

ADSORPTION

BASIC NOTION

Adsorption is a process by which a chemical component (species) from a fluid phase (gas or liquid) is removed by attachment to a solid phase. The species being adsorbed is often called the *adsorbate*, when it resides on the solid, and the solid is called the *adsorbent*.

Every adsorption at given conditions of temperature, pressure and composition of the fluid phase can be characterized by its equilibrium state and by its dynamics consisting of the kinetics of the adsorption-desorption process.

Consider for example species A in a fluid phase (f) that is adsorbed on solid sites (S^*) by a simple mechanism indicated by equation (1) below:



If we assume that all solid sites are identical in their affinity for species A, and are all equally accessible to the fluid containing A, then a single adsorption rate constant k_a , and a single desorption rate constant, k_d , are sufficient to describe the adsorption-desorption mechanism of equation (1).

The rate of adsorption can now be written as:

$$r_a = k_a (A)(S^*) \quad (2a)$$

and the rate of desorption as

$$r_d = k_d (AS^*) \quad (2b)$$

At equilibrium the two rates are equal

$$r_a = r_d \quad (3a)$$

which yields the equilibrium constant (in appropriate units):

$$K_A = \frac{k_a}{k_d} = \left[\frac{(AS^*)}{(S^*)(A)} \right]_{eq} \quad (3b)$$

Note that the total number of active sites (actually concentration of active sites) available for adsorption of A is constant and equal to $(S^*)_o$. Thus, total sites are made up of either unoccupied sites (S^*) or sites containing the adsorbate (AS^*) as expressed by equation (4):

$$(S^*)_o = (S^*) + (AS^*) \quad (4)$$

Simultaneous solution of equations (3b) and (4) yields the following expressions for the fraction of the sites covered by the adsorbate, θ_e , and for the fraction of free sites, $(1 - \theta_e)$ at equilibrium

$$\theta_e = \left(\frac{(AS^*)}{(S^*)_o} \right)_{eq} = \frac{K_A(A)}{1 + K_A(A)} \quad (5a)$$

$$1 - \theta_e = \left(\frac{(S^*)}{(S^*)_o} \right)_{eq} = \frac{1}{1 + K_A(A)} \quad (5b)$$

It is informative to plot the fraction of the surface sites covered by the adsorbate as a function of fluid phase concentration of A , $(A)_e$ with which the solid is equilibrated.

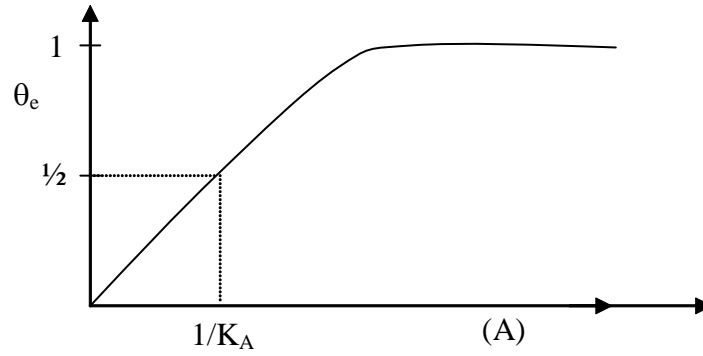


FIGURE 1: Langmuir Isotherm

This plot of equation (5a) is the so called Langmuir isotherm, i.e. the plot of the adsorbate concentration in equilibrium at constant temperature conditions with the surrounding fluid. The plot reveals that at the fluid phase concentration of the adsorbing species equal to the reciprocal of the adsorption equilibrium constant (expressed in appropriate units) the equilibrium fractional coverage of the adsorbent is exactly one half. As the fluid concentration of A is increased indefinitely (which of course has practical limitations) the equilibrium surface coverage of the adsorbent by the adsorbate tends to unity. How fast this approach to unity occurs depends on the value of the equilibrium constant K_A . For an irreversible adsorption $K_A \rightarrow \infty$ and $\theta_e = 1$ at all concentrations of A i.e. the plot in Figure 1 is a Hevisides step function at $(A)_e = 0, \theta_e = H((A)_e)$.

