CHAPTER III

THEORETICAL ASPECTS
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3.1. Biosorption modeling

Models have an important role in technology transfer from a laboratory to industrial-scale. Appropriate models can help in understanding process mechanisms, analyze experimental data, predict answers to operational conditions and optimize processes. As an effective quantitative means to compare binding strengths and design biosorption processes, employing mathematical models for the prediction of binding capacities can be useful [148, 257]. Biosorption modeling can be performed in two general ways: empirical or mechanistic equations, which are able to explain, represent and predict the experimental behaviour.

Empirical models are simple mathematical relationships, characterized by a limited number of adjustable parameters, which give a good description of the experimental behaviour over a large range of operating conditions [87]. Some frequently employed an well established empirical models involve two, three or even four parameters to model the isotherm data [254]. Although these conventional empirical models do not reflect the mechanisms of sorbate uptake, they are capable of reflecting the experimental curves [135]. Also, in most cases, the assumptions from which these models were derived are not valid for biosorption. Despite this, conventional sorption isotherm models are used with a high rate of success for replicating biosorption isotherm curves. Within the literature, the Langmuir [144] and Freundlich [95] models have been used to describe biosorption isotherm. The models are simple, well-established and have physical meaning and are easily interpretable, which are some of the important reasons for their frequent and extensive use. There are three principle advantages of biological technologies for the removal of pollutants; first, biological processes can be carried out in situ at the contaminated site; Second, bioprocess technologies are usually environmentally benign (no secondary pollution) and third, they are cost effective.

Of the different biological methods, bioaccumulation and biosorption have been demonstrated to possess good potential to replace conventional methods for the removal of metals [158, 257]. Some confusion has prevailed
in the literature regarding the use of the terms “bioaccumulation” and “biosorption” based on the state of the biomass. Herein, therefore, bioaccumulation is defined as the phenomenon of living cells; whereas, biosorption mechanisms are based on the use of dead biomass. To be precise, bioaccumulation can be defined as the uptake of toxicants by living cells. The toxicant can transport into the cell, accumulate intracellularly, across the cell membrane and through the cell metabolic cycle [158]. Conversely, biosorption can be defined as the passive uptake of toxicants by dead/inactive biological materials or by materials derived from biological sources.

Biosorption is due to a number of metabolism-independent processes that essentially take place in the cell wall, where the mechanisms responsible for the pollutant uptake will differ according to the biomass type. Biosorption possesses certain inherent advantages over bioaccumulation processes. In general, the use of living organisms may not be an option for the continuous treatment of highly toxic organic/inorganic contaminants. Once the toxicant concentration becomes too high or the process operated for a long time, the amount of toxicant accumulated will reach saturation [82]. Beyond this point, an organism's metabolism may be interrupted, resulting in death of the organism. This scenario can be avoided in the case of dead biomass, which is flexible to environmental conditions and toxicant concentrations.

Most biosorption studies employ simple closed batch systems although most envisaged industrial applications would employ some kind of flow-through or continuous process. A wide variety of biosorption systems have been used, often meaning comparisons are difficult between different studies. A whole sorption isotherm [259] is considered to be the most appropriate approach for assessing biosorbent capacity. Many such studies use a simple defined system and a single metal: biosorption is often examined under such different parameters as varying biomass density, pH, metal concentration, presence of competing cations, etc. Flow and other continuous systems are more complex, but many column studies use ‘breakthrough curves’ to assess sorbent efficiency. Fitting biosorption data to sorption isotherm equations...
provides no information about the mechanisms, and should be considered simply as numerical relationships used to fit data.

Experimental evidence is necessary before any chemical significance can be attributed to isotherm equation parameters. Further, these parameters are valid only for the chemical conditions under which the experiment was conducted. Use of these equations for prediction of metal sorption behaviour under changing pH, ionic strength and solution metal concentration is impossible. Application of sorption isotherms may also be inadequate when precipitation of metals occurs although the Langmuir isotherm has sometimes been applied to such cases despite being theoretically invalid. The criteria for choosing a isotherm or kinetic equation for biosorption data is mainly based on the goodness of curve fitting which is often evaluated by statistical analysis. However, good curve fitting in the sense of statistical evaluation may not necessarily imply that this curve fitting has true physical meaning, i.e. if a set of biosorption data is analyzed by different isotherm or kinetic equations, the best fit equation may not be the one reflecting the biosorption mechanism(s).

