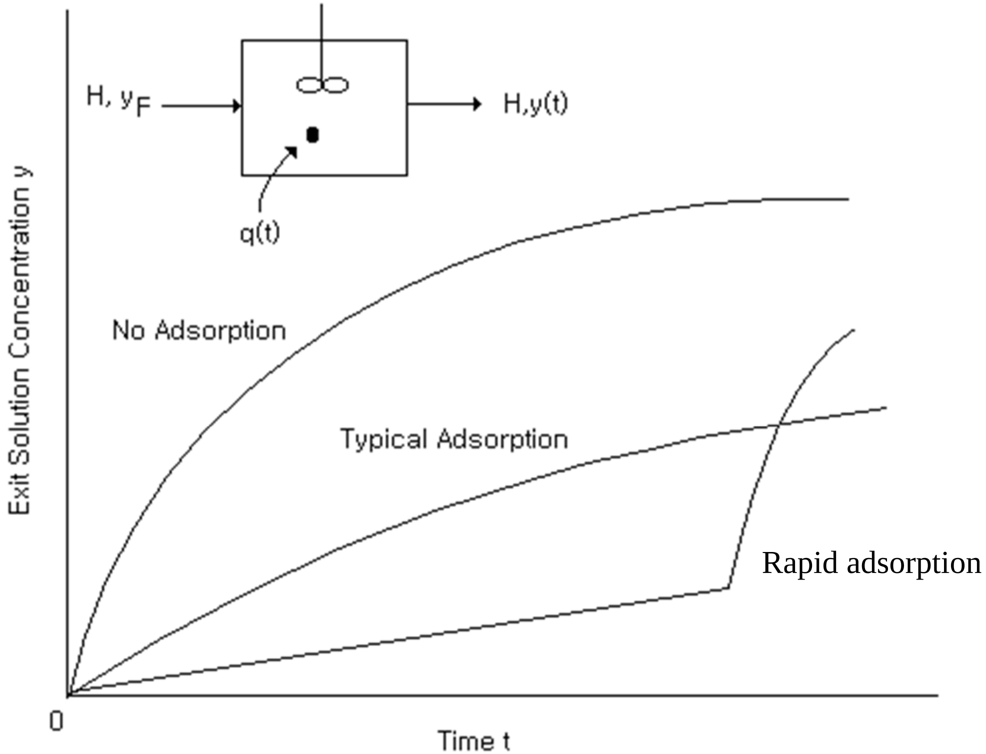
ADSORPTION

1. Batch adsorption



Mass Balance

- On the solute in the liquid

$$\varepsilon V \frac{dy}{dt} = H(y_F - y) - (1-\varepsilon) V \frac{dq}{dt} \quad (1)$$

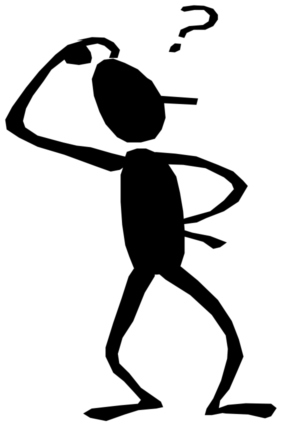
V : tank volume
y : effluent concentration
y_F : fed concentration
H : feed rate
q : adsorbed concentration

- On the adsorbent

$$(1-\varepsilon) V \frac{dq}{dt} = Vr \quad (2)$$

r : adsorption rate per tank volume

What r ?



Mechanisms

1. Adsorption is controlled by diffusion from the solution to the adsorbent.
2. Adsorption is controlled by diffusion and reaction within the adsorbent particles.

