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General Aspects of Aqueous Sorption Process in Fixed Beds

M. A. S. D. Barros, P. A. Arroyo and E. A. Silva

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<http://dx.doi.org/10.5772/51954>

1. Introduction

Adsorption as well as ion exchange share many common features. Although such phenomena are distinct (ion exchange is a stoichiometric process) they can be generically denominated as sorption processes. Then, as already known, sorption is a well-established technology in chemical engineering.

The sorption ability of different sorbents is strongly dependent on the available surface area, polarity, contact time, pH and the degree of hydrophobic nature of the adsorbent and adsorbate (Suzuki, 1990). Therefore, the selection of the sorbent is the first step in such investigation. Studies should be firstly focused on batch systems in equilibrium and isotherms should be constructed.

Equilibrium condition is attained when the concentration of the solute remains constant, as a result of zero net transfer of solute sorbed and desorbed from sorbent surface. The equilibrium sorption isotherms describe these relationships between the equilibrium concentration of the sorbate in the solid and liquid phase at constant temperature. Experimental data may provide different isotherm shapes such as: Linear, Favorable, Strongly favorable, Irreversible and Unfavorable (McCabe et al., 2001) as shown in Figure 1.

The linear isotherm starts from the origin. Although it does not show a selectivity behavior, the sorbent related to this isotherm sometimes is chosen because the linear isotherm facilitates the column modeling, mainly when equilibrium data is added to the phenomenological dynamic model (Helferich, 1995).

Sorbents that provide isotherms with convex upward curvature are denominated as favorable and strongly favorable. These shapes are often selected for dynamic studies because they show the sorbent selectivity to the sorbate of interest. Nevertheless, they are not convenient

when regeneration is required because it may be related to an unfavorable isotherm and quite long mass-transfer zones in the bed (McCabe et al., 2001). Moreover, the famous Langmuir model provides good adjustments to strongly favorable isotherms as it forms a plateau that represents in many cases, the monolayer sorption. Here, it must be remembered that the equilibrium equation is used in the modeling of fixed bed.

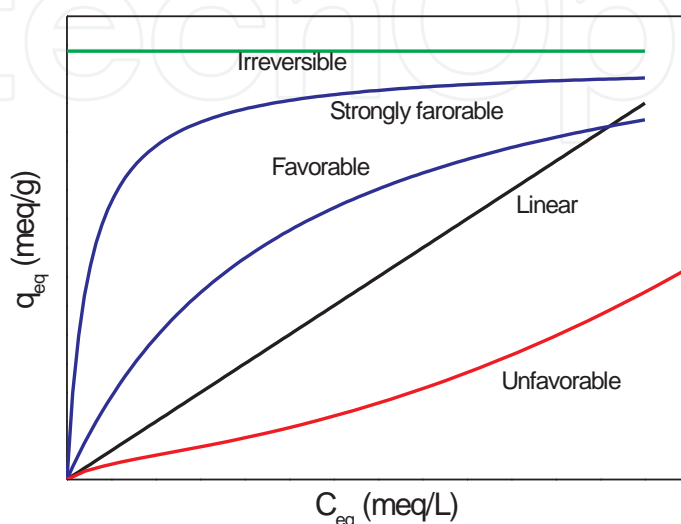


Figure 1. Adsorption isotherms

Finally, it may be emphasized that the Langmuir isotherm is derived assuming a uniform surface, which in many cases is not rigorously valid. This relation works fairly well, even with sorbents with high heterogeneity such as zeolites, clays or activated carbon. Here some aspects should be stressed. The first one is related to the model itself. Sometimes the Langmuir model represents the experimental data although it is known that there are different sites involved in the sorption process such as the ones located in the supercages or in the sodalite cages of NaX zeolite (Barros et al., 2004). On the other hand, sorbent may have high heterogeneity and only one type of site is effective in the sorption process. Then, the experimental data may be fitted successfully to such model and the assumptions previously considered are still valid. This may be the case of sorption of large molecules such as dyes.

The limiting case of the extremely favorable isotherm is the irreversible sorption represented by a horizontal line, that means a constant amount of sorbed compound. When the irreversible isotherm is obtained no regeneration is possible.

Designing of dynamic sorption processes also takes into account the multicomponent effluent. It means that studies of batch competitive systems should be relevant. Sorbents that have affinity to different sorbates may be less effective in removing the one of interest. In these cases, higher packed beds are required. The multicomponent equilibrium data are obtained considering the initial multicomponent solution. Many models have been proposed.

Some of them are derived from the single Langmuir model. As it happens with the single sorption, even when the ion exchange phenomenon is involved, release of the out-going ion is neglected (Misak 2000; Sprynskyy et al., 2006).

The Binary Langmuir Model assumes a homogeneous surface with respect to the energy of adsorption, no interaction between adsorbed species and that all adsorption sites are equally available to all adsorbed species. The Noncompetitive Langmuir Model considers that the concentration of the sorbate of interest in the sorbent depends on the concentration of the respective specie in the fluid phase only. In this case, monocomponent Langmuir can be applied for each one of the species in solution (Sánchez et al., 1999). In both cases, the Binary Langmuir Model and the Noncompetitive Langmuir Model, as there is no competition to the same sites, no overshooting is observed in the breakthrough curve. Overshooting will be discussed later.

The Langmuir Type Model was developed to describe the noncompetitive inhibition during enzymatic kinetic studies. According to the adsorption point of view such model may be applied when a synergism effect is presented due to the existence of sites containing both species (Bailey and Ollis, 1986; Sánchez et al., 1999). It means that in the dynamic sorption more adsorption occurs than the one it was expected, and the uptake on the sorbate of interest is promoted by the presence of other sorbates. No overshooting is expected to occur in this system.

Jain and Snoeyink (1973) have proposed an adsorption model for binary mixtures based on the hypothesis that a part of adsorption occurs without competition. In other words it means that there is at least one type of sorption site where the sorbate of interest is preferentially retained with no competition. In other types of sites, competition occurs. Then, it may be supposed that a slightly overshooting curvature may be evidenced in the breakthrough curve.

Myers and Prausnitz (1965) developed the ideal adsorbed solution theory (IAST) based on the Gibbs adsorption isotherm. The IAST model has the main advantage to predict the equilibrium in multicomponent systems in microporous materials through the single isotherms only. However, although the model allows its application in many complex mixtures of solutes, the IAST model limits its use in the range of concentration where the single equilibrium data were obtained. It has been used to predict the sorption process in gas phase, mainly in diluted systems.

A non-predictive thermodynamic approach called RAST (Real Adsorbed Solution Theory) extends the IAST theory to more concentrated solutes using the corresponding activity coefficients.

Finally, when the ion exchange process is much more pronounced than the adsorption process, it may be applied the Ion Exchange Model taking into account the Mass Action Law. In typical ion exchangers such as zeolites this mode are applied with successful results.

After selecting the sorbent and investigating the sorption mechanism, the second step is the dynamic studies in the fixed bed system.

2. Dynamic studies in fixed bed systems

2.1. The breakthrough curve

Most ion-exchange operations, whether in laboratory or in plant-scale processes, are carried out in columns. A solution is passed through a bed of sorbent beads where its composition is changed by sorption. The composition of the effluent and its change with time depend on the properties of the sorbent (as already discussed), the composition of the feed, and the operating conditions (flow rate, temperature etc.). Plots of the ratio C/C_o (outlet sorbate concentration/sorbate feed concentration) versus time are denominated as breakthrough curves.

