Chapter

Adsorption Isotherms: Enlightenment of the Phenomenon of Adsorption

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Abstract

Adsorption is a process in which a substance that is in a liquid phase accumulates on a solid surface and is then removed from the liquid phase. An adsorption isotherm describes the equilibrium of adsorption of a substance on a surface at a constant temperature. It represents the amount of material bound to the surface as a function of the material present in the solution. In the adsorption process, the compound to be removed is called the adsorbate and the solid on which the compound is adsorbed is called the adsorbent. The affinity of the adsorbate for the adsorbent is quantified using adsorption isotherms. Adsorption isotherms are mathematical equations that describe the relationship between the amount of adsorbate adsorbed on an adsorbent and the concentration of adsorbate in solution when equilibrium has been reached at constant temperature. Adsorption isotherms are performed by giving a volume-determined solution containing a known amount of adsorbate along with various dosages of the adsorbent. The mixture is held at constant temperature with stirring until it reaches equilibrium. When this is the case, the concentration of the adsorbate in the aqueous phase is measured and the adsorption capacity at equilibrium for each experiment is calculated from the mass balance.

Keywords: isotherms, Henry's, Langmuir, Freundlich, Temkin, Dubinin–Radushkevich, Redlich–Peterson, sips, Halsey, Harkin–Jura, Elovich, Flory–Huggins, fowler–Guggenheim, Jovanovic and Kiselev

1. Introduction

Wastewater treatment has become one of the most important issues for the development of nations. During treatment, contamination can be found that cannot be treated by biological means, but there are also other recalcitrant compounds such as heavy metals that, in certain concentrations, can make biological treatment of wastewater difficult. Treatment of these compounds requires a different type of treatment: chemical precipitation, reverse osmosis, filtration, ion exchange, electrochemical degradation, photocatalytic degradation, nanofiltration, irradiation [1], and adsorption, to name a few. There are processes that are very efficient in removing impurities at trace concentrations, such as reverse osmosis. However, they have the disadvantage that the initial cost is very high and the consumables, such as membranes and maintenance, are very expensive. One of the most promising methods for removing recalcitrant compounds such as heavy metals is adsorption. This is because it is cheap, easy to implement, and environmentally friendly [2]. To understand adsorption mechanisms, it is important to obtain equilibrium data, commonly known as adsorption isotherms. The adsorption isotherms are important for describing how the adsorbate molecules or ions interact with the surface adsorption sites. Therefore, correlation of the equilibrium data using a theoretical or empirical equation is essential for interpretation and prediction of adsorption [3]. An adsorption isotherm is an equation expressing the relationship between the amount of solute adsorbed by the adsorbent and the solute concentration in the liquid phase [4–14]. They are important because they describe how an adsorbate interacts with an adsorbent, and they are critical to the design of an adsorption process. Several equilibrium models have been developed to describe the relationship of isotherms at equilibrium. The models used are those of Henry, Langmuir, Freundlich, Temkin, Dubinin–Radushkevich (DR), Redlich–Peterson (RP), Sips, Halsey, Harkin–Jura, Elovich, Flory–Huggins, Fowler–Guggenheim, Jovanovic, and Kiselev.

2. Adsorption isotherms

2.1 Calculation of isotherms

Batch adsorption experiments are performed. A constant concentration of adsorbent is added and mixed with a constant volume of solution, progressively varying the concentration of the solute to be removed. Stir at a constant rate until equilibrium is reached. The percentage of adsorption is calculated using the following expression:

$$\%\mathrm{Adsorption} = \frac{\mathrm{C_i} - \mathrm{C_f}}{\mathrm{C_i}} \times 100 \tag{1}$$

$$q_e = \frac{C_i - C_f}{\mathrm{m}} \times \mathrm{V} \tag{2}$$

where $\mathrm{C_i}$ and $\mathrm{C_f}$ are the initial and final concentrations, respectively, of the ion to be removed ($\mathrm{mg\ L^{-1}}$), $\mathrm{q_e}$ is the adsorption capacity of the ion (adsorbate) by the adsorbent ($\mathrm{mg\ g^{-1}}$), m is the mass of the adsorbent (g), and V is the volume of the ion solution to be removed (L) [6–12, 15–17].