Diffusion controls

$$r = ka\,(y - y^*) \quad (3)$$

k : mass transfer coefficient

a : surface area

(adsorbent per tank volume)

y*: concentration(equilibrium)

$$q = K(y^*)^n \quad (4)$$

Freundlich isotherm

Diffusion and reaction

$$r = (\sqrt{D\kappa}\, a)(y - y^*) \qquad (5)$$

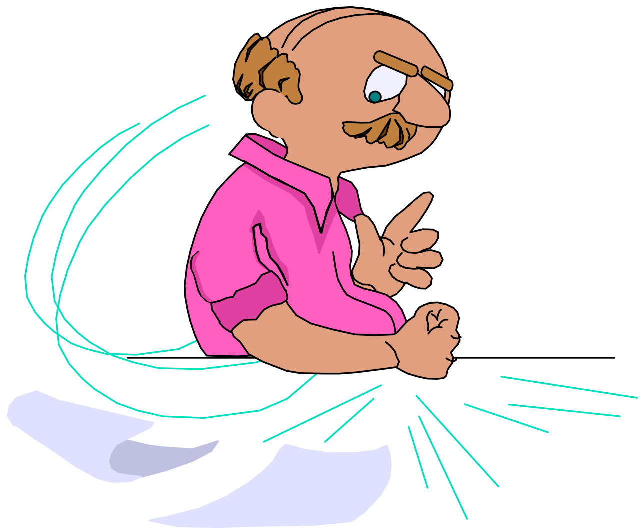
D : diffusion coefficient

κ : first order irreversible reaction

- Adsorption rate-independent of stirring-strong function of temperature

Solve y(t), q(t)

- Combining and integrating

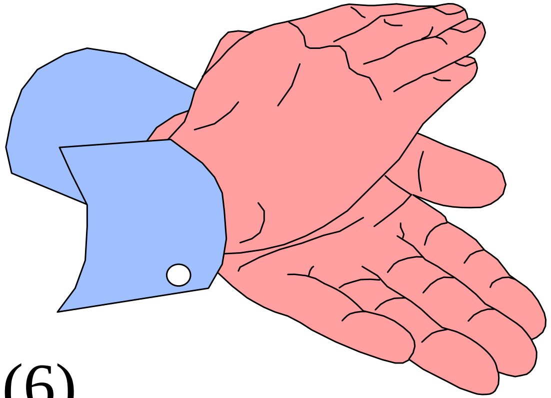


Eqs. 1 and 2 + $\begin{pmatrix} 3 \\ \text{or} \\ 5 \end{pmatrix}$

+ Equilibrium isotherm

- Assume adsorption isotherm as

$$q=Ky^*$$



- Integrate equation analytically

$$\frac{y_F-y}{y_F}=\frac{H/\varepsilon V-\sigma_2}{\sigma_1-\sigma_2}e^{-\sigma_1 t}+\frac{\sigma_1-H/\varepsilon V}{\sigma_1-\sigma_2}e^{-\sigma_2 t} \quad (6)$$

$$\frac{y_F-q/K}{y_F}=\frac{-\sigma_2}{\sigma_1-\sigma_2}e^{-\sigma_1 t}+\frac{\sigma_1}{\sigma_1-\sigma_2}e^{-\sigma_2 t} \quad (7)$$

$+ : \sigma_1$

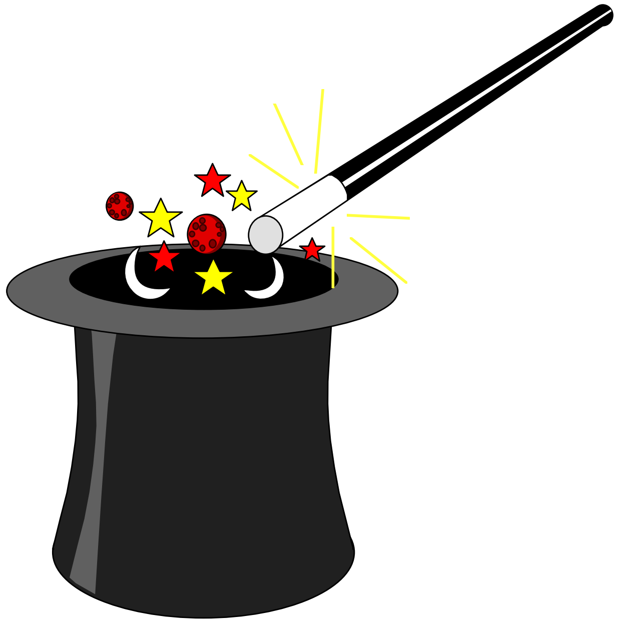
$- : \sigma_2$

$$\sigma_i=\frac{1}{2}\left[\left(\frac{H}{\varepsilon V}+ka\left(1+\frac{\varepsilon}{(1-\varepsilon)K}\right)\right)\pm\sqrt{\left(\frac{H}{\varepsilon V}+ka\left(1+\frac{\varepsilon}{(1-\varepsilon)K}\right)\right)^2-\frac{4kaH}{K(1-\varepsilon)V}}\right] \quad (8)$$

