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Lec 20

Adsorption

Adsorption → surface phenomenon

Adsorption of liq. on solid surface
steps involved -

1) Reversible Binding
2) Elute

* solid surface → adsorbent
liq. → adsorbate

Q) Why adsorption occurs? [Types of adsorption]
⇒ 1) Van der waal's forces [weak attraction]
↳ conventional [Non-specific]

Forces
2) Ion-exchange Electrostatic
3) Affinity
(Non-covalent interaction)
[eg. protein-ligand interaction]
4) Non-Polar / Hydrophobic
↳ (Reverse phase)

P.T.O.

→ Common adsorbents & functional grps -

Hydrogels
silica beads → conventional
Activated carbon → Hydrophobic

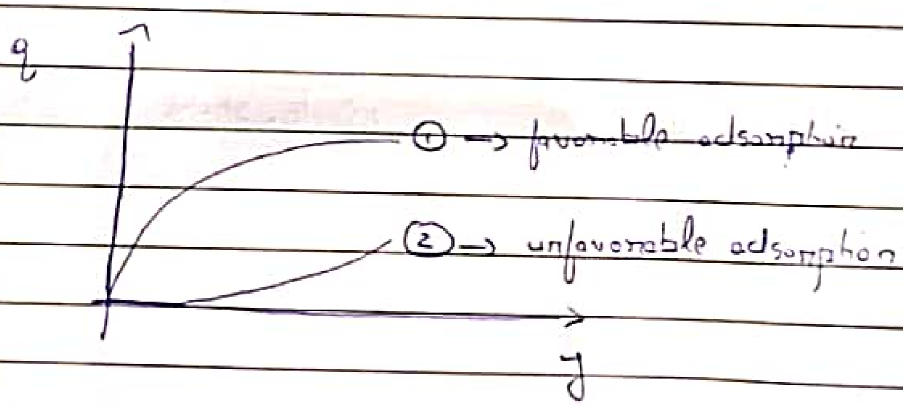
$-SO_3-$
$-COO-$
$-NR_3^+-$
} Electrostatic

* Adsorption equilibrium - [Adsorption Isotherm]

solute adsorbed solute present in solⁿ

q y

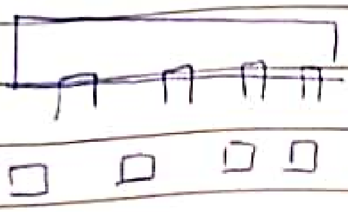
$= \dfrac{\text{Amount of solute}}{\text{Amount of adsorbent (vol or mass)}}$ $= \dfrac{\text{mass/mol of solute}}{\text{volume of sol}^n}$



1) Linear → $q = Ky$ [Seen in extremely dilute solutions]

2) Langmuir Isotherm → $q = \dfrac{q_0 y}{K+y}$ [Similar to Monod] [or michaelis - menten]

3) Freundlich Isotherm → $q = Ky^n$, $n < 1$ → favorable
$n > 1$ → unfavorable



Vacant sites → V

solute

Note - Total sites are limited

sol + vac → filled [F]

~~S → S + E → ES~~

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$$\cancel{K = \frac{[VS]}{[V][S]}} = \cancel{q}$$

$$q = \frac{q_0 y}{K + y} \Rightarrow \cancel{K = \frac{q_0 y}{q} - y}$$

$$\cancel{K = \frac{(q_0 - q)y}{q}}$$

$$V + S \rightleftharpoons F \quad (\text{Eql})$$

$$K' = \frac{[S][V]}{[F]} \quad - (1)$$

$$T = V + F \quad - (2) \quad [T = \text{Total no. of sites}]$$

$$\boxed{\begin{matrix} F \to q \\ S \to y \end{matrix}}$$

$$\Rightarrow \cancel{K' = \frac{y}{q}(T - q)} \qquad V = \frac{K'F}{S}$$

$$\Rightarrow T = \frac{K'F}{S} + F \Rightarrow T = F\left[\frac{K' + S}{S}\right]$$

$$\Rightarrow F = \frac{TS}{K' + S} \Rightarrow \boxed{q = \frac{q_0 y}{K' + y}}$$