As the run starts, most of the mass transfer takes place near the inlet of the bed, where the fluid first contacts the sorbent. If the solid contains no sorbate at the start, the concentration in the fluid drops exponentially to zero before the end of the bed is reached. This concentration profile as well as the breakthrough curve is shown in Figure 1. As the run proceeds, the solid near the inlet is nearly saturated, and most of the mass transfer takes place further from the inlet. The concentration gradient is S shaped. The region where most of the change in concentration occurs is called the mass-transfer zone. This is the real behavior of mass transfer process in fixed beds. When the axial or radial mass transfer resistances are neglected sorption occurs homogeneously and this is the ideal case. In fact, mass transfer resistances can be minimized but not effectively eliminated. Comments about such phenomenon will be better detailed. The limits of the breakthrough curve are often taken as C/C_o values of 0.05 to 0.95, unless any other recommendation is fixed. They are related to the breakpoint (t_b, C_b) and saturation point (t_s, C_s), respectively. In most of cases $C_s = C_o$. This is the case of wastewater treatment of highly toxic sorbates. When the concentration reaches the limiting permissible value, say, 1 ppm, it is considered the break point. The flow is stopped, the column is regenerated and the inlet concentration is redirected to a fresh sorbent bed.

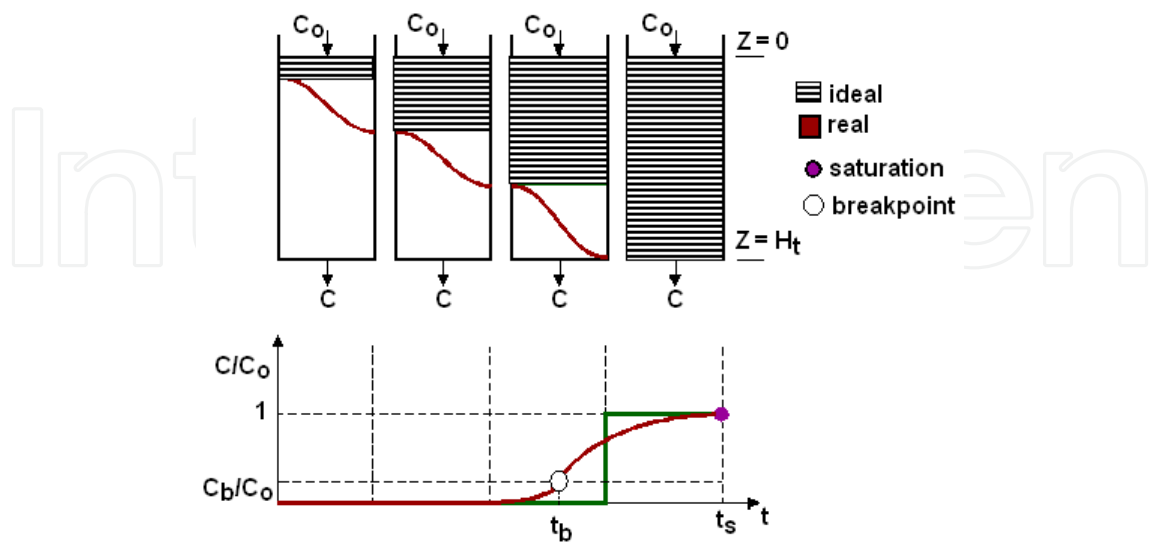


Figure 2. Breakthrough curve for the sorption process in fixed beds C_o is the concentration of the inlet solution, C_b is the concentration of the breakthrough, t_b is the breakpoint time and t_s is the saturation time.

2.2. Mass transfer in fixed beds

In fixed-bed ion exchange, the concentration in the fluid phase and in the solid phase changes with time as well as with position in the bed. The transfer process is described by the overall volumetric coefficient ($K_c a$), obtained from a metal material balance in the column assuming irreversible sorption as proposed in McCabe et al. (2001):

$$K_c a = \frac{N \cdot u_o}{H_t} \quad (1)$$

where N is the overall number of transfer units, H_t is the bed length and u_o is the superficial velocity of the fluid.

In fact, Eq. 1 can be used for modeling the breakthrough curves, if the batch isotherms can be considered as irreversible.

The overall number of transfer units may be obtained graphically by plotting C/C_o versus $N(\tau-1)$, where $N(\tau-1) = 1 + \ln(C/C_o)$ (McCabe et al., 2001). Parameter τ is dimensionless time defined as

$$\tau = \frac{u_o C_o \left(t - \frac{\epsilon}{u_o} H_t \right)}{\rho_p (1 - \epsilon) W_{sat} H_t} \quad (2)$$

The term $\frac{\epsilon}{u_o} H_t$ in Eq. 2 is the time required to displace fluid from external voids in the bed, which is normally negligible. The product is the total amount of metal fed per unit cross section of the bed up to time t and $\rho_p (1 - \epsilon) W_{sat} H_t$ is the capacity of the bed, which is equal to the time equivalent to total stoichiometric capacity of the packed-bed tower (t_t).

The time equivalent to usable capacity of the bed (t_u) and the time equivalent to total stoichiometric capacity of the packed-bed tower (t_t) if the entire bed reaches equilibrium are provided by a mass balance in the column and they are easily determined by (Geankoplis 1993):

$$t_u = \int_0^{t_b} \left(1 - \frac{C}{C_o} \right) dt \quad (3)$$

$$t_t = \int_0^{\infty} \left(1 - \frac{C}{C_o} \right) dt \quad (4)$$

where t_b is the breakpoint time.

If time t is assumed to be the time equivalent to the usable capacity of the bed (t_u) up to t_b , parameter τ may be simplified to t_u/t_t . This ratio is the fraction of total bed capacity or length utilized to the breakpoint (Geankoplis, 1993). Hence, the length of unused bed (H_{UNB}) is the unused fraction times the total length (H_t).

$$H_{UNB} = \left(1 - \frac{t_u}{t_t}\right) H_t \quad (5)$$

H_{UNB} is assumed to be constant and, as a consequence, an important tool when scaling-up processes (McCabe et al., 2001). Unfortunately it is not always true. A constant mass-transfer zone is valid for ideal sorption systems associated with sorbates of small molecular diameter and simple structures (Walker and Weatherly, 1997). Changes in pH speciation through the column may also change the MTZ (Gazola et al., 2006). It probably happens because the rate at which the sorption zone travels through the bed decreases with bed height (Walker and Weatherly, 1997). Therefore, it may be concluded that the hypothesis of a constant length of mass transfer zone for the same feed concentration can be acceptable depending on the variation of the bed height and specific sorbates.

H_{UNB} represents the mass-transfer zone (MTZ). Small values of this parameter mean that the breakthrough curve is close to an ideal step with negligible mass-transfer resistance. Moreover, in the ideal condition, no axial dispersion would occur. The velocity profile would be analogous to the one observed in a Plug Flow Reactor and the ideal breakthrough curve would be the response to a positive-step test, called the Cumulative Distribution Function or F curve. In the ideal breakthrough curve H_{UNB} is zero. This condition is never reached although it is recommended to operate the column as close as possible. The closer the column is operated to the ideal condition, the more efficient is the mass transfer zone. Therefore, the ideal situation means $H_{UNB} = 0$. In experimentally effective situation $0 < H_{UNB} < H_t$. If $H_{UNB} > H_t$ in the very beginning of the run the sorbate is presented in the outlet solution, the sorption process is highly inefficient, mainly if the sorption unit has been used for wastewater treatment. An increase in H_t is recommended.

Besides the minimum MTZ, some other mass transfer parameters may be used to identify, quantitatively, the condition with the lowest resistances over the operational conditions investigated.

