Mass Transfer Operations II
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Lecture No 27
Adsorption and Ion-exchange

Welcome back to mass transfer operations 2, we were discussing on adsorption and Ion-exchange.

Unsteady state - Fixed Bed Adsorber:

As increasing amount of fluid are passed through a stationary bed of adsorbent, solid adsorbs increasing amount of solute, and hence unsteady state prevails.

Applications:

- Recovery of valuable solvent vapors from gases
- Dehydration of gases and liquids
- Decolorization of mineral and vegetable oils

Concentration of valuable solutes from liquid solutions

Adsorption isotherm indicates the capacity of uptake of solute by adsorbent at equilibrium under a given set of physical conditions (T,P,C), but isotherm does not speak about rate or kinetics of adsorption.

The rate of adsorption in a bed depends on

- Resistance to transport of solute from bulk to adsorbent surface through stagnant film of gas.
- The resistance due to diffusion of solutes through pores (macro,meso,micro) of an adsorbent.

Physical description of adsorption by mass transfer zone (MTZ) and breakthrough

Let, Concentration of solute in feed stream is C_0.

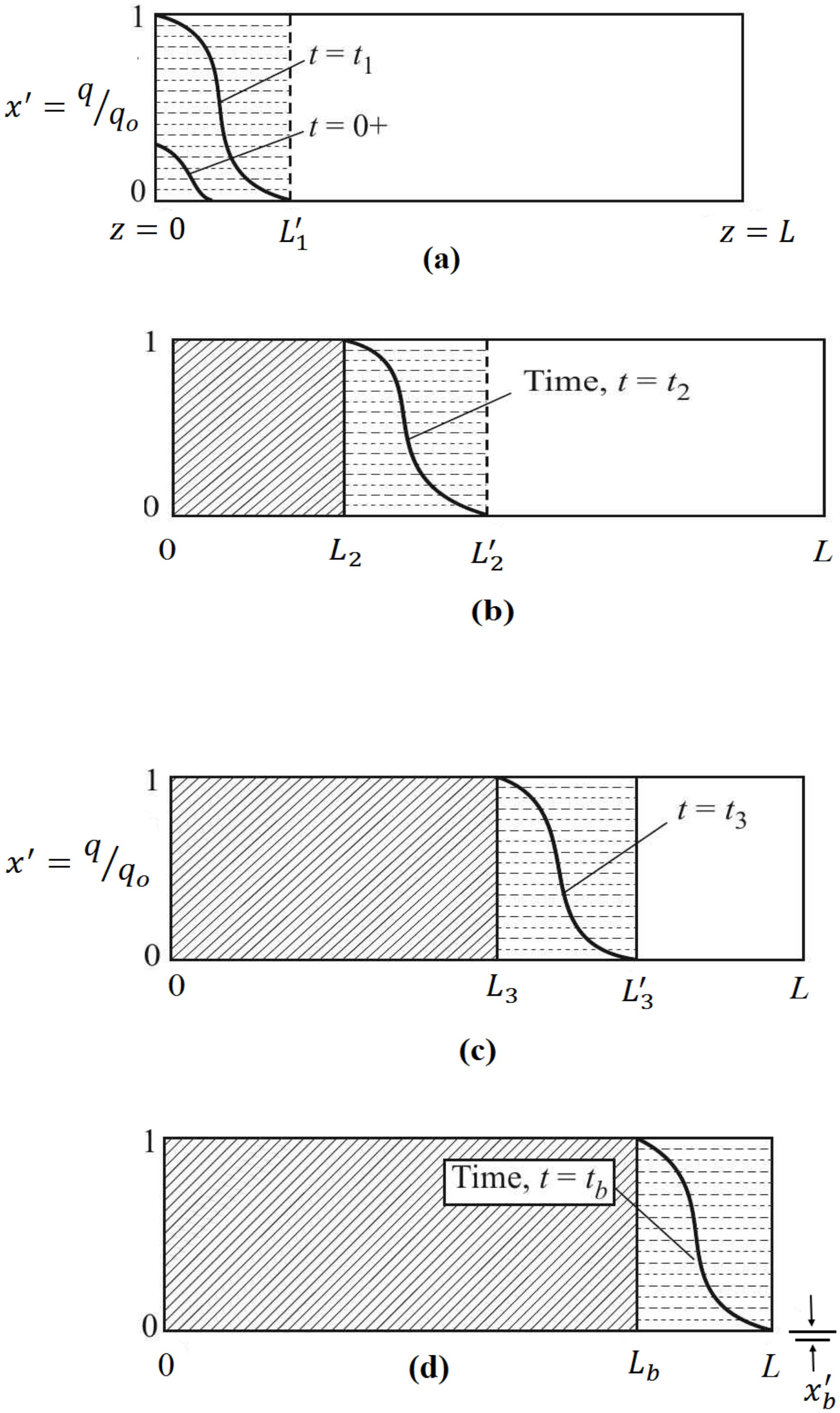
Concentration of solute in bulk gas at axial position Z of bed is C.

Concentration of solute in adsorbent in equilibrium with feed (saturated bed) is q_0.