Let us examine now the effect of temperature on the adsorption process. The true thermodynamic constant, K_A^* , for the above considered adsorption process is unit-less and given in terms of activities:

$$K_A^* = \frac{a_{AS^*}}{a_{S^*} a_A} = e^{-\Delta G^*/RT} \tag{6}$$

For species that are preferentially adsorbed on the solids sites (and we clearly speak of chemisorption here) the Gibbs free energy for adsorption is negative as the process proceeds spontaneously (i.e. $\Delta G^* < 0$). This means

$$\Delta G^* = \Delta H^* - T \Delta S^* < 0 \quad (7)$$

However, as the molecules of A get adsorbed, they lose a degree of freedom (as their motion on the surface of the solid is constrained in two dimensions compared to three dimensional motion in the fluid phase) and therefore there is a decrease in entropy due to adsorption, i.e. $\Delta S^* < 0$. Now for the left hand side of equation (7) to be negative, as it should, one must have $\Delta H^* < 0$.

The enthalpy change due to adsorption ($\Delta H^* = H_{AS^*} - H_A$) is negative, i.e. heat is evolved (released) due to adsorption. This is in accord with our common experiences as adsorption is a process akin to condensation (e.g. vapor molecules condense on a surface) which also is accompanied with heat release.

Often one talks about the heat of adsorption defined by

$$q_a = -\Delta H^* \quad (8)$$

We recall the Van t Hoff's equation is:

$$\frac{d \ln K_A^*}{dt} = \frac{\Delta H^*}{RT^2} \quad (9a)$$

or

$$\frac{d \ln K_A}{dt} = \frac{\Delta H_A}{RT^2} \quad (9b)$$

Since $\Delta H_A < 0$, K_A decreases with increased temperature, and the fractional coverage of the surface with the adsorbate, θ , decreases at given concentration of A with increased temperature. (There are few exceptions to this general rate).

We still need to consider the rates of adsorption and the appropriate units for various constants. In a liquid state we can express the activities in terms of the product of the activity coefficient and concentration $\alpha_j = \gamma_j C_j$. Then

$$K_A^* = \frac{\gamma_{AS^*} (AS^*)}{\gamma_{S^*} (S^*) (A) \gamma_A} = K_\gamma K_A \quad (10)$$

The units of K_γ are those of concentration, say (mol/L) or M, and the units of K_A then are M^{-1} . The concentration of A in the fluid is then measured in (mol/L) or M.

In gases, it is often more convenient to use the partial pressure of A, P_A (atm) as a measure of gas phase concentration of the adsorbing species A. Then, based on ideal gas equation one gets

$$K_{A_p} (\text{atm}^{-1}) = K_A (RT)^{-1} = K_A^* K_\gamma (\text{atm}^{-1}) \quad (11)$$

The equilibrium constant $K_{A_p} (\text{atm}^{-1})$ is then used in the adsorption isotherm of equation (5a) and (5b) while P_A replaces the concentration of A, (A).

The net rate of adsorption is the difference between the rate of adsorption and desorption which can be written with the help of (2a), (2b) :

$$r_{ad} = k_a (S^*)_o (1 - \theta) (A) - k_d (S^*)_o \theta \quad (12)$$

Strictly speaking based on the concepts introduced so far we would expect to measure the rate in moles adsorbed by solid per unit surface area of solid sites and unit time, i.e. $r_{net} (\text{mol}/(\text{dm})^2 \text{s})$. The use of dm is needed since $1L = 1 (\text{dm})^3$ and concentrations are measured in (mol/L). The natural measure of $(S^*)_o$ in moles per unit surface of the solid i.e. $(\text{mol}/(\text{dm})^2)$ in which case the adsorption and desorption rate constants should have the following units: $k_a ((\text{dm})^3 / \text{mol s})$ and $k_d (\text{s}^{-1})$.

