CE407 SEPARATIONS

Lecture 24

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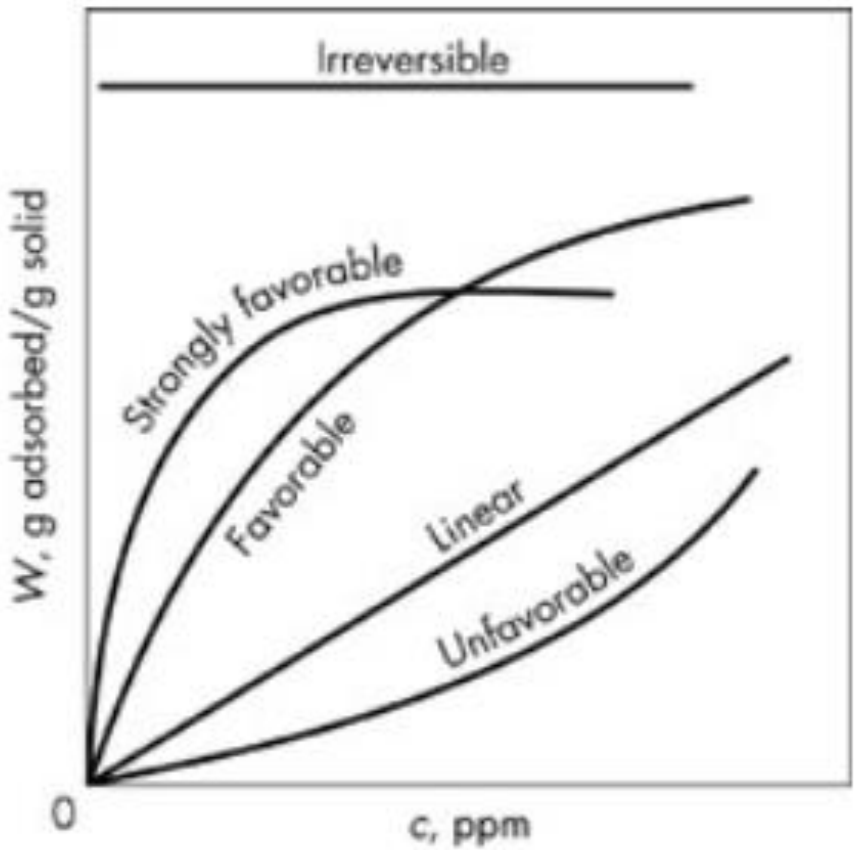
Adsorption

- Gas or liquid flows over a porous solid
  - The solid is called adsorbent
- Solute attaches to the solid, removing it from the liquid or vapor