Once the values of mass removal capacity ($\mathrm{q_e}$) and equilibrium concentration ($\mathrm{C_f}$) have been calculated using a Cartesian coordinate system to represent the two-dimensional distribution, the dispersion diagram provides a set of known points whose analysis allows a qualitative study of the relationship between the two variables. The next step is to determine the functional dependence between the two graphically represented variables that best fits the two-dimensional distribution. It is called linear regression if the function is linear.

The correlation coefficient is a technique used to study the two-dimensional distribution, indicating the intensity or degree of dependence between the variables X and Y. The correlation coefficient r is a number obtained using the following formula:

$$r = \frac{\sum\left[(x_i - \overline{x})\left(y_i - \overline{y}\right)\right]}{\sqrt{\sum (x_i - \overline{x})^2 + \sum \left(y_i - \overline{y}\right)^2}} \tag{3}$$

where r is correlation coefficient, x_i value of variable of x, $\overline{x}$ is the mean of the variable x, y_i value of variable y, $\overline{y}$ is the mean value of variable y, $\sum (x_i - \overline{x})^2$ sum of the square of the deviation x, $\sum \left(y_i - \overline{y}\right)^2$ sum of the square of the deviation y. The values of the correlation coefficient vary in the range from -1 to +1. A value of -1 indicates a perfect inverse linear correlation while a value of +1 indicates a positive linear correlation.

This last procedure can easily be done with the help of software that uses spreadsheets.

2.2 Henry's isotherm

This isothermal model adequately describes the adsorption process at low concentrations so that all adsorbate molecules are without interaction with the neighboring molecules [18]. The concentrations in the phases are associated with a linear expression. It is expressed as:

$$q_e = K_{HE} C_e \tag{4}$$

where q_e is the adsorption capacity in equilibrium (mg g^{-1}); K_{HE} is the equilibrium constant of Henry's; and C_e is the equilibrium concentration of the metal ions in the solution (mg L^{-1}). From the straight line adjusted to graph C_e versus q_e, the K_{HE} coefficient was calculated, which is represented by the slope.

2.3 Langmuir isotherm model

The Langmuir equation assumes that the maximum adsorption corresponds to a monosaturated layer of adsorbate molecules on the surface of the adsorbent, the adsorption energy is constant, and there is no transmigration of the adsorbate on the surface of the adsorbent [8]. All adsorption sites are energetically identical, and the intermolecular forces decrease with increasing distance from the adsorption surface [19]. The Langmuir model is expressed by the following equation:

$$q_e = \frac{q_m K_L C_e}{[1 + K_L C_e]} \tag{5}$$

where q_m is the maximum adsorption capacity (mg g^{-1}) and K_L is the Langmuir constant (L mg^{-1}) [6–8, 10, 12, 16, 20, 21]. The linear form of the Langmuir model is:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_L} \tag{6}$$

The values of the constants q_m and K_L are determined by the slope and the intersection of the fitted line on the abscissa C_e and the ordinate C_e/q_e, respectively. The characteristic of the Langmuir isotherm is that they can express a dimensionless constant called Balance Parameter or Separation Factor, which is expressed with the following equation:

$$R_L = \frac{1}{(1 + (K_L \times C_i))} \tag{7}$$

where R_L is the equilibrium parameter (dimensionless), and C_i is the initial concentration (mg L^{-1}). The R_L values indicate what type of adsorption can be expected. $R_L > 1$ is unfavorable, $R_L = 1$ the adsorption is linear, $R_L = 0$ is irreversible, and if $0 < R_L < 1$, adsorption is favorable [19, 22, 23].