However, in practice the net rate of adsorption is most frequently expressed as \tilde{r}_{ad} ($mol/g \text{ solid } s$) in which case the capacity of the solid absorbent for the adsorbate is expressed as $(S^*)_0$ ($mol/g \text{ solid}$). The adsorption and desorption rate constants remain unchanged. If, however, one replaces the concentration of A in equation (12), (A), with partial pressure of A, P_A (atm), then the units of the needed adsorption constant K_{a_p} become ($atm^{-1} s^{-1}$).

One should note that by subtracting the net rate of adsorption at equilibrium (which is zero) from equation (12) one can represent the rate of adsorption as being driven by the fractional surface coverage departure from equilibrium, i.e.

$$r_{ad} = [k_a (S^*)_0 (A) + k_d (S^*)_0](\theta_e - \theta) \quad (13)$$

where

$$\theta_e = \frac{K_A (A)}{1 + K_A (A)} \quad (5a)$$

One should note that the above simplified development assumes a chemisorption process, i.e. a process requiring bond formation between A and S^* which has an activation energy. It is assumed that only micro molecular coverage occurs. This development also ignores possible effect of mass transfer rates via boundary layer diffusion on the rate of adsorption. It does not consider porous solids and the effect of pore diffusion on the adsorption process.

It does, however, present a very basic notion of adsorption. Additional various types of dissociative, dual site, competitive and inhibitory adsorption mechanisms will be discussed in the appendix.

In catalytic processes often it is assumed that adsorption is rapid and equilibrated while the rate limiting step is the surface reaction that converts AS^* to a new species. The rate of that rate limiting step is then proportional to the equilibrium surface fractional coverage, θ_e .

Instead of discussing heterogeneous catalyzed reactions, that always involve adsorption as an important step, we focus here on removal of components from a gas or liquid stream by adsorption which is a frequently used “unit process” in environmental engineering.

PACKED ADSORPTION COLUMNS AND BREAKTHROUGH CURVES

When we are interested in removing a particular component from a fluid phase by adsorption, we most frequently use packed (fixed) beds of solid adsorbent. This is done because such an arrangement provides the largest possible mass of solids per unit volume of the fluid and the flow pattern of the fluid is the closest to plug flow. Both of these are conducive to achieving a high volumetric productivity and throughput rates.

Consider a cylindrical column packed with adsorbent as shown in Figure 2

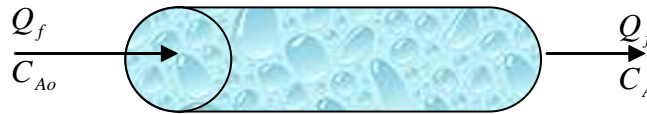


FIGURE 2: Typical Packed Bed Adsorber

The column has a diameter D and length H . Constant volumetric flow rate of fluid Q_f pumped through the column. The packing in the column is uniform and has an equivalent diameter of d_p .

Initially there is no adsorbate on the packing in the column. At time $t = 0$ we switch at the inlet from a flow of pure carrier fluid to a flow (at the same flow rate Q_f) of a stream that contains

C_{Ao} (mol A/L) in the feed. The column is kept isothermal. At the exit we monitor continuously the concentration of A, C_A , in the effluent i.e. we obtain the break through curve.

A general break through curve will have the shape indicated in Figure 3.