One of this parameter is the residence-time distribution (RTD). According to Fogler (2004), the RTD is determined experimentally by injecting a tracer in the column at some time $t=0$ and then measuring the outlet concentration as a function of time. In this case, the tracer is used to determine RTD in reactors and must be nonreactive, easily detectable, completely soluble to the mixture and more important: it should not adsorb on the walls or any other surface of the reactor. If the injection of a tracer is given as a step injection, the response is the F curve which shape is analogous to the breakthrough curve as seen in Figure 2. Then, it is possible to obtain the average residence time (t_{res}). Correlation between the F curve from the non-ideal concept and the sorption process in fixed beds can be done only in terms of the graphical shape. No more similarities are corrected.

The average residence time (t_{res}) of the fluid in the column is estimated based on principles of probability as follows (Hill, 1977):

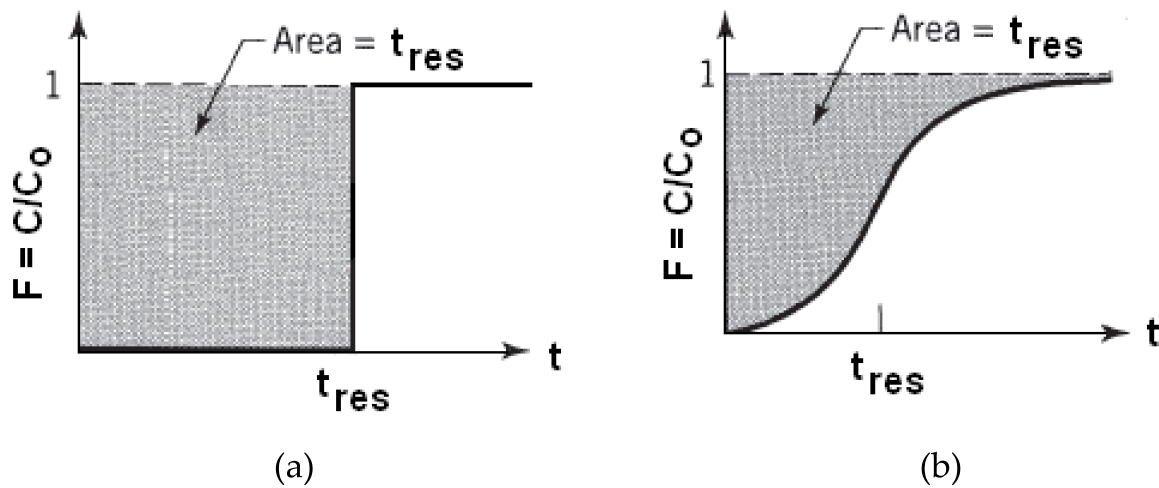


Figure 3. Breakthrough curves considering the F response of a step input: a) ideal situation ($H_{UNB} = 0$); b) real situation ($H_{UNB} > 0$).

$$t_{res} = \int_0^{\infty} t dF(t) \quad (6)$$

where $F(t)$ is the weight fraction of the effluent of an age less than t , which is equivalent to C/C_0 for breakthrough curves (Barros et al, 2003).

An indirect measure of how far from the optimum operational condition the column operates is expressed by the operational ratio (R) as (Barros et al., 2003)

$$R = \left| \frac{t_{res} - t_u}{t_u} \right| \quad (7)$$

Values of parameter R close to zero indicate that the operational conditions imposed are near the ideal condition, i.e., the optimal region of operation. Therefore, this difference may contribute to the selection of the best operational conditions in the column design.

With the average residence time it is also possible to evaluate the variance in the breakthrough curve (Hill, 1977), which is given by:

$$\sigma^2 = \int_0^{\infty} t^2 \left(\frac{dF(t)}{dt} \right) dt - t_{res}^2 \quad (8)$$

The dimensionless variance should be calculated as

$$\sigma_{\theta}^2 = \frac{\sigma^2}{t_{res}^2} \quad (9)$$

Determination of this parameter is useful to estimate the axial dispersion in the packed bed. Values of dimensionless variance close to zero mean that the behavior of the velocity profile in packed beds is close ideal plug-flow with negligible axial dispersion.

Finally, through a mass balance it is possible to obtain the amount of sorbate retained up to the breakpoint time (U^{t_b}) and up to the saturation time (U^{t_s}).

$$U^{t_b} = t_u \cdot f_R \cdot C_o \quad (10)$$

$$U^{t_s} = t_t \cdot f_R \cdot C_o \quad (11)$$

where t_u and t_t are obtained through Eqs. 3 and 4, f_R is the flow rate and C_o is the inlet concentration.

2.3. Minimum mass transfer resistances in the fixed bed

Operate the fixed bed with minimum mass transfer resistances is quite advantageous. It maximizes the sorption process as more sorption sites are available to the dynamic process. Therefore, optimizing the operational conditions is highly recommended. It can be done investigating a range of particle diameters of the sorbent or different flow rates in the column. In some cases, temperature should be also investigated. It is expected to obtain higher amount of uptaken sorbate with increasing temperatures when chemisorption and/or ion exchange are presented as the more significant mechanism. Nevertheless, if the retention is due to physisorption phenomenon, an increase in temperature is disadvantageous.

The optimal operational condition is the one that minimizes, as close as possible, the film and particle resistances, that means to maximize the pore diffusion and the solid diffusion. Figure 3 gives an idea about the mass transfer mechanism in a fixed bed.

Therefore, when the film and particle resistances are minimized it is seen that:

The mass transfer zone, the operational ratio and the dimensionless variance are minimum;

The closer the system is of the optimal condition, the closer the breakpoint time is to the saturation time;

The sorbate uptake up to breakpoint time (U^{t_b}) and up to saturation time (U^{t_s}) are the maximum. It happens when there is at least a favorable isotherm;

In most of cases, a steep breakthrough curve is observed.

Figure 4 shows an example of breakthrough curves at different flow rates. It is seen that at 11 mL/min the breakthrough curve is almost a step curve. Table 1 presents the numerical data and it is total agreement with Figure 4. It means that at this flow rate the minimum mass transfer resistance was reached considering the range investigated.

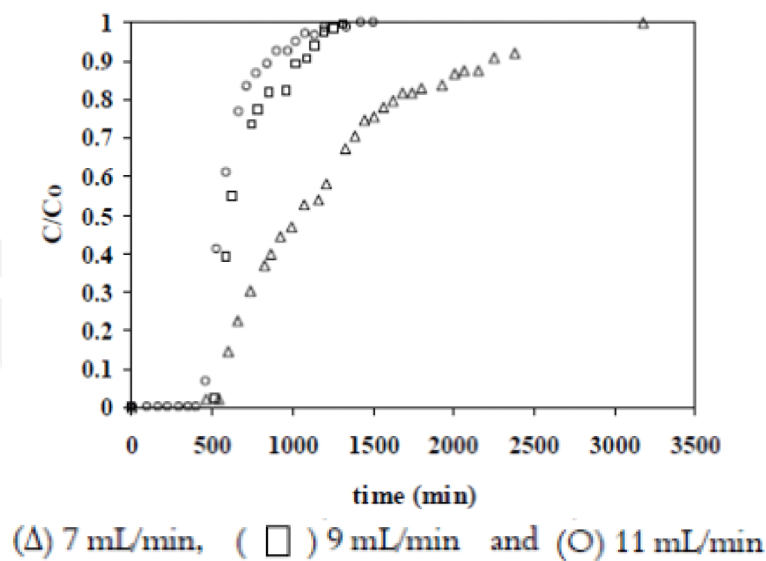


Figure 4. Breakthrough curves for Cr (III) uptake in NaA zeolite (Barros et al., 2002)

Flow rate (mL/min)	H_{UNB} (cm)	R	$\sigma_{\theta}^2 = \frac{\sigma^2}{t_{res}^2}$	$U_{Cr}^{t_b} / CEC_{bed}$
7.0	3.9	1.3	0.3	0.25
9.0	1.7	1.0	0.3	0.30
11.0	1.0	0.4	0.1	0.31

$U_{Cr}^{t_b} / CEC_{bed}$ = ratio of amount of Cr (III) retained up to the breakpoint and the cation exchange capacity of the zeolite in the bed.