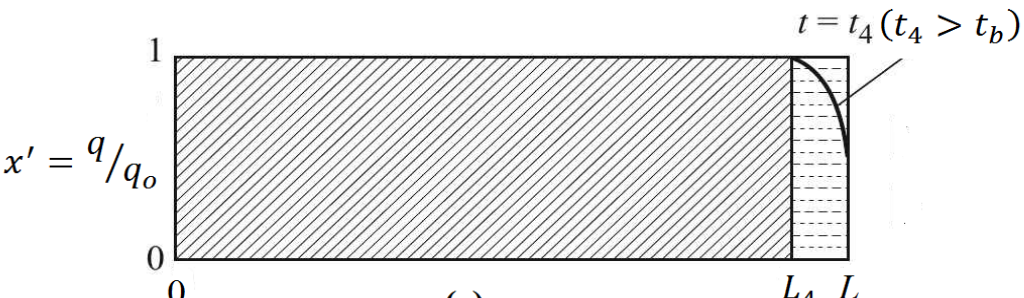
Concentration of solute in adsorbent at axial position Z is q.

$$\therefore x' = \frac{q}{q_0} = dimensionless\ solute\ concentration\ in\ the\ bed.$$

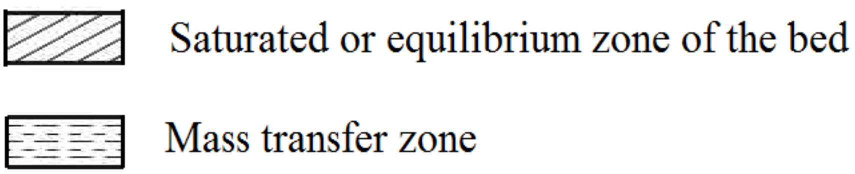
x’ = 1 at equilibrium (saturation)



1
$x' = {}^{q}/_{q_o}$
$t = t_1$
$t = 0+$
0
$z = 0$
L_1'
$z = L$
(a)
1
Time, $t = t_2$
0
0
L_2
L_2'
L
(b)
1
$x' = {}^{q}/_{q_o}$
$t = t_3$
0
0
L_3
L_3'
L
(c)
1
Time, $t = t_b$
0
0
(d)
L_b
L
x_b'



(e)



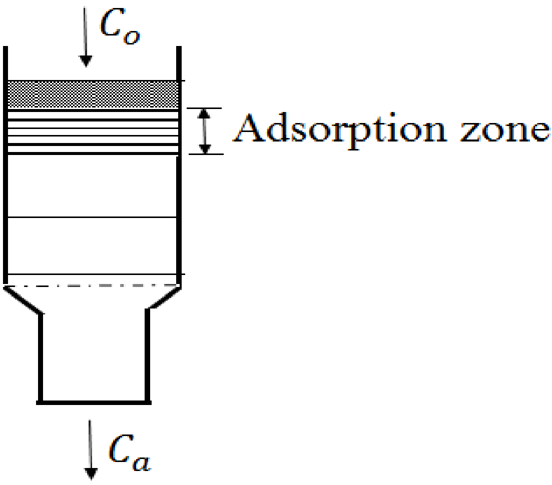
(a) Bed gets saturated near inlet *($z = 0,\ x' = 1$)*.

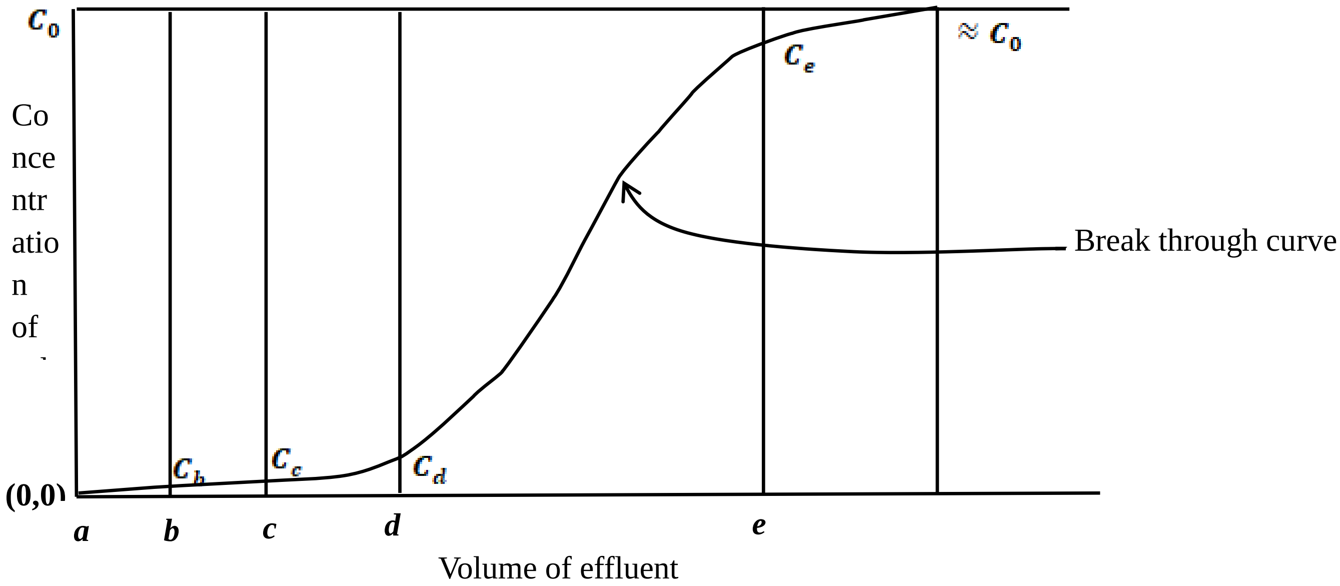
(b) Flow of feed and adsorption continues → a section of bed near inlet gets saturated.

(c) Thus Mass transfer zone moves along the bed with time like a wave.

(d) The S-shaped curves shown are called ***"mass transfer wave front"***.

