standard deviation of relative errors	s_{RE}	$\sqrt{\frac{\sum_{i=1}^{n}[(q_{e,meas}-q_{e,calc})_i-\mathrm{ARE}]_i^2}{n-1}}$	[78]
Nonlinear chi-square test	χ^2	$\sum_{i=1}^{n}\frac{(q_{e,calc}-q_{e,meas})^2}{q_{e,meas}}$	[78]
Coefficient of non-determination	K_2	–	[80]
Sum of normalized errors	SNE	–	[88]

with relative pressure ranges from 0.05 to 0.30 corresponding to a monolayer coverage lying between 0.50 and 1.50. Its extinction model related to liquid–solid interface is exhibited as:

$$q_e=\frac{q_s C_{\mathrm{BET}} C_e}{(C_s-C_e)[1+(C_{\mathrm{BET}}-1)(C_e/C_s)]} \tag{5}$$

where C_{BET}, C_s, q_s and q_e are the BET adsorption isotherm (L/mg), adsorbate monolayer saturation concentration (mg/L), theoretical isotherm saturation capacity (mg/g) and equilibrium adsorption capacity (mg/g), respectively. As C_{BET} and C_{BET} (C_e/C_s) are much greater than 1, the equation is simplified as:

$$q_e=\frac{q_s}{1-(C_e/C_s)} \tag{6}$$

Meanwhile, Frenkel–Halsey–Hill (FHH) isotherm [74], another multilayer adsorption derivation from the potential theory may be written as:

$$\ln\left(\frac{C_e}{C_s}\right)=-\frac{\alpha}{RT}\left(\frac{q_s}{q_e d}\right)^r \tag{7}$$

where d, α and r are the sign of the interlayer spacing (m), isotherm constant (J m^r/mole) and inverse power of distance from the surface (about 3), respectively. Similarly, MacMillan–Teller (MET) isotherm [75], an adsorption model interpreted from the inclusion of surface tension effects in the BET isotherm is termed as:

$$q_e=q_s\left(\frac{k}{\ln(C_s/C_e)}\right)^{1/3} \tag{8}$$

where k is an isotherm constant. When C_s/C_e is approaching unity, the logarithmic term can be approximated as:

$$q_e=q_s\left(\frac{kC_e}{C_s-C_e}\right)^{1/3} \tag{9}$$

As a note, the empirical isotherm is reasonable fit to Frenkel–Halsey–Hill (FHH) or MacMillan–Teller (MET) isotherms for relative pressures higher than 0.8 and approximately Brunauer–Emmett–Teller (BET) isotherm for relative pressures lower than 0.35.

3. Error functions

Within recent decades, linear regression has been one of the most viable tool defining the best-fitting relationship [76] quantifying the distribution of adsorbates, mathematically analyzing the adsorption systems [77] and verifying the consistency and theoretical assumptions of an isotherm model [78]. Due to the inherent bias resulting from the transformation which riding towards a diverse form of parameters estimation errors and fits distortion, several mathematically rigorous error functions (sum square error, Hybrid fractional error function, sum of absolute errors, average relative error, Marquardt's percent standard deviation, coefficient of determination, Spearman's correlation coefficient, standard deviation of relative errors, nonlinear chi-square test, coefficient of non-determination and sum of normalized errors) (Table 2) have lately drastically been addressed and confronted [79]. Concomitant with the development of computer technology in the 1980s, the progression of the nonlinear isotherm modeling has extensively been facilitated and motivated [78]. Contrary to the linearization models, nonlinear regression usually involves the minimization or maximization of error distribution (between the experimental data and the predicted isotherm) based on its convergence criteria [79].

3.1. Sum square error (ERRSQ)

Despite ERRSQ is the most widely used error function [80], at higher end of the liquid-phase concentration ranges, the magnitude and squares of the errors tend to increase, illustrating a better fit for the isotherm parameters derivation [81].

3.2. Hybrid fractional error function (HYBRID)

The error function was developed to improve ERRSQ fit at low concentrations. Hereby, each ERRSQ value is divided by the experimental solid-phase concentration with a divisor included in the system as a term for the number of degrees of freedom (the number of data points minus the number of parameters within the isotherm equation) [66].

3.3. Average relative error (ARE)

ARE model [82] which indicates a tendency to under or overestimate the experimental data, attempts to minimize the fractional error distribution across the entire studied concentration range.

3.4. Sum of absolute errors (EABS)

The approach is similar to the ERRSQ function, with an increase in the errors will provide a better fit, leading to the bias towards the high concentration data [83].

