Course: Adsorption Science and Technology: Fundamentals and Applications

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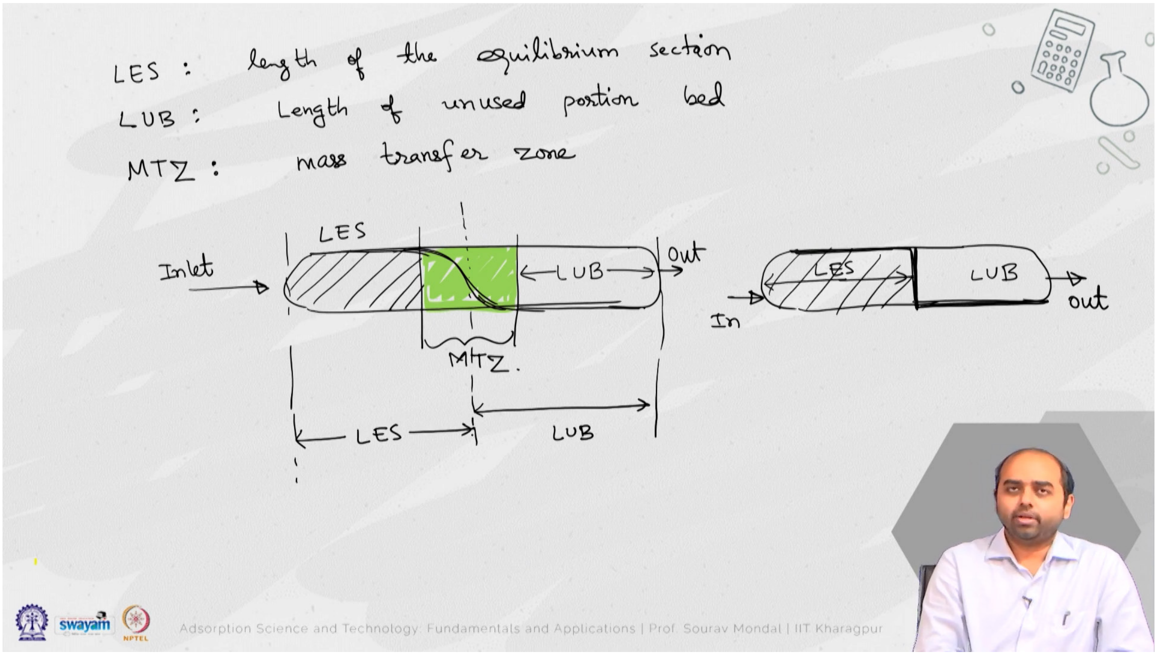
Week 05

Lecture 22 | Mass Transfer Zone Modelling

Hello everyone. So, in this lecture today we are going to continue from what we were discussing in the last class regarding the idea of this LES and the LUS and how that can be used to model you know considering an analogue of the you know ideal fixed bed absorber or when there is no mass transfer zone, which of course does not exist in the reality. But using this idea of LES and the LUS, one can consider an analogous version of the ideal wave front of a non-ideal system where there is you know finite width of the mass transfer zone. Now, in this case let me quickly remind what do we mean by the LES and the LUB. So, LES represents the length of the equilibrium section and LUB stands for the length of unused portion of the bed. MTZ represents the mass transfer zone here.