Example 1 Novobiocin Adsorption

H : 2.7 liters/hr q_o : 1.35g/liter, y_F : 640μg/cm^3,
T : 35°C, pH : 6.8~7.2
Calculate the resin loading q(t).
Then estimate the rate constant ka predicted from the simplified theory.

Time(hr)	y(μg/cm3)
0.5	138
1.0	181
1.5	217
2.0	246
3.0	313
4.0	348
5.0	375
6.0	405
7.0	418



Solution : To find the resin loading, we integrate Eq. (1) :

$$q = q_o + \frac{Hy_F t}{(1-\varepsilon)V} - \frac{H}{(1-\varepsilon)V}\int_0^t y\,dt - \left(\frac{\varepsilon}{1-\varepsilon}\right) y(t)$$

$$= 1.35\,g/liter + \left[\frac{2.7 liters}{hr}\,\frac{640\mu g/cm^3}{0.25 liter}\,\frac{10^3 cm^3}{liter}\right]t - \frac{2.7 liters/hr}{0.25 liter}\int_0^t y\,dt - \frac{0.876 liter}{0.250 liter}\,y(t)$$

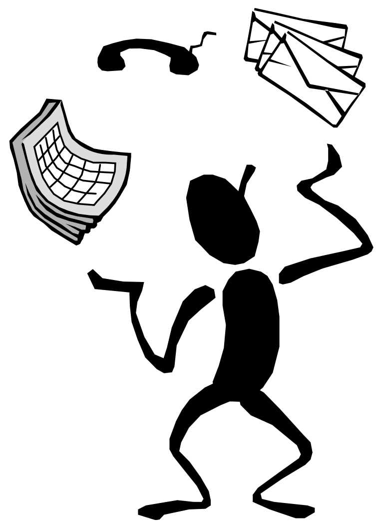
To find k, plot logarithm (y_F-y) & time(Fig. 1,next slide)

From Eq.6., slop of plot=σ_2(at larger times)

$$\sigma_2 = \frac{0.13}{hr}$$

From y and q, equilibrium constant K :

$$K = \frac{q}{y} = \frac{45 mg/cm^3}{418\mu g/cm^3}\,\frac{10^3\mu g}{mg} = 110$$