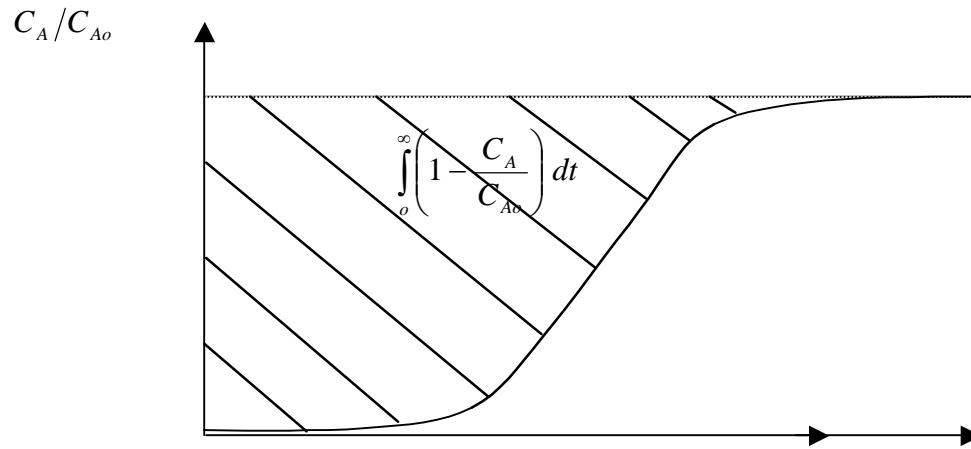


FIGURE 3: Schematic of a Breakthrough Curve

We are interested in understanding and quantifying the features of this curve. A mass balance on the adsorbing species A for the whole column requires:

$$\left(\begin{array}{c} \text{Total} \\ \text{accumulation} \\ \text{of } A \end{array} \right) = \left(\begin{array}{c} \text{Total} \\ \text{input} \\ \text{of } A \end{array} \right) - \left(\begin{array}{c} \text{Total} \\ \text{output} \\ \text{of } A \end{array} \right) \quad (14)$$

$$\left(\begin{array}{c} \text{Total} \\ \text{accumulation} \\ \text{of } A \\ \text{in column} \end{array} \right) = \left(\begin{array}{c} \text{Amount of } A \\ \text{in the column} \\ \text{at infinite time} \end{array} \right) - \left(\begin{array}{c} \text{Amount of } A \\ \text{in the column} \\ \text{at time 0} \end{array} \right)$$

$$= \varepsilon_b V C_{A0} M_A + (1 - \varepsilon_b) V \rho_p W_{A\infty} - 0 \quad (15)$$

where

$\varepsilon_b = \text{bed voidage}$

$V(L)$ = column volume $(\pi D^2/4) H$

C_{Ao} (mol/L) = molar concentration of A in the feed

M_A (kg A/mol A) = molecular weight of A

ρ_p (kg/L) = density of fresh solid adsorbent

$w_{A\infty}$ (kg A/kg solid) = saturation capacity of fresh adsorbent for A i.e. how many kg A per kg fresh sorbent can one pick up at equilibrium at C_{Ao} .

$$\left(\begin{array}{l} \text{Total} \\ \text{Input of A} \end{array} \right) = \int_0^{\infty} Q_f C_{Ao} M_A dt \quad (16a)$$

$$\left(\begin{array}{l} \text{Total} \\ \text{Output of A} \end{array} \right) = \int_0^{\infty} Q_f C_A M_A dt \quad (16b)$$

where

Q_f (L/s) = volumetric flow rate through the column

C_A (mol A/L) = exit concentration of A as a function of time

$t(s)$ = time on stream (since C_{Ao} introduced)

Equation (14) now becomes

$$\varepsilon_b V C_{Ao} + \frac{(1-\varepsilon_b)V \rho_p w_{A\infty}}{M_A} = Q_f \int_0^{\infty} (C_{Ao} - C_A) dt \quad (17)$$

This can be rewritten as:

$$\frac{\varepsilon_b V}{Q_f} + \frac{(1-\varepsilon_b)V \rho_p w_{A\infty}}{Q_f C_{Ao} M_A} = \int_0^{\infty} \left(1 - \frac{C_A}{C_{Ao}} \right) dt \quad (18)$$

