

2 Biosorption

2.1 Introduction

During the 1970's increasing environmental awareness and concern led to a search for new techniques capable of inexpensive treatment of waste waters polluted with metals. These demands led to increasing interest in biosorption.

Mining and refining industries generate a low concentration flow of metals for which standard techniques are not well suited, economically or technologically. The use of biosorbents has been proposed as an alternative, as it has proven effective on low concentration flows. Biosorption is of industrial interest, not only for its ability to remove metals from waste waters, but also for the possibility of recovering metals. The industries that may use biosorption on a large scale are, for example, metal plating, acid mine drainage and metal processing. With the accelerating depletion of natural mineral sources, there is a need for recycling metals already in use. The prices for some metals have risen over recent years, which makes recycling interesting from an economic point of view as well. Loaded biosorbents can be treated and adsorbed metal recycled.

The use of sorbents of biological origin, biopolymers, for removing heavy metals from dilute aqueous solutions has long been recognized, (Tsezos 1986). Calcium alginate has been one of the most extensively investigated biopolymers for binding heavy metals from dilute aqueous solutions (Chen et al. 1993; Jang et al. 1991). Another widely studied biopolymer is chitosan. Chitosan, a poly(D-glucosamine), is prepared from chitin by deacetylating its acetamide groups with a strong alkali solution. Chitin is a natural polymer extracted from crustacean shells, such as prawns, crabs, insects, shrimps and fungal biomasses. Chitosan has already been described as a suitable natural polymer

for the collection of metal ions, through chelation, due to the presence of an amino group of the 2-amino-2-deoxy-D-glucose (glucosamine) unit (Muzzarelli 1973; Masri et al. 1978; Maruca et al. 1982; Inoue et al. 1993).

Biosorption has advantages compared with conventional techniques (Volesky 1999). Some of these are listed below:

- Cheap: the cost for biosorbents is low since they often are made from abundant or waste material. The price for a biosorbent is around \$ 10-15/kg. In comparison, the price for ion exchange resins is \$ 30-50/kg.
- Metal selective: the metal-sorbing performance of different types of biomass can be more or less selective on different metals. This depends on various factors, such as type of biomass, mixture in the solution, type of biomass preparation and physico-chemical environment.
- Regenerative: biosorbents can be reused, after the metal is recycled.
- Process equipment known.
- No sludge generation: no secondary problems with sludge occur with biosorption, as is the case with many other techniques, for example precipitation.
- Metal recovery possible: metals can be recovered after being sorbed from the solution.
- Competitive performance: biosorption is capable of a performance comparable to the most similar technique, ion exchange treatment. Ion exchange is, as mentioned above, rather costly, making the low cost of biosorption a major factor.

In order to conduct a thorough study of the biosorption of metals, it is necessary to take into account the different areas which affect it, including a study of the mechanism of metal sorption, modelling of results and the adaptation of the sorbent.

2.2 Experimental procedure for metals sorption

In this section the methods used in a closed reactor (batch system) and then in a open reactor (dynamic system) are reported.

2.2.1 Batch system

2.2.1.1 Obtaining isotherms

The most appropriate method for assessing biosorbent capacity is the derivation of a whole sorption isotherm. The sorption isotherm is the equilibrium between the concentration in the fluid phase and the concentration in adsorbent particles at a given temperature. For liquids, concentration is usually expressed in units of mass, such as parts per million or mg of metal per litre of solution. The concentration of sorbate on the solid is expressed as mass sorbed per unit of mass of the original sorbent (Tien 1994).

An isotherm is favourable if its fixation capacity grows rapidly with concentration in equilibrium in the liquid phase, convex form. The maximum for a highly favourable isotherm is irreversible adsorption, where the amount adsorbed does not depend on the decrease in concentration down to very low values, unlike unfavourable isotherms which have a low adsorption capacity at low concentrations in equilibrium, concave form (Figure 2.1).

Figure 2.1: Shape of equilibrium isotherms (a) favorable, (b) linear, (c) unfavorable

In order to obtain the different points of the adsorption isotherm, the method in a closed reactor consists of putting different known masses of the adsorbent in contact with a given volume of solution containing the solute at an initial, known concentration. For each experiment, all the initial conditions remain constant (concentration, pH); only the amount of the adsorbent added to the reactor varies. After the adsorbent comes into contact with the solute solution, the samples are agitated in a uniform manner to reach equilibrium. The time necessary to reach equilibrium depends on the system being studied, so it is necessary to have prior knowledge of it to be sure the concentration being measured is the equilibrium concentration.

Once equilibrium has been reached, the concentration of each sample is measured, as is the final pH of the solution. The adsorption capacity is obtained by using a mass equilibrium equation. The adsorption capacity is expressed as follows:

$$q = \frac{(C_0 - C_{eq})V}{m} \quad (1)$$

C_0 and C_{eq} being the initial concentration and equilibrium concentration respectively, V the experimental volume expressed in litres, and m the adsorbent mass expressed in grams.