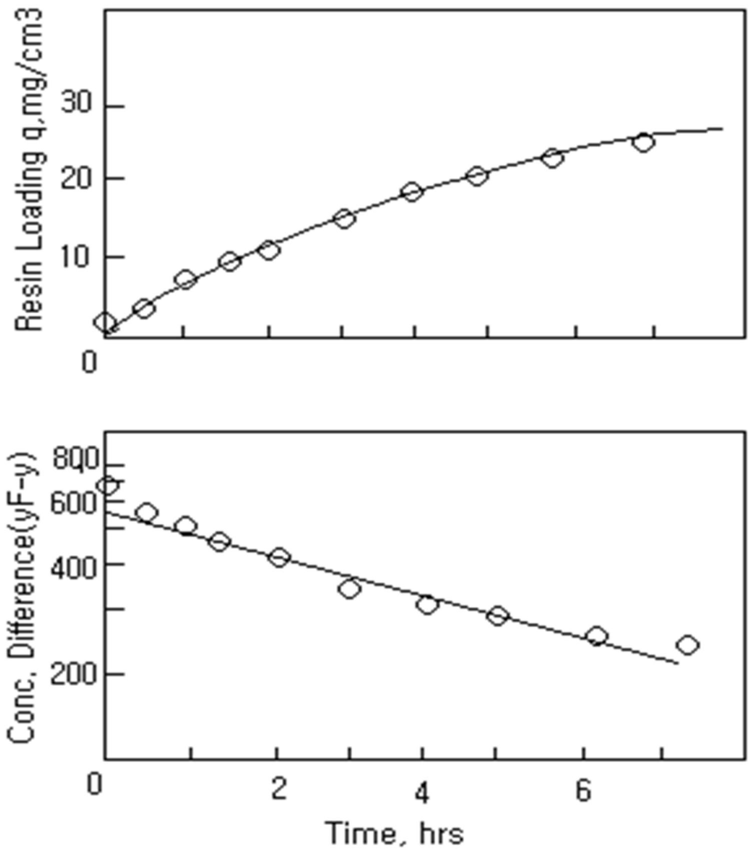


Fig.1. Novobiocin adsorption.

Result

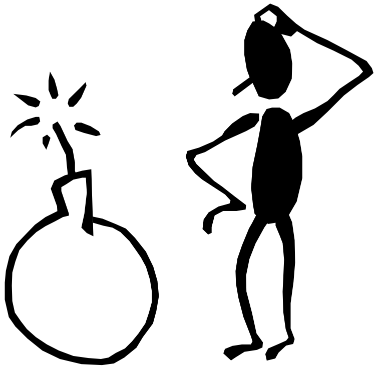
Eq. 8

$$\sigma_2 = \frac{1}{2}\left[\frac{H}{\varepsilon V} + ka\left(1 + \frac{\varepsilon}{1-\varepsilon}\right) - \sqrt{\left(\frac{H}{\varepsilon V} + ka\left(1 + \frac{\varepsilon}{(1-\varepsilon)}\right)\right)^2 - \frac{4kaH}{K(1-\varepsilon)V}}\right]$$

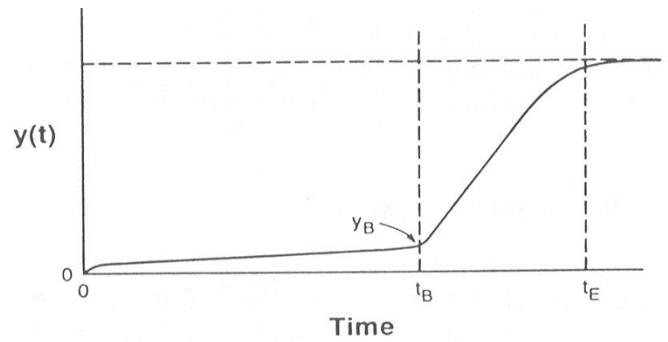
$$\frac{0.13}{hr} = \frac{1}{2}\left[\left(\left(\frac{2.7 liters/hr}{0.876 liter} + ka\left(1 + \frac{0.876 liter}{110(0.250 liter)}\right)\right) - \sqrt{\left(\frac{2.7}{8.76 hr} + ka\left(1 + \frac{0.876}{110(0.25)}\right)\right)^2 - \frac{4ka(2.7)}{110(0.250)}}\right)\right]$$

Thus

$$ka = \frac{1.3}{hr}$$



2. FIXED BEDS



y(t) : effluent conc.

Y_B : breakthrough conc.(10%)

y_E : exhaustion conc.(90%)

