An Overview of Using Error function in Adsorption Isotherm Modeling

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Abstract:

Over the past years, a large number of statistical expressions used as a measure of accuracy, collectively referred to as error functions. These functions use to determine the best fitting data. Since accurate adsorption equilibrium information are necessary for the analysis and design of adsorption, error functions are used to valuation the validity of the adsorption mathematical models with experimental results by finding the most appropriate isotherm. Therefore, this overall review provides a definition of a number of common error function and explains the use of these functions in determine optimal adsorption data and chose the right isotherm.

Keywords: Adsorption, Error function, Langmuir, Freundlich, Sips, Temkin, Radke–Prausnitz.

1.Introduction:

Adsorption commonly is a beneficial, green and low-cost technology it is frequently used in our industrial economy and in our daily life . Adsorption has highly efficient measures to remove pollutants such as a dyes, Industrial waste, pesticides, drugs, and heavy metals from wastewater [1,2,3].

Adsorption process explains the ability of certain solids to concentrate special materials from solutions (gaseous or liquid) on their surfaces to purify or isolation these fluids[2] .

The most important part of this information is adsorption equilibrium, which is necessary for correct understanding of the adsorption process and explanatory of adsorption isotherms, Isotherm models are widely used to explain

equilibrium states in the adsorption process. It is provides important data about adsorbate, adsorbents, and the adsorption system [4,5]. It assists in determining adsorbent surface area and the pores size. It also provides important information about how contaminants reaction

with the adsorbed substances and therefore important for improvement of the adsorption mechanism, express the properties of surface, adsorbent capacity, and efficient design of the adsorption systems[6,7].

The purpose of this review is to explain the role of error function in the adsorption process, where the error function is the most applicable tools to determine the suitable adsorption isotherm by determines the adsorbents distribution, analyzes the adsorption system, and check for a match of theoretical assumptions of isotherm adsorption for assessing the accuracy of the adsorption mathematical models with laboratory results, a number of error functions were clarified in this literature[8,9].

2. Isotherm adsorption models:

Adsorption is commonly defined by adsorption isotherms, which is a mathematical equation describing as a phenomenon controlling retain (or release) of a material from the hydrous porous media to a solid-phase at a given temperature [10].
Adsorption isotherms ordinarily used to description the empirical adsorption information and represent adsorbent-adsorbate equilibrium relation. The isotherm parameters give some idea about the adsorption mechanisms, the surface characteristics, and the degree of affinity of the adsorbents [11].

It is important to analyze isotherm data to find an analytical equation that accurately interpret the results and can usage in design.

There are many kinds of isotherms in this pepper we used the most common isotherms by many researchers for describing adsorption systems.

2.1. The Langmuir isotherm:

The equation of Isotherm Langmuir is the first homogenously developed theoretically, which derived using thermodynamic and statistical comparisons. This empiricist model supposes that adsorption process happen at specific localized sites, and there is no reaction between adjacent adsorbed molecules when a mono molecule takes a mono surface site (monolayer adsorption)[12,13].This isotherm based on the presumption of the structurally homogeneous systems it can find by the following:

$$qe = \frac{q\mathrm{m}KaCe}{1+KaCe} \qquad (1)$$

Where q_m and K_a represent Langmuir equation parameters. This isotherm can write in linear form (2):

$$\frac{\mathrm{Ce}}{qe} = \frac{1}{qmKa} + \frac{Ce}{qm} \qquad (2)$$

A plot of C_e/q_e against C_e give a straight line were slope is $1/q_m$ and the intercept is $1/ (K_aq_m)$.

2.2.The Freundlich isotherms:

The Freundlich isotherm is the oldest and most widely used, it is simple and able to cover a wide range of concentration values. This isotherm is a limiting form of the Langmuir isotherm and is Applicable only for vapor pressure in the middle ranges[14] . This completely experimental isotherm can utilize for non-ideal, reversible and not finite to the forming of monolayer adsorption[15].The equation describes the amount adsorbed that collected on all sites, where the strongest binding sites are first taken so that the adsorption energy capacity decreased significantly and thus the adsorption process achieved. It is most important isotherm for heterogeneous systems expressed by the following equation[16] :

$$q_e = K_F C_e^{1/n} \qquad (3)$$

It can also be a linear equation by taking the logarithm of both sides.

$$\mathrm{Log}\ (q_e) = 1/n \log\ (C_e) + \log\ (K_F) \qquad (4)$$

The plot of log (q_e) versus log (C_e) gave "1/n" as slope and log (K_F) as an intercept, where K_F and 1/n are Freundlich constants.