Isotherms

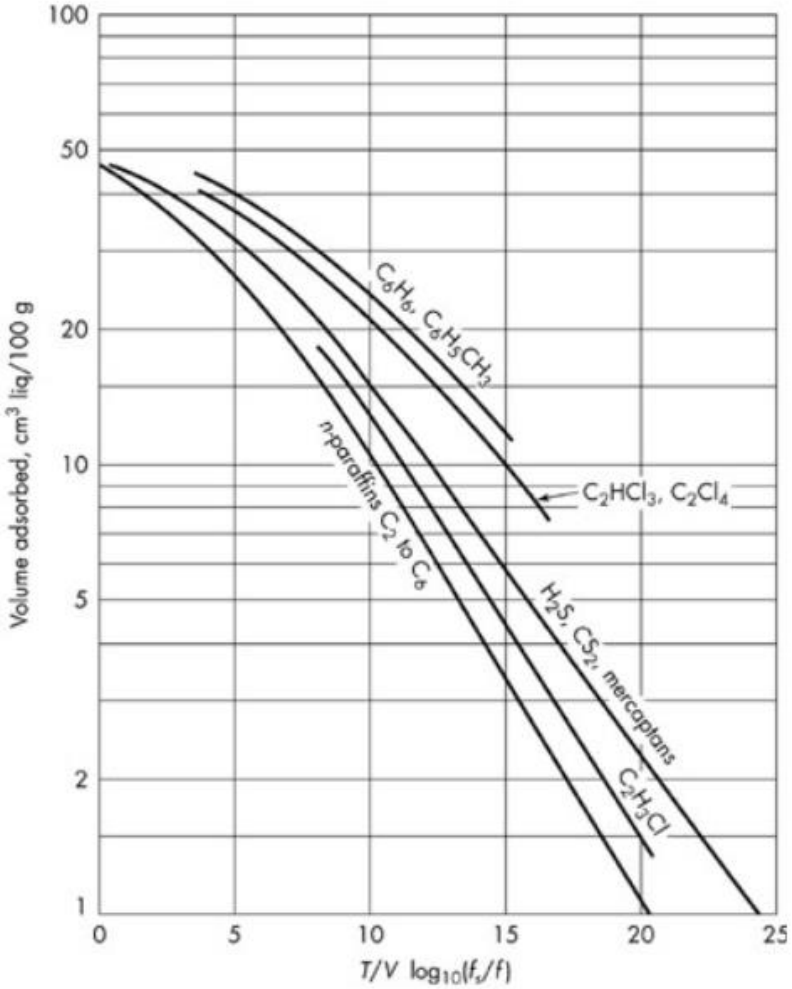
- Isotherms are the equilibrium data for Adsorption
- $\boldsymbol{W = \frac{Mass\ of\ adsorbate\ on\ solid}{Original\ Mass\ of\ solid}}$
- Adsorbate is the solute which has become attached to the solid (adsorbent)
- You can see that if the fluid has a higher concentration then the amount adsorbed increases
- "Favorable" indicates that there is high adsorption, W, even at lower concentrations

Isotherm Properties

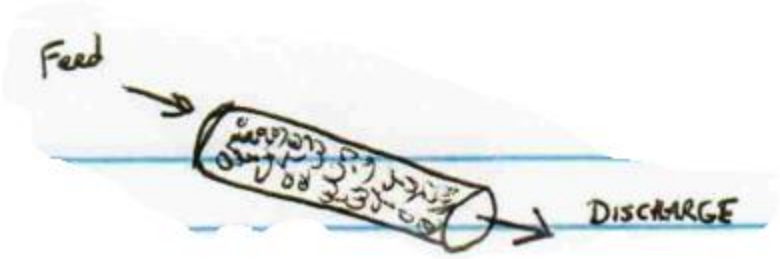
- All systems show decrease in the amount adsorbed as temperature increases

Temperature Dependence

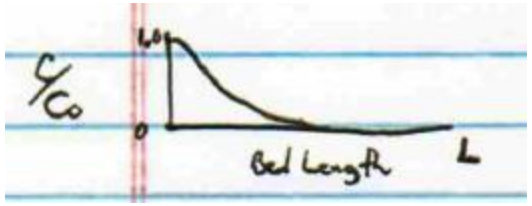
- Abcissa of graph is $\left(\frac{T}{V}\right) \log_{10}\left(\frac{f_S}{f}\right)$
- Where
  - **T** is adsorption temperature in Kelvin
  - **V** is the molar volume of the liquid at its boiling point
  - f_S is the fugacity of saturated liquid at temperature **T**
    - $f_S \approx P^{sat}(T)$
  - f is the fugacity of the vapor
    - $f \sim partial\ pressure = \ y_i\ P$
- As **T** increases **V** and f are relatively constant
- As **T** increases **T** and f_S increase
- We therefore move to the right on the graph and the ability to adsorb decreases