Knowledge of adsorption isotherms is most important; in addition to informing us of the adsorption capacity, it enables us to evaluate to what extent an adsorption system can be improved, as well as helping us to foresee the type of conditions in which we have to work in order to broaden our study to adsorption in an open reactor and estimate the necessary operating conditions for the system to be as effective as possible.

2.2.1.2 Study of Sorption Kinetics

Kinetic tests show the time-concentration profile for adsorption. The sorption reaction itself is inherently an extremely fast one. It is mainly the particle mass transfer which controls the overall adsorption kinetics (sorbent particle size, porosity, sorbate size and mixing in the sorption system). Monitoring a kinetic experiment enables us to see how the system is affected by these factors and to understand the stages which limit adsorption. The sorption kinetics thus constitutes a major criterion in the determination of the interest of sorption processes (Volesky 1999).

Kinetic studies are carried out by mixing an amount of sorbent with a given volume of metal solution, with various metal concentrations. The different tank reactors are agitated at the same speed. Alternatively, we can keep the same metal concentration and vary the amount of adsorbent (or other factors). In both cases the samples were regularly withdrawn, filtered and analysed. The values of the different concentrations are represented on a timescale. We can also represent the evolution of sorption capacity over time.

It is particularly important to analyse the kinetics with a prior knowledge of the isotherms. Isotherms enable us to know at all times the deviation from

equilibrium which drives the transfer. The isotherm also enables us to know if the kinetic has led to the saturation of the sorbent. We must bear in mind that the last point of the kinetics refers to the equilibrium concentration; by applying the material balance we can obtain the sorption capacity in equilibrium; this should coincide with the curve of the sorption isotherm obtained previously.

2.2.2 Dynamic Sorption

A study of sorption in an open reactor is based on determining the effluent-time concentration curves or the effluent-volume concentration curves, which are a function of the sorber geometry, the conditions of the operation and also the equilibrium sorption data. The effluent-time (or if applicable effluent-volume) concentration curve is generally known as "breakthrough" and is obtained by passing a fluid containing an sorbable solute with an initial concentration of C_0 through a bed packed with sorbent particles (column); as the fluid passes through the column, the solute is retained and the sorbent becomes saturated until the concentration at the outlet is equal to the initial concentration, establishing a distribution of the concentration inside the column as shown in Figure 2.2. In cases of ideal flow, with piston type reactors, there is no axial dispersion and the head is flat. In real cases, the sorption kinetic intervenes and perturbation appears due to axial dispersion (Wase and Forster 1997).

After time t_i , the solute starts to appear at the outlet of the column. Time t_b is defined as the time necessary to reach the changeover point concentration, indicated as C_b . This is the maximum permissible concentration of effluent. Time t_e is the time after which the bed is saturated with the sorbate. At this time, the bed is exhausted and has to regenerate. The time period from t_i to t_e is the thickness of the adsorption area or mass transfer in the bed and is related to the sorption process. The area under the curve represents the amount sorbed by the column, which is one point over the equilibrium isotherm.