3.5. Marquardt's percent standard deviation (MPSD)

Marquardt's percent standard deviation (MPSD) error function [84] has previously practiced by a number of researchers in the isotherm studies [26,83,85,86]. According to the number of degrees of freedom in the system, it is similar to some respects of a modified geometric mean error distribution [87].

3.6. Coefficient of determination (R^2), Spearman's correlation coefficient (r_s) and standard deviation of relative errors (s_{RE})

Coefficient of determination, which represents the percentage of variability in the dependent variable (the variance about the mean) is employed to analyze the fitting degree of isotherm and kinetic models with the experimental data [88]. Its value may vary from 0 to 1 [89] where Spearman's correlation coefficient and standard deviation of relative errors are individually determined to evaluate the global correlation and the dispersion of its relative errors [78].

3.7. Nonlinear chi-square test (χ^2)

Nonlinear chi-square test is a statistical tool necessary for the best fit of an adsorption system, obtained 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). Small χ^2 value indicates its similarities while a larger number represents the variation of the experimental data [78].

3.8. Coefficient of non-determination (K_2)

Another statistical term, coefficient of non-determination, is much useful in describing the extent relationship between the transformed experimental data and the predicted isotherms, and minimization of the error distribution [90].

3.9. Sum of normalized errors (SNE)

Consequence of different error criteria is likely to produce different sets of isotherm parameters, a standard procedure normalizing and combining various errors for better and meaningful comparison between the parameter sets (for the single isotherm model) is adopted [44,78,83,91]. The calculation orientation is revealed as follows:

(a) Selection of an isotherm model and error function, and determination of the adjustable parameters which minimize the error function.
(b) Determination of all other error functions by referring to the parameter set.
(c) Computation of other parameter sets associated with their error function values (initiation of the procedure by minimizing the error function).
(d) Normalization and selection of the maximum parameter sets with respect to the largest error measurement.
(e) Summation of each parameter set which generates the minimum normalization error.

4. Literature review on applications of linear and nonlinear forms of isotherm models

An accuracy of an isotherm model is generally a function of the number of independent parameters, while its popularity in relation to the process application is an indicative of its mathematical simplicity [37]. Undoubtedly, linear regression analysis has frequently been employed in accessing the quality of fits and adsorption performance [44], primarily owing to its wide usefulness in a variety of adsorption data [91] and partly reflecting the appealing simplicity of its equations [92]. However, during the last few years, a development interest in the utilization of nonlinear optimization modeling has been noted [65]. A number of researches have been advocated to investigate the applicability of linear or nonlinear isotherm models in describing the adsorption of dyes, heavy metals and organic pollutants onto activated carbons, zeolites, chitosans, bentonites, montmorillonites, kaolinites and a list of low-cost adsorbents (Table 3).

In 1984, Harter [103] had firstly examined Langmuir isotherm model in an ions adsorption system (adsorption of ion phosphate, zinc, and copper by soil). Without sufficient ranges of adsorbate concentration, he emphasized that the estimation of maximum adsorption capacity could be quite misleading (in error by 50% or more), reducing the variability of its linearity. In 1988, Persoff and Thomas [104] had proposed the use of nonlinear least-squares (NLLS) curve-fitting method for determination of the Michaelis–Menten and Langmuir adsorption isotherm constants (from the experimental data). From the application, they concluded that weighted NLLS yielded a more precise and accurate estimation. More recently, similar observations have been reported by several researchers [24,63,78,79,96,101]. The authors suggested that the linearized equations apparently generate real problems and errors arising from the complexities and complications for simultaneous transformation of data, leading to the violation of theories behind the isotherms.

In certain cases, it has been illustrated that a different axis setting (different linearized models) would alter the regression results, influencing its consistency and accuracy [97]. Such tendency (more statistical functions are valid for nonlinear than linear analysis) could be directly proportional to the distortion of the experimental errors, creating an inherent errors estimation problem which limits the validity of the studied tools [35]. Moreover, linear analysis method assumes that the scatter vertical points around the line follows a Gaussian distribution, and the error distribution is uniform at every value of the liquid-phase residual concentration (X-axis) [89]. Nonetheless, such behavior is practically impossible with the equilibrium relationships (since isotherm models had nonlinear shape),

Table 3
Previous researches of the linear and nonlinear isotherm studies.