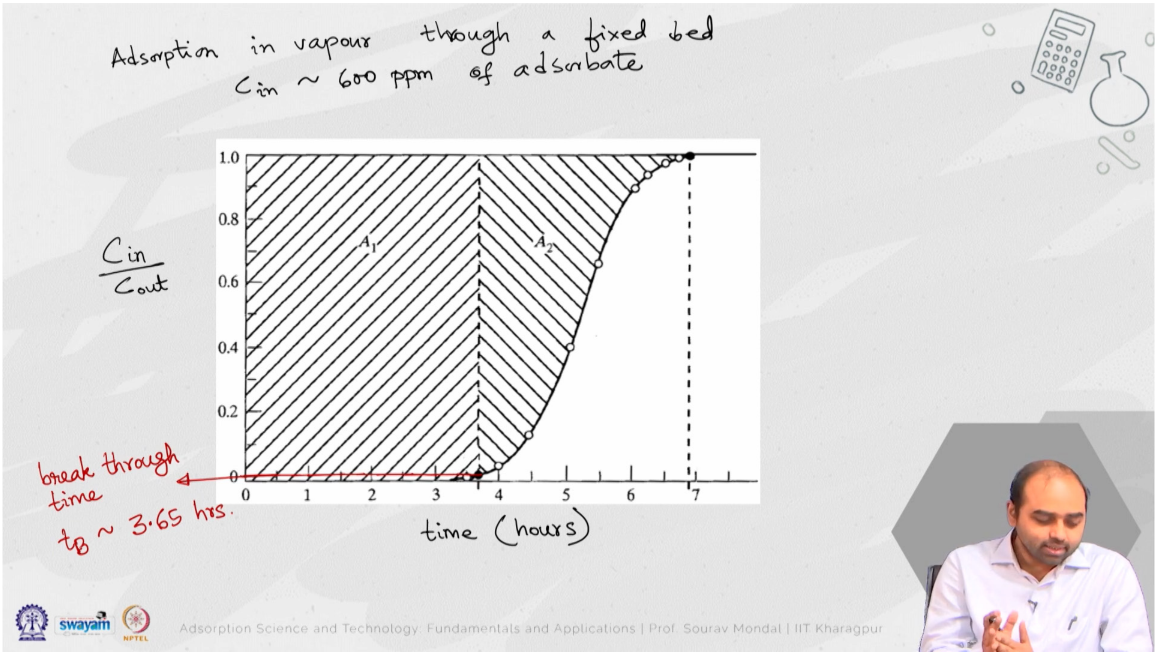
So, typically if this is an adsorption bed and this is the adsorption front. So, this is like the equilibrium portion. So, this is LES this is the unused portion. So, this is LUB and in between these two we have the portion of the mass transfer limitation, or the mass transfer zone or the active zone of adsorption where all this dispersion, you know, adsorption, kinetics, diffusion, transports, etc., takes place, mass transfer zone. So this is like a, this is like a system where, and in the case of an ideal scenario, this adsorption front is actually like a shock wave there is absolute plug flow and you know all the ideality conditions are maintained. Then it is reasonable to approximate there is mass transfer zone is 0. So, this is like the equilibrium portion and this is the unutilized portion. So, in both of these scenarios we consider this is like inlet and this is outlet.



So this is in, this is out. Let us try to use this idea that in the case of when the mass transfer width is non-zero there is a finite width we consider halfway in between so that half from that half we consider the remaining portion of the bed on the downstream side as the unutilized portion and on the upstream side of the inflow is considered as the equilibrium section. Now, let us try to look into a example problem and as this is best understood with the help of a example. So, this is a sample you know profile of the breakthrough plot. So, here this left hand side represents the C in by C out and the this x axis represents the time in hours.

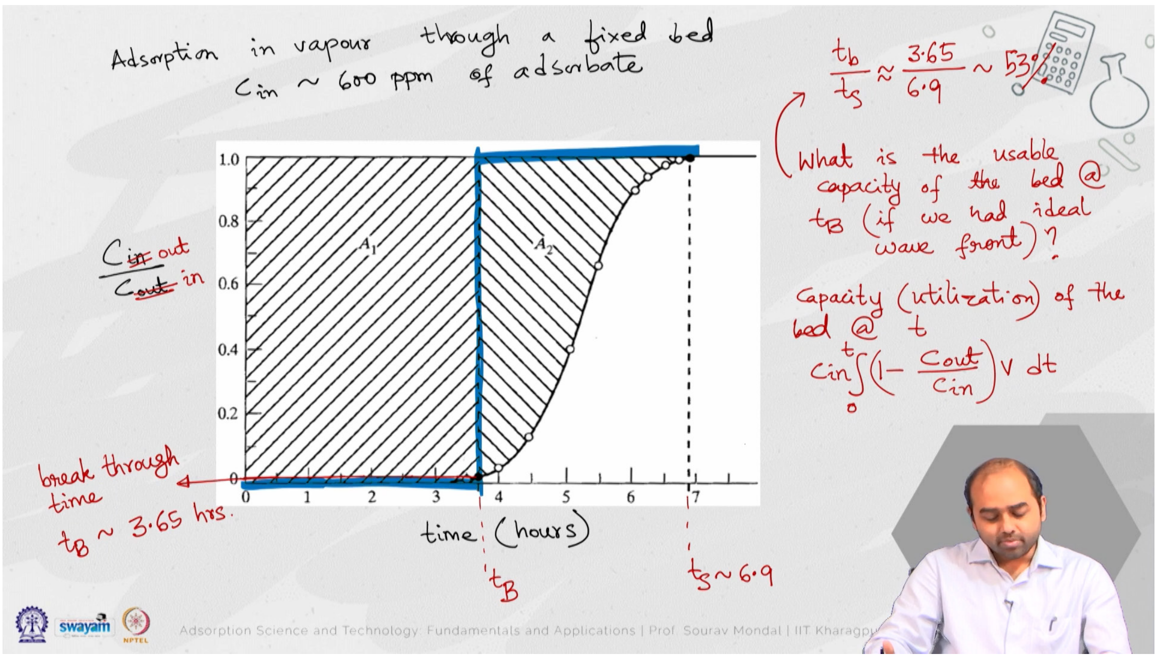
So this is a particular experiment of adsorption in vapour through a fixed bed. The inlet concentration of this vapour is around 600 ppm of adsorbate. Although that is not very important in this case, that information, but still for the knowledge I am writing it down. It is the relative ratio with respect to the output to the input is what is important. Now in the output section the first time the first thing that it should be understood is that what is the sort of the you know this breakthrough time that one can consider.