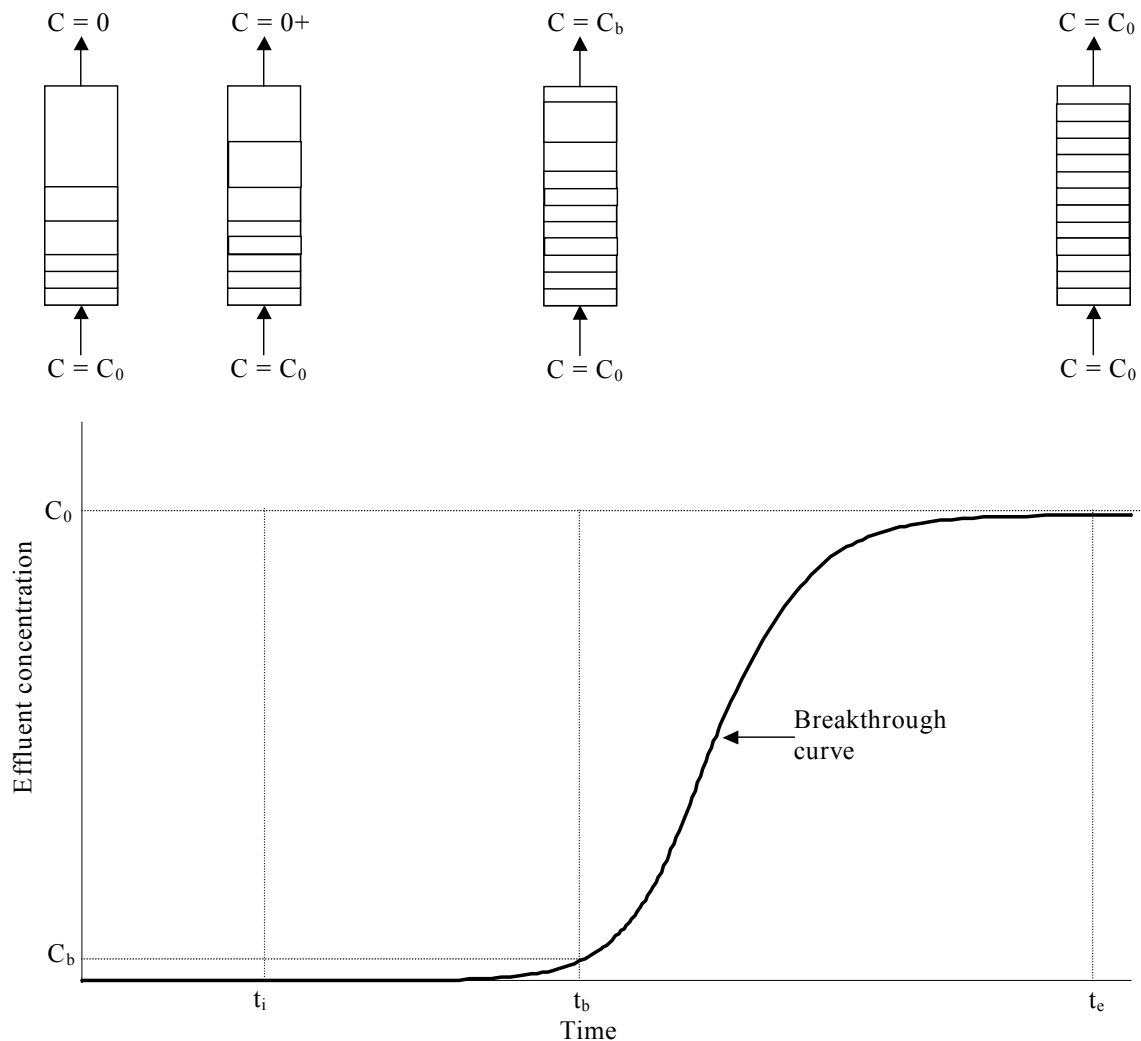


Figure 2.2: Adsorption wavefront

2.3 Desorption

The possibility of regeneration of loaded biosorbent is crucially important to keeping the process costs down and to opening the possibility of recovering the metal(s) extracted from the liquid phase. The deposited metals are washed out (desorbed) and biosorbency regenerated for another cycle of application (Volesky 1999). The desorption process should result in:

- high-concentration metal effluent;
- undiminished metal uptake upon re-use;
- no biosorbent physical-chemical damage.

The desorption and sorbent regeneration studies might require somewhat different methodologies. Screening for the most effective regenerating solution is the starting point.

Different affinities of metal ions for the biosorbent result in a certain degree of metal selectivity on the uptake. Similarly, another selectivity may be achieved upon the elution-desorption operation, which may serve as another means of eventually separating metals from one another if desirable.

The Concentration Ratio (CR) is used to evaluate the overall concentration effectiveness of the whole sorption process:

$$\text{CR} = \frac{\text{Eluate metal concentration}}{\text{Feed metal concentration}}$$

Obviously, the higher the CR, the better the overall performance of the sorption process, making the final recovery of the metal more feasible with higher eluate concentrations.

Following the desorption of the metal(s), the column may still be pre-treated for optimum operation in the subsequent metal uptake cycle. The type of pre-treatment may vary and could be used to optimise the column performance.

2.4 The Mechanism of Metal Biosorption

Sorption and desorption studies invariably yield information on the mechanism of metal biosorption: how the metal is bound within the biosorbent. This knowledge is essential for understanding the biosorption process and it serves as a basis for quantitative stoichiometric considerations which constitute the foundation for mathematical modelling of the process (Volesky 1999).

A number of different metal binding mechanisms has been postulated to be active in biosorption such as:

- chemisorption: by ion exchange, complexation, coordination, chelation;
- physical adsorption, microprecipitation.

There are also possible oxidation/reduction reactions taking place in the biosorbent. Due to the complexity of the biomaterials used it is quite possible that at least some of these mechanisms act simultaneously to varying degrees, depending on the biosorbent and the solution environment.

When the metal-biomass interaction mechanism(s) are reasonably understood, they offer possibilities for:

- optimising the biosorption process on the molecular level;
- developing economically attractive analogous sorbent materials;
- simplifying and effectively guiding the screening process.

Simple and economically feasible biomaterial procedures for suitable pre-treatment procedures for suitable biomaterials may be devised, based on a better understanding of the metal biosorbent mechanism(s).

2.5 Modelling

Mathematical modelling of biosorption offers an extremely powerful tool for a number of tasks on different levels. It is essential for process design and optimisation. The dynamic nature of the sorption process application (columns, flow-through contactors) makes this approach mandatory. When reaction kinetics is combined with mass transfer which is, in turn, dependent on the particle and fluid flow properties computer program is both extremely useful and necessary (Volesky 1999).

The mass transfer between the solution and the solid phase is modelled by several equations or concepts in both static and dynamic contact. Sorption isotherms show the distribution of solute between the liquid and solid phases.