Adsorbent	Adsorbate	Isotherm models	Determination	Preference types	Reference
Wheat bran	Cadmium ions	Freundlich, Langmuir	R^2	Nonlinear	[15]
Babasse fly ash	Orange-G dyeMethyl Violet dye	Freundlich, Langmuir, Redlich–Peterson, Temkin, Dubnin–Radushkevich, Elovich	R^2	Nonlinear	[19]
Peat	Divalent metal ions	Freundlich, Langmuir, Redlich–Peterson, Temkin, Dubnin–Radushkevich, Toth	R^2, ERRSQ, ARE, HYBRID, MPSD, SAE, SNE	Both	[23]
Water hyacinth	Methylene blue dye	Freundlich, Langmuir	R^2	Nonlinear	[24]
Rice husk	Safranin	Freundlich, Langmuir, Redlich–Peterson	R^2	Nonlinear	[30]
Fibrous biomass	Direct Solophenyl Brown dye	Langmuir, Redlich–Peterson, Temkin, Dubnin–Radushkevich, Elovich	ARED, EABS, MPSD, HYBRID, R^2, RESID	Nonlinear	[35]
Iron oxide-coated cement	Arsenic	Freundlich, Langmuir, Redlich–Peterson, Temkin	SAE, ARE, HYBRID, MPSD, EABS	Both	[44]
Montmorillonite, kaolinite	Heavy metals	Freundlich, Langmuir	R^2	Both	[55]
Yeast biomass	Ochratoxin A	Freundlich, Langmuir, BET, Redlich–Peterson	R^2, EABS, HYBRID, ARE, SAE, MPSD	Nonlinear	[63]
Activated carbon	Malachite green dye	Freundlich, Langmuir, Redlich–Peterson	R^2	Nonlinear	[76]
Activated carbon	Tetrahydrothiophene	Langmuir	R^2, r_s, EABS, RSS, ARE, s_{RE}, HYBRID	Nonlinear	[78]
Activated carbon	Methylene blue	Freundlich, Langmuir, Redlich–Peterson	R^2, ERRSQ, ARE, HYBRID, MPSD, EABS	Nonlinear	[79]
Activated carbon	Malachite green dye	Freundlich, Langmuir, Redlich–Peterson	R^2	Nonlinear	[80]
Rice husk ash	Brilliant green dye	Freundlich, Langmuir, Redlich–Peterson, Temkin, Dubnin–Radushkevich	SSE, SAE, ARE, HYBRID, MPSD	Both	[81]
Chitosan	Lead	Freundlich, Langmuir, Redlich–Peterson	ERRSQ, ARE, HYBRID, MPSD, EABS	Nonlinear	[83]
Zeolite	Ammonium	Freundlich, Langmuir	R^2	Nonlinear	[88]
Activated carbon	Basic dyes	Freundlich, Langmuir, Redlich–Peterson	R^2	Nonlinear	[89]
Activated carbon	Basic red 9	Freundlich, Langmuir, Redlich–Peterson	R^2, EABS HYBRID, ARE, SAE, MPSD	Nonlinear	[90]
Alumina cement granules	Fluoride	Freundlich, Langmuir, Dubnin–Radushkevich	R^2, SNE, EABS HYBRID, ARE, SAE, MPSD	Both	[92]
Eucalyptus bark	Cadmium ions	Freundlich, Langmuir	R^2	Nonlinear	[93]
Zeolite	Methylene blue	Freundlich, Koble–Corrigan, Langmuir, Redlich–Peterson, Temkin	SAE, ARE, ARS, EABS	Both	[94]
Bagasse fly ash	Brilliant green dye	Freundlich, Langmuir, Redlich–Peterson, Temkin, Dubnin–Radushkevich	SSE, SAE, ARE, HYBRID, MPSD	Both	[95]
Activated carbon	Basic blue 9 dye	Freundlich, Langmuir, Redlich–Peterson	R^2, ERRSQ, χ^2	Nonlinear	[96]
Sugarcane dust	Basic dyes	Freundlich, Langmuir, Redlich–Peterson	R^2 χ^2	Nonlinear	[97]
Fly ash	Dyes	Freundlich, Langmuir	R^2	Nonlinear	[98]
Rice husk	Bismarck brown dye	Freundlich, Langmuir, Redlich–Peterson	R^2	Nonlinear	[99]
Bentonite	Strontium	Freundlich, Langmuir	RMSE	Nonlinear	[100]
Ca-alginate beads	Zinc (II) ions	Freundlich, Langmuir	R^2	Nonlinear	[101]
Mansonia wood sawdust	Methyl violet	Freundlich, Langmuir, Redlich–Peterson	R^2	Both	[102]

as the error distribution tends to get altered after transforming into a linearized order [26].