$$q = \frac{q_0 y}{K+y} \Rightarrow \frac{K+y}{q_0 y} = \frac{K}{q_0 y} + \frac{1}{q_0} = \frac{1}{q}$$

$$\Rightarrow \cancel{\frac{q_0}{q} = 1 + \frac{K}{y}}$$

$$\frac{1}{q} = \frac{1}{q_0} + \left(\frac{K}{q_0}\right)\frac{1}{y}$$

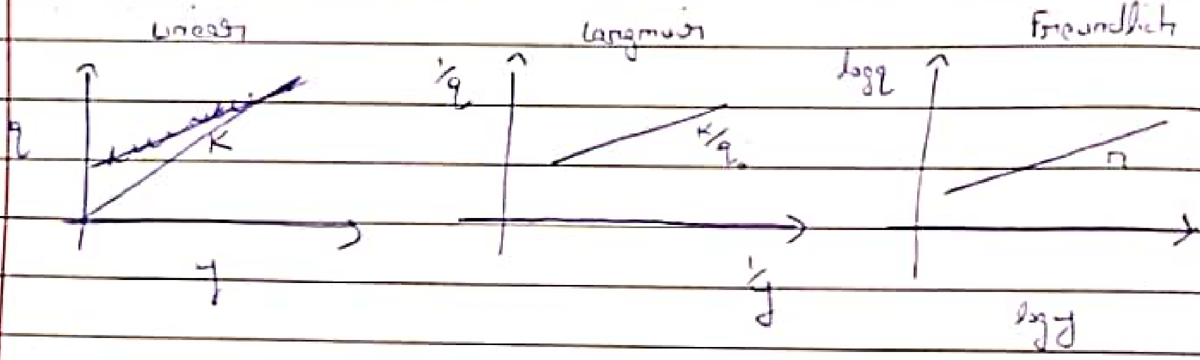
∈ Plot $1/q$ v/s $1/y$

slope → K/q_0

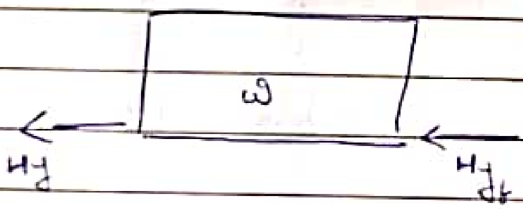
intercept → $1/q_0$

For Freundlich –

$$\log q = n \log Ky = n \log K + n \log y$$



* Batch adsorption – (Same as liq-liq extraction)