are used to infer behavior at time t_B within the column

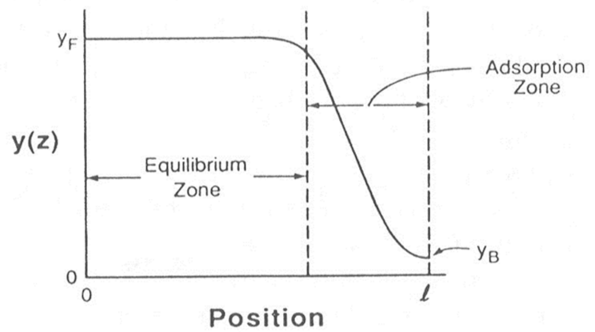
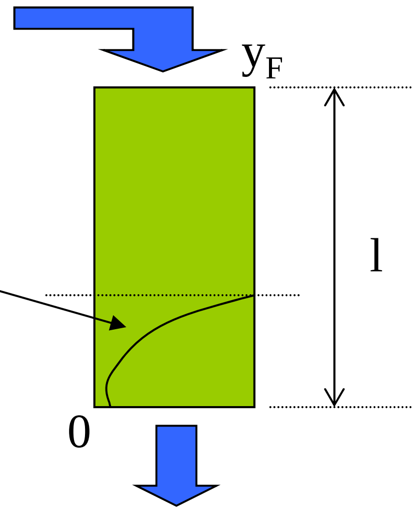
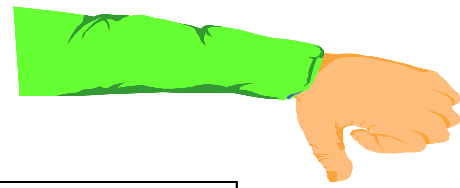


Figure 6.4-1. Breakthrough curves for packed bed adsorption. Performance in this most common case cannot be accurately predicted. As a result, the analyses given in the text should only be used to scale up laboratory results.





Basic Equations

Mass balance in liquid

$$\varepsilon \frac{\partial y}{\partial t} = -v \frac{\partial y}{\partial z} + E \frac{\partial^2 y}{\partial z^2} - (1-\varepsilon)\frac{\partial q}{\partial t} \quad (9)$$

ε : void fraction in the bed
v : superficial velocity(H/A)
E : dispersion coefficient

Mass balance on the adsorbed solute

$$(1-\varepsilon)\left(\frac{\partial q}{\partial t}\right) = r \quad (10)$$

r : adsorption rate(controlled by mass transfer
from bulk solution to the surface of the adsorbent)

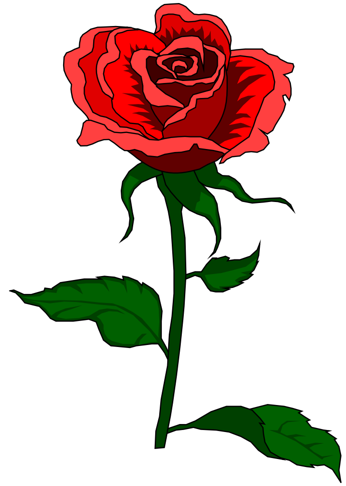
$$r = ka(y - y^*) \quad (11)$$

r : rate per bed volume
ka : rate constant
y* : concentration in solution at equilibrium

Isotherm

$$q = K(y^*)^n \quad (12)$$

Equilibrium(adsorbent and solution concentrations)



- Nonlinear
- Coupled Equations.
- Numericallyn solved

- For aproximate analysis
  - first : breakthrough curves as a ramp
  - second : two parameters (characteristic time, standard deviation)
  - third : adsorption equilibrium is linear
  - fourth : mimic graphical analysis

2.1 An approximate analysis

- Depend completely on experiments
- 1. Equilibrium zone saturated
  2. Adsorption zone long

- Equilibrium zone

$$q(\text{equilibrium}) = q(y_F)$$

- Adsorption zone contains half of $q(y_F)$ as a good approximation

$$q(\text{adsorption}) = \frac{1}{2} q(y_F)$$

- Fraction of the bed which is loaded

$$\Theta = \frac{q(y_F) l (1 - \Delta t / t_B) + \frac{1}{2} (y_F)(l - l(1 - \Delta t / t_B))}{q(y_F) l} = 1 - \frac{\Delta t}{2 t_B} \qquad \text{(A)}$$

2.2 Two parameter model

$$\frac{y}{y_F} = \frac{1}{2}\left(1 + \text{erf}\left[\frac{t - t_o}{\sqrt{2}\sigma t_o}\right]\right)$$

Two parameters : 1. Characteristic time
2. Standard deviation

t_o : time at half feed concentration
σt_o : standard deviation(slope of curve)

TABLE 1. Typical characteristics of the standard deviation for breakthrough curves