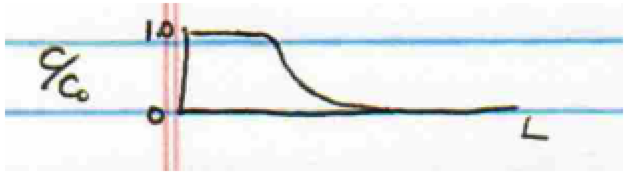
Fixed Beds



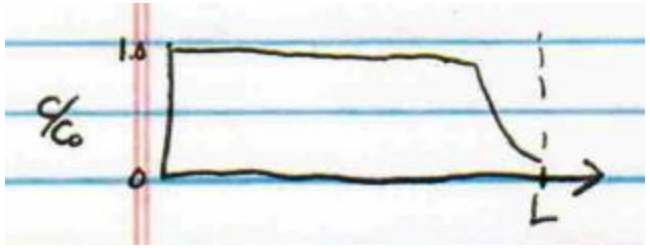
- Initially $W = W_0$ across the entire bed
  - $W_0 = 0$ for fresh material
- The first fluid to enter the bed has its solute adsorbed early in the bed
- The discharge at this point has $c = 0$



- Soon the solids at the entrance to the bed become saturated relative to c_0

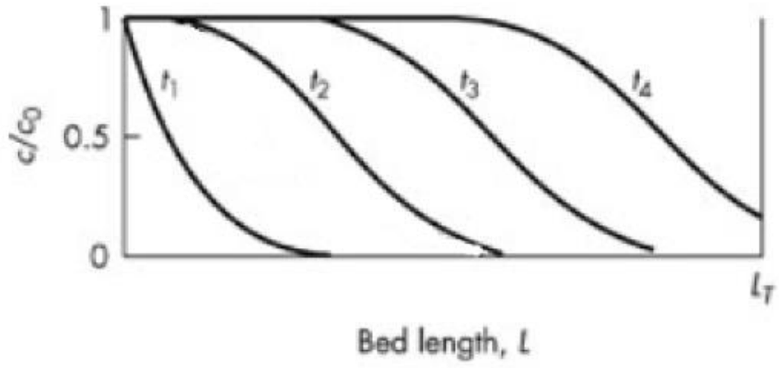


- Eventually this profile travels down the bed as more adsorbent becomes saturated
- The discharge now becomes $c \neq 0$



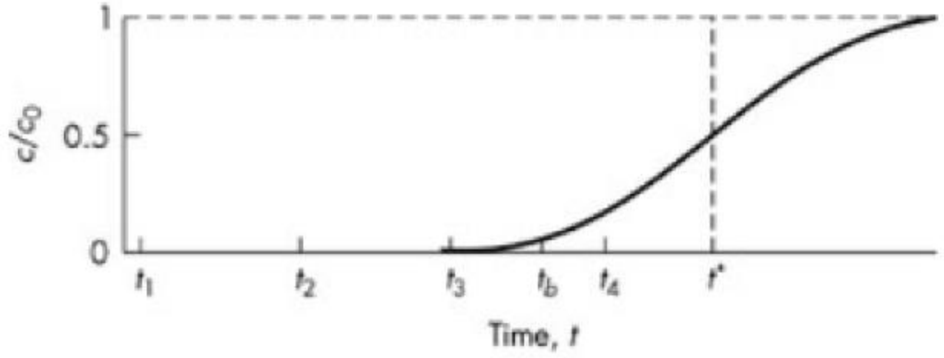
Fixed Beds – concentration profiles

- Diagram (a) shows profiles of concentration c/c_0 versus position in the bed
  - The various curves show how the profile progresses with time



(a)

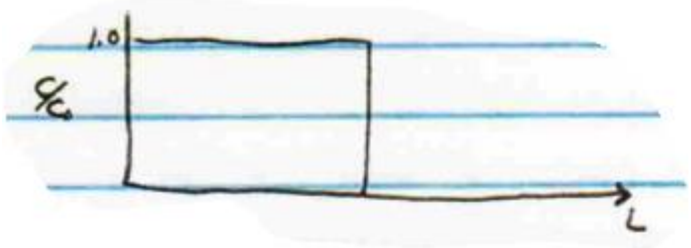
- Diagram (b) shows how the concentration of the discharge c/c_0 changes with time