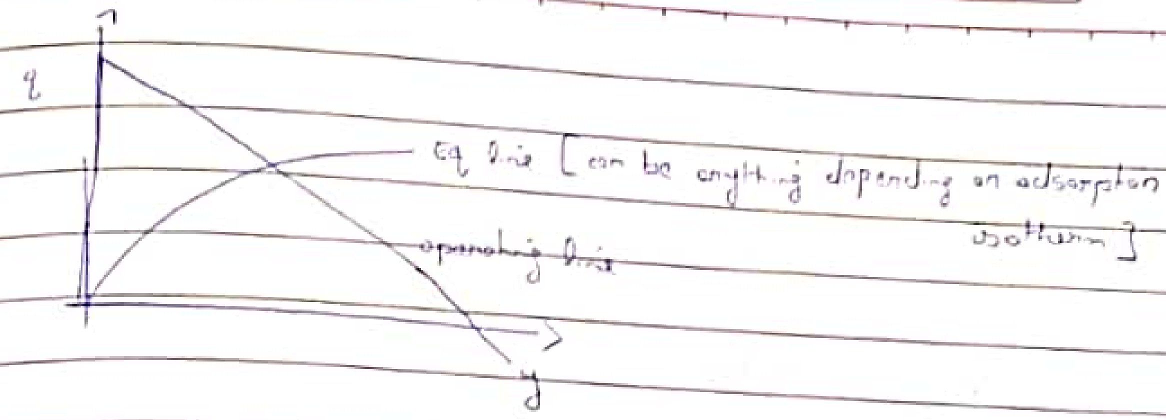
Adsorption Isotherm

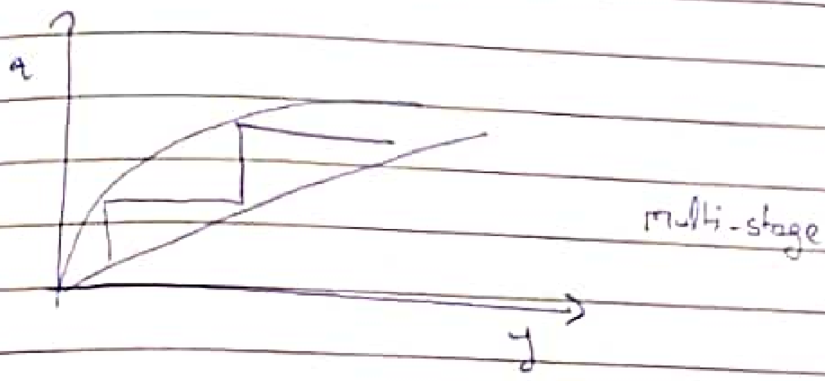
$q = f(y)$ — (1)

Amount of adsorbent → w

q_f q

$$Hy_f + w q_f = Hy + w q \Rightarrow q = q_f + \frac{H}{w}(y_f - y) \quad (2)$$





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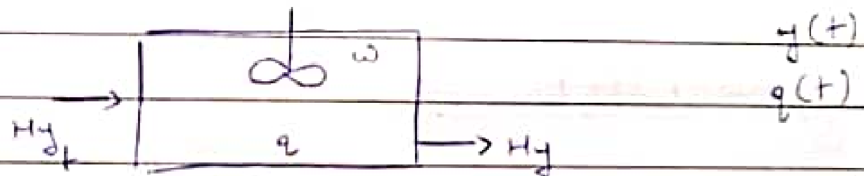
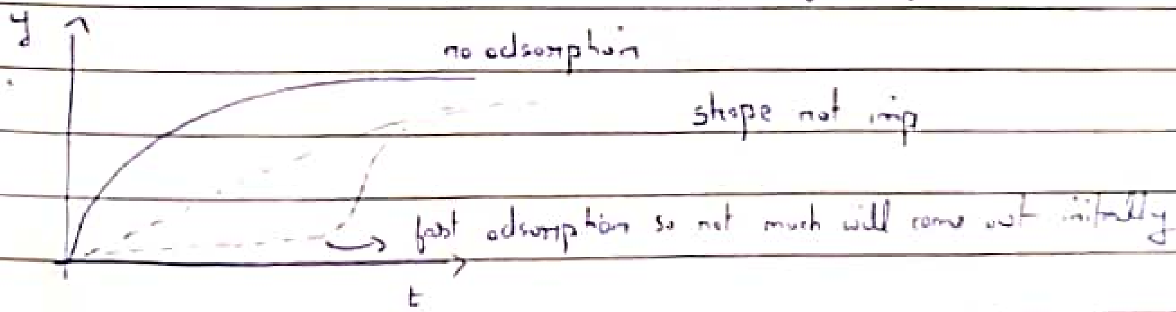
* CSTR -

No equilibrium



Mass transfer of solute from liq. to solid

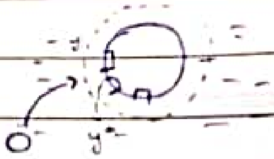


→ <u>Determine Kinetics of adsorption</u>

1) mass Balance on solute in liq. phase
2) Rate of solute transfer from liq. to adsorbent
3) Rate eqn
4) Adsorption Isotherm

* <u>Rate eqn</u> -

1) MT of solute from liq to solid
2) solute diffusion to find & interact with site
3) Reaction / Interaction of solute & vacant site



→ <u>overall MB on solute in reactor</u> -

$\cancel{\frac{Hy}{d_t} = Wq + Dty}$

(similar to)

Rate of solute accumulation in reactor (liq) = Rate of sol incoming - outgoing - Rate of adsorption

liq   liq   liq.   solid

$$\varepsilon V \frac{dy}{dt} = Hy_f - Hy - (1-\varepsilon) V \frac{dq}{dt} \quad - \ (1)$$

ε → void fraction in adsorbent

ε → liq. fraction

$(1-\varepsilon)$ → adsorbent fraction

⇒ $(1-\varepsilon) V \frac{dq}{dt} = V r$ - (2), r → rate of adsorption hypothetical conc. → liq. phase that would be in equilibrium with q

Rate of adsorption ??