It therefore seems that many isotherm and kinetic studies of biosorption are basically a simple mathematical exercise. It has been stated that selection of kinetic equations should be based on the mechanisms [114]. Consequently, to formulate a mathematical expression of biosorption, models with strong theoretical characteristics are needed rather than simple curve fitting [150]. In view of the previously discussed uncertainties about mechanisms, this may not be possible and the application of biosorption isotherms may remain dubious in many studies [99].

3.2. SORPTION REACTION MODELS

In the past decades, several mathematical models have been proposed to describe sorption data, which can generally be classified as sorption reaction models and adsorption diffusion models. Both models are applied to describe the kinetic process of sorption; however, they are quite different in nature. sorption diffusion models are always constructed on the basis of three consecutive steps [157]
✓ diffusion across the liquid film surrounding the sorbent particles, i.e., external diffusion or film diffusion;
✓ diffusion in the liquid contained in the pores and/or along the pore walls, which is so-called internal diffusion or intra-particle diffusion;
✓ Sorption and desorption between the adsorbate and active sites, i.e., mass action.

However sorption reaction models originating from chemical reaction kinetics are based on the whole process of adsorption without considering these steps mentioned above. Sorption systems have been investigated to assess their suitability for application in the field of water pollution control. The cost and performance of a product or the mode of application are always of concern to control process efficiency. Therefore the sorption capacity and required contact time are two of the most important parameters to understand. Two important physicochemical aspects for evaluation of a sorption process as a unit operation are the equilibrium of the sorption and the sorption kinetics. Sorption equilibrium is established when the concentration of sorbate in the bulk solution is in dynamic balance with that of the interface.

An equilibrium analysis is the most important fundamental information required to evaluate the affinity or capacity of a sorbent [265]. However, thermodynamic data can predict only the final state of a system from an initial non-equilibrium mode. It is therefore important to determine how sorption rates depend on the concentrations of sorbate in solution and how rates are affected by sorption capacity or by the character of the sorbent. From the kinetic analysis, the solute uptake rate, which determines the residence time required for completion of the sorption reaction, may be established.

Sorption processes may include ion exchange, chelation, physical and chemical sorption. When the chemical reaction at the solid phase is rapid and is not associated with solid-phase transport processes, the liquid-phase transport process determines the overall rate of reaction, e.g., transport in the bulk liquid phase, diffusion across the liquid film surrounding the solid particles, diffusion in liquid-filled macropores [7]. Sorption mechanisms depend on the sorbate-sorbent interaction and the system conditions. Therefore it is impossible to classify sorption mechanisms by the solute type.
To predict the time to achieve the equilibrium state of sorption and to establish the reaction mechanism, knowledge of the rate equations explaining the reaction system is required. A number of equations have been used to describe kinetic reactions in biosorbents [81, 107, 141, 265, 4537]. These include first-order, second-order and two-constant rate equations.

3.3. Pseudo First-order forward reaction

The Lagergren rate equation (1) may have been the first rate equation for the sorption in liquid/solid systems based on solid capacity. The Lagergren rate equation

\[ \frac{dq_t}{dt} = k_1(q_m - q_t) \] ................................. (1)

Is the most widely used rate equation for sorption of a solute from a liquid solution? (1) Integrating this for the initial and end conditions \( t = 0 \) to \( t = t \) and \( q_t = 0 \) to \( q_t = q_t \), the above equation (1) may be rearranged for linearised data plotting as shown by equation (2):

\[ \log(q_m - q_t) = \log q_m - \frac{k_1}{2.303} t \] ................................. (2)

When equation (2) is applied and the parameter \( q_m \) is evaluated, using experimental data, it generally differs from a true first-order equation in two ways [7,265]:

The parameter \( q_m \) does not represent the number of available sites.
The parameter \( \log(q_m) \) is an adjustable parameter and it is not often equal to the intercept of a plot of \( \log(q_m - q_t) \) against \( t \), whereas in a true first order system, \( \log(q_m) \) should be equal to the intercept of a plot of \( \log(q_m - q_t) \) against \( t \).