So now in this case the breakthrough time can be considered to be the point when the you know this value or this value of c by cF reaches a particular level that I was referring to in the last class. So for example in this case let us identify this point something like 1% of the inlet can be considered as the point when the bed no longer actually performs or delivers desirable output below the permissible value can be considered as the breakthrough time. So this breakthrough time In this case, let us assume or let us consider this point the black dot. So, it is roughly around 3.65 hours, in this problem here.



Of course, depending on what is the level of concentration if someone wants to set the level of concentration here in this case as something like 0.2 then the breakthrough time would be different. But whatever it is the breakthrough time is the point when we consider that this is just the onset of the sigmoidal curve starting from a non-zero value which could be like 1 percent or less than 1 percent depending on what is the level of output that is desired now the next question for this using this curve that you can work out is that what is the usable capacity of the bed at this breakthrough time if an ideal you know let me write it down what is the usable capacity of the bed at this breakthrough time if we had ideal wave front which means that there is no mass transfer resistance. So, in this case the ideal wave front you know capacity would be the ratio of the shaded areas of A1 particularly on the onset of the breakthrough time with respect to the total area. So, what I mean here is that one can consider the ideal breakthrough time or the ideal you know this wave front in that case would be essentially the the break through curve or the shock wave curve in that scenario would look something like this at the break through time it reaches the sigmoidal is reaches to the value at equal to 1.

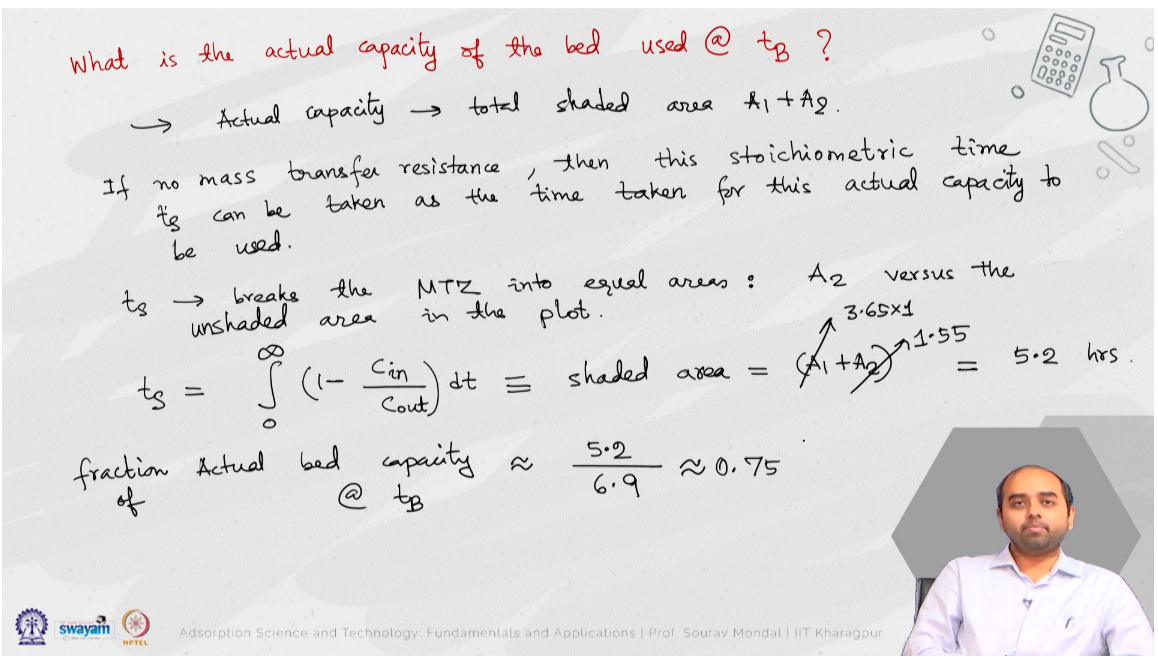
So, this would be like if we are considering that the bed attains break through right at the break through point then what is the usable capacity. So, in that case one can if you see here the capacity of the bed. The total capacity of the bed or the capacity of the bed or the utilization of the bed capacity or utilization of the bed at any time t, is represented by the area of the you know curve with respect to the time. So, the capacity of the bed can be represented as whatever the outlet concentration that is achieved right in this case that would be in this scenario the amount of the species that is adsorbed which is actually removed from the you know solution can be represented by whatever the outlet concentration what one gets minus the inlet concentration sorry this would be 1 minus c out by c in. Of course, multiplied with the volume with respect to time 0 to time.