The right hand side of equation (18) represents the dashed area in Figure 3. Hence, a breakthrough experiment, on a model free basis, provides direct information on the adsorption saturation capacity of the solid. The first term on the left hand side is the mean residence time of the flowing fluid external to the packing. It tells us how long it takes to replenish the volume of the fluid in the column with incoming flow rate. It also tells us how long on the average a fluid element stays in the fluid phase of the column. The second term on the left hand side is the ratio of the capacity of the solid adsorbent in the bed for adsorbate A to the carrying capacity of the inlet flow for A . It tells us how long a time the inlet flow rate must be sustained to provide enough A to saturate the whole bed. In a way it is a measure of the average residence time of the adsorbate on the adsorbent.

Equation (18) and the above discussion make it clear that from a breakthrough experiment one can calculate the adsorbent saturation capacity $w_{A\infty}/M_A$ ($mol A/g solid$) which corresponds to fluid phase concentration C_{Ao} . By repeating the breakthrough experiments at different levels of C_{Ao} one can find the adsorption isotherm of $w_{A\infty}/M_A$ vs C_A .

We recognize now that the area represented by $\int_0^{\infty} (1 - C_A/C_{Ao}) dt$ is directly proportional to the

saturation capacity of the bed. Next we examine the shape of the curve. Let us call $F_A = \frac{C_A}{C_{Ao}}$ to be the dimensionless F-curve, or breakthrough curve, for the adsorbate A .

Also consider $F_i = C_i/C_{i0}$ as a step response, breakthrough curve, of a non-adsorbing inert species i . Then the following situations depicted in Figure 4 may arise.