(b)

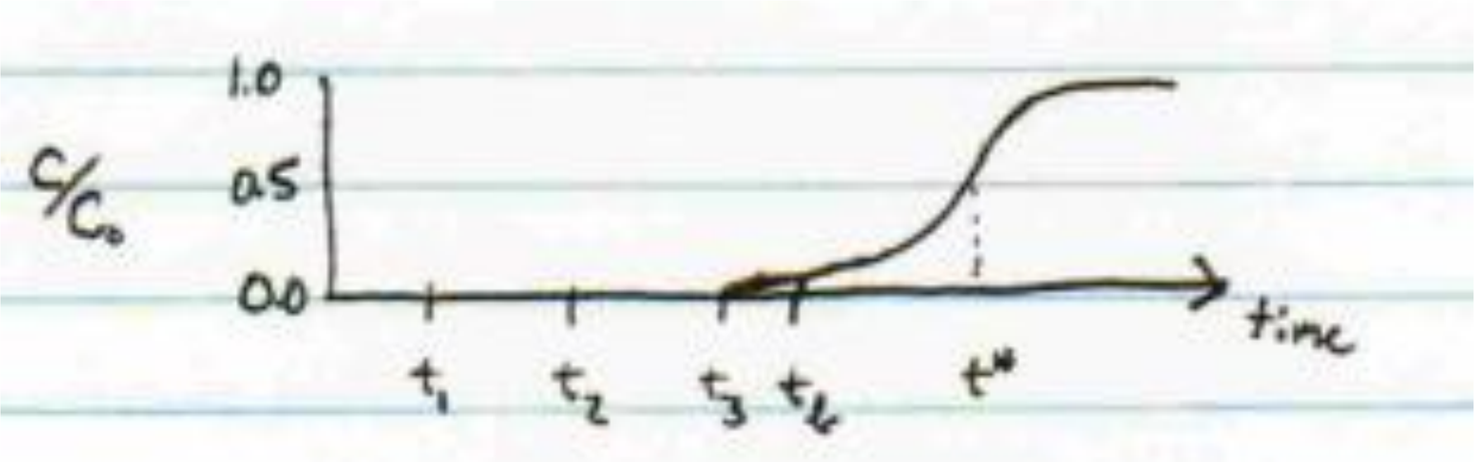
Fixed Beds – ideal concentration profile

- Requirements
  - Plug flow of fluid
  - Adsorption is immediate
- This would lead to a concentration profile where the adsorbent at one location fully saturates before adsorbent immediately adjacent begins to adsorb any solute
- This won't be observed because
  - There will most likely be a velocity profile other than true plug flow
  - The solute needs to work its way into the pores so it takes time to saturate the adsorbent at any given location and the concentration profile will spread out



Breakpoint

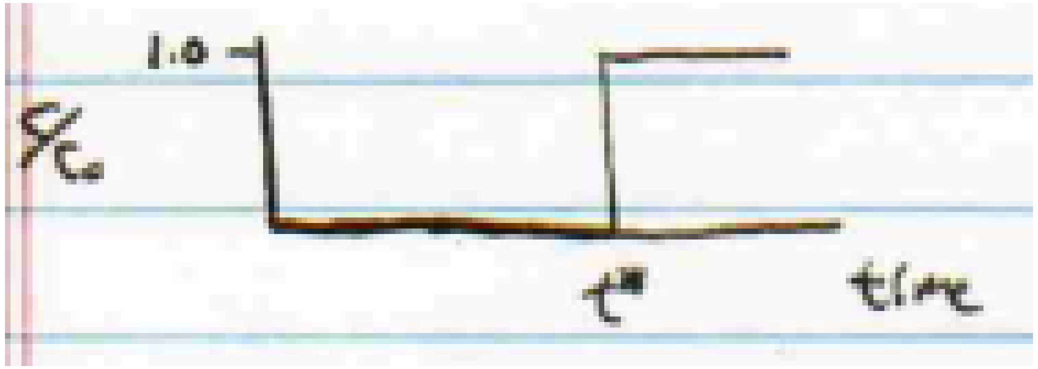
- Concentration profile: Discharge Concentration versus Time