(3) $\quad r = \underbrace{k}_{\text{MTC}} a \,(y - y^*)$, $\quad a$ = Surface area of adsorbent per tank ~~vol~~ volume

Rate i) Diffusion controlled adsorption

	Linear	Freundlich
Adsorption Isotherm	$q = Ky^*$	$q = K(y^*)^n$ — (4)

$\rightarrow \; y^* = \left(\frac{q}{K}\right)^{1/n}$

subs (2) & (3) in (1),

$$\varepsilon V \frac{dy}{dt} = H(y_1 - y) - Vka(\underbrace{y - y^*}_{y^* = \left(\frac{q}{K}\right)^{1/n}}) \quad - (5)$$

$$(1-\varepsilon)\cancel{V}\frac{dq}{dt} = \cancel{V}ka\left[y - \left(\frac{q}{K}\right)^{1/n}\right] \quad - (6)$$

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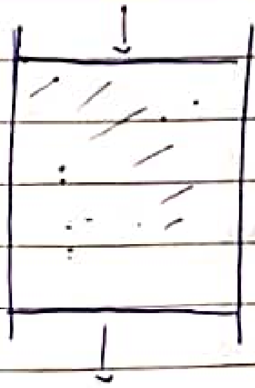
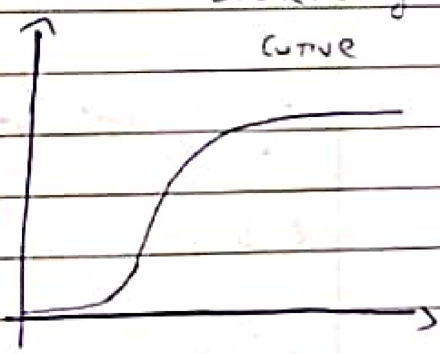
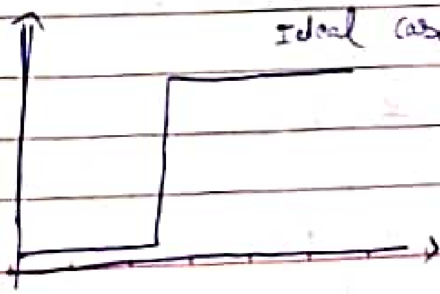
* Packed-Bed -