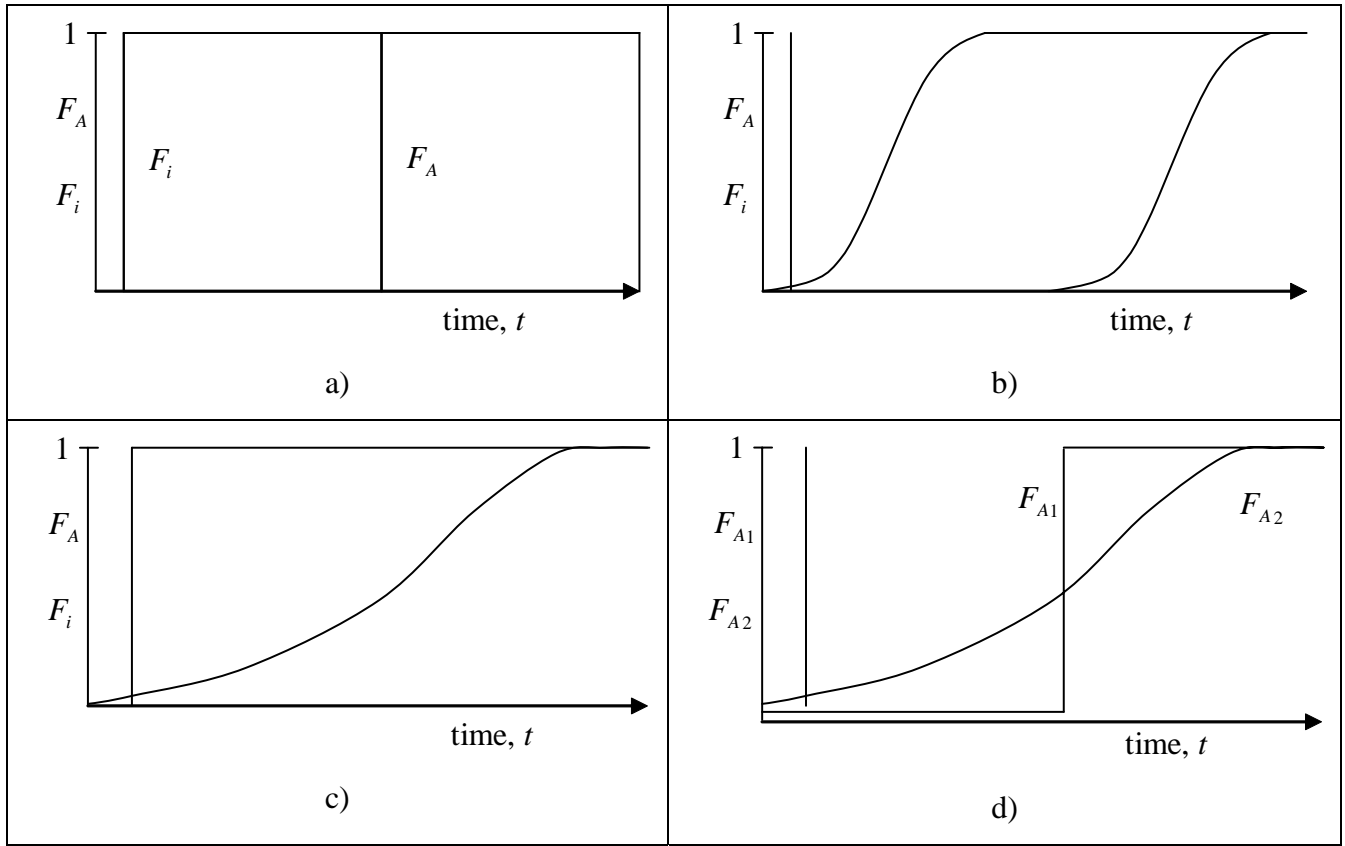


FIGURE 4: Schematic of Breakthrough Curves of Inert (Nonadsorbing) and Adsorbing Species

In Figure 4a, the breakthrough, F_i , of an inert (nonadsorbing) species is shown together with the breakthrough of the adsorbate A . The sharp step-wise rise of the F_i curve indicates that the flow in the column is plug flow, (piston flow) as all the fluid elements that enter together flow together until the exit. The area $\int_0^{\infty} (1 - F_i) dt = \bar{t}_f$ is the mean residence time of the fluid. The fact that F_A is also a sharp rising step indicates that all adsorption-desorption processes are instantaneous on the time scale of flow. The area is given by equation (18).

In Figure 4b, the fact that F_i is of sigmoidal S shape indicates the response of a flow profile other than plug flow, and points to possibilities of flow maldistribution. Since F_A is the same in shape as F_i , but just translated in time, indicates that the rate processes involved in adsorption-desorption are

still instantaneous on the time scale of flow. The area $\int_0^{\infty} (1 - F_A) dt$ equals the sum of the two terms on the left of equation (18) while the area $\int_0^{\infty} (1 - F_1) dt$ equals the first term on the left of equation (18).

In Figure 4c, the sharp step-like rise of F_1 indicates a perfect plug flow pattern in the column. The fact that F_A is now of sigmoidal S-shape is indicative of the presence of substantial resistances in the adsorption-desorption process. In other words, the kinetics, diffusion and other factors affecting the adsorption must be described to predict the shape of the S-curve.

Figure 4d compares two breakthroughs, F_{A_1} and F_{A_2} of species A_1 and A_2 , respectively.

The solid adsorbent has the same adsorption capacity for both A_1 and A_2 e.g.

$\int_0^{\infty} (1 - F_{A_1}) dt = \int_0^{\infty} (1 - F_{A_2}) dt$. Since F_{A_1} is a sharp rising step-wise curve this indicates that the flow in the column is plug flow and all the steps involved in adsorption of A_1 , are essentially instantaneous on the time scale considered. Clearly, major resistances are present in adsorption of A_2 which results in the sigmoidal F_{A_2} curve.

In adsorption the goal often is to remove a component from the fluid phase and, hence, when that component “breaks through” at an undesired level, the flow must be stopped and switched to another adsorption column. Clearly then in Figure 4d the adsorbent used is excellent for removal of A_1 but does not yield a good breakthrough curve for A_2 adsorption.