Other examples can be found in Pereira et al. (2006).

Table 1. Mass-transfer parameters obtained for Cr(III) uptake in NaA zeolite packed bed (Barros et al., 2002)

2.4. Sorption in competing systems

When the feed solution is composed by different sorbates, the competition for the sorption sites may occur. Uptake of the sorbate of interest is well evidenced by the dynamic capacity of the column. Thus, the term $U_{i-mix}^{t_b}$ is defined as the amount of sorbate uptaken at t_b prior to the sorbate i breakpoint (Valdman et al., 2001).

The effect of competitive systems on the sorption process may be represented by the ratio of the uptake capacity for the sorbent i in multicomponent solution and in single solution, that is the removal ratio $\left(U_{i-mix}^{t_b} / U_{i-single}^{t_b} \right)$ -Mohan and Chander, (2001).

Thus if the removal ratio:

> 1 : uptake is promoted by the presence of other sorbates;

$=1$: no interaction exists between the sorbates;

< 1 : uptake is suppressed by the presence of other sorbates.

Therefore, the evaluation of the removal ratio at the time equivalent to usable capacity of the bed t_u for sorbate i may be useful to investigate the influence of different sorbates on the uptake of such sorbate (Barros et al., 2006).

Moreover, in the competing systems, sometimes the breakthrough curves for the competing sorbates may have values higher than one that is called overshooting. When the ion exchange phenomenon is dominant, it is also called sequential ion exchange (Barros et al., 2006). Figure 5 shows an example of a sequential ion exchange. The ion exchange preferentially occurs up to the occupation of all available sites. As the sorption proceeds, the competing sorbates are released at different running times with continued feed of the multicomponent solution. Potassium ions are smaller than the other ions. Then, they diffuse faster into the ion exchanger framework and are firstly retained. Calcium ions are larger and probably face some difficulties in diffusing as fast as the potassium ions. Nevertheless, once they diffuse, they are preferentially retained due to its higher charge, displacing the potassium ions. Finally, chromium ions are the largest ones with the highest charge. They diffuse slowly into the exchanger framework. They displace the calcium ions. The consequence of such process is the presence of two overshooting waves: one related to the release of potassium ions and another related to the release of the calcium ions. In this competing ion exchange process it is seen that $\left(\frac{U_{Cr-mix}^{t_b}}{U_{Cr-single}^{t_b}} \right)$ is 0.79, which means that there is a decrease of 21% in the chromium uptake. Probably the presence of potassium and mainly the presence of calcium ions suppressed the chromium uptake due to competition towards the exchanging sites located in the large cages of the zeolite NaY.

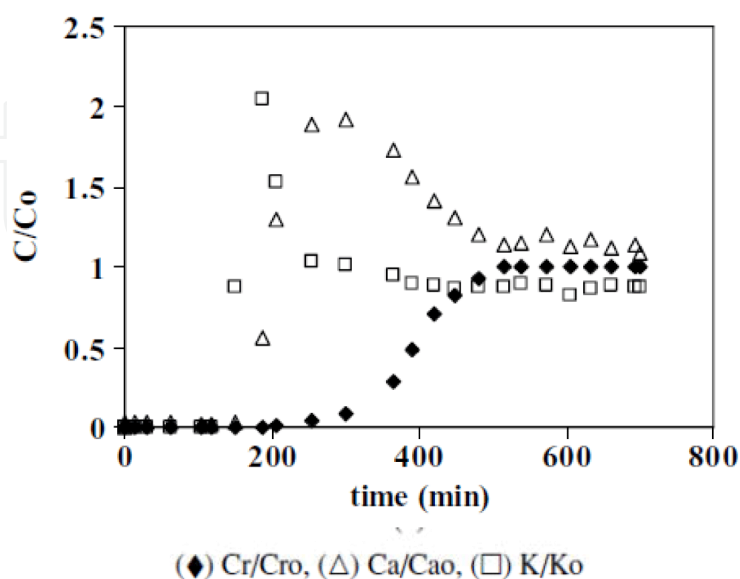


Figure 5. Breakthrough curves for competitive system Cr/Ca/K in NaY zeolite (Barros et al., 2006)

Overshooting may occur in different sorbents such as activated carbons (Mohan and Chander, 2001), biosorbents (Sağ et al., 2000) or even ion exchanger membranes (Labanda et al., 2011). It depends on the selectivity of the sorbent, the sorption mechanism (that can be seen through the isotherms) and on the operational conditions imposed. If the operational condition is the one that minimizes the mass transfer resistances of one sorbate is imposed, it is expected a pronounced overshooting when the optimal operational conditions of the other sorbates are different from the one of interest. When the optimal conditions are close, there should be some overshooting depending of the selectivity provided by the isotherms and the concentration of the sorbates, as shown in Figure 6.