In fact, is only an approximate solution to the first order rate mechanism. In order to fit to experimental data, the equilibrium sorption capacity, \( q_m \), should be known. In many cases \( q_m \) is unknown, as chemisorptions tends to become unmeasurably slow while the amount sorbed is still significantly smaller than the equilibrium amount. In most cases from the literature, the pseudo-first order equation of Lagergren does not fit well over the range of contact times under investigation. Furthermore, one has to
find some means of extrapolating the experimental data, or treat \( q_m \) as an adjustable parameter to be determined by trial and error. For this reason, it is necessary to use a trial and error solution method to obtain the equilibrium sorption capacity, \( q_{\text{max}} \). If film diffusion is rate controlling, the constant of the rate equation will vary inversely with the particle size and the film thickness; if the exchange is chemically rate controlled, the rate constant will be independent of particle diameter and flow rate and it will depend only on the concentrations of the ions in solution and the temperature. [45,265]

### 3.4. Pseudo-first-order rate equation

Lagergren (1898) presented a first-order rate equation to describe the kinetic process of liquid-solid phase adsorption of oxalic acid and malonic acid onto charcoal, which is believed to be the earliest model pertaining to the adsorption rate based on the sorption capacity.

\[
\frac{dq_t}{dt} = k_1 (q_e - q_t) \tag{3}
\]

It can be presented as follows: where \( q_e \) and \( q_t \) (mg/g) are the adsorption capacities at equilibrium and time \( t \) (min), respectively. \( k_1 \) (min\(^{-1}\)) is the pseudo-first-order rate constant for the kinetic model. Integrating with the boundary conditions of \( q_t = 0 \) at \( t = 0 \) and \( q_t = q_t \) at \( t = t \), yields [114] which can be rearranged to:

\[
\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \tag{4}
\]

To distinguish kinetic equations based on adsorption capacity from solution concentration, Lagergren’s first order rate equation has been called pseudo-first-order [116].

### 3.4.1. Pseudo-first-order irreversible sorption reaction model

The equation applicable to experimental results generally differs from a true first-order equation in two ways [7];

The parameter \( q_e - q_t \) does not represent the number of available sites and the parameter \( \log(q_e) \) is an adjustable parameter which is often not found equal to the intercept of a plot of \( \log(q_e - q_t) \) against \( t \), whereas in a true first-order sorption reaction \( \log(q_e) \) should be equal to the intercept of a plot of \( \log(q_e - q_t) \) against \( t \). [44]

\[
\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \tag{4}
\]
In order to fit to experimental data, the equilibrium sorption capacity, $q_e$, must be known. In many cases $q_e$ is unknown and as chemisorptions tends to become un measurably slow, the amount sorbed is still significantly smaller than the equilibrium amount. [249] In most cases in the literature, the pseudo-first-order equation of Lagergren does not fit well for the whole range of contact time and is generally applicable over the initial 20 to 30 min of the sorption process. Furthermore, one has to find some means of extrapolating the experimental data to $t = 8$ or treat $q_e$ as an adjustable parameter to be determined by trial and error. For this reason, it is necessary to use trial and error to obtain the equilibrium sorption capacity, $q_e$, in order to analyze the pseudo-first-order model kinetics. The pseudo-first-order kinetic model has been used extensively to describe the sorption of metal ions onto sorbents. The main disadvantages of this model are [44].

Does not give theoretical $q_e$ values that agree with that the linear experimental $q_e$ values and that the plots are only linear over the first 30 min, approximately. Beyond this initial 30 min period the experimental and theoretical data do not correlate well. Various authors have made proposals for these deviations. One suggestion for the differences in the $q_e$ values is that there is a time lag, possibly due to a boundary layer or external resistance controlling at the beginning of the sorption process. [7,162]. This time lag is difficult to quantify and does little to help rationalize the differences in experimental and theoretical $q_e$ values. In terms of the short time correlation between experimental and theoretical data for the pseudo-first order model [141]. It has been proposed that another first-order reaction [220,228,251] supersedes the first or another reaction of another order becomes predominant.