In another study, linearization isotherms models (Langmuir and Freundlich isotherm models) have been demonstrated inappropriate in predicting the goodness of fit for a particular set of conditions [95], and unable for providing a fundamental understanding of the ions adsorption systems, resulting in an improper conclusion. On the contrary, the nonlinear isotherm models are conducted on the same abscissa and ordinate, thus avoiding such drawbacks of linearization [92]. Nevertheless, a few researchers [23,44,94,95,102] also indicated the similarities and consistency of both linear and nonlinear isotherms, lying into the same error distributions and structures. Under such conditions, it would be more rational and reliable to interpret adsorption data through a process of linear and nonlinear regression [92]. Irrespective of its technique (either the linear or the nonlinear method), the availability and usefulness of the equilibrium data should be sufficient enough to effectively represent an efficient and complete isotherm model [76].

5. Conclusion

The past 10 years has seen a developing interest in the preparation of low-cost adsorbents as alternatives to activated carbons in water and wastewater treatment processes. To date, limited success of adsorbents in the field applications has raised apprehensions over the use of adsorption capacity (generated from equilibrium data) as a measure of their effectiveness in drinking water treatment. Over the past few decades, linear regression has been developed as a major option in designing the adsorption systems. However, recent investigations have indicated the growing discrepancy (between the predictions and experimental data) and disability of the model, propagating towards a different outcome. Despite this obvious inherent bias of the model, linearization remains a confident option in the literature, applied in over 95% of the liquid-phase adsorption systems. Hence, the next real challenge in the adsorption field is the identification and clarification of both isotherm models in various adsorption systems. Further explorations on developing in this area are recommended.