This relation is used in several models of dynamic studies for the prediction of breakthrough curves, assuming various hypotheses as regards mechanisms and performances.

This section presents the different models applied in the study of sorption by the processes used, such as the study of sorption in a closed reactor and the system in an open reactor.

2.5.1 Sorption Isotherms

A wide array of equilibrium-based models have been used to describe sorption on solid surfaces. These include the usual isotherms equations such as those described by Freundlich, Langmuir, Brunauer Emmett and Teller or Sips (Kinniburgh 1986).

The Langmuir equation was developed by Irving Langmuir in 1918 to describe the adsorption of gas molecules on a planar surface. It was first applied to soils by Fried and Shapiro in 1956 and Olsen and Watanabe in 1957 to describe phosphate sorption on soils. Since that time, it has been widely employed in many fields to describe sorption on solid surfaces. The Langmuir model suggests, as a hypothesis, that uptake occurs on an homogenous surface by monolayer sorption without interaction between sorbed molecules. This model is described by the equation:

$$q = \frac{q_m b C_{eq}}{1 + b C_{eq}} \quad (2)$$

where q_m is the maximum sorption capacity for monolayer coverage ($\text{mg}\cdot\text{g}^{-1}$), and b is the affinity coefficient ($\text{L}\cdot\text{mg}^{-1}$), while q ($\text{mg}\cdot\text{g}^{-1}$), and C_{eq} ($\text{mg}\cdot\text{L}^{-1}$) represent sorption capacity and metal concentration in the solution at equilibrium respectively.

Another widely used sorption model is the Freundlich equation. The Freundlich model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, and with interactions between sorbed molecules, as described by the equation:

$$q = k_F C_{eq}^{1/n} \quad (3)$$

where k_F and n represents the Freundlich coefficients (n dimensionless; k_F : $\text{mg}^{1-1/n} \cdot \text{g}^{-1} \cdot \text{L}^{1/n}$).

Model parameters q_m , b , n and k_F are obtained by nonlinear regression analysis to avoid statistical bias (Kinniburgh 1986).

2.5.2 Sorption Kinetics

The sorption of solutes on solid particles has been extensively studied (Tien 1994). The overall mechanism can be described as the succession of various steps (Figure 2.3): (1) solute transfer from the bulk solution to the boundary film, (2) solute transport from the boundary film to the surface of the sorbent (external diffusion), (3) transfer of the solute from the surface of the sorbent to the intraparticle active sites (intraparticle diffusion), (4) uptake of the solute on the active sites.

The first and fourth steps are considered as non limiting as the agitation provided is sufficient to avoid a concentration gradient in the solution, whereas the sorption is seen as a quasi instantaneous mechanism. So, external mass transfer resistance and intraparticle mass transfer resistance are the major controlling stages.

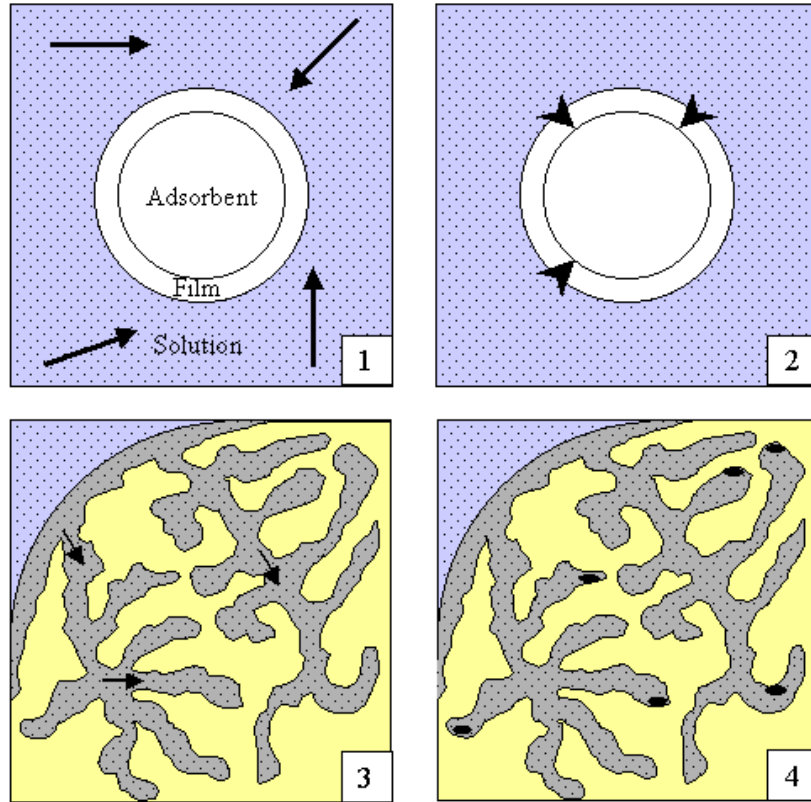


Figure 2.3: Steps of mechanism

The study of the rate laws is preceded by a brief discussions of the fundamental equation which form the basis for the quantitative treatment of ion-exchange and sorption kinetics.