Controlling	The Quantity σ^2 is Proportional to	The Variance $(t_o\sigma)^2$ is Proportional to
Equilibrium	$1/l$	l/v^2
Kinetics of adsorption	v/l	l/v
Mass transfer	$v^{1/2}/l$	$l/v^{3/2}$
Dispersion	v/l	l/v
Diffusion	$1/lv$	l/v^3

2.3 Linear adsorption model

Linear isotherm

$$q = Ky^* \qquad (13)$$

Eqs. 9,10,11 and 13 combined

$$0 = -v\frac{\partial y}{\partial z} - ka\left(y - \frac{q}{K}\right)$$

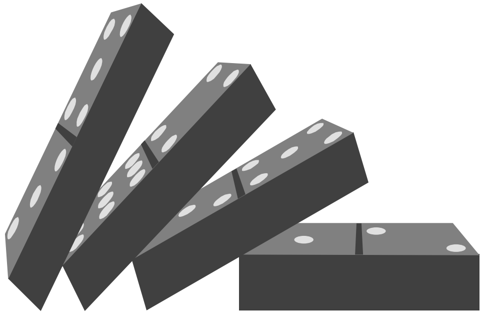
and

$$(1-\varepsilon)\frac{\partial q}{\partial t} = ka\left(y - \frac{q}{K}\right)$$

conditions

t=0, all z, q=0
t>0, z=0, y=y_F

Neglects terms : $E\partial^2/\partial z^2$ and $\partial y/\partial t$ in Eq. 9



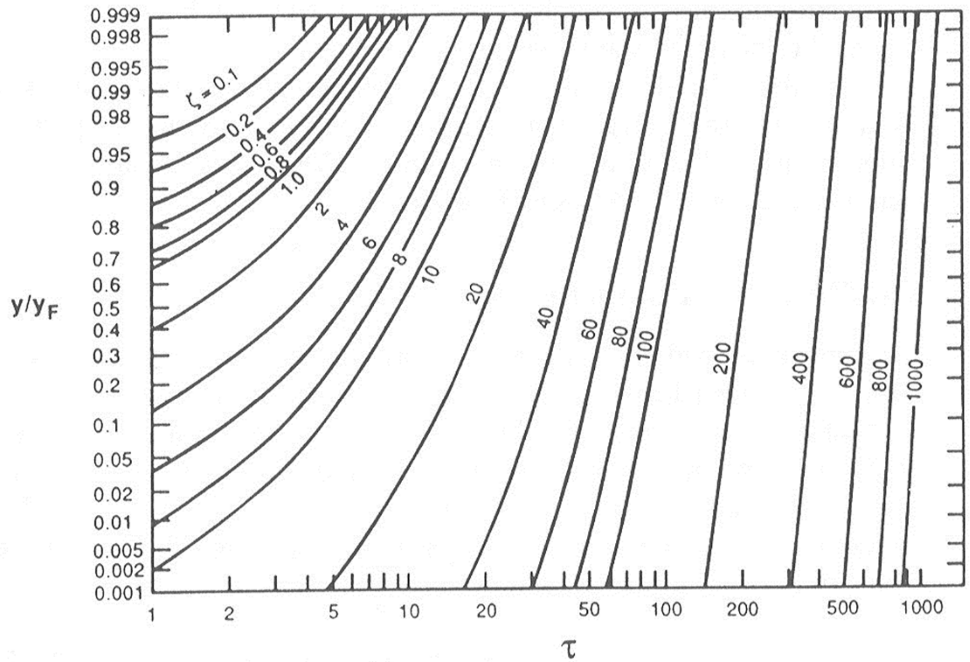


Figure 6.4-2. Predicted packed bed concentrations versus position and time. The dimensionless position ζ is defined as (zka/v); the dimensionless time τ is given by $[ka(t - z/v)/K(1 - q)]$. These curves are based on a linear isotherm (After Vermeulen *et al*, in Perry's *Chemical Engineers Handbook*, McGraw, 1973).