Breakthrough:





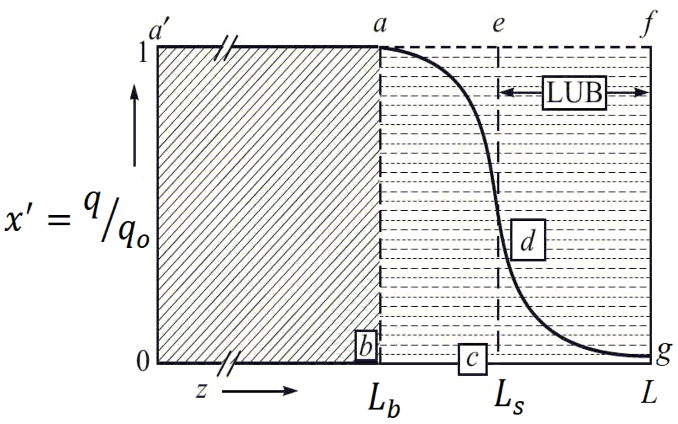
When flow of feed starts, initial rate of adsorption is pretty fast. As gas flows through bed, concentration of solute decreases due to adsorption.

bed gets saturated near inlet (Z=0, x'=1).

1. Flow of feed and adsorption continues a section of bed near inlet gets saturated.
2. Thus Mass transfer zone moves along the bed with time like a wave.
3. The S-shaped curves shown are called mass transfer wave front.
4. Effluent concentration, C_a, C_b, C_c, C_d, C_e

The upper most layer of bed is saturated. As solution continues to flow, mass transfer zone (MTZ) moves downward as a wave. At d, lower portion of the adsorption zone has reached bottom of the be, and solute concentration in the effluent has suddenly risen to an appreciable value C_d . The system is said to have reached the breakpoint.Then solute concentration in the effluent risen rapidly as MTZ passes through the bottom of the bed and at e, it has reached the initial feed concentration (C_0). The portion of the effluent concentration curve between position d and e is termed as breakthrough curve. (solute in the feed has been able to breakthrough the barrier of the bed of the adsorbent). Equilibrium time t_{eq} (time required to get saturated). (solute in the feed has been able to breakthrough the barrier of the bed of the adsorbent). Equilibrium time t_{eq} (time required to get saturated).

Length of unused bed (LUB):



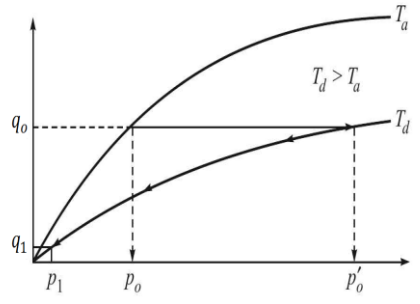
$0 - a' - a - d - g - c - b - 0$ $\rightarrow$ *Used adsorption capacity*

$a - d - g - f - e - a$ $\rightarrow$ *Unused adsorption capacity*

Region $c - d - g - c$ and $a - d - e - a$ are equal

$L - L_s \Rightarrow LUB$

Thermal Swing Adsorption (TSA):



- Regeneration temperature is selected on the basis of the adsorption equilibrium or isotherm at different temperatures.
- Heat requirement for regeneration is ~2.5 times the enthalpy of desorption.
- Higher temperature and lower pressure.
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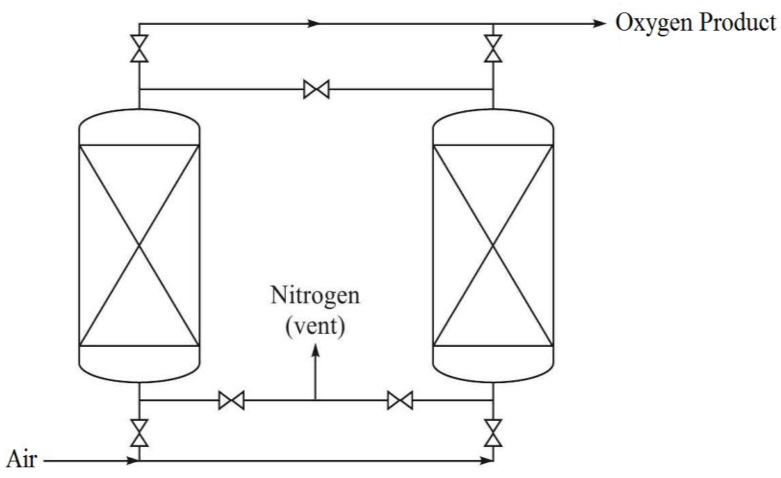
Pressure Swing Adsorption (PSA):

Four steps for Skarstrom cycle:



1. Adsorption – feed gas flows at a higher pressure through bed.
2. Depressurization – the pressure in the vessel is reduced.
3. Purging – small fraction of product gas from other bed is passed through vessel.
4. Repressurization – Feed is supplied (no product is drawn during this step).

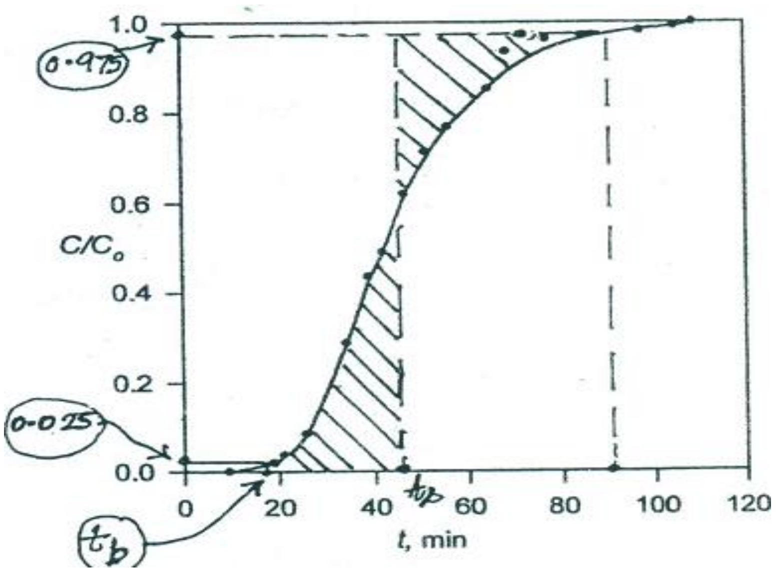
Problem 6:

Adsorption equilibrium data for Cr (III) adsorption from tannery effluent on Spirulina platensis is give as follows:

Time (min)	10	20	22.5	25	30	35	37.5	40	42.5
C/C_0 in effluent	0	0.017	0.04	0.1	0.2	0.3	0.35	0.45	0.502
Time (min)	45	50	60	70	80	90	100	105	110
C/C_0 in effluent	0.55	0.64	0.8	0.95	0.96	0.965	0.99	0.995	1.0

Temperature is 20°C, bed height is 2 m, superficial gas velocity is 0.29 m/s, C_0 is 0.11 gm mole/m3, bed density is 700 kg/m3. If maximum permissible limit of is C/C_0 0.03,
(a) calculate breakthrough time. Calculate the length of mass transfer zone (MTZ).
(b) Using the above data, design a bed for the treatment of 500 m3/min of the effluent if adsorption half cycle of 480 min is allowed. What is the average loading of the bed at breakthrough point? Calculate maximum solid loading at the given inlet concentration of Cr(III) in effluent?

Solution:



Now we need to solve the problem in terms of say breakthrough time calculation etcetera. The given parameter are temperature is 20 degree Celsius, bed height is 0.2 meter then superficial gas velocity 0.29 metres per second. Then C0 is 0.11 gram mole per metre cube, then bed density is 700 kg per meter cube. If maximum permissible limit is C by C0 is 0.025

then we need to calculate the breakthrough time. We need to calculate the length of the mass transfer zone also MTZ, we will be getting this one very easily if we are able to plot this we can say x prime by we can say Z from there we will be getting what is the length of this MTZ.

Then using the about data, design a bed for the treatment of 50 metre cube per minute or 3000 m cube per hour of this effluent if adsorption half cycle is 480 minutes or we can say this one 8 hours that is allowed, so what is the average loading of the bed at breakthrough point? And we need to calculate the maximum solid loading at a given inlet concentration of the chromium 3 effluent. We will be solving this problem, so we will recapitulate this one so firstly we have the C by C0 data is there with time so I think we will be able to plot the breakthrough curve there, so we will be solving this step-by-step we will be doing the solution.

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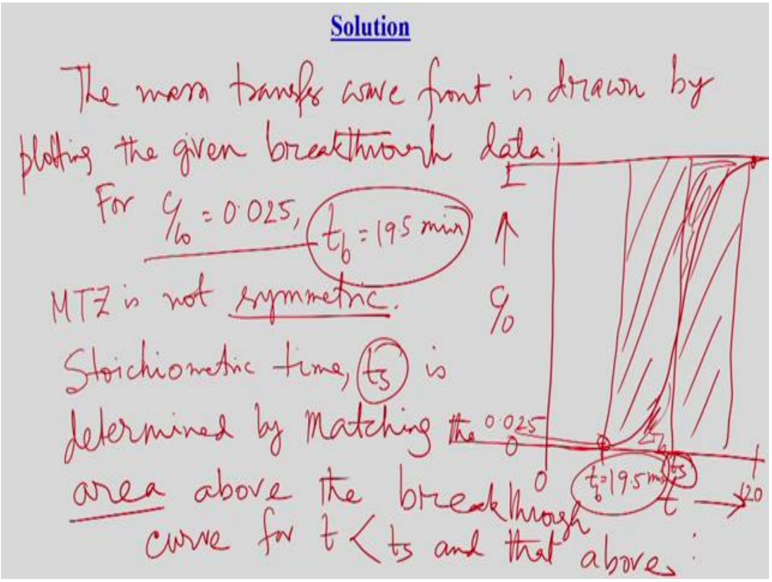

Temperature is 20°C, bed height is 0.2 m, superficial gas velocity is 0.29 m/s, C_0 is 0.11 gm mole/m^3, bed density is 700 kg/m^3. If maximum permissible limit of is C/C_0=0.025,

(a) Calculate breakthrough time. Calculate the length of mass transfer zone (MTZ).

(b) Using the above data, design a bed for the treatment of 50 m^3/min of the effluent if adsorption half cycle of 480 min is allowed. What is the average loading of the bed at breakthrough point? Calculate maximum solid loading at the given inlet concentration of Cr(III) in effluent.

Like the mass transfer wave front that is will be drawing this one is drawn by plotting the given breakthrough data like this one it is tabulated like this and let us take for solving this problem we need to use the graph paper like this, so here we will be plotting time and here we will be plotting this C by C0 then we will be getting definitely getting this type of S shaped curved but for the time being we are writing this one without the scale but whenever we will be solving this one we need the graph paper, we need to solve this one in the graph paper.

Let us take this is 1 and this is 0 and time t is equal to 0 and let us say up to 110 minutes actually the data point is given, say we will take (())(33:56) we will be taking this up to 120 minutes which is 2 hours will be taking this one before that in 110 minutes it has become 1, C by C0 has become one like this and then we will be getting this we can say. We can say this allowable, the maximum permissible limit for C by C0 is 0.025, so we can say let us take this for C by C0 is equal to 0.025 we can say.

That time we can say this one time t will be like this from here we can say whenever just it will start entering into this we can say the breakthrough curve like that time you can say whenever this 0.025 from here suppose this is 0.025, so from this graph paper you find this one this time will be is equal to, so whatever I have got this one is 19.5 this minute. So we can say this t is equal to say t breakthrough like this, so this is 19.5 minutes. So I can say it is tb will be is equal to 19.5 minutes, so we got this one from the graph like this.