For single-species sorption with spherical particles, the external mass-transfer rate may be expressed as

$$\frac{\partial \bar{q}}{\partial t} = k_L A (C - C_s) \quad (4)$$

where

\bar{q} = average sorbed-phase concentration ($\text{g} \cdot \text{kg}^{-1}$)

C and C_s = solute concentration in the bulk of fluid and on the particle surface ($\text{g} \cdot \text{m}^{-3}$)

A = surface area for the unit mass of sorbent ($\text{m}^2 \cdot \text{kg}^{-1}$)

k_L = interphase (or external) mass transfer coefficient ($\text{m} \cdot \text{s}^{-1}$)

The magnitude of k_L , of course, depends upon the flow conditions around the particle.

In a second step, the intraparticle diffusion is the preponderant rate controlling factor. The diffusion of solute through the particle was assumed to follow Fick's law. When the diffusion is considered radial, the diffusion equation for a constant diffusion coefficient takes the form

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) \quad (5)$$

where r is the radial variable and D is the global diffusion coefficient in the solid ($\text{m}^2 \cdot \text{min}^{-1}$ or $\text{m}^2 \cdot \text{s}^{-1}$).

The mass transfer in the fixed-bed sorption is described by the following system of equations:

the balance equation of process dynamics,

$$\frac{\partial C}{\partial t} + u_0 \frac{\partial C}{\partial Z} + \frac{(1-\varepsilon)}{\varepsilon} \rho_p \frac{\partial q}{\partial t} = D \frac{\partial^2 C}{\partial Z^2} \quad (6)$$

where

C = solute concentration in the liquid and phase ($\text{g} \cdot \text{m}^{-3}$)

q = solute concentration in the solid phase ($\text{g} \cdot \text{kg}^{-1}$)

t = time (s)

Z = distance from the column inlet (m)

D = axial diffusion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$)

u_0 = linear flow rate ($\text{m} \cdot \text{s}^{-1}$)

ε = fixed-bed porosity (m^3 voids/ m^3 bed = m^3 fluid/ m^3 bed)

the equation of process kinetics,

$$\frac{\partial q}{\partial t} = \Phi(C, q) \quad (7)$$

the system equilibrium, that is the sorption isotherm,

$$q_i = f(C_i) \quad (8)$$

The application of these equations are rather complex, even in the comparatively simple limiting cases which have so far been solved. In a rigorous quantitative treatment of complicated systems, for example, adsorption or ion exchange columns, mathematical difficulties are encountered. Simplified models are widely used. In the literature on ion exchange and adsorption there is no lack of such equations; some of them are empirical and others are based on simplified models or plausible assumptions. Most of these models were found to hold quite well in the systems investigated by their originators. However, they might well fail under only slightly different conditions. Then, various models which have been suggested and used are showed.

2.5.2.1 External Mass Transfer

A number of single resistance models have been proposed to determine the effect of external mass transfer in a sorbent system. The model proposed by Findon et al. in 1993 was the boundary method. The Boundary Model assumes that the surface concentration of metal ion is negligible at $t=0$, and consequently, intraparticle diffusion is negligible.

The change in solute concentration with respect to time is related to the liquid-solid film mass transfer coefficient, k_L , by the equation:

$$\frac{dC}{dt} = -k_L S (C - C_s) \quad (9)$$

where,

k_L = liquid-solid film mass transfer coefficient ($m \cdot s^{-1}$)

C = solute concentration in the solution at time t ($g \cdot m^{-3}$)

C_s = solute concentration in the solution on the surface sorbent ($g \cdot m^{-3}$)

S = the specific outer surface of sorbent particles per unit of volume of present particles (m^{-1}), which is obtained using the following equation:

$$S = \frac{6m}{d_p \rho_p (1 - \varepsilon)} \quad (10)$$

with,

$$m = \frac{w}{V} \quad (11)$$

being,

w = mass of sorbent (kg)

V = volume occupied for the particles (m^3)

d_p = mean particle diameter (m)

ρ_p = density of sorbent particles ($kg \cdot m^{-3}$)

ε = void fraction in the adsorption bed (m^3 void/ m^3 bed)

As $t = 0$, $C_s \rightarrow 0$ and $C = C_0$ the Eq. (9) becomes:

$$\left[\frac{dC}{dt} \right]_{t=0} = -k_L S C_0 \quad (12)$$

Given that with $t > 0$ $C_s > 0$ and $C < C_0$ the Eq.(16) becomes,

$$\left[\frac{d(C/C_0)}{dt} \right]_{t>0} = -k_L S \quad (13)$$

Hence, in a plot of C/C_0 versus time, k_L can be determined from the slope as $t \rightarrow 0$.