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References

[1] K.Y. Foo, B.H. Hameed, Utilization of biodiesel waste as a renewable resource for activated carbon: application to environmental problems, Renew. Sust. Energy Rev. 13 (9) (2009) 2495–2504.
[2] K.Y. Foo, B.H. Hameed, Value-added utilization of oil palm ash: a superior recycling of the industrial agricultural waste, J. Hazard. Mater. (2009), doi:10.1016/j.jhazmat.2009.07.091.
[3] N. Marti, A. Bouzas, A. Seco, J. Ferrer, Struvite precipitation assessment in anaerobic digestion processes, Chem. Eng. J. 141 (1–3) (2008) 67–74.
[4] Z. Liang, Y.X. Wang, Y. Zhou, H. Liu, Coagulation removal of melanoidins from biologically treated molasses wastewater using ferric chloride, Chem. Eng. J. 152 (1) (2009) 88–94.
[5] R. Bürger, F. Concha, F.M. Tiller, Applications of the phenomenological theory to several published experimental cases of sedimentation processes, Chem. Eng. J. 80 (1–3) (2000) 105–117.
[6] A.L. Macfarlane, R. Prestidge, M.M. Farid, J.J.J. Chen, Dissolved air flotation: a novel approach to recovery of organosolv lignin, Chem. Eng. J. 148 (1) (2009) 15–19.
[7] T. Deuschle, U. Janoske, M. Piesche, A CFD-model describing filtration, regeneration and deposit rearrangement effects in gas filter systems, Chem. Eng. J. 135 (1–2) (2008) 49–55.
[8] H. Valdés, J. Romero, J. Sanchez, S. Bocquet, G.M. Rios, F. Valenzuela, Characterization of chemical kinetics in membrane-based liquid–liquid extraction of molybdenum(VI) from aqueous solutions, Chem. Eng. J. 151 (1–3) (2009) 333–341.
[9] K.Y. Foo, B.H. Hameed, A short review of activated carbon assisted electrosorption process: An overview, current stage and future prospects, J. Hazard. Mater. 171 (2009) 54–60.
[10] G.B. Zhu, Y.Z. Peng, B. Ma, Y. Wang, C.Q. Yin, Optimization of anoxic/oxic step feeding activated sludge process with fuzzy control model for improving nitrogen removal, Chem. Eng. J. 151 (1–3) (2009) 195–201.
[11] H. Delmas, C. Creanga, C. Julcour-Lebigue, A.M. Wilhelm, AD–OX: a sequential oxidative process for water treatment—adsorption and batch CWAO regeneration of activated carbon, Chem. Eng. J. 152 (2009) 189–194.
[12] M.A. Abdullah, L. Chiang, M. Nadeem, Comparative evaluation of adsorption kinetics and isotherms of a natural product removal by Amberlite polymeric adsorbents, Chem. Eng. J. 146 (3) (2009) 370–376.
[13] N. Miladinovic, L.R. Weatherley, Intensification of ammonia removal in a combined ion-exchange and nitrification column, Chem. Eng. J. 135 (1–2) (2008) 15–24.
[14] K.Y. Foo, B.H. Hameed, An overview of landfill leachate treatment via activated carbon adsorption process, J. Hazard. Mater. (2009), doi:10.1016/j.jhazmat.2009.06.038.
[15] L. Nouri, I. Ghodbane, O. Hamdaoui, M. Chiha, Batch sorption dynamics and equilibrium for the removal of cadmium ions from aqueous phase using wheat bran, J. Hazard. Mater. 149 (2007) 115–125.
[16] D. Mohan, C.U. Pittman Jr., Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water, J. Hazard. Mater. 137 (2006) 762–811.
[17] E.N. El Qada, S.J. Allen, G.M. Walker, Influence of preparation conditions on the characteristics of activated carbons produced in laboratory and pilot scale systems, Chem. Eng. J. 142 (2008) 1–13.
[18] K.Y. Foo, B.H. Hameed, Recent developments in the preparation and regeneration of activated carbons by microwaves, Adv. Colloid Interface Sci. 149 (2009) 19–27.
[19] Md. Ahmaruzzaman, Adsorption of phenolic compounds on low-cost adsorbents: a review, Adv. Colloid Interface Sci. 143 (1–2) (2008) 48–67.
[20] D. Kalderis, D. Koutoulakis, P. Paraskeva, E. Diamadopoulos, E. Otal, J.O. del Valle, C. Fernández-Pereira, Adsorption of polluting substances on activated carbons prepared from rice husk and sugarcane bagasse, Chem. Eng. J. 144 (1) (2008) 42–50.
[21] V.V. Srivastava, M.M. Swamy, I.D. Mall, B. Prasad, I.M. Mishra, Adsorptive removal of phenol by bagasse fly ash and activated carbon: equilibrium, kinetics and thermodynamics, Colloids Surf. A 272 (2006) 89–104.
[22] F. Gimbert, N. Morin-Crini, F. Renault, P.M. Badot, G. Crini, Adsorption isotherm models for dye removal by cationized starch-based material in a single component system: error analysis, J. Hazard. Mater. 157 (2008) 34–46.
[23] Y.S. Ho, J.F. Porter, G. Mckay, Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems, Water Air Soil Pollut. 141 (2002) 1–33.
[24] M.I. El-Khaiary, Least-squares regression of adsorption equilibrium data: comparing the options, J. Hazard. Mater. 158 (2008) 73–87.
[25] G. Thompson, J. Swain, M. Kay, C.F. Forster, The treatment of pulp and paper mill effluent: a review, Bioresour. Technol. 77 (2001) 275–286.