- When c/c_0 reaches a limiting permissible level, aka the Breakpoint
  - Perhaps $c/c_0 = \mathbf{0.05}$
- Flow is stopped or diverted to a fresh bed (if running multiple beds in parallel)
- This low concentration material is blended into all of the relatively pure material that preceded it so the overall concentration of material collected is still very close to 0
- t_b is the time where c/c_0 reaches the specified breakpoint

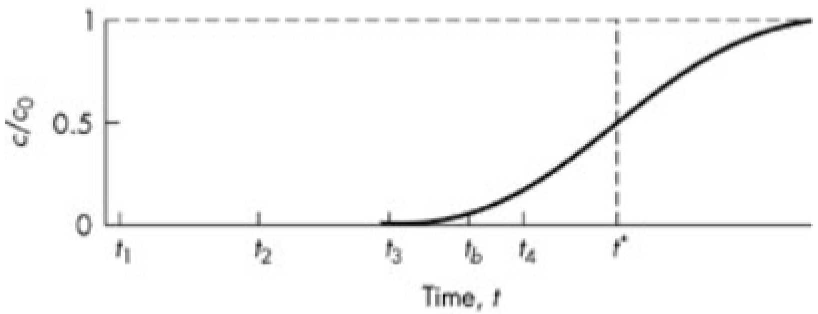
Vertical Breakthrough

- t^* is the ideal adsorption time for vertical breakthrough
  - The time at which discharge concentration c/c_0 goes from 0 to 1 instantaneously



Calculations…

- The area between the line $c/c_0 = 1$ and the concentration curve is proportional to the total solute that has been adsorbed
  - When $c/c_0 = 0$, all of the material that has entered the bed has been adsorbed and therefore the fluid being discharged is free of solute
  - When $c/c_0 = 1$ the fluid being discharged is at its feed concentration and therefore no more solute is being adsorbed



Calculations…

- **Solute feed rate** $= u_0\, c_0\, S$
  - u_0 = superficial velocity
  - c_0 = feed concentration
  - S = cross-sectional area of the bed
    - This is for the whole bed and does not take into account the adsorbent filling up space

- **Solute Flux** $= \dfrac{Solute\ Feed\ Rate}{cross\text{-}sectional\ area} = \dfrac{u_0\, c_0\, S}{S} = u_0\, c_0 = F_A$