2.5.2.2 Intraparticle Mass Transfer

Morris and Weber (1964) and McKay and Poots (1980) demonstrate that in diffusion studies rate processes are usually expressed in terms of the square root of the time. So q_t or fraction metal sorbed $(1-C_t/C_0)$ is plotted against $t^{0.5}$. Initial slope is determined by the derivative (at $t=0$) of the polynomial linearisation of $(1-C_t/C_0)$ versus $t^{0.5}$. Following $(1-C_t/C_0)$ determination, the sorption rate (slope of q_t versus $t^{0.5}$) is calculated according to the conversion:

$$q_t = (C_0 - C_t)V / m = (1 - C_t / C_0)VC_0 / m \quad (14)$$

The slope of $(1-C_t/C_0)$ plot, multiplied by VC_0/m , gives the intraparticle diffusion rate.

Crank (1975) proposed a model whereby diffusion is controlled only by intraparticle mass transfer for a well-stirred solution of limited volume (V), assuming the solute concentration to always be uniform (initially C_0), and the sorbent sphere to be free from solute. Under these conditions after integration of Eq. (5), the total amount of solute M_t ($\text{mg}\cdot\text{g}^{-1}$) in a spherical particle after time t , expressed as a fraction of the corresponding quantity after infinite time (M_∞ , $\text{mg}\cdot\text{g}^{-1}$), is given by:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha + 1)\exp(-D_i g_n^2 t / d_p)}{9 + 9\alpha + g_n^2 \alpha^2} \quad (15)$$

where g_n 's are the non-zero roots of:

$$\tan g_n = \frac{3g_n}{3 + \alpha g_n^2} \quad (16)$$

and $\alpha = \frac{3V}{(4\pi a^3)}$, the ratio of the volumes of solution and sphere, or if there is a partition factor k between solute in equilibrium in the sphere and the solution, $\alpha = \frac{3V}{(4\pi a^3 k)}$. The parameter α is expressed in terms of the final fractional uptake of solute by the sphere by the relation:

$$\frac{M_{\infty}}{VC_0} = \frac{1}{1 + \alpha} \quad (17)$$

The fractional approach to equilibrium, FATE (M_t / M_{∞}), may be used to estimate the intraparticle diffusion coefficient D , when the external diffusion coefficient being neglected.

Urano and Tachikawa (1991) proposed an intraparticle diffusion coefficient D'_i based on the concentration in solids, assuming simple hypotheses such as the following: the sorption rate is independent of the stirring speed, and external mass transfer is non-limiting. The mass transfer is governed by the differential Eq. (5).

The solution of this differential equation, assuming boundary and mechanism hypotheses, is given by the following equation:

$$f(q_t / q_m) = -[\log(1 - q_t / q_m)^2] = \frac{4\pi^2 D'_i t}{2.3d_p^2} \quad (18)$$

where q_t and q_m are the metal concentration in the solid, at t and at equilibrium $t \rightarrow \infty$, and d_p is the mean particle diameter. The ratio q_t / q_m represents the fractional approach to equilibrium. So the diffusion coefficients, D'_i , is obtained by evaluation of the initial slope of $f(q_t / q_m)$ *versus* time, between 0 and 120 min.

In the models presented above, the external mass transfer resistance coefficients and the intraparticle diffusion (pore and/or solid diffusions) constants were examined separately, but numerous, more sophisticated models were investigated, amongst which we could mention the shrinking core model (SCM), (Levenspiel 1999), with special definitions for film diffusion, intraparticle diffusion, and chemical reaction control. This model was developed for the first time by Yagi and Kunii (1961). Tien (1994), describes a model which include external, intraparticle diffusion and sorption isotherm. Yiacoumi and Tien 1995, describe and compare sorption kinetics controlled by either reaction or diffusion mechanisms.

2.5.2.3 Modelling of Breakthrough Curves

Much has been written about the prediction of breakthrough curves. Recently, Ko et al. (1999), have analyzed the data using a model originally proposed by Bohart and Adams (1920) for the adsorption of chlorine and hydrogen chlorine on carbon. Considering a given portion of adsorbing material, its adsorption capacity diminishes at a rate given by

$$\frac{\partial N}{\partial t} = -kNC \quad (19)$$

considering the liquid phase, the solute concentration is diminishing at a rate given by

$$\frac{\partial C}{\partial Z} = -\frac{k}{u_0}NC \quad (20)$$

where

N = volumetric sorption capacity ($\text{g}\cdot\text{m}^{-3}$), $[N = q\rho_p(1 - \varepsilon)]$

C = solute concentration in solution ($\text{g}\cdot\text{m}^{-3}$)

k = kinetic constant ($\text{m}^3\cdot\text{g}^{-1}\cdot\text{s}^{-1}$)

u_0 = linear flow rate ($\text{m}\cdot\text{s}^{-1}$)

Z = distance from the column inlet (m)