Several researchers [103, 116, 2216, 247, 279, 280] have tested the Lagergren pseudo-first-order reaction model for Cu(II); Cr(III) and Cu(II); Cr(VI); Cu(II); for Pb(II); and Cu(II) and for Cu(II). In general, most of the fits are moderate to poor. However, it should be noted that the limited model by Lagergren is generally restricted to only the initial 20% to 40% of the adsorption capacity. The equation needs further modification for longer sorption times and higher fractional surface coverages. Hence, when the
Experimental data are inspected; several sets of results have very few data points in the initial 20% and 40% period, and therefore the rejection of a pseudo-first-order reaction model on the grounds of poor model fitting may not be the correct reason. A more logical approach would be to analyze the likely mechanism of a first-order metal ion sorption uptake process on chitosan and compare this with a model where involving a second-order or higher process seems more likely. [44]

3.4.1. Pseudo-second-order irreversible sorption model

If the rate of sorption has a second-order mechanism, the pseudo-second-order chemisorption kinetic rate equation is expressed as:

\[ \frac{dq_t}{dt} = k_2(q_e - q_t)^2 \]  \hspace{1cm} (5)

Where \( q_e \) and \( q_t \) are the sorption capacity at equilibrium (mmol g\(^{-1}\)) and at time \( t \), respectively, and \( k_2 \) is the rate constant of pseudo-second-order sorption (g mmol\(^{-1}\) min). For the boundary conditions \( t = 0 \) to \( t = t \) and \( q_t = 0 \) to \( q_t = q_t \), the integrated form of equation (5) becomes.

\[ \frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \]  \hspace{1cm} (6)

which is the integrated rate law for a pseudo-second-order reaction.

Equation (6) can be rearranged to obtain:

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \]  \hspace{1cm} (7)

which has a linear form does not have the problem of assigning an effective \( q_e \). The pseudo-second-order kinetic model has been the most widely tested model for the sorption of metal ions and organic pollutants from wastewater since it was proposed [116]. The main deficiency of this extremely useful model stems from the fact that it is a pseudo-kinetic model, so a specific but different rate constant is obtained for each change in system variable. So it is important to develop an equation for correlating the pseudo-rate constant with each variable. [44, 62]

3.4.2. Pseudo-second-order reversible sorption reaction

Depending on the method of preparation of the chitosan and the treatment conditions, the chitosan produced is often in flake form or irregular in shape. Since many researchers consider the chitosan flake to be fairly impermeable and nonporous, metal ion uptake would be expected to be
largely limited to the external surface of the chitosan flake/sheet. On this basis, a second-order reversible model was developed [65] to predict the sorption of copper from solution. The steps are outlined next. In the second-order reversible reaction model, it is assumed that the interaction that occurs between a metal ion and the binding site at the adsorbent surface may be represented by a reversible reaction of the form:

\[ M + A \xrightleftharpoons{\frac{k_{+2}}{k_{-2}}} MA \]  

(8)

Where M is the metal ion in solution, A is the adsorption site, and MA is the metal–adsorbent complex. The parameters \( k_{+2} \) and \( k_{-2} \) are the second-order forward and first-order reverse rate constants, respectively. The rate of metal uptake by the sorbent in an interaction described by equation (8) is given by

\[ \frac{dq_t}{dt} = k_{+2}C_t(q_m - q_t) - k_{-2}q_t \]  

(9)

Where \( q_t \) and \( C_t \) are respectively the adsorbent-phase metal concentration and solution-phase metal concentration at time \( t \).

At equilibrium, equation (9) reduces to the Langmuir isotherm equation where:

\[ \frac{1}{a_L} = \frac{k_{-2}}{k_{+2}} \]

The extent of metal ion uptake as a function of time can be found from the integration of equation (6) together with the appropriate initial conditions and the mass balance equation for a batch system. The analytic solution of equation (6) is given by Skidmore and Chase [230]:

\[ \frac{C_t}{C_0} = 1 - \frac{1}{a_L} \frac{m}{v} \left( b^2 - \frac{C_0q_m}{V} \right) \left( \frac{1}{a_L} \left( b + a \right) \left( \frac{b + a}{b - a} \right) \exp \left[ -2a(\frac{m}{v})k_{+2}t \right] \right) \]  