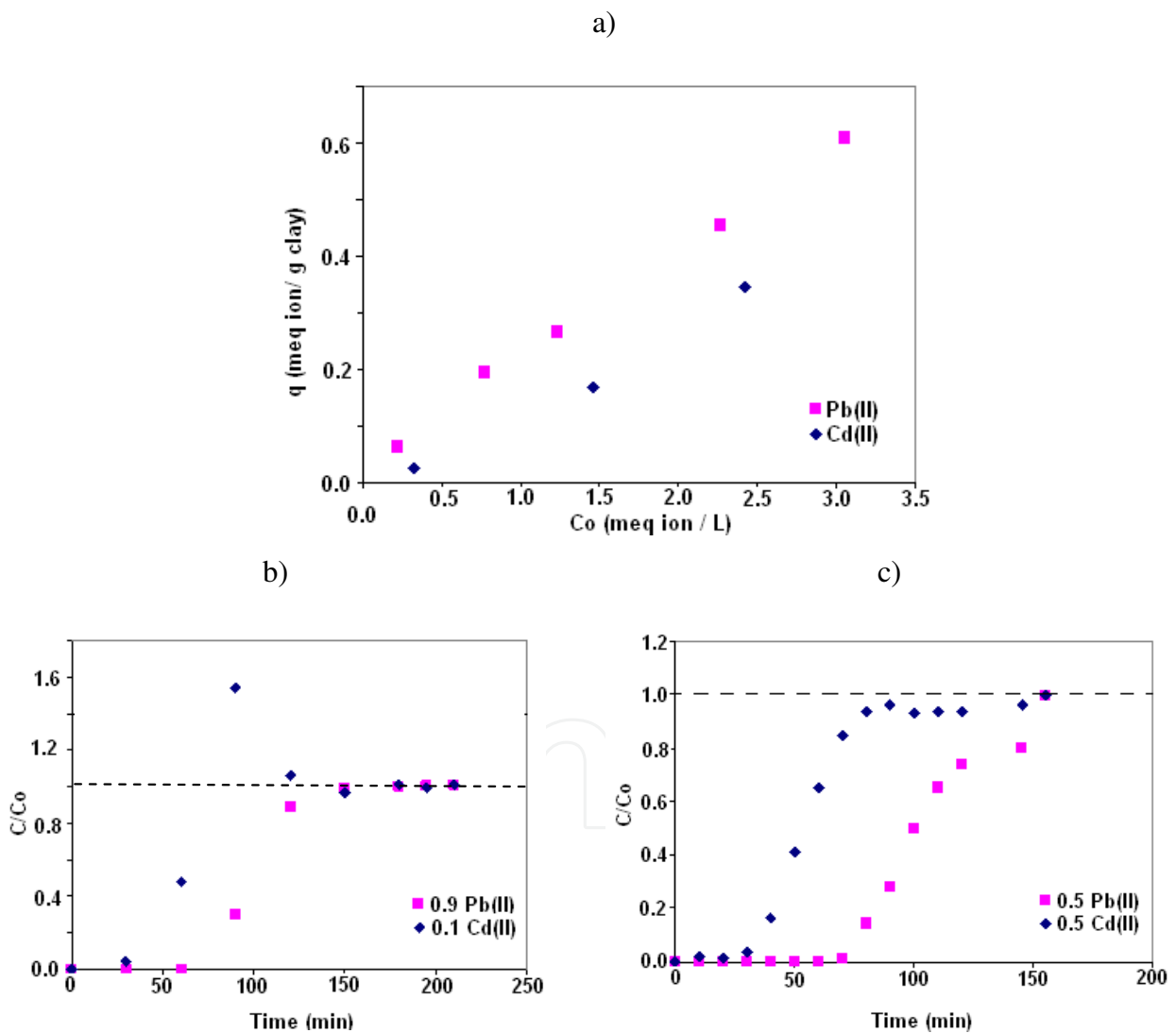


Figure 6. a) Dynamic isotherm (see item 2.5) of Pb (II)/Cd (II) in bentonite clay pretreated with calcium at 30 °C and 2 mL/min; b) breakthrough curve at 2 mL/min and total concentration of 3.0 meq/L, 90% Pb (II), 10% Cd (II); c) breakthrough curve at 2 mL/min and total concentration of 3.0 meq/L, 50% Pb (II), 50% Cd (II).

In Figure 6a it is seen the bicomponent dynamic isotherm of Cd (II) and Pb(II) ions in bentonite clay from Boa Vista-PB-Brazil. The clay sample was pretreated with calcium in order to obtain, as far as possible, a homoionic sample. The concept of dynamic isotherm will be discussed in section 2.5. In this system, the flow rate of 2 mL/min may be considered as the optimal condition that minimize the mass transfer resistances of both Cd(II) and Pb(II) uptake. It is seen that the clay sample has more affinity to lead ions, probably due to its electro-negativity (Kang et al., 2004).

Figures 6b and 6c show the breakthrough curves for two different inlet percentages of cadmium and lead and the same total concentration of 3 meq/L. In the first case the inlet concentration was composed by 90% Pb (II), 10% Cd (II) (2.7 meq/L of Pb (II) and 0.3 meq/L of Cd (II). In the second case the composition was 50% for each ion, or 1.5 meq/L of Pb (II) and 1.5 meq/L of Cd (II). The overshooting is clearly observed in Figure 6b due to the higher selectivity to lead ions. When cadmium concentration was increased no overshooting was observed although, according to the breakpoint times, it is also seen the preference of lead as its breakpoint occurs later.

2.5. Dynamic isotherms

Most separation and purification processes that employ the sorption technology use continuous-flow columns. In order to understand and to model the dynamic process, a deep knowledge of the equilibrium in the fixed bed is essential. For the complete comprehension of the whole process, information about the equilibrium and the kinetics of the process should be combined with the mass balance. Kinetic investigations in a column are almost exclusively restricted to those processes of which the equilibria either can be represented by a linear or a Langmuir isotherm or satisfy the law of mass action. However, the results of this study of industrially applicable commercial products have shown that the above equilibria usually fail to fit the experimental results adequately. Furthermore, the customary procedures of determining the equilibria in batch systems are not, in general, applicable to all types of sorbents (Klamer and Van Krevelen, 1958). For example, the batch isotherm was not able to represent correctly, the breakthrough curve of Cr (III) sorption in NaX zeolite modeled by a phenomenological model. Such model will be discussed in section 2.6. Figure 7 presents the batch isotherm of Cr (III) in zeolite NaX and its use in a LDF model. It is clearly seen that it is totally inadequate.

The dynamic isotherm surged to better describe the sorption mechanisms involved in a dynamic process where kinetics and equilibrium acts simultaneously. In fixed beds, solution is fed continuously, and, at equilibrium, concentration and pH are equal to their respective feed values that do not occur in batch isotherms. Its procedure is based on the breakthrough data. Each run up to the saturation is related to one point of such data, that is, the amount of sorbate retained up to saturation plotted against the inlet concentration (Barros et al., 2004). The dynamic isotherm has the advantage of controlling the fluid-phase concentration. Results of the column dynamic simulations depend on the selection of an appropriate mathematical relation used to represent the equilibrium. Therefore, in order to model the dynamic

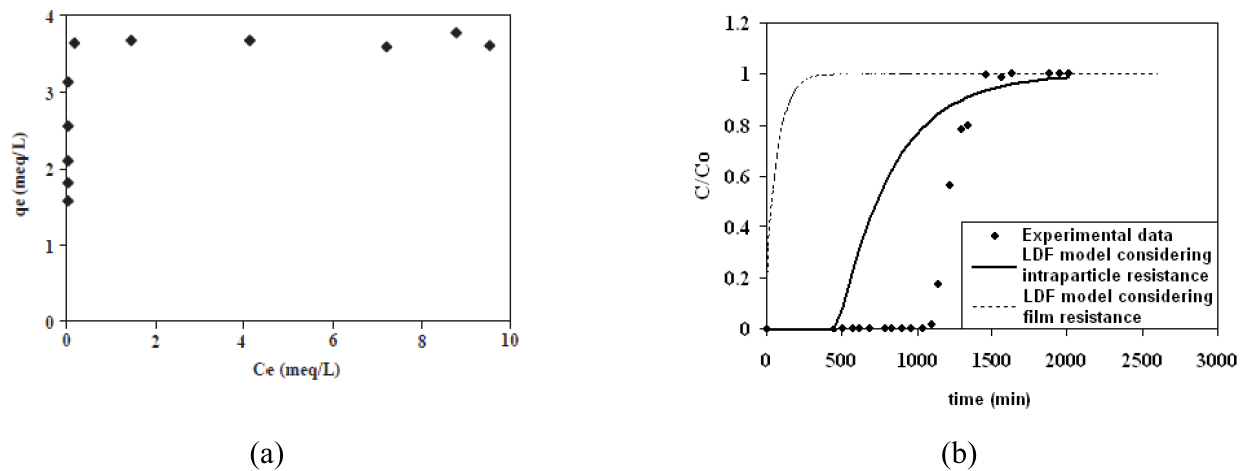


Figure 7. a) Batch isotherm of Cr (III) in zeolite NaX at 30 °C (Barros et al., 2004); b) Use of batch isotherm to model Cr (III) breakthrough data in NaX columns

sorption, dynamic isotherms should be considered instead of the frequently used batch isotherms as they better represent equilibrium in fixed bed (Barros et al., 2009).

The dynamic isotherm of Cr (III) in NaX is shown in Figure 8 at the optimal particle size and flow rate previously determined (Barros et al., 2004). Its shape is totally different, as one can see comparing Figures 8 and 7a.

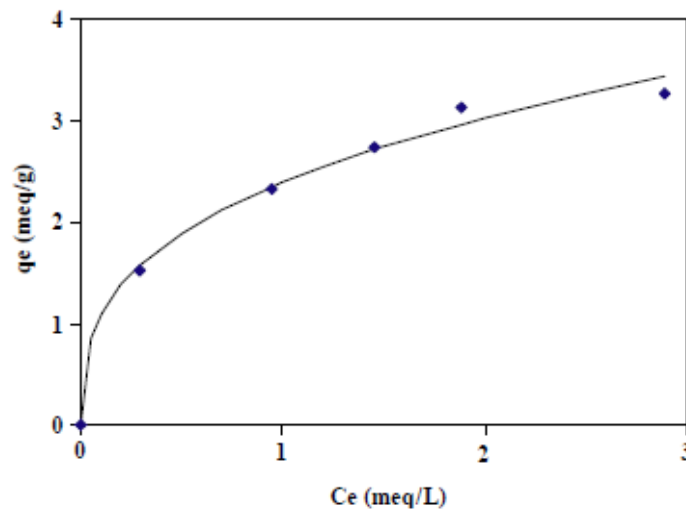


Figure 8. Dynamic isotherm of Cr (III) in zeolite NaX at 30 °C (Barros et al., 2004)

2.6. Modeling of the breakthrough curve

The phenomenological mathematical models are important tools in the design of sorption in fixed bed columns. The validation is done by experimental data obtained in laboratory scale. Mathematical models are useful for designing and optimizing purposes in industrial scale.