If N_0 is the maximum volumetric sorption capacity and C_0 is the initial solute concentration in solution, the following non-dimensional parameters can be defined:

$$N' = \frac{N}{N_0}; \quad C' = \frac{C}{C_0}; \quad Z' = \frac{kN_0 Z}{u_0} \quad \text{and} \quad t' = kC_0 t$$

its derivatives being as follows:

$$\frac{\partial N'}{\partial N} = \frac{\partial N}{N_0}; \quad \frac{\partial C'}{\partial C} = \frac{\partial C}{C_0}; \quad \frac{\partial Z'}{\partial Z} = \frac{kN_0}{u_0} \frac{\partial Z}{\partial Z} \quad \text{and} \quad \frac{\partial t'}{\partial t} = kC_0 \frac{\partial t}{\partial t}$$

introducing these new parameters into the Eq. (19) and (20):

$$\frac{\partial N'}{\partial t'} = -N'C' \quad (21)$$

$$\frac{\partial C'}{\partial Z'} = -N'C' \quad (22)$$

On the following initial conditions:

$$\text{when } t' = 0 \Rightarrow C' = 1 \quad (21 \text{ bis})$$

$$\text{when } Z' = 0 \Rightarrow C' = 1 \quad (22 \text{ bis})$$

Integrating Eq. (21) with the initial condition (21 bis), the following is obtained:

$$N' = e^{-t'} \quad (23)$$

Integrating Eq. (22) with the initial condition (22 bis), the following is obtained:

$$C' = e^{-Z'} \quad (24)$$

If Eq. (24) is divided by $(C')^2$:

$$-\frac{\partial C' / (C')^2}{\partial Z'} = \frac{N'}{C'} \quad (25)$$

Introducing Eqs. (23) and (24) into Eq. (25):

$$-\frac{\partial C' / (C')^2}{\partial Z'} = e^{(Z'-t')} \quad (26)$$

Integrating Eq. (26):

$$\frac{1}{C'} = e^{(Z'-t')} - f(t') \quad (27)$$

Introducing the initial condition (22 bis) into Eq. (27):

$$f(t') = e^{-t'} - 1 \quad (28)$$

Then, introducing Eq. (28) into Eq. (27):

$$\frac{1}{C'} = e^{(Z'-t')} - e^{-t'} + 1 \Rightarrow \frac{1}{C'} - 1 = (e^{Z'} - 1)e^{-t'} \quad (29)$$

Applying logarithms to Eq. (29):

$$\ln\left(\frac{1}{C'} - 1\right) = \ln(e^{Z'} - 1) - t' \quad (30)$$

Doing again the change of initial variables, Eq. (30) remains:

$$\ln\left(\frac{C_0}{C} - 1\right) = \ln\left(e^{kN_0Z/u_0} - 1\right) - kC_0t \quad (31)$$

Because the exponential term, e^{kN_0Z/u_0} , is usually much higher than unity, the unity term within the brackets on the right-hand side of the Eq. (31) is often neglected. A linear relationship between the bed depth and service time can be written as

$$t = \frac{N_0Z}{C_0u_0} - \frac{1}{kC_0} \ln\left(\frac{C_0}{C} - 1\right) \quad (32)$$

For the current system, the critical bed depth, Z_0 , is the theoretical depth of sorbent to prevent the solute concentration from exceeding the breakthrough solute concentration (C_b) at $t = 0$. By letting $t = 0$ in Eq. (32), Z_0 is obtained:

$$Z_0 = \frac{u_0}{kN_0} \ln\left(\frac{C_0}{C_b} - 1\right) \quad (33)$$

According to Eq. (32), the service time, t , and the bed depth, Z can be correlated with the process parameters: the initial solute concentration, the solution flow rate, the sorption capacity, and the sorption rate constant. Eq. (32) is the bed depth service time (BDST) equation with the form of straight line $t = mZ + b$, as suggested by Hutchins (1973). Thus, the slope of the BDST plot, which equals N_0 / C_0u_0 , is the time required to exhaust a unit length of the sorbent in the column under the test condition. The intercept on the ordinate wave front to pass through the critical bed depth and is given by

$$b = \left(\frac{-1}{kC_0}\right) \ln\left(\frac{C_0}{C_b} - 1\right) \quad (34)$$

Wolborska (1989), shows that the phenomenon obeys the following equations,

the balance equation of process dynamics:

$$\frac{\partial C}{\partial t} + u_0 \frac{\partial C}{\partial Z} + \frac{\partial a}{\partial t} = D \frac{\partial^2 C}{\partial Z^2} \quad (35)$$

where:

C = solute concentration in the liquid and phase ($\text{g}\cdot\text{m}^{-3}$)

a = solute concentration in the solid phase ($\text{g}\cdot\text{m}^{-3}$)

t = time (s)

Z = distance from the column inlet (m)

D = axial diffusion coefficient ($\text{m}^2\cdot\text{s}^{-1}$)

u_0 = linear flow rate ($\text{m}\cdot\text{s}^{-1}$)

and the kinetic equation:

$$\frac{\partial a}{\partial t} = \beta(C - C_i) \quad (36)$$

being,

β = kinetic coefficient of the external mass transfer (s^{-1})

C_i = solute concentration at the solid-liquid interface ($\text{g}\cdot\text{m}^{-3}$)

The initial conditions are as follows:

$$t = 0 \quad C = 0 \quad \forall Z \quad (37)$$

$$t = 0 \quad a = 0 \quad \forall Z \quad (38)$$

The boundary conditions are:

$$Z = 0 \quad C = C_0 \quad \forall t \quad (39)$$

$$Z = \infty \quad C = 0 \quad \forall t \quad (40)$$

New variables were introduced:

time $\tau = t$ and bed height $h = Z - vt$, where v corresponds to the migration velocity of concentration fronts in the bed ($\text{m}\cdot\text{s}^{-1}$).