- Five parameters : (y/y_F), t, v, K, k

- four parameter found
- then fifth found

2.4 Differential contacting model

-Moving countercurrently
-Infinitely long, steady state
-equilibrium, y_F and $q(y_F)$
-exit solution conc. zero

- Mass balance

$$H(y-0)=W(q-0)$$

← Between the exit and some arbitrary position

- Steady state mass balance on the solute in solution

accumulation=solute flow(in-out) - solute adsorbed

$$0 = Av(y|_{z} - y|_{z+\Delta z}) - kaA\Delta z(y - y^*)$$

→ Negligible dispersion

Dividing by the volume $A\Delta z$ and taking the limit as this volume goes to zero

$$0 = -v\frac{dy}{dz} - ka(y - y^*)$$

Initial condition

$Z=0, \quad y=y_F$

$$l = \int_0^l dz = \frac{v}{ka} \int_y^{y_F} \frac{dy}{(y - y^*(q))}$$

Evaluate

- choosing y, integral numerically and reading q
- operating line
- using q to find y* from equilibrium

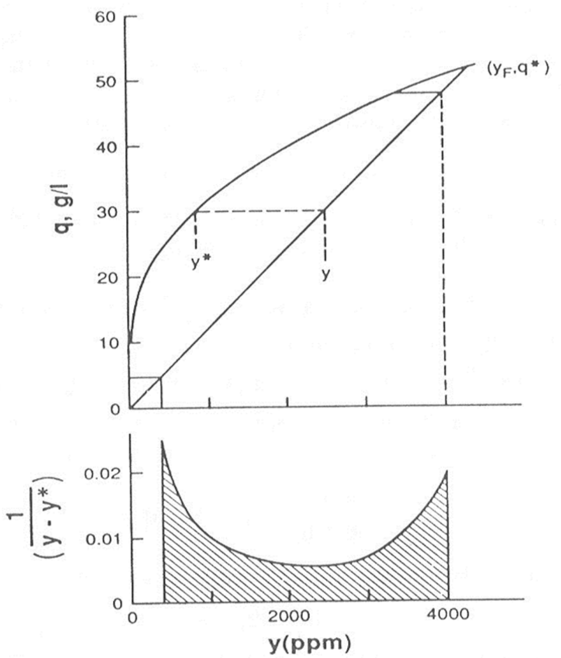


Figure 6.4-3. Packed bed adsorption as a differential contactor. This method of analysis argues that the column's behavior can be described with an equilibrium line and a type of operating line, dodging the unsteady operation of the bed. The numerical values given are those for Example 6.4-2.

Example 1. Lactate dehydrogenase adsorption

L=1.3m, diameter=7cm, void fraction=0.3, feed conc.=1.7mg/liter
linear isotherm :
q(in mg/cm^3)=38y(in mg/cm^3)
breakthrough 6.4hr, bed exhausted 10hr.
(a) the length of the adsorption zone at breakthrough
(b) the length of the equilibrium zone at breakthrough
(c) the fraction of the bed's capacity which is being used.

Solution

a) 10-6.4=3.6hr, so (3.6hr/6.4hr)×1.3m=0.73m
b) 1.3-0.73=0.57m
c) By approximate analysis and from Eq. A
θ=1-(3.6hr/2(6.4hr))=72%

Example 2. Cephalosporin adsorption

q(g/liter resin)=32(y(g/liter solution))$^{1/3}$
bed length : 1.0m, diameter : 3.0, density : 0.67cm^3 resin/cm^{3}bed
feed conc. : 4.3g/liter, superficial bed velocity : 2m/hr

a) Calculate how much of the feed is lost if we stop the adsorption when y=0.4g/liter
b) Estimate what fraction of the bed's capacity is used at this breakthrough. Assume the bed is exhausted when y=4.0g/liter
c) Estimate the rate constant in the bed
d) If we double the flow rate, how much of the will have been lost when the exit concentration is 0.4g/liter?