So, this is like the amount of the material or the amount of the adsorbate species that is actually removed over this time. So, this is essentially what is contributed. So, from this ratio of of this 1 minus of c out by c in. Sorry this should be c out i wrote this wrong, with respect to c in. That is how we relate it from 0 to 1 so in this case this is like the amount of the you know solute that is actually removed from this system of course this has to be multiplied with c of t.

So, that is what I mean that the difference in the concentration and how much of the fraction that is removed is represents the capacity of the spade. Now, in some way this is linked to the to the portion of the shaded area. So, the shaded area reflects the capacity of the bed or at least the fractional capacity of the bed can be related with respect to the shaded area here like the area of A 1 by sorry with respect to this area present here. Now, in this case since we are considering it to be an ideal wave front. So, the area of the rectangle of this portion before it reaches breakthrough and after it reaches breakthrough in the non ideal scenario the differ the ratio of these two time would be sufficient enough.

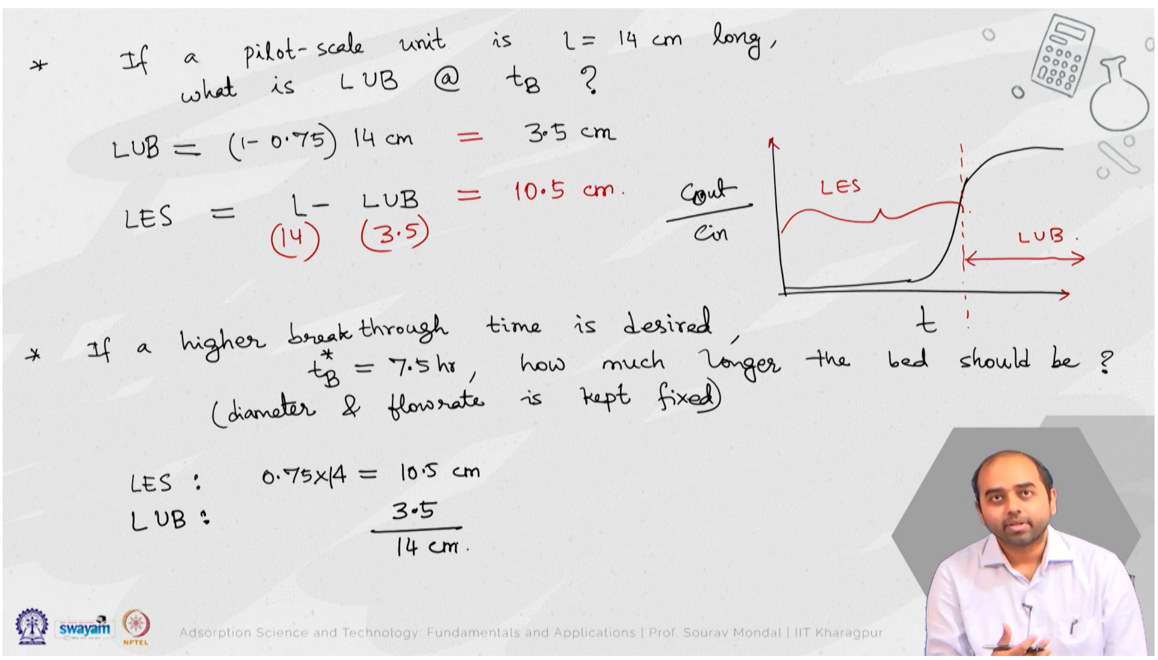
So in this case, the breakthrough time here, in the case of this ideal wave front or the breakthrough time that it is considered, let us consider this as like the tB and this is like the saturation time when the bed has reached almost this saturation limit. In this case, this is around 6.9. So, in this case of this you know ideal scenario this capacity instead of doing this integration under this curve since this would be like the square areas or the rectangular areas this capacity here usable capacity for the ideal wave front, can be related to the ratio of these two times as tB by tS and in that case this would be 3.65 by 6.9 hours which is roughly equal to 53 percent. So, considering an ideal wave front and since this you know in this case since the area of this rectangular square whatever the other unit is like unity. So, we can one can easily represent instead of considering the you know area you can easily consider the time or the ratio of these two time when it reaches saturation and when it reaches breakthrough in the instance of ideal wave front this can be related. So, the next point is what is the actual fraction. Now, if we do not have this ideality condition what is the actual fraction of the bed capacity which is used at this you know breakthrough.