[26] Y.C. Wong, Y.S. Szeto, W.H. Cheung, G. McKay, Adsorption of acid dyes on chitosan-equilibrium isotherm analyses, Process Biochem. 39 (2004) 693–702.
[27] S. Hong, C. Wen, J. He, F.X. Gan, Y.S. Ho, Adsorption thermodynamics of Methylene Blue onto bentonite, J. Hazard. Mater. (2009), doi:10.1016/j.jhazmat.2009.01.014.
[28] Y.S. Ho, Selection of optimum sorption isotherm, Carbon 42 (2004) 2113–2130.
[29] R.P. Han, Y. Wang, W.H. Zou, Y.F. Wang, J. Shi, Comparison of linear and non-linear analysis in estimating the Thomas model parameters for methylene blue adsorption onto natural zeolite in fixed-bed column, J. Hazard. Mater. 145 (2007) 331–335.
[30] K.V. Kumar, S. Sivanesan, Sorption isotherm for safranin onto rice husk: comparison of linear and non-linear methods, Dyes Pigments 72 (2007) 130–133.
[31] Y.S. Ho, Second-order kinetic model for the sorption of cadmium onto tree fern: a comparison of linear and non-linear methods, Water Res. 40 (2006) 119–125.
[32] G. Limousin, J.P. Gaudet, L. Charlet, S. Szenknect, V. Barthes, M. Krimissa, Sorption isotherms: a review on physical bases, modeling and measurement, Appl. Geochem. 22 (2007) 249–275.
[33] S.J. Allen, G. Mckay, J.F. Porter, Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems, J. Colloid Interface Sci. 280 (2004) 322–333.
[34] M. Ghiaci, A. Abbaspur, R. Kia, F. Seyedeyn-Azad, Equilibrium isotherm studies for the sorption of benzene, toluene, and phenol onto organo-zeolites and as-synthesized MCM-41, Sep. Purif. Technol. 40 (2004) 217–229.
[35] M.C. Ncibi, Applicability of some statistical tools to predict optimum adsorption isotherm after linear and non-linear regression analysis, J. Hazard. Mater. 153 (2008) 207–212.
[36] E. Bulut, M. Ozacar, I.A. Sengil, Adsorption of malachite green onto bentonite: equilibrium and kinetic studies and process design, Micropor. Mesopor. Mater. 115 (2008) 234–246.
[37] A. Malek, S. Farooq, Comparison of isotherm models for hydrocarbon adsorption on activated carbon, AIChE J. 42 (11) (1996) 3191–3201.
[38] I. Langmuir, The constitution and fundamental properties of solids and liquids, J. Am. Chem. Soc. 38 (11) (1916) 2221–2295.
[39] J.H. De Boer, The Dynamical Character of Adsorption, second ed., Oxford University Press, London, 1968.
[40] A.L. Myers, J.M. Prausnitz, Thermodynamics of mixed gas adsorption, AIChE J. 11 (1) (1965) 121–129.
[41] M.M. Dubinin, The potential theory of adsorption of gases and vapors for adsorbents with energetically non-uniform surface, Chem. Rev. 60 (1960) 235–266.
[42] D.M. Ruthven, Principles of Adsorption and Adsorption Processes, Wiley, New York, 1984.
[43] K. Vijayaraghavan, T.V.N. Padmesh, K. Palanivelu, M. Velan, Biosorption of nickel(II) ions onto Sargassum wightii: application of two-parameter and three parameter isotherm models, J. Hazard. Mater. B133 (2006) 304–308.
[44] S. Kundu, A.K. Gupta, Arsenic adsorption onto iron oxide-coated cement (IOCC): regression analysis of equilibrium data with several isotherm models and their optimization, Chem. Eng. J. 122 (2006) 93–106.
[45] A.B. Pérez-Marín, V. Meseguer Zapata, J.F. Ortuno, M. Aguilar, J. Sáez, M. Llorens, Removal of cadmium from aqueous solutions by adsorption onto orange waste, J. Hazard. Mater. B139 (2007) 122–131.
[46] E. Demirbas, M. Kobya, A.E.S. Konukman, Error analysis of equilibrium studies for the almond shell activated carbon adsorption of Cr(VI) from aqueous solutions, J. Hazard. Mater. 154 (2008) 787–794.
[47] T.W. Webber, R.K. Chakkravorti, Pore and solid diffusion models for fixed-bed adsorbers, AIChE J. 20 (1974) 228–238.
[48] H.M.F. Freundlich, Over the adsorption in solution, J. Phys. Chem. 57 (1906) 385–471.
[49] A.W. Adamson, A.P. Gast, Physical Chemistry of Surfaces, sixth ed., Wiley-Interscience, New York, 1997.
[50] J. Zeldowitsch, Adsorption site energy distribution, Acta Phys. Chim. URSS 1 (1934) 961–973.
[51] F. Haghseresht, G. Lu, Adsorption characteristics of phenolic compounds onto coal-reject-derived adsorbents, Energy Fuels 12 (1998) 1100–1107.
[52] M.M. Dubinin, L.V. Radushkevich, The equation of the characteristic curve of the activated charcoal, Proc. Acad. Sci. USSR Phys. Chem. Sect. 55 (1947) 331–337.
[53] A. Gunay, E. Arslankaya, I. Tosun, Lead removal from aqueous solution by natural and pretreated clinoptilolite: adsorption equilibrium and kinetics, J. Hazard. Mater. 146 (2007) 362–371.
[54] A. Dabrowski, Adsorption—from theory to practice, Adv. Colloid Interface Sci. 93 (2001) 135–224.
[55] O. Altin, H.O. Ozbelge, T. Dogu, Use of general purpose adsorption isotherms for heavy metal–clay mineral interactions, J. Colloid Interface Sci. 198 (1998) 130–140.