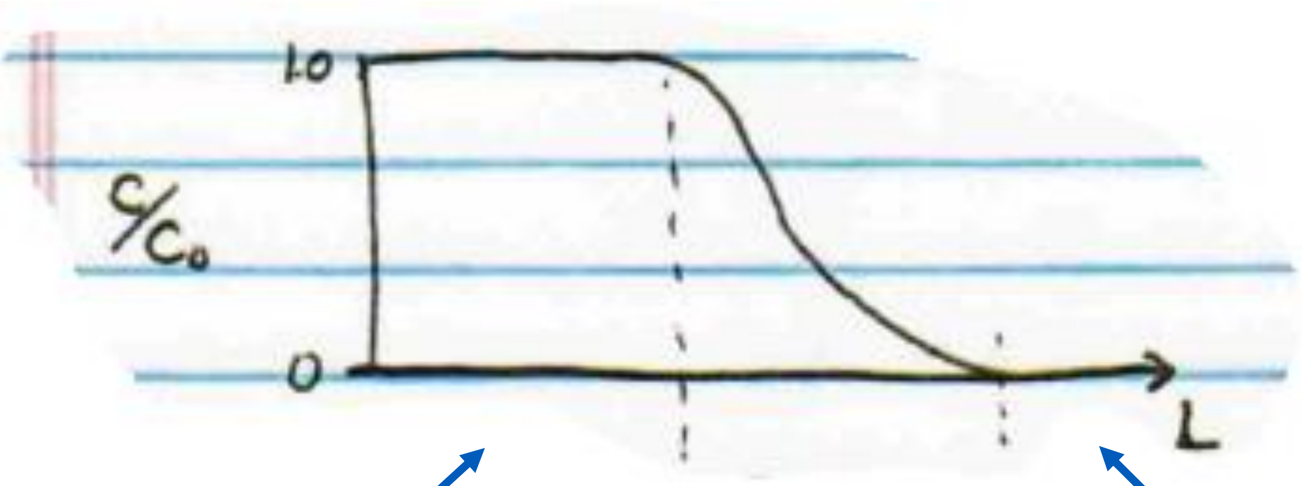
- For an ideal breakthrough curve all the solute fed is adsorbed from time $t = 0$ up until time $t = t^*$ at which point the discharge concentration goes from $c/c_0 = 0$ to $c/c_0 = 1$
- Also at the this time the concentration of solute on the adsorbent is w_{sat}
- w_{sat} is the saturated concentration on the solid relative to c_0
  - This is the value obtained from the isotherm

Calculations…

- At the time of ideal breakthrough, $\boldsymbol{t^*}$, the amount of solute fed is equal to the amount of solute adsorbed
- $\boldsymbol{u_0\, c_0\, S\, t^* = S\, L\, \rho_b\, (w_{sat} - w_0)}$
  - $\boldsymbol{S}$ is the cross sectional area of the bed
  - $\boldsymbol{L}$ is the length of the bed
  - $\boldsymbol{\rho_b}$ is the bulk density of the adsorbent in the bed
  - $\boldsymbol{S\, L\, \rho_b}$ is therefore the mass of adsorbent in the bed
  - $\boldsymbol{w_{sat} - w_0}$ is the change in mass of solute per mass of adsorbent
  - The breakthrough time can be calculated as:

$$t^* = \frac{L\, \rho_b\, (w_{sat} - w_0)}{u_0\, c_0}$$

Mass Transfer Zone



Adsorbent is saturated
∴ No mass transfer

Liquid has no solute
∴ No mass transfer

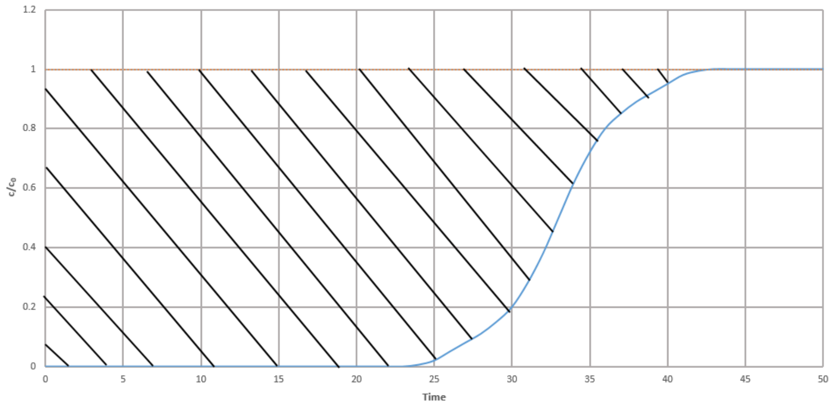
Mass transfer is occurring here

Breakpoint

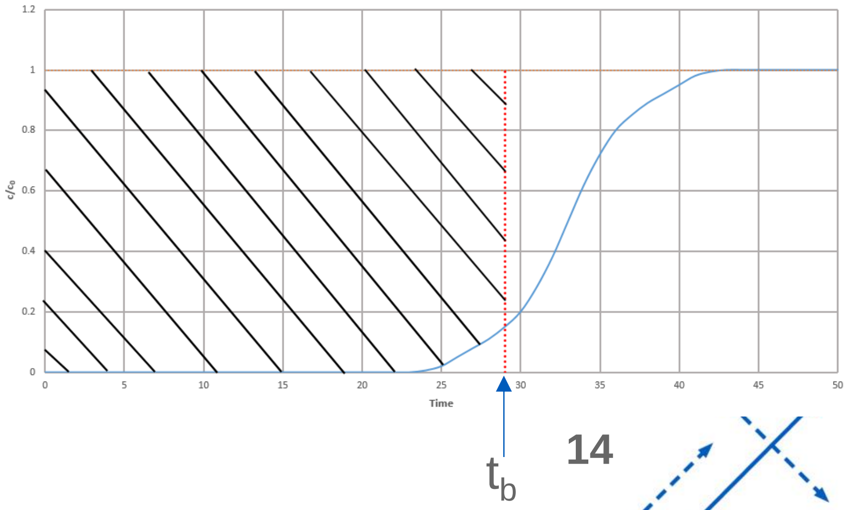
- Defined as the time, $\boldsymbol{t_b}$, where c/c_0 reaches a specified cutoff level
- At this point you need to stop using the bed and regenerate the adsorbent
  - You can stop the process or you can switch to a parallel bed
  - There are energy costs with the regeneration so you don't want to regenerate any more often than you have to
  - The longer you wait to regenerate, the more solute that you allow to pass through the bed
- The adsorbent in the Mass Transfer Zone is not saturated
  - We are therefore not getting the full utilization of the bed
- A wide Mass Transfer Zone means more of the bed is underutilized at time $\boldsymbol{t_b}$

Bed Utilization

- Complete breakthrough is at the time where c/c_0 reaches a value of 1
- Integrate the area between the line $c/c_0 = 1$ and the discharge concentration curve up to complete breakthrough. This is proportional to the capacity of the bed to adsorb.



- Integrate the area between the line $c/c_0 = 1$ and the discharge concentration curve up to the breakpoint. This is proportional to the amount of solute actually adsorbed.
  - Note the area under the concentration curve that is not included in the integral
- The ratio of these two areas is the fraction of the bed capacity that has been utilized at the breakpoint



Bed Utilization

- The mass of material adsorbed on the bed at a given time is

$$w(t) = \frac{\int_0^t F_{A\,in}\left(1 - \frac{c}{c_0}\right) dt}{L\,\rho_{bed}}$$

- $F_{A\,in}$ is the solute mass flow rate per cross-sectional area of the feed
- $L\,\rho_{bed}$ is the mass of adsorbent per cross-sectional area

- $w_b = w(t_b)$ is the mass of solute adsorbed on bed at time t_b
- $w_{sat} = w(\infty)$ is the mass of solute adsorbed when the bed is saturated
  - Note that time ∞ is any time AFTER $\frac{c}{c_0}$ has reached a value of 1