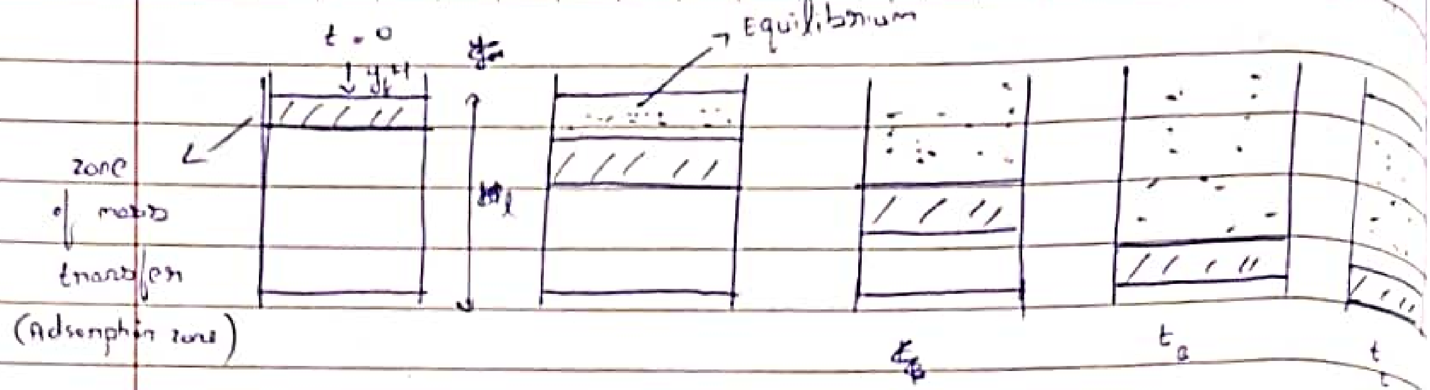
Break Through Curve



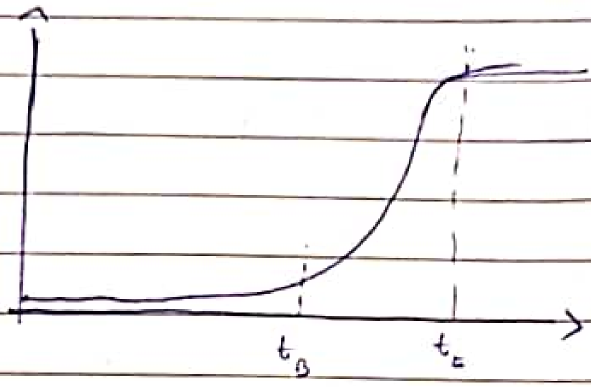
Ideal case

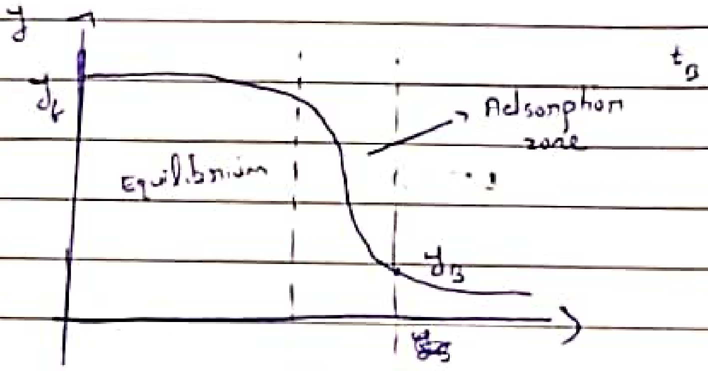


Exit conc. starts increasing once adsorption is complete



Zone of M.T. is moving through the column





If we don't want solute loss → stop at t_B

Shape of Breakpoint → design & operate

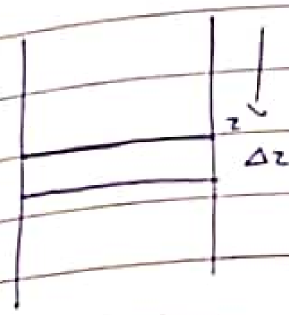
~~Solute loss~~ ~~Bed capacity~~ use

* Factors influencing B.P. curve -

1) Feed rate

1) Column capacity
3) Nature of adsorption / Equilibrium
4) Packing

->



Accumulation in liq + Accum in solid adsorbent = Solute in by convection ~~Solute out~~ $\pm$ dispersion/diffusion - solute out

* M.B. for Δt ->

$$(A\Delta z)\varepsilon\left[y|_{t+\Delta t} - y|_t\right] + (A\Delta z)(1-\varepsilon)\left[q|_{t+\Delta t} - q|_t\right]$$

$$= \left[A\varepsilon\left[vy - E\frac{\partial y}{\partial z}\right]_z - A\varepsilon\left[vy - E\frac{\partial y}{\partial z}\right]_{z+\Delta z}\right]\Delta t$$

Limits, Δt & $\Delta z \to 0$

Dividing by $(A\Delta z)\varepsilon\Delta t$,

$$\cancel{\frac{1}{\Delta t}\left[y|_{t+\Delta t} - y|_t\right]} = \cancel{\frac{1}{\Delta z}}$$

Convective transfer → Dispersion

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

$$\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\partial q}{\partial t} = r \quad - (2)$$