So the mass transfer zone, so it is, here actually it is not symmetric one like this one this is not symmetric one, so we can say this mass transfer zone, so whenever we will be plotting this one will find that it is not purely symmetric whatever we have discussed this one during this mass transfer zone calculation there it was assume that it is the symmetric one that is why this portion will come and it will be sitting here, so then unused bed is obtained from here but in this case it is not symmetric actually from this data point it is not symmetric, so that is why can say as it is not symmetric so we can say we need to get this stoichiometric time so that is why this, say time ts actually we can say like this one is ts stoichiometric time, so that is actually is determined by matching the area above the breakthrough point. We can say this one t less than we can say this ts.

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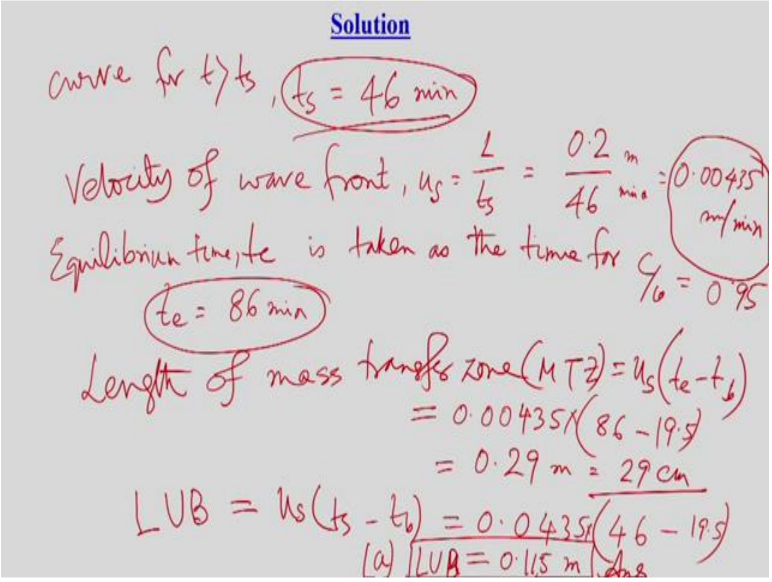

And that above the curve for t greater than ts like this one so from there actually whenever we will be doing this one that time we will be getting ts is equal to from the graph actually we will be getting is that this 46 minutes, so we will be getting this we can say this stoichiometric time that may not be in the middle but say from this we can say this area under the curve we will be getting this ts is equal to 46 minutes like this.

So now we have this velocity of this wave front is already given, so velocity of wave front this u s will be equal to we can say L by ts that this is equal to we can say 0.2 meter by ts equal to 46 minutes, so meter per minute so that is we can say this meter per minute, so it is coming out as 0.00435 meter per minute, so this is we can say velocity of the wave front we have got this one that 0.00435 meter per minute and this equilibrium time, so te is taken as the time for C by C0 is equal to, so we can say this one 0.095. So for that case we can say this one say 0.95 actually, so here we can say so for this 0.95 and then 0.95.

So that time actually we can say this one the will be like this te is equal to, so from the curve we will be getting this one that 86 minutes, so from their curve actually we will be getting this t is equal to 86 minutes, so we need to get this length of mass transfer zone that is MTZ that is nothing but this us into t minus tb. So that is coming out as us is equal to 0.00435 into t is equal to 86 minus tb is equal to 19.5, so from there actually we will be getting this one as 0.29 meter or we can say this 29 centimetre.

So this length of this mass transfer zone is 29, so length of unused bed that is the one question that is asked that what will be the length of unused bed that LUB that will be nothing but we can say this us into ts minus tb, so that will be like this us is equal to say again 0.0435 into ts is equal to that 46 minus 19.5, so it is coming out as 0.115 meter, so LUB is equal to 0.115 meter. So that is one this is the answer of 1st problem what is the length of unused bed. Now the 2nd problem is, so that is the answer of problem a.

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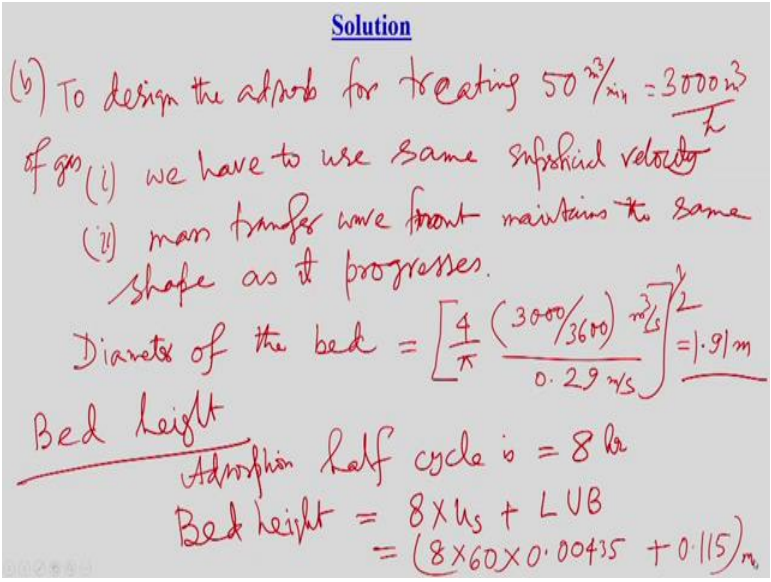