2.4 Freundlich isotherm model

The Freundlich model takes into account the heterogeneity of the surface of the adsorbent and an exponential distribution of the active sites and their energies. The Freundlich model is expressed by the following equation:

$$q_e = K_F + C_e^n \tag{8}$$

where K_F is Freundlich's constant in (mg g^{-1}), and n is the Freundlich exponent related to the intensity of the adsorption; it is dimensionless. The equation of this model can be linearized as follows:

$$log\, q_e = \frac{1}{n}\, log\, C_e + log\, K_F \tag{9}$$

The values of the constants K_F and n are determined by the intercept and the slope of the graphical line on the ordinate ln q_e and the abscissa ln C_e, respectively. The range of values of $1/n$ is between 0 and 1 showing the degree of nonlinearity between the concentration of the solution and the adsorption. If the value of $1/n$ is equal to 1, the adsorption is linear [6–8, 10, 12, 16, 21, 24]. High values of n indicate a relatively uniform surface, where low values mean high adsorption at low concentrations of solution. In addition, low values of n indicate the existence of a high proportion of high-energy active sites [25].

2.5 Temkin isotherm model

The Temkin isotherm model contains a factor that explicitly considers the adsorption interactions between the species and the adsorbate [14, 26]. The Temkin model is described with the following equation:

$$q_e = BLn(K_T C_e) \tag{10}$$

where $B = RT/b$, b is Temkin's constant, K_T is the Bound Equilibrium Constant (L g^{-1}), and B is related to the heat of adsorption (J mol^{-1}) [27]. The Temkin isotherm model is presented in linear form with the following equation:

$$q_e = BLnC_e + BLnK_T \tag{11}$$

To obtain the constants B and K_T defined by the slope and intersection of the lines, respectively, plot q_e on the ordinate and Ln C_e on the abscissa.

2.6 Dubinin–Radushkevich isotherm model (D–R)

The model of the Dubinin–Radushkevich isotherm (D–R) not assumes a homogeneous surface or a constant adsorption potential. The model is described with the following equation:

$$q_e = q_s e^{-K_{DR}\varepsilon 2} \tag{12}$$

where q_s is the adsorption capacity (mol g^{-1}), K_{DR} is the Dubinin–Radushkevich constant (mol^2/KJ^2), and ε is correlated with the following expression:

$$\varepsilon = RTLn\left(1+\frac{1}{C_e}\right) \tag{13}$$

where ε is the potential of Polanyi, C_e is the concentration in equilibrium (mol L^{-1}), q_e is the equilibrium concentration in the adsorbent (mol g^{-1}), R is the universal gas constant (8.314×10^{-3} KJ mol^{-1} K^{-1}), and T is the absolute temperature °K. The linear form of this isotherm is expressed with the following equation:

$$q_e = -K_{\mathrm{DR}}\varepsilon^2 + Lnq_s \tag{14}$$

where q_s is the saturation capacity of the isotherm (mg g^{-1}). The isotherm constants q_s and K_{DR} are obtained from the intercept and the slope, respectively, from plotting on the ordinate Ln q_e and on the abscissa ε^2. The constant K_{DR} gives the mean of the free energy, E, is the adsorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated using the following relationship:

$$E = \frac{1}{\sqrt{-2}K_{\mathrm{DR}}} \tag{15}$$

The magnitude of E is used to estimate the type of adsorption process. The adsorption process is a chemical absorption if the magnitude of E is greater than 16 KJ mol^{-1}. In turn, when the magnitude of E is less than 8 KJ mol^{-1}, the type of absorption can be defined as a physical process [14, 27, 28]. There is talk of an ion exchange if $8 < E < 16$ KJ mol^{-1} [29].

2.7 Redlich–Peterson isotherm model (R–P)

This model is a combination of the Langmuir and Freundlich isotherms. It is used to describe the adsorption on both homogeneous and heterogeneous surfaces. It is considered as a comparison between these two models [30]. This isotherm is expressed with the following expression:

$$q_e = \frac{K_{\mathrm{R}}C_e}{\left(1+\alpha RC_e^{\beta}\right)} \tag{16}$$

where K_{R} is the constant of Redlich–Paterson (L g^{-1}), Redlich–Paterson constant αR (L mg^{-1}), β constant of Redlich-Paterson (dimensionless). The values of β fluctuate between 0 and 1. At low concentrations, the Redlich–Paterson isotherm approximates Henry's law [31]. When the constant β is very close to 1, it is the same as the Langmuir equation and in high concentrations its behavior approaches that of the Freundlich isotherm, since the β exponent tends to zero [32, 33]. From the transformation of the original equation, two linear forms are obtained. One of the linear forms of this isotherm is expressed with the following equation:

$$log\left[\left(K_R\frac{C_e}{q_e}\right)-1\right]=\beta logC_e+log\,(\alpha R) \tag{17}$$