So, the question is next what is the actual capacity of the bed used at this breakthrough condition. So, in this case first we have to find the actual capacity from the total shaded area represented by this A1 plus A2. Now of course, this A1 plus A2 represents the stoichiometric capacity. The stoichiometric term is actually evolved from the fact that this is like the mass balance or the total amount of the capacity of the bed that it can adsorb is should be equal to the you know this the amount of the species the mass of the species that is removed, from this system which is nothing, but equal to the inlet concentration times the volumetric flow rate that gives us with and multiplied with the time that gives us what is the amount that is removed and that is equal to the equilibrium capacity. That is why it is related to as the stoichiometric capacity.

So, if no mass transfer, mass transfer resistance was there, then this stoichiometric time tS can be taken as the time taken for this actual capacity to be used. So, essentially this stoichiometric time breaks the mass transfer zone into equal areas which is like A2 versus unshaded area in the plot. So, this breakthrough time can be related sorry this stoichiometric time can be related something like this. So this represents the shaded area of A1 plus A2. So, this if the you know mathematics of this integration is done of course, the first part is straight.

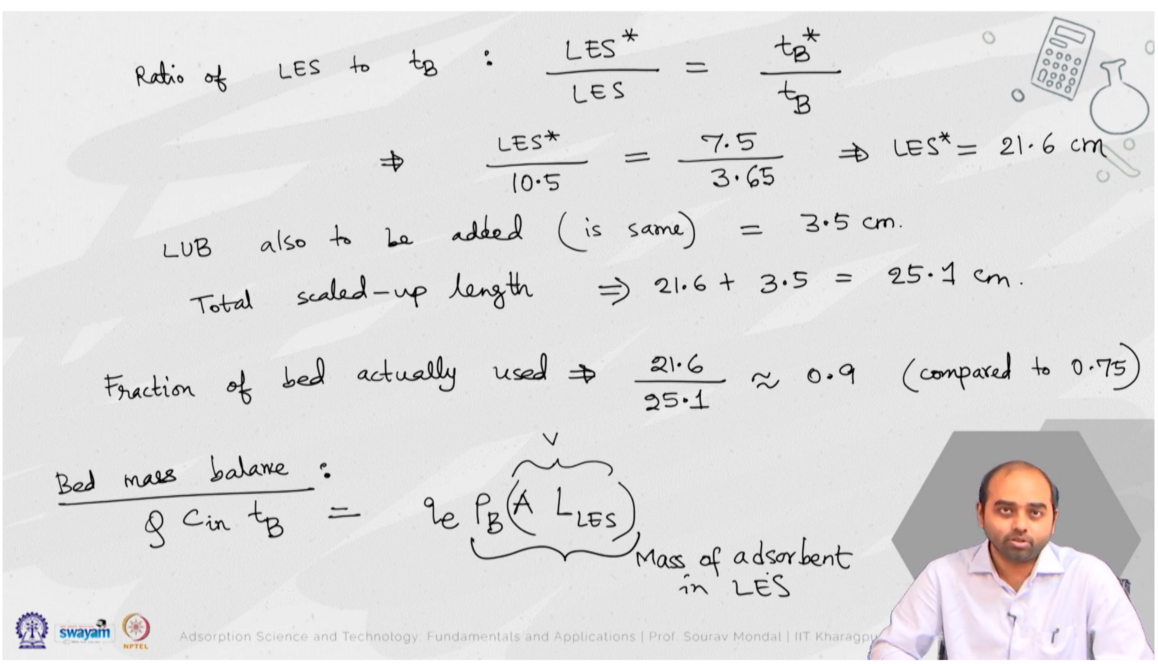
So, this area A 1 is 3.65 into 1 and if you work out this from this profile the area under the curve on the other side this would be 1.55. So, this total gives you a value of 5.2 hours. So, this is the you know the capacity of the bed or the equivalent time it needs to attain this actual capacity.



So, in fractional or the actual bed capacity that is used here is at breakthrough is 5.2 divided by the breakthrough time it needs it is 6.9 in this case this turns out to be 75 percent or 0.75. So, please note that here considering the actual bed capacity is at 75 percent compared to the ideal bed capacity if there is a constant wave you know constant wave front that is produced at the stoichiometric sorry at the break through time in that case one would get a much less bed capacity of 52 percent.