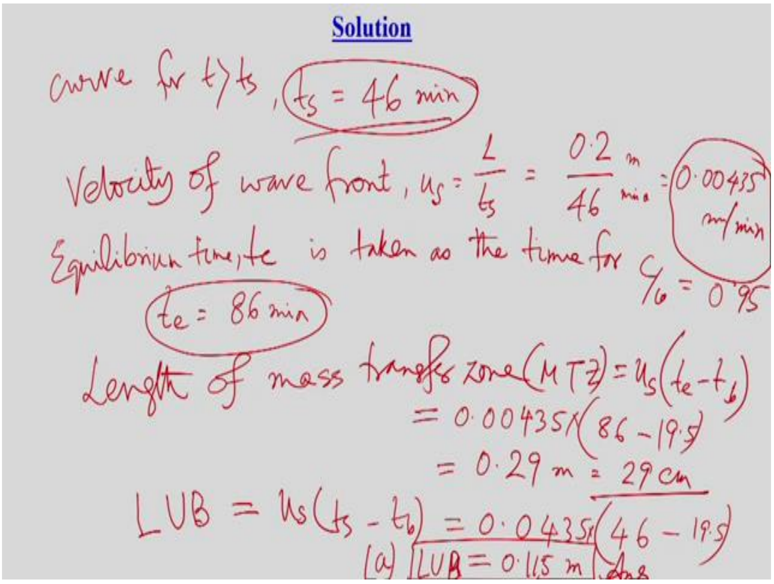

Now we will be solving for the problem b, we have to design this adsorber. To design the adsorber for treating say 50 meter cube per minute are is equal to 3000 meter cube per hour of gas, so firstly we have to use the same superficial velocity and that is there in the problem and then that mass transfer wave front maintains the same shape like this s shape as it progresses and then we can say this one we need to get the diameter of the bed from this superficial velocity from the bed will be like this 4 by pi into say 3000 per hour that is meter cube per second by 0.29 meter per second to the power half that is coming out as 1.91 meter so that is what we can say diameter of the bed.

So we got this one at 1.91 meter. Now we need to get the bed height, so for that we can say adsorption half cycle is given is equal to 8 hours. And so bed height will be like this total we can say total time into say us plus how much amount of unused bed is there, means how much amount of it is utilised and how much amount of unutilised bed is there, so there will be getting like this 8 into that us is equal to that is hours, minutes into this us is equal to 0.00435 this plus length of unused bed that is 0.115 meter.

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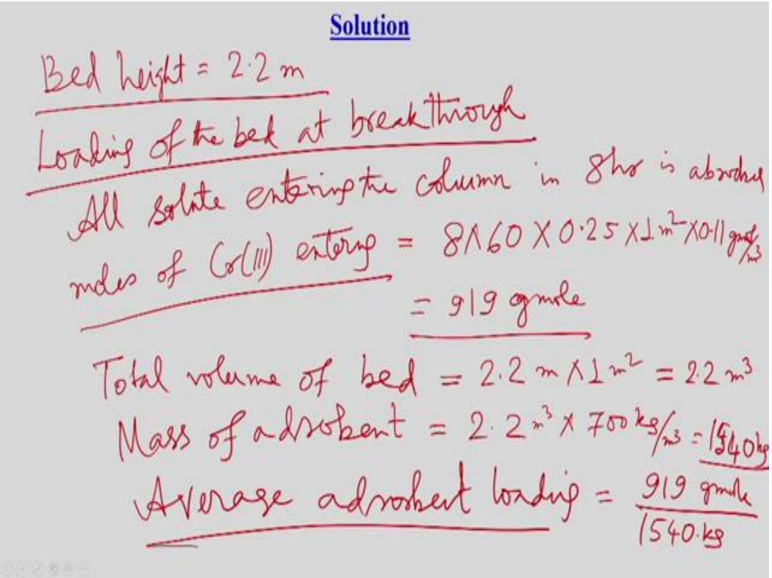

So total height is in meter that is coming out as so bed height is equal to 2.2 meter, so this is one answer and now we need the loading of this bed at breakthrough that this we need to get loading of the bed at breakthrough, so all solute actually we can say entering the column in 8 hours that is the half cycle adsorbed and say we can say the moles of chromium 3 entering is equal to say 8 into 60 into this us so that is 0.29 into say 1 meter square into say 0.11 gram mole per metre cube, so it is coming out as 919 gram mole.

So that is we can say how much amount of moles of the chromium 3 is entering, so in the, we can say this column. So then we have this one total volume of the bed that will be 2.2 meter into 1 meter square that is equal to 2.2 meter cube. So mass of adsorbent because this density is given, so that way we can say the volume is known, so 2.2 meter cube into density it says 700 kg per metre cube, so equal to you can say 1540 KG, 1540 kg is there, so average we can say this adsorbent loading will be like we can say 919 gram mole per 1540 kg.

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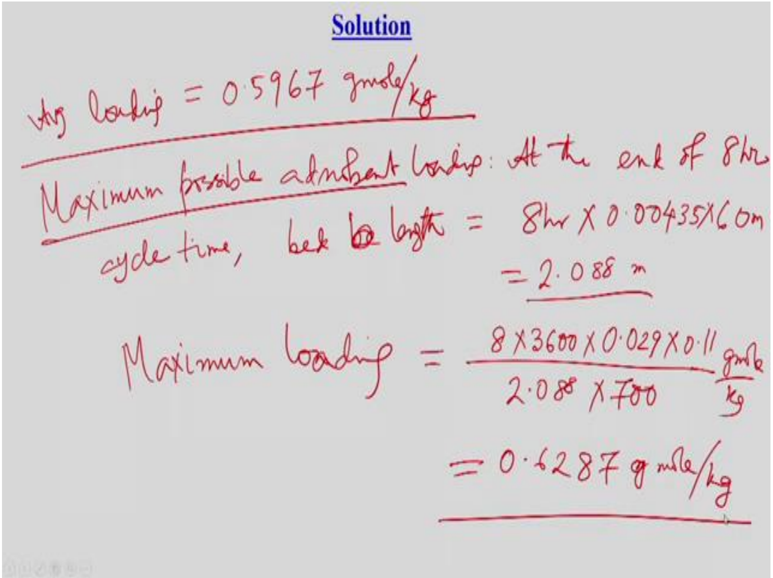

So that is coming out as that is is equal to you can say 0.5967 gram mole per kg, so that is we can say this one average loading okay, so average loading is equal to this one so we can say this maximum possible adsorbent loading. So at the end of 8 hour of cycle like this half cycle 8 hours of this we can say this adsorption cycle actually. Then bed length will be, so this is nothing but 8 into 0.00435 into 60 that is coming out as 2.088 meter.