2.3.The Redlich–Peterson isotherm:

This isotherm is a hybrid isotherm comprises the trait of two isotherm Langmuir and Freundlich. This isotherm includes three parameters. It is generally utilized to calculate effect of porous structure of the adsorbent and differentiate between the physical and chemical adsorption of metal ions by analyzing free energy of each adsorbate molecule. It can use for a wide domain of concentrations and then it can applied to both homo- and heterogeneous system. It can be described as following[17,18] :

$$q_e=K_R C_e/1+\alpha_R C_e^{\beta} \qquad (5)$$

Where, β is a constant parameter. The linear equation gives as:

$$C_e/q_e=1/K_R+a_R C_e^{\beta}/K_R \qquad (6)$$

Plotting C_e/q_e versus C_e^{β} gave a straight line with slope=a_R/K_R" and intercept =$1/K_R$

2.4. Sips isotherm:

The Sips model is an additional experimental model that has both model combinations of Langmuir and Freundlich isotherm. Sips model fundamentally utilized to description heterogeneous adsorption systems[19]. From its mathematical expression, with low concentrations of adsorbent, it follows the Freundlich isotherm, while at high concentrations; it expects the ability of monolayer adsorption similar to that predicted by Langmuir. There are three Parameters in this model, q_{max}, K_s and 1 / n, and it can write as[20] :

$$q_e = (q_{max}K_sC_e^{1/n})/(1+K_sC_e^{1/n}) \qquad (7)$$

Where K_s is constant, q_{max} is maximum sorption capacity (mmol/ g), and 1/n is degree of heterogeneity.

2.5. Temkin isotherm:

The Temkin isotherm depends on the assumption that the absorption temperature will decrease linearly instead of logarithmic with coverage. This isotherm used to characterized sorption on heterogeneous surface energy systems (Irregular distribution of sorption heat).This model given by the following[21] :

$$q_e = RT/b_t \ln (a_tC_e) \qquad (8)$$

Where R is the gas constant, T the temperature in Kelvin, b_t Temkin isotherm constant and a_t is Temkin isotherm equilibrium binding constant (L/g).

3. Error function:

Throughout the years, error function has been used to select the appropriate model for adsorption[22].

Their main usefulness is to quantify the distribution of the adsorbent, provide mathematical analysis of the results, and most importantly to verify the consistency of the experimental results, which have led to the generation of the adsorption isotherm[23]. The statistical analysis, in this work, has completed by evaluating each adsorption model using 11different error functions and all of them could calculate by using Microsoft Office Excel. Table(1) summary the error function.

Table1: Common error functions.

Error function	Expression	best fit	Ref.
Residual Sum of Squares (RSS)	$\sum_{i=1}^{n} \lvert q_{e,observed}-q_{e,calc}\rvert_i^2$	smallest value	24
Sum of absolute errors (SAE)	$\sum_{i=1}^{n} \lvert q_{e,meas} - q_{e,calc}\rvert_i$	smallest value	25
Sum square error (SSE)	$\sum_{i=1}^{n} (q_{e,calc}-q_{e,meas})_i^2$	smallest value	26
Hybrid function fractional error (HYBRID)	$\frac{100}{\text{p-n}} \sum_{i=1}^{p} [\frac{(q_{e,meas} - q_{e,calc})_i^2}{q_{e,meas}}_i]$	smallest value	13

Average relative error (ARE)	$\frac{100}{n} + \sum_{i=1}^{n} \left\| \frac{q_{e,meas} - q_{e,calc}}{q_{e,meas}} \right\|_i$	smallest value	26
Marquardt's percent standard deviation (MPSD)	$100 \sqrt{\frac{1}{n-p} \sum_{i=1}^{n} \left(\frac{q_{e,meas} - q_{e,calc}}{q_{e,meas}} \right)_i^2}$	smallest value	13
Nonlinear chi-square test (X^2)	$\sum_{i=1}^{n} \frac{(q_{e,exp} - q_{e,calc})^2}{q_{exp}}$	smallest value	26
Coefficient of determination (R^2)	$\frac{\left(q_{e,meas} - \overline{q_{e,calc}}\right)}{\sum\left(q_{e,meas} - \overline{q_{e,calc}}\right)^2 + (q_{e,me}}$	1or close to1	27
corresponding coefficient of determination (r^2)	$1 - \frac{6 \sum_{i=1}^{n} \left(q_{e,meas} - q_{e,calc}\right)_i^2}{n(n-1)^2}$	1or close to1	26
Sum of normalized errors (SNE)	$\sum_{i=1}^{n} \frac{f_i}{f_{i\,max}}$	minimize the error distribution	28
Coefficient of non-determination (K^2)	(Unexplained variance)/(Total variance)	minimize error distribution	29
"q_{cal}: calculated sorption capacity, q_{exp} : experimental capacity of adsorbate, n: number of experimental data, p: number of facter in each Isotherm model".			

3.1. Residual Sum of Squares:

Residual Sum of Squares (RSS) is the widely applied technique to foretelling the optimum isotherm at low concentrations[24] .

3.2. Sum of absolute errors:

Although Sum of absolute errors (SAE) function is similar to the RSS model, but it give better fit at high concentrations than the RSS model[30] .

3.3. Sum square error:

Sum square error (SSE) is the most commonly utilized error; the disadvantages of applying SSE are that when the concentration higher, the squares of error increases. This provides a good match most often and the best value when we get close to zero[31].

3.4. Hybrid function fractional error:

Hybrid function fractional error (HYBRID) error used to improvement SSE error at low concentrations values by dividing the calculated value. It also involved the number of degrees of freedom for the system as a divisor[32] .