The effects of mass transfer in breakthrough curves are complex, mainly if the isotherms are expressed by non-linear mathematical equations. The concentration of the sorbate varies with the position and time. Therefore, the phenomenological model is represented by partial differential equations, which are difficult to be solved analytically.

Due to such complexity, the phenomenological mathematical models have many simplifications to make them feasible to obtain an analytical solution. Bohart and Adams (1920) developed one of the first mathematical models. The respective equation is given by Equation 12. This model was firstly used to describe the dynamic sorption of chlorine in columns packed with activated carbon and are still widely used by several researchers (Singh et al., 2012; Kumar et al., 2011; Rao et al., 2011; Trgo et al., 2011, Chu et al., 2011; Martin-Lara et al., 2010, Muhammad et al., 2010, Borba et al., 2008.). The model Bohart Adams considers that the limiting step of the mass transfer is controlled by the kinetics of sorption which is represented by a second-order reaction.

$$\frac{C_{out}}{C^F} = \begin{cases} 0 & t < t_F \\ \frac{1}{(e^A + e^{-B} - 1)e^B} & t > t_F \end{cases} \quad (12)$$

$$\text{where: } A = \frac{L}{u_0} \beta, B = \frac{(-tu_0 + L)\beta}{\alpha u_0}, \alpha = \frac{\rho_{bed} q^*}{C^F \varepsilon}, \beta = k_a C^F \alpha \text{ and } t_F = \frac{L}{u_0}$$

Bohart and Adams model presented only one adjustable parameter that is the rate constant k_a . The parameter q^* has been also reported as an adjustable parameter. However, its value can be determined is the saturation point of the breakthrough curves.

The model developed by Thomas (1944) has also analytical solution. The sorption rate is described by Langmuir adsorption kinetics. Both models, Thomas and Bohart and Adams consider negligible film and particle resistances as well as the dispersion within the column.

The Thomas mathematical model is obtained by mass balances of the sorbate in the fluid phase and in the solid phase. Such mass balances originate an equation that describe the equilibrium in the system. The mass balance in the fluid phase results in the following equation:

$$\frac{\partial C}{\partial t} + \rho_{bed} \frac{(1-\varepsilon)}{\varepsilon} \frac{\partial q}{\partial t} = -u_0 \frac{\partial C_j}{\partial z} + D_L \frac{\partial^2 C_j}{\partial z^2} \quad (13)$$

with the following initial and boundary conditions:

$$C(0, z) = 0 \quad (14)$$

In the inlet sample in the column ($z=0$):

$$D_L \frac{\partial C}{\partial z} = u_0 (C(t, 0) - C^F) \quad (15)$$

In the outlet sample in the column ($z = L$):

$$\frac{\partial C}{\partial z} = 0 \quad (16)$$

A rigorous mathematical model that takes into account the variation of the concentration of the adsorbate within the particle is described by the Fick's second law. In these cases, solution of equations of the bed and the particle should be solved simultaneously, which increases the complexity and computational effort. One alternative for reducing the computational effort is to replace Fick's Law by the simplified kinetics equation. (Hsuen, 2000). The approach mostly used to replace the Fick's Law is the LDF model (Linear Driving Force). It applies the expression of the first order kinetics represented by Equation (17). Several authors have used such models with successful results for sorbents and biosorbents.

$$\frac{\partial q}{\partial t} = -K_s (q - q_{eq}) \quad (17)$$

In the adsorption models represented by Equation (17), it is assumed that the driving force for mass transfer is linear with the concentration of the sorbate in the solid. Moreover, it means the equilibrium condition at the interface between the local phase fluid, as illustrated in Figure 9. The equilibrium in the adsorption process is usually represented by adsorption isotherms, such as: Langmuir, Freundlich, Tóth, Sips. Figure 9 also illustrates the mechanism of the external mass transfer occurs around the surface of the particle. From the interface solid-fluid, the mass transfer occurs, which is represented by following equation:

$$-K_s (q - q^*) = \frac{K_F a \varepsilon}{\rho_{bed}} (C - C_{eq}) \quad (18)$$

The mathematical model that considers both mass transfer resistances (external and intraparticle) is called double resistance model. This model is composed by the set of Equations (13)-(18). When the mass transfer is predominantly intraparticle, that is ($C^{eq} \approx C$), the equilibrium concentration of the sorbate in the solid is directly related to the concentration in bulk phase. In cases where the mass transfer resistance is in the film, that is ($C^{eq} \approx C$), the rate of sorption can be expressed by the following below:

$$\frac{\partial q}{\partial t} = \frac{K_F a \varepsilon}{\rho_{bed}} (C - C_{eq}) \quad (19)$$

When the operational condition is experimentally optimized, the film and intraparticle resistances of the sorption processes (adsorption, ion exchange or adsorption + ion exchange) are minimized in the experimental range investigated. It means that the film thickness is the thinnest one and there is no significant steric resistance of the sorbate in the particle pores.

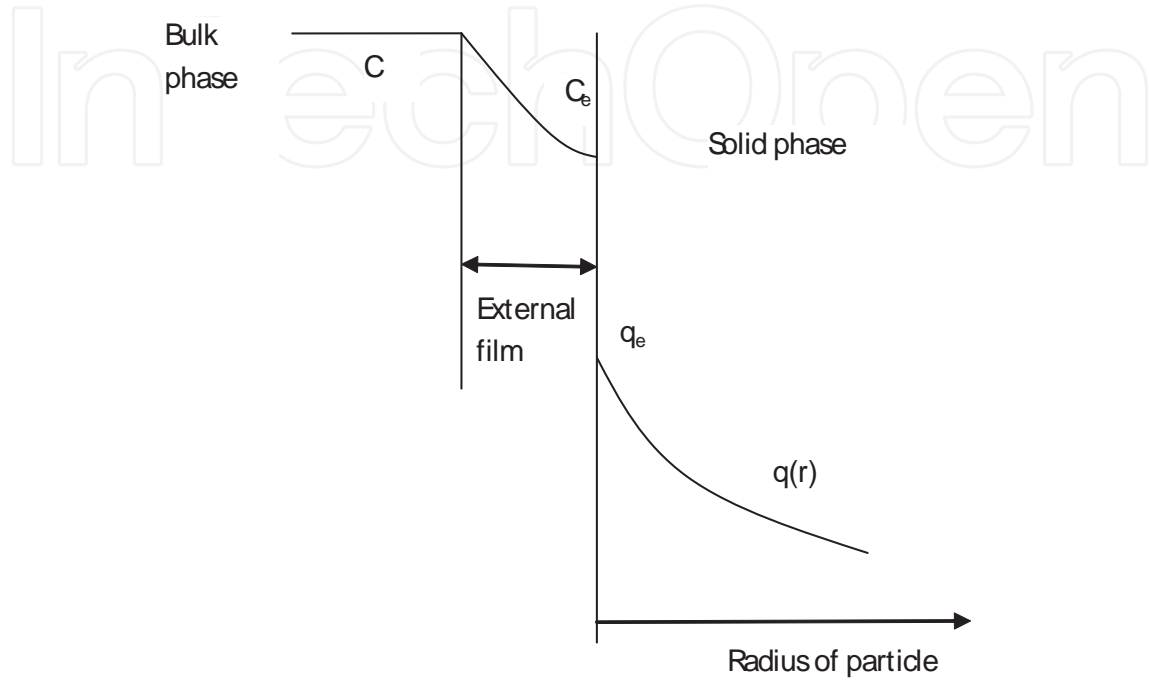


Figure 9. Mass transfer in adsorption process

Some parameters of the model can be calculated from the correlation, namely: axial dispersion coefficient (D_L) and external mass transfer coefficient. The relationship for calculating the axial dispersion is usually expressed from the dimensionless groups: Reynolds (Re), Peclet (Pe), Schmidt (Sc). Delgado (2006) presents several correlations for calculating of axial dispersion of gases and liquids in packed beds. There are many correlations for calculating external mass transfer coefficients in porous media, usually expressed in terms of Reynolds (Re_p), Schmidt and Sherwood (Sh_p). Wakao and Funazkri (1978) developed the following expression for $3 < Re_p < 2000$:

$$Sh_p = 1 + 1.1 Re_p^{0.6} Sc^{1/3} \quad (20)$$

Where: $Sh_p = \frac{K_F d_p}{D}$, $Re_p = \frac{u_0 d_p}{\nu}$, $Sc = \frac{\nu}{D}$

The mass transfer coefficient in the solid (K_s) is an adjustable parameter of the model obtained from the experimental breakthrough curves.

2.6.1. Examples of breakthrough modeling

Example 1 – Modeling of Breakthrough curves

Table 2 shows the experimental data of breakthrough curve of zinc in fixed bed columns using Na-Y zeolite as adsorbent obtained by Ostroski (2007) and Table 3 shows the operational conditions and bed parameters.

Time (min)	C_{out} / C^F
0.00	0.0000
22.00	0.0000
31.00	0.0000
55.00	0.0050
68.00	0.0156
74.00	0.1980
87.00	0.3564
93.00	0.5916
118.00	0.7721
136.00	0.8500
147.00	0.9248
180.00	0.9490
205.00	0.9655
230.00	0.9788
250.00	0.9874
260.00	0.9913
280.00	0.9963
307.00	1.0000

Table 2. Experimental data of zinc breakthrough curve

C^F - Feed concentration of adsorbate (meq / cm ³)	2.447x10 ⁻³
L -Height of the bed (cm)	3.0
m_s - Weight of the adsorbent (g)	0.8
u_0 - Interstitial velocity (cm/min)	25.104
ϵ - Bed porosity	0.5
ρ_{bed} - Bed density (g / cm ³)	0.4192

Table 3. Operational conditions and bed parameters.

From these data it will be tested the Bohart and Adams and the LDF models that consider intraparticle resistance only. Both models have only one adjustable parameter: (k_a) for Bohart and Adams and (K_s) for LDF model.

Bohart and Adams model

From the experimental breakthrough curve it is calculated the capacity of the adsorbent (q^*), since the column experiments are carried out up to the complete exhaustion of the column (saturation point), ie, when the concentration of sorbate in the outlet of the column is equal to the feed concentration. From a mass balance in the column, one can obtain the following equation:

$$q^* = \frac{C^F \dot{Q}}{1000 m_s} \int_0^{t_{END}} \left(1 - \frac{C_{out}}{C^F} \right) dt \quad (21)$$

Where:

q^* -Capacity of the adsorbent (meq/g);

C_{out} -Concentration of zinc in the outlet of the column (meq/L);

C^F -Feed concentration of zinc (meq/L);

\dot{Q} -Volumetric flow rate (cm³/min);

t -time (min);

m_s -Weight of adsorbent (g).

The capacity of the adsorbent was calculated from the area determinate by term $\left(1 - \frac{C_{out}}{C^F} \right)$ calculate by experimental breakthrough curve, illustrated in Figure 10. The integral $\int_0^{t_{END}} \left(1 - \frac{C_{out}}{C^F} \right) dt = 102.78 \text{ min}$, calculated by trapeze method.

$$q^* = \frac{C^F \dot{Q}}{1000 m_s} \int_0^{t_{END}} \left(1 - \frac{C_{out}}{C^F} \right) dt = \left(\frac{2.447 \times 8}{1000 \times 0.8} \right) \times 102.78 = 2.515 \text{ meq/g}$$

$$\alpha = \frac{\rho_{bed} q^*}{C^F \varepsilon} = \left(\frac{0.4192 \times 2.515}{2.447 \times 10^{-3} \times 0.5} \right) = 861.7 \text{ meq/g}$$

$$\beta = k_a C_0 \alpha = k_a \times 861.7 \times 10^{-3} \times 2.447 = 2.1086 k_a$$

$$A = \frac{L \beta}{u_0} = \frac{0.8 \times 2.1086 k_a}{25.104} = 67.20 k_a$$

$$B = \frac{(-t u_0 + L) \beta}{\alpha u_0} = \frac{(-t \times 25.104 + 3) \times 2.1086 k_a}{861.7 \times 25.104} = 9.75 \times 10^{-5} \times (3 - t \times 25.104) k_a \text{ min}$$

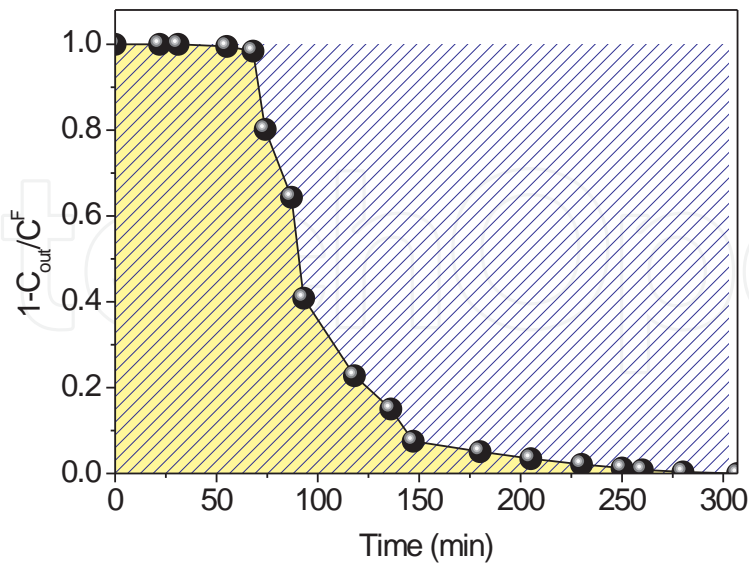


Figure 10. Area of curve $\left(1 - \frac{C_{out}}{C^F}\right)$

Applying in the Equation (12), it follows that: $t_F = \frac{L}{u_o} = \frac{0.8}{25.104} = 0.03187$

The parameter (k_a) estimated from the experimental data of breakthrough curve and applied method for one-dimensional optimization golden search, minimizing the following objective function:

$$F = \sum_{j=1}^{n_{exp}} \left(\left(\frac{C_{out}}{C^F} \right)_j^{EXP} - \left(\frac{C_{out}}{C^F} \right)_j^{EXP} \right)^2 \quad (22)$$

Where:

$F = \sum_{j=1}^{n_{exp}} \left(\left(\frac{C_{out}}{C^F} \right)_j^{EXP} - \left(\frac{C_{out}}{C^F} \right)_j^{EXP} \right)^2$ -Ratio of the concentrations in the outlet of the column and feed determined experimentally

$\left(\frac{C_{out}}{C^F} \right)_j^{EXP}$ -Ratio of the concentrations in the outlet of the column and feed determined by model

$\left(\frac{C_{out}}{C^F} \right)_j^{MOD}$ -Number of experimental data

The value of adjustable parameter k_a was 22.35 (meq / cm³ min).