↳ rate of rxn/adsorption

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

$$q = K (y^*)^n \quad - (4) \qquad \text{[Assuming Freundlich]}$$

* ~~Approximate solutions -~~

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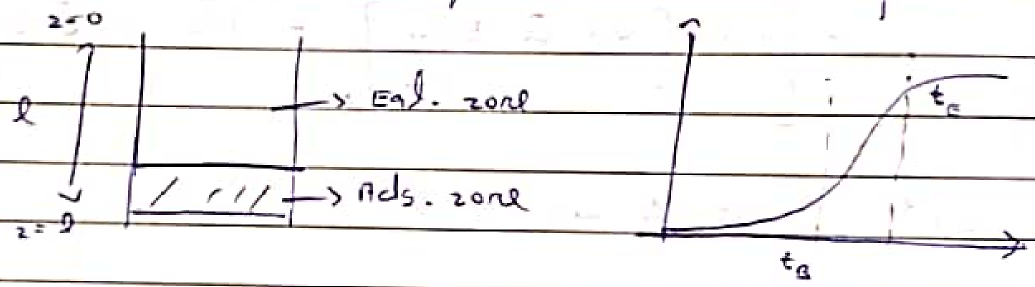
* Approximate solutions -
    ↳ using experimental data

1) Model this as a ramp
    ↳ divide into equilibrium zone & adsorption zone



- Eql. zone ranges from → $z = 0$ to $z = l\left[1 - \dfrac{\Delta t}{t_B}\right]$

    $\Delta t = t_E - t_B$

- Ads. zone → $l\left(\dfrac{\Delta t}{t_B}\right)$

- $q\,(\text{eqm zone}) = q(y_b)$

- $q\,(\text{ads zone}) = \dfrac{1}{2} q(y_b)$ [Approximation]

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- Fraction of bed used (θ) $= \dfrac{\left[q(y_f)\, l\left(1-\frac{\Delta t}{t_B}\right) + \frac{q(y_f)}{2}\, l\left(\frac{\Delta t}{t_B}\right)\right] A(1-\varepsilon)}{q(y_f)\, l A(1-\varepsilon)}$

$$= \cancel{\tfrac{1}{2} - \frac{\Delta t}{2t_B} + \frac{\Delta t}{t_B}\,\theta}$$

$$= \cancel{\frac{1}{2}\left[1 + \frac{\Delta t}{t_B}\right]}$$

$$1 - \frac{\Delta t}{t_B} + \frac{\Delta t}{2t_B} = \cancel{1 - \frac{\Delta t}{2t_B}}$$

$$= \boxed{1 - \frac{\Delta t}{2t_B}}$$

** Note - 2nd Approximation (2-parameter model) from bolter not in syllabus

2) Linear Adsorption Model -

Assumptions -

1) $q = Ky^*$ [Replace Freundlich with linear]

2) Neglect $\frac{\partial^2 y}{\partial z^2}$ & $\frac{\partial y}{\partial t}$

i.e. neglect dispersion & assume steady state in liq. phase

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

$$ka\left(y - \frac{q}{K}\right) = (1-\varepsilon)\frac{dq}{dt} \quad - \quad \text{II}$$

Boundaries $\rightarrow$ $t = 0$, all z, $q = 0$

$t > 0$, $z = 0$, $y = y_f$

Can be solved by non-dimensionalizing the time & location (distance), & concentration.

$\Rightarrow$ $\phi = \dfrac{y}{y_b}$

$\xi_e = \dfrac{zka}{vE}$

$\tau = \dfrac{ka\,(t - z/v)}{K\rho}$ ↳ bed density

} will be given in exam if asked

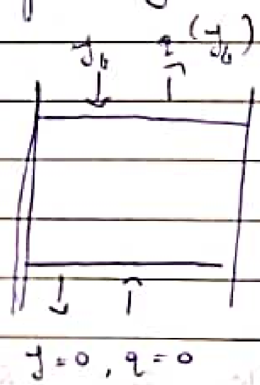
Explained in Harrison (pg. 212)

Solving using these, we get Bessel functions.

3) Differential contacting model –

↳ (similar to differential extraction)

Think of ~~many~~ bed



Assume – 1) bed is infinitely long
2) Equil. at top of the bed
$\Rightarrow q(y_b)$ & y_b in eqb.
3)

$\rightarrow$ $H(y_b - 0) = w\,[q(y_b) - 0]$ (Using Mass Balance)

Steady state $\rightarrow$ All solute coming in liq $\Rightarrow$ Adsorbed on solid adsorbent

$\Rightarrow \dfrac{\partial y}{\partial t} = 0$

Neglect dispersion