[56] J.P. Hobson, Physical adsorption isotherms extending from ultra high vacuum to vapor pressure, J. Phys. Chem. 73 (1969) 2720–2727.

[57] M.I. Tempkin, V. Pyzhev, Kinetics of ammonia synthesis on promoted iron catalyst, Acta Phys. Chim. USSR 12 (1940) 327–356.

[58] C. Aharoni, M. Ungarish, Kinetics of activated chemisorption. Part 2. Theoretical models, J. Chem. Soc. Faraday Trans. 73 (1977) 456–464.

[59] Y. Kim, C. Kim, I. Choi, S. Rengraj, J. Yi, Arsenic removal using mesoporous alumina prepared via a templating method, Environ. Sci. Technol. 38 (2004) 924–931.

[60] M. Horsfall, A.I. Spiff, Equilibrium sorption study of Al^{3+}, Co^{2+} and Ag^{2+} in aqueous solutions by fluted pumpkin (Telfairia occidentalis HOOK) waste biomass, Acta Chim. Slov. 52 (2005) 174–181.

[61] A.V. Hill, The possible effects of the aggregation of the molecules of haemoglobin on its dissociation curves, J. Physiol. (London) 40 (1910) iv–vii.

[62] L.K. Koopal, W.H. Van Riemsdijk, J.C.M. de Wit, M.F. Benedetti, Analytical isotherm equation for multicomponent adsorption to heterogeneous surfaces, J. Colloid Interface Sci. 166 (1994) 51–60.

[63] D. Ringot, B. Lerzy, K. Chaplain, J.P. Bonhoure, E. Auclair, Y. Larondelle, In vitro biosorption of ochratoxin A on the yeast industry by-products: comparison of isotherm models, Bioresour. Technol. 98 (2007) 1812–1821.

[64] O. Redlich, D.L. Peterson, A useful adsorption isotherm, J. Phys. Chem. 63 (1959) 1024–1026.

[65] R.K. Prasad, S.N. Srivastava, Sorption of distillery spent wash onto fly ash: kinetics and mass transfer studies, Chem. Eng. J. 146 (1) (2009) 90–97.

[66] J.C.Y. Ng, W.H. Cheung, G. McKay, Equilibrium studies of the sorption of Cu(II) ions onto chitosan, J. Colloid Interface Sci. 255 (2002) 64–74.

[67] L. Jossens, J.M. Prausnitz, W. Fritz, E.U. Schlünder, A.L. Myers, Thermodynamics of multi-solute adsorption from dilute aqueous solutions, Chem. Eng. Sci. 33 (1978) 1097–1106.

[68] R. Sips, Combined form of Langmuir and Freundlich equations, J. Chem. Phys. 16 (1948) 490–495.

[69] J. Toth, State equations of the solid gas interface layer, Acta Chem. Acad. Hung. 69 (1971) 311–317.

[70] R.A. Koble, T.E. Corrigan, Adsorption isotherms for pure hydrocarbons, Ind. Eng. Chem. 44 (1952) 383–387.

[71] A.R. Khan, R. Ataullah, A. Al-Haddad, Equilibrium adsorption studies of some aromatic pollutants from dilute aqueous solutions on activated carbon at different temperatures, J. Colloid Interface Sci. 194 (1997) 154–165.

[72] A.R. Khan, I.R. Al Waheab, A.A. Al-Haddad, Generalized equation for adsorption isotherms for multicomponent organic pollutants in dilute aqueous solution, Environ. Technol. (1996) 13–23.

[73] S. Bruanuer, P.H. Emmett, E. Teller, Adsorption of gases in multimolecular layers, J. Am. Chem. Soc. 60 (1938) 309–316.

[74] T.L. Hill, Theory of physical adsorption, Adv. Catal. 4 (1952) 211–258.

[75] W.G. McMillan, E. Teller, The assumptions of the B.E.T. theory, J. Phys. Colloid Chem. 55 (1) (1951) 17–20.

[76] K.V. Kumar, Comparative analysis of linear and non-linear method of estimating the sorption isotherm parameters for malachite green onto activated carbon, J. Hazard. Mater. B136 (2006) 197–202.

[77] D.H. Lataye, I.M. Mishra, I.D. Mall, Adsorption of 2-picoline onto bagasse fly ash from aqueous solution, Chem. Eng. J. 138 (1–3) (2008) 35–46.

[78] B. Boulinguiez, P. Le Cloirec, D. Wolbert, Revisiting the determination of Langmuir parameters application to tetrahydrothiophene adsorption onto activated carbon, Langmuir 24 (2008) 6420–6424.

[79] K.V. Kumar, K. Porkodi, F. Rocha, Isotherms and thermodynamics by linear and non-linear regression analysis for the sorption of methylene blue onto activated carbon: comparison of various error functions, J. Hazard. Mater. 151 (2008) 794–804.

[80] K.V. Kumar, S. Sivanesan, Pseudo second order kinetics and pseudo isotherms for malachite green onto activated carbon: comparison of linear and non-linear regression methods, J. Hazard. Mater. B136 (2006) 721–726.

[81] V.S. Mane, I.D. Mall, V.C. Srivastava, Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green dye from aqueous solution by rice husk ash, J. Environ. Manage. 84 (2007) 390–400.

[82] A. Kapoor, R.T. Yang, Correlation of equilibrium adsorption data of condensable vapours on porous adsorbents, Gas Sep. Purif. 3 (1989) 187–192.

[83] J.C.Y. Ng, W.H. Cheung, G. McKay, Equilibrium studies for the sorption of lead from effluents using chitosan, Chemosphere 52 (2003) 1021–1030.