So, now in this case considering this idea of the LES and the LUS we move forward and let us say that if the lab scale or if a pilot scale unit you know is like 14 centimetre long what is the length unused portion of the bed at break through time. Now at the breakthrough time the fraction of the bed which is unused in this case comparing you know this portion of the sigmoidal curve and taking the half value at that zone. So, which represents that 1 minus of 75 percent of the bed which is used times 14 centimeter roughly gives us the value of 73.5 centimeter. So, this is the length of the unused portion of the bed.

Now the length of the you know portion of the bed or the equilibrium part or the equilibrium section is actually the total length minus the length of the LUB because we only segregate this entire bed. So, in this case only this entire bed is actually segregated into only two parts unused portion and used portion, where considering while calculating the unused portion, we are considering the time when it reaches the breakthrough at halfway the value. So, let me once again reemphasize this. So, this C in sorry C out by C in here, with respect to time this is the problem that we are working here and in this case this is split at half way here and that is the point we are considering that below this portion can be used for the you know this un-equilibrium section and this is the portion for the unused portion of the bed. Of course this diagram is not with respect to x but with respect to time but in this zone or in this period or whatever the capacity that is utilized in this portion of the bed represents the you know fraction of the bed which is already utilized and whatever is unutilized is from this breakthrough analysis of the curve that we have seen in the previous slide can be worked out.



So in this case, this is the equilibrium portion is 10.5 centimeters so this is 14 and this is 3.5. So if you subtract this then the unutilized equilibrium section is 10.5. Now the important question or the scale up question that is posed here that if you want if a higher, you know breakthrough time breakthrough time is desired let us say instead of three point six five which is the previous case now we want a breakthrough time of new breakthrough time of seven point five hours how much longer the bed should be of course, we say that diameter and flow rate is kept fixed. So, in this case it may be noted that currently we have the LES portion as 75 times of 14 centimeter as 10.5 and LUB is 3.5, and that makes the total of 14 centimeter. Now, we want this breakthrough time to be increased from 3.65 to 7.5, then how will we calculate that? So, in this case, in this case, we will use the theory that this ratio of LES to breakthrough time is essentially constant. So, which means the LES of the new state represented by * with respect to LES at the current value is equal to the you know this time tB at the this target value or the breakthrough time with respect to the current state would be constant. So, in this case the break the new LES that is desired is unknown, the existing LES is 10.5. In this case the new theta new breakthrough time that is asked is 7.5, and the existing breakthrough time was 3.65. So, with this logic the new LES is 21.6 centimeter right. Of course, to this the unused portion of the bed also needs to be added, and this unused portion of the bed for a particular you know this adsorbate adsorbent system provided flow rate and diameter are not same is constant or is same that is 3.5 centimeter. So, if you go back here. So this is like current situation and this is like the desired situation or the scaled up value. So, this is for the case of when the breakthrough time is 3.65 and this is when the breakthrough time is 7.5. In this case the LES is 21.6 centimetre, LUB stands at 3.5 centimetre. The total bed length becomes 25.1 centimetre. So, this is how you can scale up or you can work out what would be the scaled up length of the bed, you know length of the bed provided you have the information of the breakthrough for a smaller bed in in you know with respect to time.

So, this is 25.1cm. So, the LUB this is an important point I am saying that the LUB is of the same length that is to be added for any scaled up um you know system because the LUB is essentially um is the portion of the unutilized part of the bed which actually takes up the portion when the breakthrough curve starts to rise. So, in this case the fraction of bed actually used is also increased. In this case this is 21.6 divided by the total length of 25.1 and this is substantially higher compared to the previous value of 75 percent.