Solution

a) From next slide , breakthrough occurs at 6.3hr
thus fraction lost by numerical integration =0.02 $= \dfrac{\int_0^{6.3hr} y\,dt}{y_F(6.3hr)}$

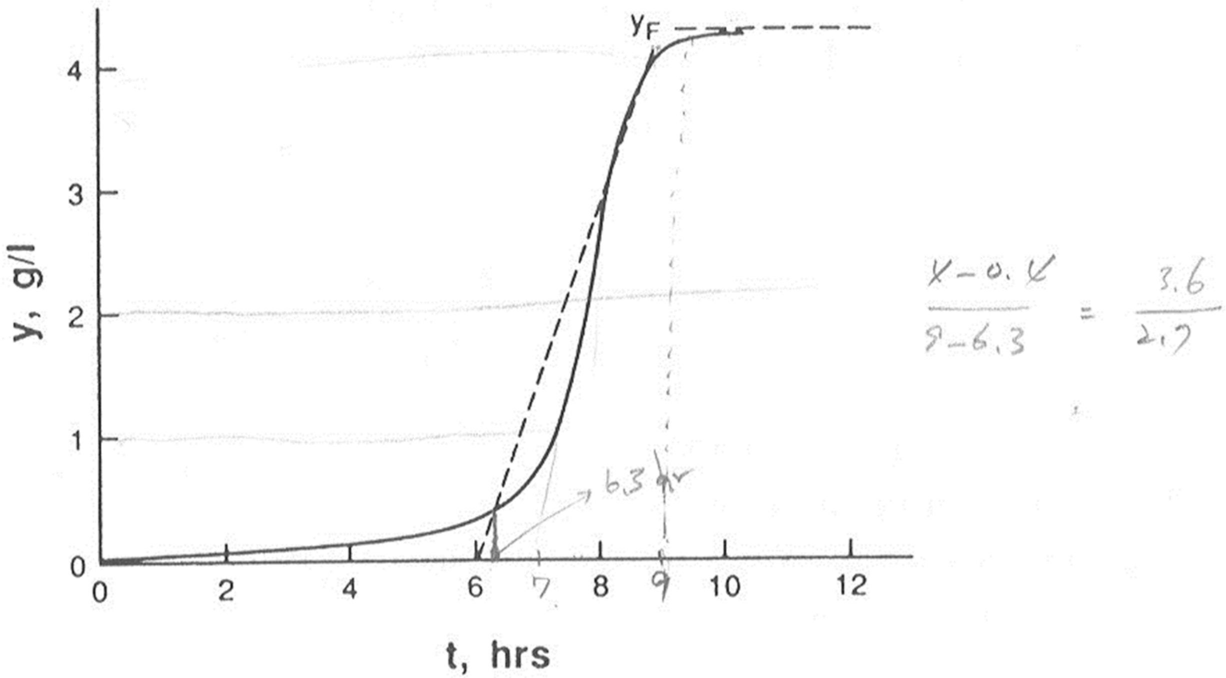


Figure 6.4-4. Cephalosporin adsorption in a packed bed. The breakthrough curve shown can be analyzed with any of the four methods given in this section. Results are similar, as detailed in Example 6.4-2.

b) From the figure, breakthrough = 6.3hr and exhausted = 9.0hr
from Eq. (A)

$$\Theta = 1 - \frac{\Delta t}{2t_B} = 1 - \frac{9.0 - 6.3}{2(6.3)} = 79\%$$

c) By linear adsorption model

$$\xi = \frac{zka}{\varepsilon v} = \frac{1m(ka)}{0.33(2m/hr)} = \frac{1.5ka}{hr}$$

$$\tau = \frac{ka}{K\rho}\left(t - \frac{z}{v}\right) = \frac{ka}{12(0.67)}\left(t - \frac{1m}{2m/hr}\right) = 0.124ka(t - 0.5hr)$$

d) By two parameter model

t_o=7.8hr(inversely proportional to the velocity)

σ=0.15(σ^2 will be directly proportional to the velocity(cf. Table 1))

$t_o\sigma$: slope of curve

$$\frac{y}{y_F}=\frac{1}{2}\left[1+\mathrm{erf}\left(\frac{(t/7.8/2))-1}{\sqrt{2}0.15}\right)\right]$$

y/y_F=(0.4/4.0), t=2.4hr

lost : about 5%