The values of αR and β for the above equation can be determined from the intercept and the slope, respectively, of the straight line of graphing $log\left[\left(K_R\frac{C_e}{q_e}\right)-1\right]$ versus log C_e [34]. Several values of the constants must be tested before obtaining the optimal line, in order to obtain the values of these. The range of values of these constants is very wide, ranging from 0.01 to several hundred, so it is not easy to obtain the correct values [31]. Another linear form of this equation is:

$$\frac{C_e}{q_e}=\frac{1}{K_R}+\frac{\alpha R}{K_R}C_e^{\beta} \tag{18}$$

The constants of the Redlich–Paterson isotherm can be determined from the graph between C_e^{β} and C_e/q_e. However, its application is very complex since it includes three unknown parameters αR, K_R, and β. Therefore, a minimization procedure is adopted to obtain the maximum value of the coefficient of determination R^2, between the theoretical data for q_e obtained from the linearized form of the isotherm equation of Redlich–Peterson and the experimental data [30]. By trial and error, values of β are adopted to obtain an optimal line. In the specific range, the values of b are limited, and it is easy to obtain the correct value [31].

2.8 Sips isotherm model

The Sips isotherm is a combined form of Langmuir and Freundlich isotherms applied for the prediction of heterogeneous adsorption systems. The Sips model avoids the inconveniences and limitations of the Langmuir or Freundlich models. At low concentrations, the adsorbate becomes Freundlich's isotherm and, therefore, does not obey Henry's law [35]. While in high concentrations, the isothermal formula of Langmuir is reduced [36]. The equation of the Sips isotherm is characterized by containing a dimensionless heterogeneity factor, βs. If βs = 1, the Sips equation is reduced to the Langmuir equation, which indicates that the adsorption process is homogeneous. The Sips isotherm constant (β_s) confirms that the surface of the adsorbent is heterogeneous or not [33]. The Sips isotherm is expressed with the following equation:

$$q_e=\frac{K_SC_e^{\beta_s}}{1+asC_e^{\beta_s}} \tag{19}$$

where K_S is the equilibrium constant of the Sips isotherm (L mg^{-1}), as is the maximum adsorption capacity (mg g^{-1}), and β_s is the model exponent (dimensionless) [35, 37, 38]. The linear form of the Sips isotherm is [39]:

$$Ln\left(q_e\right) = \beta_s Ln(C_e) + Ln\left(K_S - a_s \times q_e\right) \tag{20}$$

The coefficients of the Sips isotherm are calculated from graphing $\ln(C_e)$ versus ln (q_e), where β_s is slope.

2.9 Halsey isotherm model

This model is used to evaluate multilayer adsorption in a system where metal ions are located relatively far from the surface of the adsorbent. The model is expressed with the following Equation [40]:

$$q_e = exp\left(\frac{ln\,K_H - \,ln\,C_e}{n_H}\right) \tag{21}$$

The linear form from Halsey isotherm is [62, 63]:

$$Ln\left(q_e\right) = -\frac{1}{n_H}Ln\frac{1}{C_e} + \left[\left(\frac{1}{n_H}\right)Ln(K_H)\right] \tag{22}$$

where n_H is the constant of the equation, and K_H is Halsey's equilibrium constant. The constants of the isotherm may be calculated graphing $\ln(1/C_e)$ versus $\ln(q_e)$ and from the straight line obtained, the slope is n_H, and the intercept represents K_H [41].

2.10 Harkins–Jura isotherm model

The Harkins–Jura model describes a multilayer adsorption and the existence of a heterogeneous distribution of the pores of the adsorbent. The model is defined with the following expression:

$$\frac{1}{q_e^2} = -\frac{1}{A_{HJ}}\,log\,(Ce) + \frac{B_{HJ}}{A_{HJ}} \tag{23}$$

where B_{HJ} is a model constant, and A_{HJ} is another model constant. Graphing $1/q_e^2$ versus $\log(C_e)$, the model constants are calculated with slope A_{HJ} and intercept B_{HJ} [41].