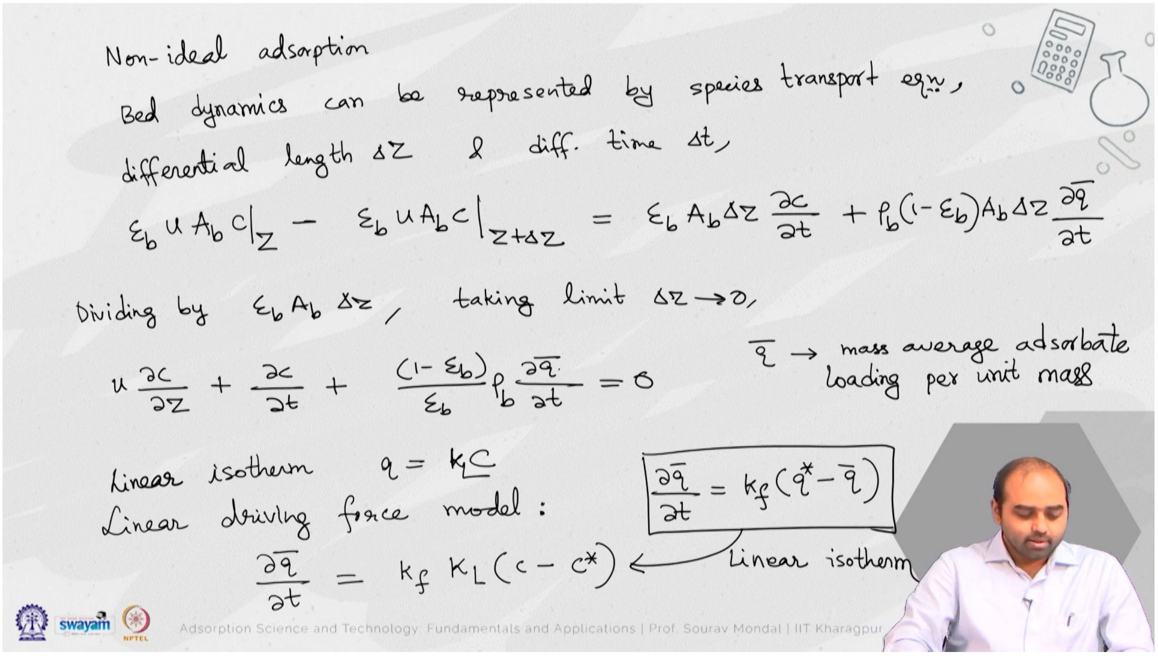
In this LES I would like to make a you know bed mass balance if Q is the flow rate of the stream. C is in the concentration of the adsorbate species in the fluid and this is the breakthrough time. So, this represents the amount of material that has gone into the bed from the solution phase. This is the equilibrium qe that is loaded. This is the density of the bed this is the cross section of the bed and this is the length of the sorry length of the equilibrium section of the bed where actually this you know this mass is getting captured.

So, this is the volume of the equilibrium portion of the bed multiplied with the bed density gives the mass of the. So, this gives us the mass of adsorbent in the equilibrium portion and multiplied with Q e the equilibrium value tells us that how much of the amount of the solute is in the solid phase. So, whatever is this solute that is incoming into the system is actually taken up by the adsorbent. So, that is the outlet concentration in this case close to close to 0 or almost 0 value. Because there is always some adsorbent which is taking up the you know this species adsorbate species from the system.

Now, this is unlike the scenario in a batch where the equilibrium concentration is in the solution phase is nonzero, but here the since the adsorbate sorry the adsorbent phase is in excess with respect to as long as the bed is unsaturated is in excess with respect to the amount that is coming from the incoming solute or the incoming stream the all of these you know species is getting adsorbed by this bed. This is the whole idea of the fixed bed adsorption and from here we can do this mass balance. So next I am going to talk about what happens when we have the non-ideal scenario. So this non-ideal adsorption happens. In this case, the breakthrough curve stiffness is slightly reduced and it takes the sigmoidal shape.

So in this case, the bed dynamics can be represented by the mass transfer, this species transport equation. So considering a differential volume differential length of delta z and differential time of delta t, you can just quickly make a mass balance that this is the bed porosity. U is the, I mean this is like the simple mass balance of in, mine and out equal to the accumulation plus the disappearance due to adsorption. So this is the flow rate or the linear velocity U Ab sorry U Ab is the area and C is the concentration of Z. So this is equal to you know at a particular location Z and then you have at Z plus delta Z which is equal to epsilon B AB delta Z del C by del t.

This is the accumulation term. And this is the disappearance term due to adsorption. It is very similar to chemical reaction. dQ by dt, right. So, considering dividing by epsilon B Ab delta Z and taking limit delta Z tending to 0, we get the differential equation as the classical species transport equation.