Intraparticle model

In this model considerate that the internal diffusion is controller the mass transfer, the LDF approximation was used to represent the diffusion, described by Equation (17). This model also has only one adjustable parameter (K_s). To solve the equations of the model is also necessary to define an equation for the isotherm and the coefficient of axial dispersion. The Langmuir isotherm, represented by Equation (23), was used in the simulation. The values of parameters used were as follows: $D_L = 8.96 \times 10^{-3} \text{ cm}^2/\text{min}$, $q_{\max} = 2.83 \text{ meq / g}$ and $b = 3.06 \text{ L / meq}$ (Ostroski, 2007). The parameter coefficient of mass transfer from adjusted breakthrough curve was: $K_s = 0.0431 \times 10^{-3} \text{ min}^{-1}$.

$$q_{eq} = \frac{q_{\max} b C_{eq}}{1 + b C_{eq}} \quad (23)$$

The phenomenological model can provide good results only if the equilibrium model used is appropriate to make this analysis. Its should compare the values of the equilibrium concentrations of the adsorbent predicted by the model, in this case calculated by Equation (21) and the experimental value obtained from Equation (23).

$$\text{Adsorption capacity predicted by the model} = q_{eq} = \frac{q_{\max} b C_{eq}}{1 + b C_{eq}} = 2.497 \text{ meq/g}$$

$$\text{Experimental adsorption capacity} = 2.515 \text{ meq/g}$$

In this case, the deviation between predicted adsorption capacity and experimental was 0.7%. It demonstrates that the equilibrium model is appropriated to use in the modeling of the column. When the deviation is high, it is not possible to achieve good adjustments for the breakthrough curves. In these cases, one must first search different isotherm models or theories (RAST –Real Adsorption Solution Theory, VSM - Vacancy Solution Model) to correlate the equilibrium data. In electrolytic systems it can used the Law of Action Mass.

When the parameters of model equilibrium are estimated from batch systems, the model accurately describes the behavior of the equilibrium curve. However, these values are different from the one obtained in the capacity of the column. Such behavior occurs generally for electrolyte systems. Several authors (Bajracharya and Vigneswaran 1990; Silva et al. 2002; Palma et al. 2003; Barros et al 2004; Izquierdo^{a,b} et al., 2010) reported the differences between batch and column capacity of adsorption. In these cases for modeling the dynamic adsorption column fixed bed must perform the adjustment of the parameters from the equilibrium data obtained in fixed bed column at different feed concentration. See section 2.5.

To solve the partial differential equations (Eq. 13 and Eq.17) it was used the lines method, which transforms the partial differential equations in a system of ordinary differential equations by approximating the spatial derivatives by finite differences. Further details of the resolution method used can be found in Silva (2001). The results obtained with the LDF model (Numerical solution) and Adams Bohart (analytical solution) is shown in Figure (11).

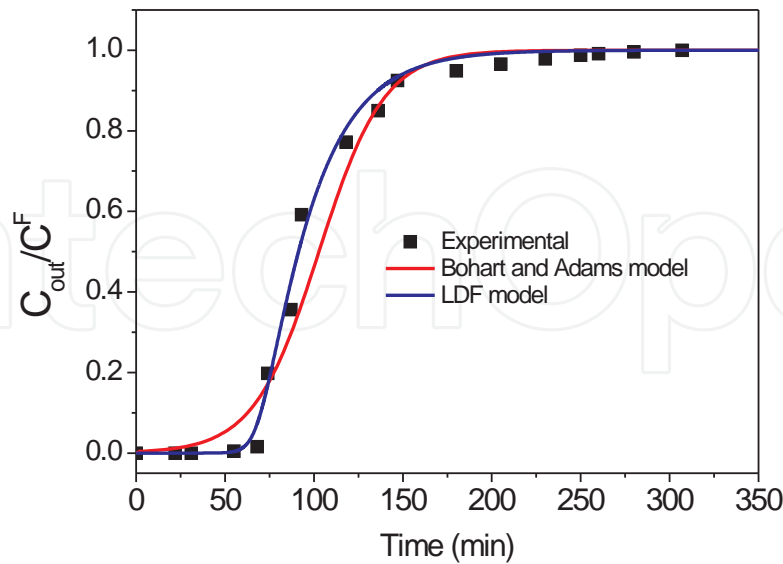


Figure 11. Zinc Breakthroughs curves

In this example, the model LDF described more accurately the behavior of zinc breakthrough curve due the consideration of mass transfer controlled by the intraparticle diffusion. It is more realistic than consideration that the kinetics is phase controller, which is the hypothesis of the Bohart and Adams model.

3. Final comments

Design of dynamic sorption is considered a simple process. Nevertheless, to reach higher and higher efficiencies is always a challenge.

Differences in packing procedures may provide quite different breakthrough behavior. Therefore, much attention should be paid to avoid channeling and bubbles of different fluid phase. Channeling promotes undesired dispersion in the bed keeping the system away from plug-flow behavior. Bubbles create additional mass transfer resistances and diminish the uptake efficiency. Much attention should be paid in the operational conditions imposed to the column. The ones that minimize the mass transfer resistances are always recommended.

Mathematical modeling of dynamic behavior with analytical solutions, such as: Bohart and Adams and Thomas considers that the limiting step is controlled by adsorption kinetics and can be applied only to monocomponent systems. The advantage of these models is that the estimation is simpler. Models with a numerical solution is more realistic because they take into account various aspects related to mass transfer (axial dispersion, external film diffusion and intraparticle diffusion) are more suitable for use in the design and optimization of

sorption processes in industrial scale. The phenomenological models are generated by mass balances of adsorbate in fluid and solid phase and require information of mass transfer mechanism and equilibrium. A prerequisite for phenomenological models is the theory and / or model used to represent the equilibrium of adsorption (isotherms, the law of mass action, RAST, VSM). Particularly in electrolyte systems, it is recommended that the equilibrium data are obtained in columns experiments on the basis of no pH correction. As already seen, the equilibrium conditions are different in batch and in dynamic systems. In the batch system, the counter ions are in solution, whereas in systems in a fixed bed column is loaded by the feed solution. The LDF model is an approximation to represent the intraparticle diffusion and has been shown to be efficient to describe the behavior of breakthrough curves for different systems (monocomponent and mixtures).

Nomenclature

a -Mass transfer area per unit bed volume (m^{-1})

$\frac{2.83 \times 3.06 \times 2.447}{1 + 3.06 \times 2.447}$ -Concentration of the adsorbate in the fluid phase (mmol / L);

C -Feed concentration of the adsorbate in the fluid phase (mmol / L);

C^F -Equilibrium concentration of the adsorbate fluid phase (mmol / L);

C_{eq} -Particle diameter (m);

d_p -Molecular coefficient diffusion (m^2/min);

D -Axial dispersion coefficient (m^2/min);

D_L -Height of bed (m);

L -Mass transfer coefficient in the solid (min^{-1})

k_a -Kinetics parameters of Bohart and Adams model ($\text{L} / \text{mol min}$)

K_S -External film mass transfer coefficient (m/min^{-1})

u_0 -Interstitial velocity (m/min);

K_F -Coordinated in the axial direction (m);

z -Bed porosity;

ε -Bed density (g / L);

ρ_{bed} -Kinematic viscosity (m^2/min);

Author details

M. A. S. D. Barros¹, P. A. Arroyo¹ and E. A. Silva²

¹ Department of Chemical Engineering, State University of Maringá, Maringá, Brazil

² Department of Chemical Engineering, West Paraná State University, Jardim La Salle, Toledo, Brazil

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