Thus runs of small adsorption columns could rapidly determine the suitability of various adsorbents for removal of different adsorbates. A steep breakthrough curve with a long breakthrough time is sought.

Often adsorption columns are used in periodic operation. The adsorption step is followed by the desorption step in which the adsorbate is released in a new fluid phase frequently in concentrated

form. For example, adsorption at low temperature can be followed by desorption at elevated temperature upon heating the column. In gas phase high pressure adsorption can be followed by low pressure desorption. This swing pressure adsorption process is used extensively in industrial applications.

One should also note that the theory of adsorption columns is intimately tied to the theory of chromatography. For example, if we define

$$E_i = \frac{d F_i}{dt} \text{ and } E_A = \frac{d F_A}{dt} \quad (19)$$

Then E_i and E_A represent the impulse response of the column to a delta function (instantaneous) unit injection of inert I and species A.

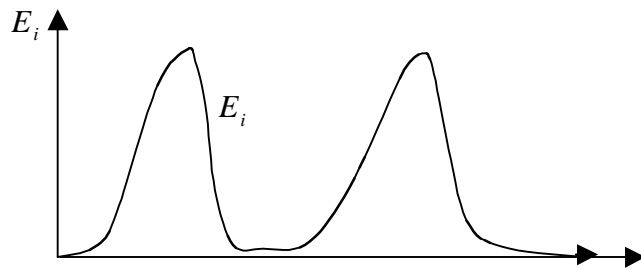


FIGURE 5: Impulse Responses for Figure 4b

Impulse responses derived from breakthrough curves of Figure 4b are shown in Figure 5. The centroid of these can be shown to be

$$\int_0^{\infty} t E_i(t) dt = \frac{\varepsilon_b V}{Q_f} \quad (20a)$$

$$\int_0^{\infty} t E_A(t) dt = \frac{\varepsilon_b V}{Q_f} + \frac{(1 - \varepsilon_b) V \rho_p w_{A\infty}}{Q_f C_{Ao} M_A} \quad (20b)$$

This is precisely the principle used in chromatographic columns to separate components that have different adsorption equilibrium constants ($w_{A\infty}/M_A C_{Ao}$).

We examine now engineering models for the breakthrough curve.

ENGINEERING MODELS FOR BREAKTHROUGH CURVES

The task is to have a robust not overly complex model for prediction of the breakthrough time and the sigmoidal shape of the breakthrough curve and the ability to calculate the model parameters both by fitting experimental breakthrough curves and to predict then the theory. It is important that the model has the ability to assess the effect of the change in scale of the column, or with operating conditions, on the shape of the breakthrough curve.

For many systems, including adsorbers, it is possible to represent the dimensionable impulse response to a unit delta function input in the inlet in terms of the incomplete gamma function

$$E_i(\theta) = \frac{\theta^{(1/\sigma_D^2)} \exp(-\theta/\sigma_D^2)}{\Gamma(1/\sigma_D^2)} \quad (21)$$

where $\theta = t/\bar{t}$ with \bar{t} being given by equation (20b) and

$$\theta_D^2 = \frac{\sigma^2}{\bar{t}^2} \quad (22)$$

where

$$\sigma^2 = \int_0^{\infty} (t - \bar{t})^2 E_i(t) dt \quad (23)$$

where σ^2 is derived from a model of adsorption, flow, transport in the bed.

For details see Linek and Dudukovic (1982).

The use of such a representation in describing the performance of a cyclic mode of operation is described for heat regenerators by Dudukovic and Ramachandran (1985, 992). The analogy to adsorbers should be self evident.

References:

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3. Linek, F. and M.P. Dudukovic, "Representation of Breakthrough Curves for Fixed-Bed Adsorbers and Reactors Using Moments of the Impulse Response", *The Chem. Eng. Journal* 23, 31-36 (1982).