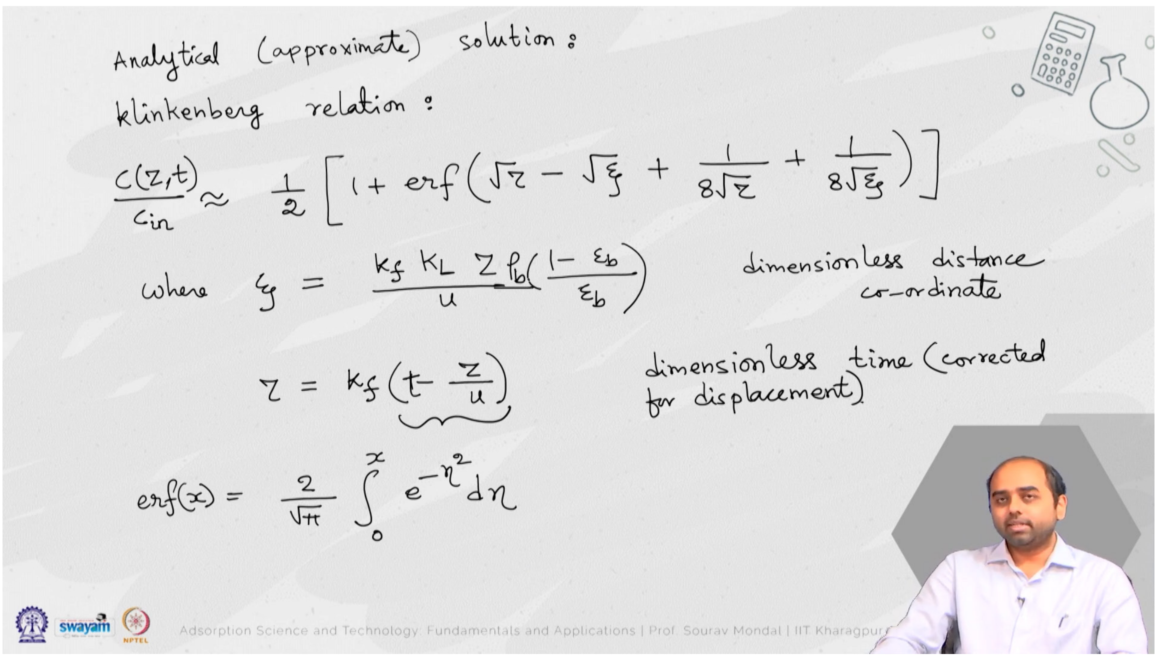


Please note that this Q is like the volume average. But if you are considering it to be the, you know, mass average, then this has to be multiplied with the density of the bed. So let us multiply that with the density of the bed. So in this case now, then Q represents the mass average adsorbate loading per unit mass. So of course you can use the linear driving force equation so and considering you know isothermal linear isotherm that q is equal to k into c. I will write this as k L and using a linear driving force this dq/dt.

So, the internal mass transport resistance or the diffusion or the intra particle these things if we ignore or you know if that can be considered to be negligible then you can use the you know this linear driving force relation and d q by d t would be like the mass transfer coefficient k f the equilibrium coefficient k L if for a linear isotherm of course, for a non-linear model this would be different. c minus c*, where of course c* is the solute loading at the equilibrium concentration and q is the average. If you want to write in, if you do not want to consider for a linear isotherm, so in general the dq dt relation stands as kf into q minus q star minus q. This is something which we have already discussed in the last week lectures.

So, this is the generic form. Now, for this is applicable when we are considering linear isotherm models. Now for the case of you know this and solution of this equation the solution of this equation and this analytical solution. I would say analytical approximate solution is given by the Klinkenberg relation where this c out by c in is given by this formula. So, for details you can look into the famous Klinkenberg paper.

This parameter represents. So, this is some sort of a dimensionless distance coordinate. So, please note that c would be a function of should not say c out, but rather c is a function of z and t. And the dimensionless time is represented by this. This is like dimensionless time coordinate, but this is corrected for displacement. So, t minus z of u represents the characteristic dimension of the time.



And this erf represents the error function. So, erf of x is generally defined as is a classical mathematical function is the error function. So these are this epsilon and z are like the coordinate transformation both for time and distance. So I must add this density also here for the bed which I missed. So please note that in the dimensionless distance coordinate there would be the value of this dimensionless distance dimension less sorry the density that would be also used and appropriately the value of the this coefficients kL is the unit in the isotherm equation. So, this Klinkenberg equations actually helps in relating or trying to get an idea of the mass transfer zone or the you know, the sigmoidal shape of the wave front in the non-ideal case.

But this is like solving for analytically or numerically solving the species transport equation. A complete equation, you know, the solution of that equation in terms of the

Bessel function for heating, etc., is also provided by Anzelius. But these are highly complicated techniques and that is something we would not be focusing too much on this course. But I wanted to give you an idea about the Klinkenberg relation that can be useful.

This is an approximate relation of course that is useful to work out the nature of the solution profile in this case for non-ideal situation. So, with this I would like to close the lecture for today. In the next class we will see other semi-empirical and you know detailed first principle based models for the modeling the you know performance or the solution profiles species concentration in the fixed bed adsorption column. Thank you. I hope all of you found this lecture to be useful in the design of design and scale up of fixed bed adsorption particularly in the case of you know some approximate situations or some assumptions of limiting mass transfer resistances or negligible mass transfer resistances. Thank you. Hope you all find it useful.