(10)

Where the parameters \( a \) and \( b \) are defined as

\[ a = b^2 - C_0q_m \frac{v}{m} \]

\[ b = 0.5 \left( C_0 \frac{v}{m} + q_m + \frac{1}{a_L} \frac{v}{m} \right) \]

Alternatively, the interaction that occurs between a metal ion and the adsorbent may be represented by a second-order irreversible reaction of the form:
Where $k_2$ is the second-order rate constant. The rate of change of solution phase metal concentration in an interaction described by equation (11) is given by [232]:

$$\frac{dC_t}{dt} = -k_2C_t(C_t - C_e) \tag{12}$$

The analytic solution of equation (12) can be found by integration with the appropriate initial conditions and is given by

$$C_t = \frac{C_e}{C_0 - (C_0 - C_e) \exp(-C_e k_2 t)} \tag{13}$$

When the equilibrium relationship of the sorption system is of Langmuir form, $C_e$ for a batch system is given by: [44]

$$C_e = \frac{-b + \sqrt{b^2 + 4C_0(\frac{1}{a_h})}}{2} \tag{14}$$

Where the parameter $h$ is defined as

$$h = \frac{1}{a_h} - C_0 + q_m \frac{m}{V}$$

### 3.5. Other Kinetic Sorption Reaction-Based Models

#### 3.5.1. RITCHIE $n$TH-ORDER SORPTION MODEL

Ritchie [208] proposed a method for the kinetic sorption of gases on solids. The author assumed that $\theta$ was the fraction of surface sites that are occupied by adsorbed gas, $n$ is the number of surface sites occupied by each molecule of adsorbed gas, and $k_n$ is the rate constant.

Then

$$\frac{d\theta}{dt} = k_n(1 - \theta)^n \tag{39} \tag{15}$$

When $t = t$, $\theta = \frac{q_t}{q_{m,\infty}}$, and $t = 0$ and $\theta = 0$.

The integrated form of equation (15) becomes

$$\frac{q_{m,\infty}^{-1}}{(q_{m,\infty} - q_t)^{n-1}} = (n - 1)k_nt + 1 \quad \text{for } n = 2, 3, \ldots, i. \tag{16}$$

If metal ion sorption in aqueous solution is considered to be a second-order reaction, then equation (16) becomes

$$\frac{q_m}{(q_m - q_t)} = k_n t + 1 \tag{17}$$

Rearranging equation (17) to the linear form, it becomes:

$$\frac{1}{q_t} = \frac{1}{k_n q_m t} + \frac{1}{q_m} \tag{18}$$
Ritchie proposed plotting $1/q_t$ against $1/t$. The sorption capacity $q_m$ and rate constant $k_n$ can be calculated from the intercept and the slope of linear second-order equation. If the results were plotted directly according to equation (18), a reasonable straight line is obtained. However, the intercept at $t = 0$ may not be equal to 1.0. The author could not interpret these results but indicated that a significant sorption was shown at time $t = 0$. To interpret these results, the new boundary conditions of equation (18) should be defined at $t = 0$, at $q = q_0 = 0$. Assume the pre-second-order reaction occurs very rapidly at $t \sim 0$. [44]

$$\frac{d\theta}{dt} = k_n (1 - \theta)^n \quad \text{................................................................. (19)}$$

When

$$\theta_0 = \frac{q_0}{q_m}, \quad \text{at } t = 0$$

$$\frac{1}{(1-\theta)^{n-1}} = (n-1)k_n t + \frac{1}{(1-\theta)^{n-1}}$$

When $n = 2$, $\beta = q_t/q_m$, and $\beta_0 = \frac{1}{(1-\theta_0)}$, the equation becomes:

$$\frac{q_m}{(q_m-q_t)} = k_n t + \beta_0 \quad \text{................................................................. (20)}$$

Rearranging equation (20) gives the nonlinear form:

$$q_t = q_m \left[ \frac{(\beta_0-1)+k_n t}{\beta_0+k_n t} \right] \quad \text{................................................................. (21)}$$

The linear form becomes:

$$\frac{1}{q_t} = \frac{1}{q_m(\beta_0-1)+k_n t} + \frac{1}{q_m} \quad \text{................................................................. (22)}$$

When $\theta_0 = 0$ (no surface coverage) at $t = 0$, then $\beta_0 = 1$, and equation (21) becomes equation 22).