Balanced Eq. (35) takes the form of the ordinary differential equation:

$$(u_0 - v) \frac{\partial C}{\partial h} - v \frac{\partial a}{\partial h} = D \frac{\partial^2 C}{\partial h^2} \quad (41)$$

and Eq. (36) becomes:

$$-v \frac{\partial a}{\partial h} = \beta(C - C_i) \quad (42)$$

Moreover, initials and boundary conditions are transformed in :

$$\tau = 0 \quad C = 0 \quad \forall h \quad (37 \text{ bis})$$

$$\tau = 0 \quad a = 0 \quad \forall h \quad (38 \text{ bis})$$

$$h = 0 \quad C = C_0 \quad \forall \tau \quad (39 \text{ bis})$$

$$h = \infty \quad C = 0 \quad \forall \tau \quad (40 \text{ bis})$$

For the other hand, as $C_i \ll C$ and when $\tau \rightarrow 0 \Rightarrow \beta = \beta_0$, Eq. (42) remains:

$$-v \frac{\partial a}{\partial h} \cong \beta_0 C \quad (43)$$

Substituting Eq. (43) into Eq. (41), upon transformations, the equation describing mass transfer in the bed at the initial stage of the process was obtained:

$$\frac{\partial^2 C}{\partial h^2} - \left(\frac{u_0 - v}{D} \right) \frac{\partial C}{\partial h} - \frac{\beta_0 C}{D} = 0 \quad (44)$$

The integration of this equation with initials and boundary conditions proposed before takes to the following solution:

$$\frac{C}{C_0} = \exp\left[-\frac{(u_0 - v)h}{2D} \left(\sqrt{1 + \frac{4\beta_0 D}{(u_0 - v)^2}} - 1\right)\right] \quad (45)$$

Then, the parameter β_a (the effective kinetic coefficient) (Zolotarev et al. 1972) can be defined as following:

$$\beta_a = \frac{(u_0 - v)^2}{2D} \left(\sqrt{1 + \frac{4\beta_0 D}{(u_0 - v)^2}} - 1\right) \quad (46)$$

Therefore, Eq. (45) becomes:

$$\frac{C}{C_0} = \exp\left[-\frac{\beta_a}{(u_0 - v)} h\right] \quad (47)$$

When the effect of the axial dispersion is negligible, the Eq. (47) has the form:

$$\frac{C}{C_0} = \exp\left[-\frac{\beta_0}{(u_0 - v)} h\right] \quad (48)$$

Moreover, the migration velocity according to the Wicke law can be determined by:

$$v = \frac{u_0 C_e}{a_e + C_e} \quad (49)$$

where C_e, a_e = the sorbate concentrations in both phases under equilibrium conditions.

For $a_e \gg C_e$ and moreover, assuming that the process conditions are steady for low concentrations of the breakthrough curve $a_e = N_0$ and $C_e = C_0$, the Eq. (49) becomes:

$$v = \frac{u_0 C_0}{N_0} \quad (50)$$

For the other hand, $v \ll u_0$, therefore:

$$u_0 - v \cong u_0 \quad (51)$$

Substituting Eq. (51) into Eqs.(47) and (48), these are transformed to:

$$\frac{C}{C_0} = \exp\left[-\frac{\beta_a}{u_0} h\right] \quad (52)$$

$$\frac{C}{C_0} = \exp\left[-\frac{\beta_0}{u_0} h\right] \quad (53)$$

Doing again the change of initial variable, $h = Z - vt$, and Eq. (50) is introduced, before Eqs. finally becomes:

■ in the process with the axial dispersion:

$$\ln \frac{C}{C_0} = \frac{\beta_a C_0}{N_0} t - \frac{\beta_a}{u_0} Z \quad (54)$$

with

$$\beta_a = \frac{u_0^2}{2D} \left(\sqrt{1 + \frac{4\beta_0 D}{u_0^2}} - 1 \right) \quad (55)$$

■ in the process without the axial diffusion:

$$\ln \frac{C}{C_0} = \frac{\beta_0 C_0}{N_0} t - \frac{\beta_0}{u_0} Z \quad (56)$$

The expression of the Wolborska solution is usable in the low concentrations range and is equivalent to the Adams-Bohart relation if coefficient k is equal to β_a / N_0 . So the drawing of $\ln C/C_0$ *versus* t would give information on both models.