So that is actually we can say this one effectively saturated then we can say this maximum loading will be, so that is the question maximum loading will be like this 8 hours means 8 into 3600 seconds into 0.029 into 0.11 divided by 2.088 into 700, so that is we can say this gram mole for kg. So it is coming out as 0.6287 when gram mole per KG, so this is the last answer that is what is the maximum loading required for this adsorption process that is 0.6287 gram mole per KG.

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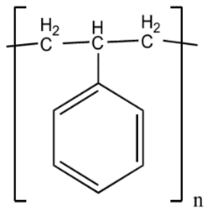
Ion Exchange:

Ion exchange is a separation process in which a solid containing mobile, replaceable ions is contacted with a solution of an ionizable species, when mobile ions of the solid are exchanged by ions of similar charge(+ve or –ve) in the solution.

Eq. $ca^{2+}(aq) + 2\,Na^{+}R^{-} \rightarrow 2\,Na^{+}(aq) + CaR_2$ (R^- Anionic resin)

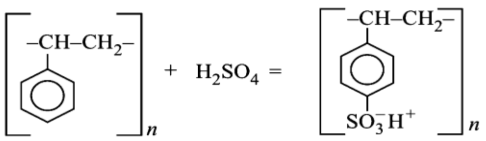
Polymeric ion exchange resins:

Polystyrene, cross linked with a small quantity of divinyl benzene (DVB) is base material.

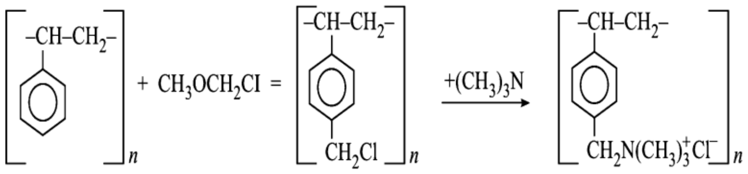


A cationic site $\rightarrow$ by sulphonation of the benzene rings in polystyrene.

An anion – exchange site $\rightarrow$ by chloromethylation of the benzene rings followed by amination.



$\rightarrow$ Preparation of strong - acid cation-exchange resin



$\rightarrow$ Preparation of strong-base anion-exchange resin

Industrial application of ion exchange resins:

- Softening and demineralization of water for boiler and chemical process
- Catalysis (esterification catalyst)
- High purity water production for semiconductor industry
- Separation of metal ions from waste water
- Electrodialysis

Ion exchange equilibrium:

The ion exchange reaction can be expressed as

$$A^+ + \bar{B}^+R^- + X^- \quad \rightarrow \quad \bar{A}^+R^- + B^+ + X^-$$

→ A^+ and X^- are formed in solution by dissociation of the compound AX.

→ $\bar{B}^+R^-$ and $\bar{A}^+R^-$ stand for cation – exchange resin.

→ A superscript 'bar' on an ion indicates that it presents in the resin phase.

→ The concentrations of ions in a phase may be expressed as 'gmole per litre' (or kgmole per m^3).

C_i → Concentration of the counter ions of type *i* in solution in gmole/litre.

$\bar{C}_i$ → Concentration in the same unit in the resin phase.

C_e → Total ionic concentration in solution (eq./litre).

$\bar{C}_e$ → Total ionic concentration in the resin phase.

x_i → Equivalent fraction of the counter ion *i* in the solution.

y_i → Equivalent fraction of the counter ion *i* in the resin.

y_i → Charge of the ion *i*.

$$x_i = \frac{z_i C_i}{C_e} \text{ and } y_i = \frac{z_i \bar{C}_i}{\bar{C}_e}$$

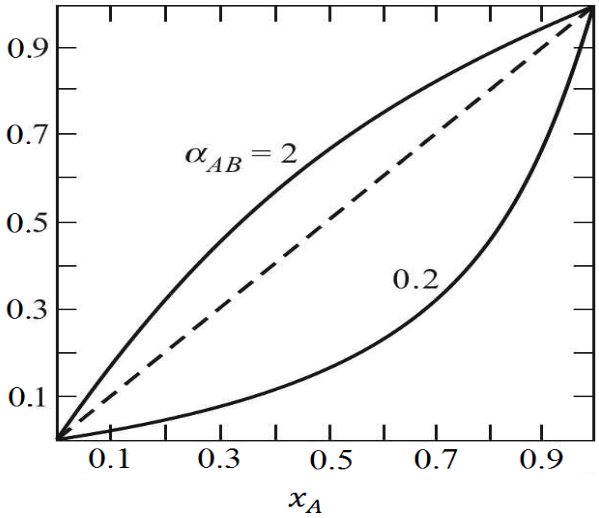
$$K_{AB} = \frac{\bar{C}_A C_B}{C_A \bar{C}_B} = \frac{\bar{C}_e y_A C_e x_B}{C_e x_A \bar{C}_e y_B} = \frac{y_A x_B}{x_A y_B}$$

Since only two types of counter ions , A and B, are involved.

$$y_A + y_B = 1 = x_A + x_B$$

$$\frac{y_A}{y_B} = K_{AB}\frac{x_A}{x_B} \quad \Rightarrow \quad K_{AB} = \frac{y_A/(1-y_A)}{x_A/(1-x_A)}$$

Separation factors in Ion-Exchange:



Ion Exchange Isotherm

If valency is same, K_{AB} is identical with separation factor for ion exchange , i.e.,

$$\alpha_{AB} = \frac{y_A x_B}{x_A y_B}$$

If $\alpha_{AB} > 1 \rightarrow$ favourable

Separation factor for exchange of B ion by A ion is

$$\alpha_{AB} = \frac{y_A / y_B}{x_A / x_B}$$

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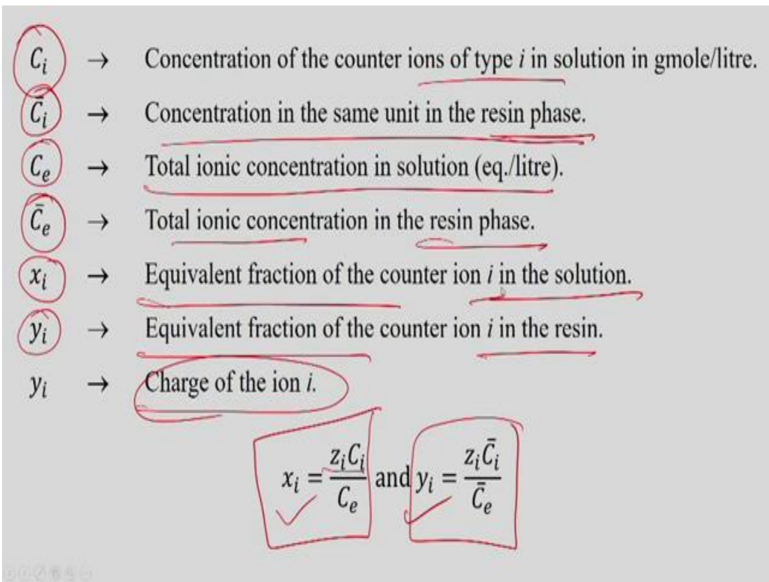

Now you see this Ci we can say concentration of the counter ion this one type i in the solution in gram mole per litre and whenever it is Ci bar then it will be in the resin phase. Ce also we can say this total ionic concentration in the solution wherever it is the Ce bar then we can say it is in the resin phase total ionic concentration, so xi is the equivalent fraction of the counter ion i in the solution this yi will be like this equivalent fraction of the counter ion i in the resin and we can say the charge of the resin is we can say this one I, so from there we can say this xi is equal to you can say this zi into ci by ce and yi is equal to we can say this zi into Ci bar by Ce bar, so these are 2 we can say this one parameters we need to calculate for this ion exchange equilibrium.

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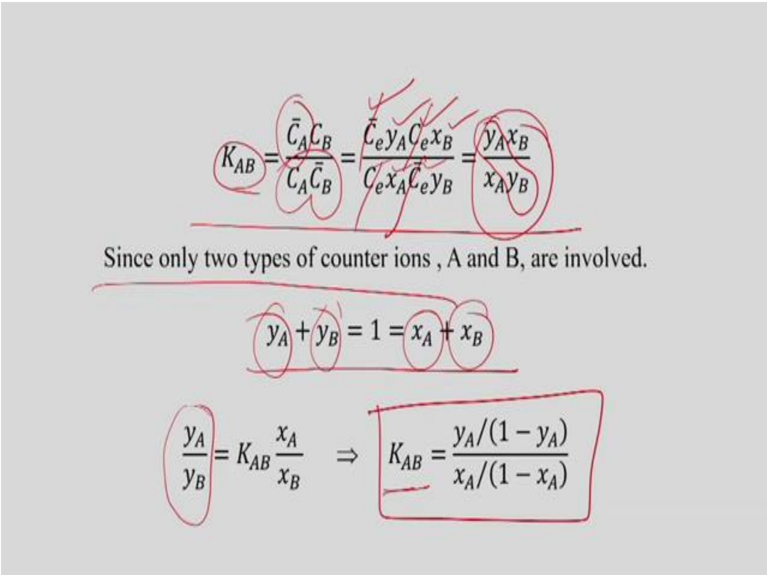

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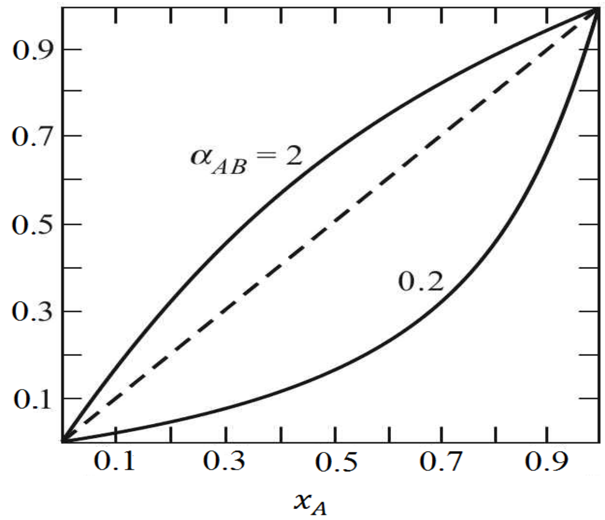
Separation factors in Ion-Exchange:



Ion Exchange Isotherm

And separation factors in the ion exchange like this sometimes it may be favourable it may not be favourable so we can say this if the valency is same like for both a and b valency are same, suppose plus single cation, single anion or we can say this binary cation binary anion, then KAB will be just identical with the separation factor for the ion exchange like this alpha AB will be equal to yA into xB by xA into yB.

So in all the cases we can say this one if we say this is the favourable one then alpha AB will be always greater than 1 like 1 alpha AB is equal to 2 so then we can say it is a favourable one if alpha AB is less than 1 then we say this process ion exchange process is not favourable at all, so that is why we can say separation factor for the exchange of B ion by A ion will be alpha AB is equal to yA by yB by xA by xB. So that we can say this one whenever this separation factor is greater than 1 then it is favourable and where separation factor is less than 1 that is we can say unfavourable.

References

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Thank you.

In the next class, we will be discussing the crystallisation process this new mass transfer operations.