### 3.6. SORPTION MODEL SELECTION

Due to the large array of models, as shown in this paper, the selection of a sorption model for testing is not an easy or obvious choice. Furthermore, the mathematical model should be consistent with a proposed mechanism for sorption although the identification of a potential mechanism alone is usually not sufficient to define the rate controlling kinetic or diffusion process. An additional complicating factor is that the initial rate controlling process may change throughout the duration of the sorption process, for example, initially external film diffusion, may give way to reaction which after a further time...
period may become diffusion controlled. Therefore, in order to identify the correct sorption model usually involves selecting and testing several models and system variables over the entire sorption range, from \( t = 0 \) until sorbent saturation is achieved. [265]

### 3.6.1. Step 1—Mechanism

A preliminary appraisal of the sorbent-sorbate system may provide information indicating the sorption mechanism. For instance, are there any chemical groups on the sorbent which can undergo chemical reaction to form a chemical bond? Acid groups on the sorbent could provide ion exchange sites for metal ions and ionic dyes, amine groups can provide a lone pair of electrons for chelation with metal ions etc. Relatively inert sorbent surfaces may only provide physical sites for diffusional controlled bond formation. In order to identify the exact mechanism it is necessary to carry out experiments to study several system variables, namely, initial concentration, sorbent particle size, solution temperature, solution pH and agitation and analyse the data for different order kinetic reactions or for pore/solid phase diffusion mechanisms. The correlation coefficients between experimental and theoretical data will provide the ‘best fit’ model. The suitability of this model still needs to be confirmed by proposing a mechanism appropriate to the sorption model. The difference between kinetic sorption and diffusion sorption can be confirmed by analyzing experimental data in a number of ways. Usually more than one system variable is required as several different mathematical model equations can fit a limited number of experimental data points with a high degree of accuracy.[265]

### 3.6.2. Step 2—Kinetic versus Diffusion Control

The distinction between these two processes is often difficult to characterize. For example, the removal of a metal ion from an effluent by an ion exchanger is obviously an ion-exchange mechanism, which is often rapid and not rate controlling. Rate control could be the intraparticle diffusion of the metal ions throughout the pores of the ion exchange sorbent. As a very general guideline, from the literature presented in this paper, if equilibrium is achieved within three hours, the process is usually kinetic controlled and above twenty four hours, it is diffusion controlled. Either or both kinetic and
sorption processes may be rate controlling in the three to twenty four hour period. Another very general guideline is that changes in pH have a greater effect on the sorption of solutes in reaction controlled sorption processes. A more appropriate quantitative approach to distinguishing between kinetic and diffusion rate control is to perform the square root of contact time analysis according to equation (29). A plot of the amount of pollutant adsorbed, $q_t$, against the square root of time, $t_{0.5}$, yields a straight line plot of slope $k_d$, a diffusional rate parameter. This straight line, passing through the origin, indicates intraparticle diffusion control. This approach has been successful in many cases [275, 217, 126, and 92]. In cases of adsorbents whose pore size range is extensive including micro-, meso and macropores up to three linear sections have been obtained [35,184]. Additional confirmation of a diffusion mechanism should be obtained by analyzing the effect of the system variables on $k_d$. For intraparticle diffusion controlling systems: - $k_d$ should vary linearly with reciprocal particle diameter; the product of $k_d$ times sorbent mass should vary linearly with sorbent mass. Furthermore, it is possible to determine the sorption energy by carrying out sorption studies at different temperatures. The rates of reaction sorption increase more rapidly than those of diffusion processes with temperature. When $k_d$ is plotted against reciprocal temperature (Arrhenius plot) for diffusion controlled processes the energy of adsorption is usually less than 25–30 kJ/mol. [265]

3.6.3. Step 3–Kinetic versus Combined Mass Transport

In order to distinguish between a reaction kinetic model and a model controlled by coupled reaction and diffusion, it is necessary to carry out a kinetic analysis. Linearisation of data and statistical analysis of data using correlation coefficients enables the “best fit” model to be determined.