2.11 Elovich isotherm model

It assumes that the adsorption sites increase exponentially with adsorption, which implying a multilayer adsorption. This is expressed with [18, 41–43]:

$$\frac{q_e}{q_m} = K_E C_e\, exp\left(-\frac{q_e}{q_m}\right) \tag{24}$$

The linear form is expressed:

$$Ln\frac{q_e}{C_e} = -\frac{1}{q_m}q_e + LnK_E q_m \tag{25}$$

where q_m is the maximum adsorption capacity of Elovich (mg g^{-1}), and K_E is the equilibrium constant of Elovich (L mg^{-1}). K_E and q_m are calculated from the intercept and slope, respectively, of the straight line of $\ln(q_e/C_e)$ versus q_e [18, 41–43].

2.12 Flory-Huggins isotherm model

This model assumes the degree of coverage of the adsorbate on the adsorbent and expresses the degree of feasibility and spontaneity of the adsorption process. It included a parameter indicating the degree of coverage of the surface of the adsorbent, expressed as θ. The general form is given by the following Equation [43]:

$$\frac{\theta}{C_0} = K_{FH}(1-\theta)^n \tag{26}$$

The linear form of it is expressed:

$$log\,\frac{\theta}{C_0} = nlog(1-\theta) + log\,K_{FH} \tag{27}$$

$$\theta = \left(1 - \frac{C_e}{C_0}\right) \tag{28}$$

where K_{FH} is the equilibrium constant of Flory–Huggins (L mg^{-1}), n is the exponent of the model, and θ is the coverage parameter of the adsorbent surface. For the calculation of the isotherm parameters, $\log \theta/C_0$ versus $\log(1-\theta)$ should be plotted, where the slope and the intercept represent n_{FH} and K_{FH}, respectively. The constant K_{FH} can be used to calculate the spontaneity of Gibbs free energy [32, 43]. For its calculation is used the following Eq. (32):

$$\Delta G^{\circ} = RTlnK_{FH} \tag{29}$$

where ΔG° Gibbs free energy change (KJ mol^{-1}). The negative values of ΔG° indicate that the adsorption is thermodynamically spontaneous and feasible [44].

2.13 Fowler–Guggenheim isotherm model

It is one of the simplest equations that takes into account the lateral interaction of adsorbate molecules. Its general form is expressed below:

$$K_{FG}C_e = \frac{\theta}{1-\theta}\,exp\left(\frac{2\theta W}{RT}\right) \tag{30}$$

The linear form of it is expressed:

$$ln\left[\frac{C_e(1-\theta)}{\theta}\right] = \frac{2W}{RT}\theta - \,ln\,K_{FG} \tag{31}$$

where K_{FG} is the equilibrium constant of Fowler–Guggenheim (L mg^{-1}), and W is the energy of interaction between the molecules of the adsorbate (KJ mol^{-1}) [37, 42]. The parameters of the equation are calculated by graphing $\ln[C_e(1-\theta)/\theta]$ versus θ.

From this straight line the intercept and the slope represent K_{FG} and W, respectively. The charge and heat of adsorption vary linearly. When the values of W are greater than zero, it indicates that the interaction between the adsorbate molecules is attractive, but if the values of W are negative, the interaction is of the repulsion type, and if $W = 0$, there is no interaction [42].

2.14 Jovanovic isotherm model

This model assumes a superficial adsorption, it is an approximation of adsorption in a monolayer as expressed in the Langmuir model, but it assumes that there is no lateral interaction between the molecules. This model tolerates surface vibration of an adsorbed species [42] and allows some mechanical contact between the adsorbate and the adsorbent [18]. This model is expressed with the following expression [42]:

$$q_e = q_m\left(1 - e^{K_J C_e}\right) \tag{32}$$

Its linear form is [18]:

$$q_t = K_J t^{\frac{1}{2}} \tag{33}$$

where K_J is the equilibrium constant of Jovanovic (L mg^{-1}). When plotting ln q_e versus C_e, the slope and the intercept are K_J and q_m, respectively.