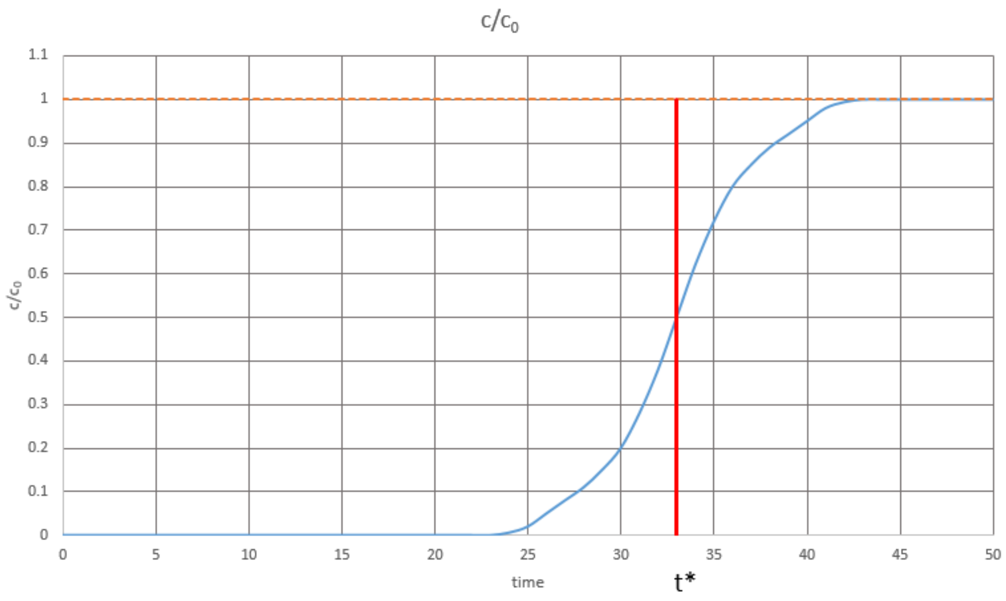
$$\frac{w_b}{w_{sat}} = fraction\ of\ bed\ utilized$$

Bed Utilization

- $1\ - ratio\ of\ areas = 1 - \frac{w_b}{w_{sat}}$ = **UNUSED fraction of bed**
- **UNUSED fraction of bed** $*$ **L = LUB** **LUB** = Length of Unused Bed

$$t_b = t^*\ * fraction\ of\ bed\ utilized = t^*\ * \left(1 - \frac{LUB}{L}\right)$$

- For a symmetric curve: t^* is also the time where $\frac{c}{c_0} = 0.5$



Scale Up Principles

- **Must** used same Adsorbent Particles and have the same superficial velocity
- When using an adsorbent with a Favorable Isotherm, the Mass Transfer Zone concentration curve obtains a characteristic shape and width early on and then that shape progresses down the bed without changing
- Meaning that for the same system (solute, solvent, adsorbent, temperature, etc) the LUB is independent of the length of the bed

$$t_b = t^* * \left(1 - \frac{LUB}{L}\right)$$

- Increasing L from L_1 to L_2 will increase t_b by two different factors:

$$t_2^* / t_1^* = L_2 / L_1$$

- and the factor $\left(1 - \frac{LUB}{L_1}\right)$ becomes $\left(1 - \frac{LUB}{L_2}\right)$

Scale Up Principles

$$t_b = t^* * \left(1 - \frac{LUB}{L}\right)$$

- Therefore the ratio of ${}^{t_{b\,2}}/_{t_{b\,1}}$ becomes

$$ {}^{t_{b\,2}}/_{t_{b\,1}} = \frac{t_2^* * \left(1 - \frac{LUB}{L_2}\right)}{t_1^* * \left(1 - \frac{LUB}{L_1}\right)}$$

- Which is

$$ {}^{t_{b\,2}}/_{t_{b\,1}} = \frac{L_2 * \left(1 - \frac{LUB}{L_2}\right)}{L_1 * \left(1 - \frac{LUB}{L_1}\right)}$$

Scale Up Principles

- We start with bench top / pilot plant experiments to determine LUB and breakthough time, $t_{b\,1}$
  - Use the same solute and solvent as in proposed production scale bed
  - Use the same Adsorbent as in proposed production scale bed
  - Use greatly reduced flow rate of solution
- Determine the needed diameter of Production Scale Bed
  - This diameter will give same superficial velocity with the production flow as was used in the experimental testing
- Select a targeted Breakthrough time, $t_{b\,2}$
- Determine the required length of the Production Scale Bed to obtain the desired breakthrough time
  - LUB is constant from the test bed to the production bed!

$$t_{b\,2}/t_{b\,1} = \frac{L_2 \ * \left(1 - \frac{LUB}{L_2}\right)}{L_1 \ * \left(1 - \frac{LUB}{L_1}\right)}$$