3.6.4. Step 4–External Film Transport

When the plots in step 2 or step 3 do not pass through the origin, this is indicative of some degree of external film mass transfer or boundary layer control. For most systems reported in the literature, there is some evidence of film resistance in the initial stages of the sorption process. However, the concentration driving force, bulk concentration minus surface liquid concentration, decreases rapidly and so its influence is usually limited to the
early stages of adsorption. Equation (2) describes film transport and is analogous to the pseudo-first-order equation, however, a series of agitation and particle size variation experiments will usually distinguish which mechanism is controlling. External film diffusion can be identified on a theoretical basis by plotting the mathematical function for kinetic sorption (first order, second order etc.) against time or for diffusion sorption \( (q_t) \) versus square root of time. [265]. If the plots do not go through the origin it is indicative of external film control and the film mass transfer parameter can be determined from equations. External film diffusion is best identified by carrying out a series of agitated batch contact time experiments at different agitation speeds. Agitation shears the film boundary layer reducing this mass transfer resistance and can be easily seen from plots of solute concentration versus time. As the agitation speed is changed, the rate controlling process may also change from film to reaction or diffusion. Another ‘external’ phenomenon is a surface enhancement often associated with highly energetic heterogeneous surfaces. This results in a high rapid uptake of solute on the sorbent before the system stabilizes. This effect is seen on similar plots to those used in the identification of external film mass transport; but in this case, varying agitation speed has little influence on the rate of uptake. [265]

3.7. MODELLING OF BATCH EQUILIBRIUM ISOTHERMS

To examine the relationship between sorbed \((q_e)\) and aqueous concentrations \((C_e)\) at equilibrium, sorption isotherm models are widely employed for fitting the data, of which the Langmuir and Freundlich equations are the most commonly used. The capacity of a sorbent can be described by its equilibrium sorption isotherm, which is characterized by certain constants whose values express the surface properties and affinity of the sorbent.

3.7.1. Freundlich Biosorption Isotherm Model

The Freundlich isotherm is an empirical isotherm that can be used for non-ideal adsorption and expressed as follows:

\[
q = K_f C^{1/n}
\]

The Freundlich model is also widely used but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model. [95]
3.7.2. Langmir Biosorption Isotherm Model

In 1916, Irving Langmuir published an isotherm for gases adsorbed on solids, which retained his name. It is an empirical isotherm derived from a proposed kinetic mechanism. The Langmuir isotherm is probably the most widely applied sorption isotherm. It is based on four hypotheses: [144]

- The surface of the adsorbent is uniform, that is, all the adsorption sites are equal.
- Adsorbed molecules do not interact.
- All adsorption occurs through the same mechanism.
- At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

This model can be mathematically described as:

\[ q_e = K q_{\text{max}} C_e / (1 + K C_e) \]

3.8. MODELLING OF CONTINUOUS BIOSORPTION PROCESS

3.8.1. THE Bed Depth–Service Time (BDST)

The Bed depth–service time (BDST) model, proposed by Bohart and Adams and subsequently modified by Hutchins is based on physically measuring the capacity of the bed at different breakthrough values. This simplified design model ignores the intraparticle mass transfer resistance and the external film resistance such that the sorbate is sorbed onto the sorbent surface directly. The BDST model states that bed height (Z) and service time (t) of a column is presented by the equation:

\[ t = \frac{N_0 Z}{C_0 V} \cdot \frac{1}{K_a C_0} \ln \left( \frac{C_0}{C_b} - 1 \right) \]

3.8.2. Thomas Model

The data obtained in column in continuous mode studies was used to calculate maximum solid phase concentration of metals on biosorbent and the adsorption rate constant using the kinetic model developed by Thomas. The Thomas solution is one of the most general and widely used methods in column performance theory. The expression by Thomas for an adsorption column is given as follows:
\[
\frac{c_t}{c_0} = \frac{1}{1 + \exp\left[\left(\frac{K_{TH}(q_0 x - c_0 V_{eff})}{v}\right)\right]}
\]