[84] D.W. Marquardt, An algorithm for least-squares estimation of nonlinear parameters, J. Soc. Ind. Appl. Math. 11 (1963) 431–441.

[85] I.D. Mall, V.C. Srivastava, N.K. Agarwal, I.M. Mishra, Adsorptive removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon-kinetic study and equilibrium isotherm analyses, Colloid Surf. A 264 (2005) 17–28.

[86] I.D. Mall, V.C. Srivastava, N.K. Agarwal, I.M. Mishra, Removal of Congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analyses, Chemosphere 61 (2005) 492–501.

[87] A. Seidel, D. Gelbin, On applying the ideal adsorbed solution theory to multicomponent adsorption equilibria of dissolved organic components on activated carbon, Chem. Eng. Sci. 43 (1988) 79–89.

[88] D. Karadag, Y. Koc, M. Turan, M. Ozturk, A comparative study of linear and non-linear regression analysis for ammonium exchange by clinoptilolite zeolite, J. Hazard. Mater. 144 (2007) 432–437.

[89] K.V. Kumar, S. Sivanesan, Isotherm parameters for basic dyes onto activated carbon: comparison of linear and non-linear method, J. Hazard. Mater. B129 (2006) 147–150.

[90] K.V. Kumar, K. Porkodi, F. Rocha, Comparison of various error functions in predicting the optimum isotherm by linear and non-linear regression analysis for the sorption of basic red 9 by activated carbon, J. Hazard. Mater. 150 (2008) 158–165.

[91] F.J. Rivas, F.J. Beltran, O. Gimeno, J. Frades, F. Carvalho, Adsorption of landfill leachates onto activated carbon equilibrium and kinetics, J. Hazard. Mater. B131 (2006) 170–178.

[92] S. Ayoob, A.K. Gupta, Insights into isotherm making in the sorptive removal of fluoride from drinking water, J. Hazard. Mater. 152 (2008) 976–985.

[93] I. Ghodbane, L. Nouri, O. Hamdaoui, M. Chiha, Kinetic and equilibrium study for the sorption of cadmium(II) ions from aqueous phase by eucalyptus bark, J. Hazard. Mater. 152 (2008) 148–158.

[94] R.P. Han, J.J. Zhang, P. Han, Y.F. Wang, Z.H. Zhao, M.S. Tang, Study of equilibrium, kinetic and thermodynamic parameters about methylene blue adsorption onto natural zeolite, Chem. Eng. J. 145 (2009) 496–504.

[95] V.S. Mane, I.D. Mall, V.C. Srivastava, Use of bagasse fly ash as an adsorbent for the removal of brilliant green dye from aqueous solution, Dyes Pigments 73 (2007) 269–278.

[96] A. Jumasiah, T.G. Chuah, J. Gimbon, T.S.Y. Choong, I. Azni, Adsorption of basic dye onto palm kernel shell activated carbon: sorption equilibrium and kinetics studies, Desalination 186 (2005) 57–64.

[97] Y.S. Ho, W.T. Chiu, C.C. Wang, Regression analysis for the sorption isotherms of basic dyes on sugarcane dust, Bioresour. Technol. 96 (2005) 1285–1291.

[98] D. Mohan, K.P. Singh, G. Singh, K. Kumar, Removal of dyes from wastewater using fly ash, a low-cost adsorbent, Ind. Eng. Chem. Res. 41 (2002) 3688–3695.

[99] K.V. Kumar, S. Sivanesan, Prediction of optimum sorption isotherm: comparison of linear and non-linear method, J. Hazard. Mater. B126 (2005) 198–201.

[100] S.C. Tsai, K.W. Juang, Comparison of linear and nonlinear forms of isotherm models for strontium sorption on a sodium bentonite, J. Radioanal. Nucl. Chem. 243 (3) (2000) 741–746.

[101] Y.L. Lai, G. Annadurai, F.C. Huang, J.F. Lee, Biosorption of Zn(II) on the different Ca-alginate beads from aqueous solution, Bioresour. Technol. 99 (2008) 6480–6487.

[102] A.E. Ofomaja, Y.S. Ho, Effect of temperatures and pH on methyl violet biosorption by Mansonia wood sawdust, Bioresour. Technol. 99 (2008) 5411–5417.

[103] R.D. Harter, Curve-fit errors in Langmuir adsorption maxima, Soil Sci. Soc. Am. J. 48 (1984) 749–752.

[104] P. Persoff, J.F. Thomas, Estimating Michaelis–Menten or Langmuir isotherm constants by weighted nonlinear least squares, Soil Sci. Soc. Am. J. 52 (1988) 886–889.