3.5. Average relative error :

Average relative error (ARE) endeavors to minify the fractional error apportionment through the full concentration range[26] .

3.6. Nonlinear chi-square test :

Nonlinear chi-square test (X^2) test a useful test to explain if the experimental result histogram matched the expected data, the X^2 is a parametric test based on the distribution of the difference from normal distribution)[33].Small data values of chi-square test refer their resemblance, whilst a larger number refer to the difference of the empirical result[26].

3.7. Marquardt's percent standard deviation:

Marquardt's percent standard deviation(MPSD) has reported in isotherm studies by several researchers. It is follows of geometric mean error distribution named according to the number of degrees of freedom of the system[34].

3.8. Coefficient of determination:

Coefficient of determination (R^2) is calculate of the proportion of the variance in one variable that accounted for by another variable. The R^2 value lies between (0–1) and the perfect fit of R^2 when it value close to one[34].

3.9. Corresponding coefficient of determination:

It is represents the percentage of variability in the rely variable used to analyze the appropriate degree of isotherm models experimental[29] . The r^2 value lies between (0-1). The higher values of r^2 mean that the model is more useful[31] .

3.10. Sum of normalized errors:

When studying different types of error functions, they give different results that make it difficult to choose the best model, So SNE used to know the best error functions, which makes it easier to compare. SNE performed by dividing the error value of the various functions at the highest error for given isotherm parameters[34].

3.11. Coefficient of non-determination"

Coefficient of non-determination (K^2) very beneficial in identifying the best error functions and check which error function minimizes the

error distribution between the empirical and expected isotherm models[22] .

4.Linearand non-linear fitting application:

For explain the role of the error function in determining the appropriate isotherm for the adsorption process. Five types of isotherm studied: Langmuir, Freundlich, Sips, Radke–Prausnitz, Temkin isotherm. As shown in Table (2), a series of previous studies used to clarify the role of the error function in determining the best isotherm

Table 2:Linear and non-linear adsorption isother

Adsorbent	adsorbate	Statistical error	isotherm	Ref
NanNiO	Co(II)	X^2	Langmuir, Freundlich, Tempkin, Redlich–Peterson, Sips	35
Diatomite	Pb (II)	R^2, X^2	Langmuir, Freundlich, Redlich-Peterson , Sips	28
Cobalt oxide	Doxycycline hyclate	R^2, X^2	Langmuir , Freundlich	36
Shrimp shell	Heavy metal from coalacids	ARE, MPSD, HYBRID , SSE	Langmuir, Temkin, Sips, Freundlich	21
Activated carbon W G12 and WG12 modified by ZnCl2 and KOH	Carbone dioxan	SSE, HYBRID , ARE, MPSD, SAE, SNE	Langmuir, Freundlich, Sips, Radke–Prausnitz	8
Treated Martil sand	Cu(II)	r^2, SSE, SAE, ARE, HYBRID , MPSD	Freundlich, Langmuir, Temkin, Redlich-Peterson	11
Saccharumarundinaceum.	Cadmium	R^2, X^2, RSS,	Freundlich, Langmuir, Temkin	23

		ARE, EABS		
Activated carbon	Methylene blue	SSE, r^2, k^2, ARE,HYBRID SRE, MPSD	Freundlich, Langmuir, Redlich–Peterson	37
maize silk powder	Methylene blue	X^2, SSE, HYBR, MPSD,	Langmuir, Freundlich	24
		ARE, SAE	Temkin, Redlich–Peterson	
Lemna Minor	Tetracycline	R^2, X^2, RSS	Langmuir ,Freundlich	13
Nano $ZnCl_2$–MCM-41.	Hg(II)	SSE,R^2, X^2, ARE, SRE, MPSD	Freundlich, Langmuir, Temkin, Redlich–Peterson	38

The use of coefficient of determination (R^2) insufficient to verify that isotherm is suitable for adsorption because (R^2) is finite to solve linear forms of isotherm equation, which in linear plots calculated only the difference between theoretical data and experimental, but not the errors in non-linear form of isotherm curves. Soto finding the best isotherm modeling, other statistical error we utilized .

The adsorption of Co (II) by Nano NiO, The values of R^2 were >0.99 for all isotherms. Therefore to determine the best isotherm, error analyses used by calculating X^2 values. Based on the error functions, isotherm models arranged by the following direction:

Redlich–Peterson>Sips >Freundlich>Tempkin>Langmuir.

We also can used the statistical error as evidence to support the findings of the researcher through the highest R^2 value and the lowest values of error function as show in adsorption of Methylene blue in maize silk powder and activated carbon or adsorption of doxycycline hyclate on cobalt oxide.

Error function can optimization to choice which error effect on isotherm parameters. SNE and K^2can be used to comparison between different parameter, as show in adoption of Carbone dioxan and Methylene blue.

5.Conclusion:

When studying the adsorption process, the researcher needs to ascertain the accuracy of the results to use in the design of the successful adsorption system and therefore needs to use the appropriate tools. Therefore, error functions are useful techniques in determining optimum isotherm and thus help to assess the adsorption process and its suitability for the purpose for which it used.

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