2.15 Kiselev isotherm

This model is known as the model of the localized monomolecular layer and is only valid when $\theta \geq 0.68$. Its linear expression is [18]:

$$\frac{1}{C_e \times (1 - \theta)} = K_i \frac{1}{\theta} + K_i K_n \tag{34}$$

where K_i is Kiselev's constant (L mg^{-1}), and K_n is the equilibrium constant of complex formation between the molecules of the adsorbate. Constants are calculated by plotting $1/[C_e \times (1 - \theta)]$ versus $1/\theta$ where the slope and the intercept represent K_i and $K_i \times K_n$, respectively [18].

2.16 Evaluating the suitability of the isothermal equations using experimental data

Statistical tools are used to evaluate the suitability of the values calculated with the selected isotherm equation in comparison with the experimentally determined values. To measure the differences between the experimentally observed values and the values calculated with the isothermal model, the so-called goodness of fit is used. Among the best known are the following:

2.16.1 Average relative error (%ARE)

To evaluate the goodness of fit of the isothermal equations against the experimentally obtained data, the average relative error (% ARE) can be used. It is explained by the following equation:

$$\%ARE = \frac{100}{n} \sum_{i=1}^{n} \left\| \frac{q_{i,cal} - q_{i,exp}}{q_{i,exp}} \right\| \tag{35}$$

where n is the data number, $q_{i,cal}$ are the equilibrium values calculated with the mathematical isotherm expression (mg g^{-1}), and $q_{i,exp}$ are values obtained experimentally (mg g^{-1}) [14, 28, 43]. An average relative error lower than or equal to 5% is considered adequate.

2.16.2 Chi-square (χ^2)

To determine the best-fitting isothermal model, the linear Chi-square values (χ^2) were used along with the linear regressions (R^2). The Chi-square test statistic is basically the sum of the squared errors of the differences between the experimental data and the data obtained by calculations with the models. Each square difference is divided by the corresponding data obtained by calculations using the models. If the values obtained using a model are similar to the experimental values, the value of χ^2 is very small and close to zero. High values of χ^2 imply a high discrepancy between the experiment and the model. Therefore, the analysis of the dataset of the Chi-square test may confirm the isotherm that best fits the adsorption system. The mathematical expression of the Chi-square test is explained below [29].

$$x^2 = \sum_{i=1}^{n} \frac{\left(q_{i,exp} - q_{i,cal}\right)^2}{q_{i,cal}} \tag{36}$$

If values $\chi^2 \leq 0.05$, the experimental data and the data obtained by calculations using the models have a statistically significant association.

3. Conclusions

The adsorption process of various compounds and elements is one of the most important environmental issues of the last decade due to its relevance, especially in emerging countries. To better understand how a solute can interact with the surface of a solid, it is useful to use the adsorption isotherm.

The effect of different variables on the adsorption process is of great importance for the development of treatment systems. The use of isotherms helps to determine these effects.

The analysis of equilibrium data is necessary to understand and interpret the adsorption mechanism and predict the removal of contaminants. They are necessary to know the mechanisms or transport phenomena that control the adsorption rate and thus be able to calculate, scale, and design an adsorption treatment system.

The obtained equilibrium data used to calculate isotherms can be used to scale up to a pilot plant experiment.

Among all the phenomena that determine the mobility of substances in porous aqueous media and in the aquatic environment, the transfer of substances from a mobile phase (liquid or gas) to a solid phase is the relevant phenomenon.

An isotherm is a curve describing the retention of a substance in a solid at different concentrations. It is an important tool for describing and predicting the mobility of this substance in the environment.

The adsorption process is a widely accepted treatment method because it is easy to apply and effective even at low concentrations. Adsorption has advantages over other treatment methods because it has low start-up and installation costs, is easy to operate, has low environmental risk, is resistant to toxic components, and offers significant potential for removing hazardous and unsafe contaminants.

The description of equilibrium data is valuable when using an equation that has a physical meaning, as it is then possible to correlate what is observed in one experiment with what is physically seen in a larger experiment.

Conflict of interest

The authors declare no conflict of interest.

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