Course: Adsorption Science and Technology: Fundamentals and Applications

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Week 07

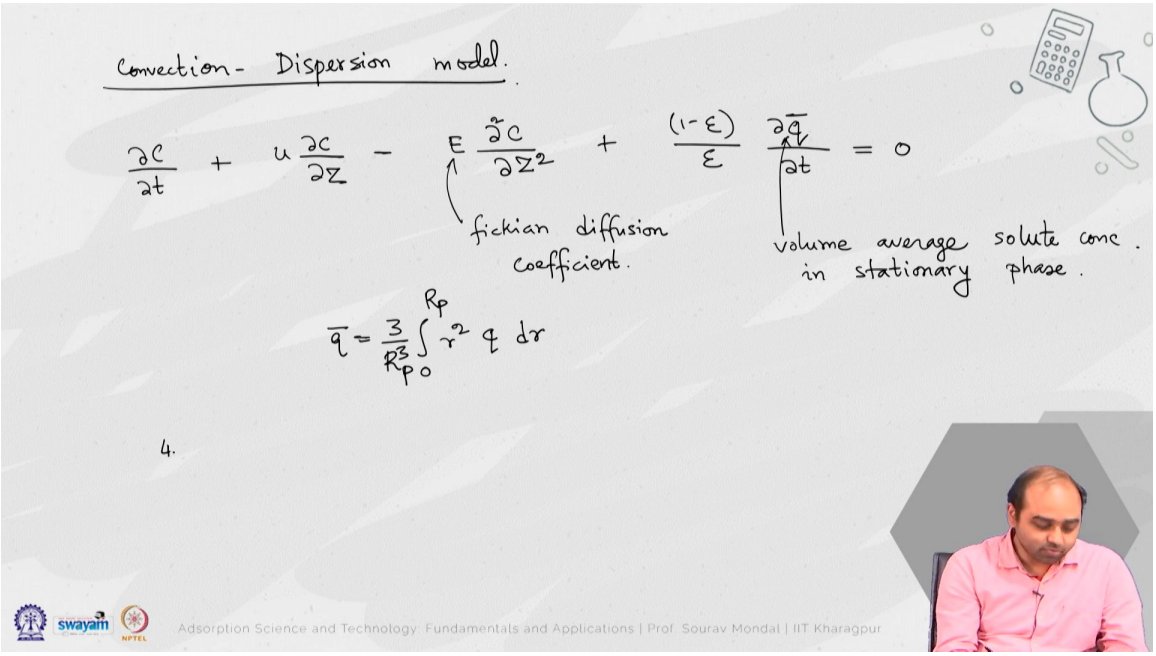
Lecture 33 | Column Chromatography

Welcome to this lecture today on column chromatography. Here we are going to talk about the properties of the peak of the chromatogram and how the particularly this Gaussian distribution profile can be explored to study different aspects of the you know this number of this units of the theoretical equivalent units of this column and height of each theoretical plate. Now, typically this chromatogram or whatever this you know packed bed adsorption column that we are talking about in this case for chromatography. The convection dispersion model can be written down as something like this. So here specifically we write the diffusion component. So this is like the Fickian diffusion coefficient equal to or sorry plus this one minus epsilon by epsilon del u bar by dt.

Of course, we know that if the dispersion or this sorry if the diffusion does not exist then this equation can be used to find out the solute you know the front capacity. This q bar represents the volume averaged solute concentration in the stationary phase. So the average can be written down something like this. Of course, if you consider that the particle mass transfer effects are not so important then the average can be considered as to be same as the surface concentration.

But if that is not the scenario then one has to couple the you know surface concentration with this particle you know and the bulk between the particle and the bulk. So in that case you know this approximation does work good considering the linear driving force model in utilized as something like this. Like KC or K overall or something like this. Alpha minus this C. So, this is what we can relate based on the driving force model on the particle surface and this can be used to find out or to relate this dq / dt term and one can approach this solution of this convection dispersion model.

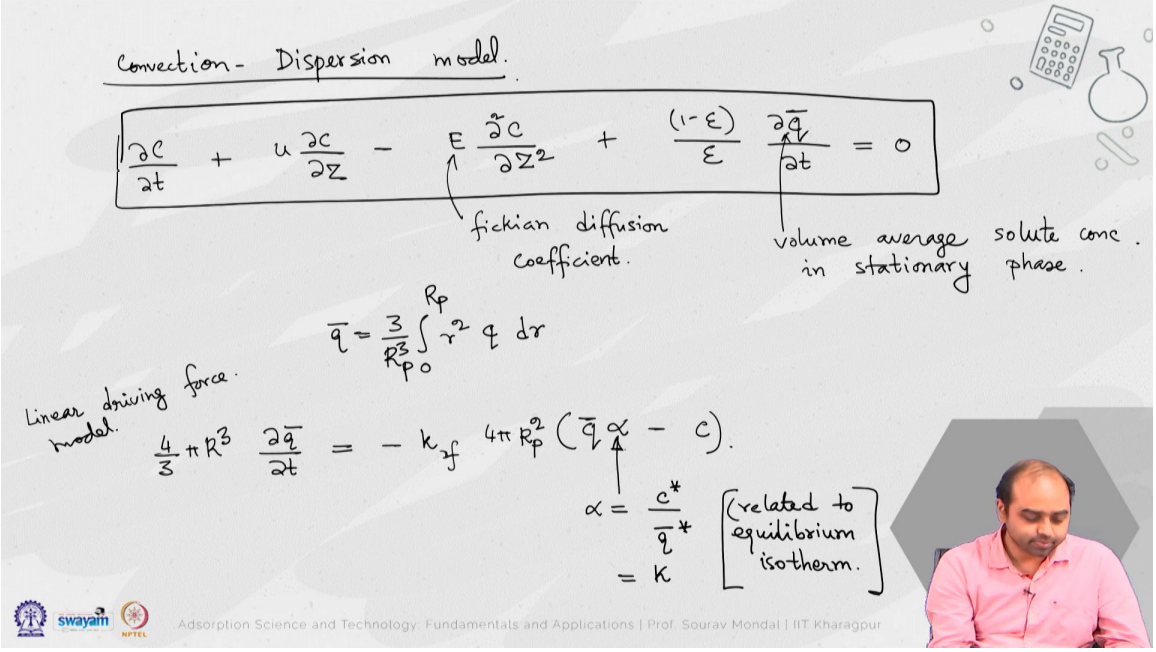
Now, here particularly the important thing that I have mentioned is this alpha. So, alpha represents the you know this partitioning coefficient of the solute between the bulk and the stationary phase or between the mobile phase and the this stationary phase. So, alpha can be related as the ratio of C with respect to alpha. And of course, this is can be related with the equilibrium isotherm. So, this can be related to equilibrium.



So, I can consider both of these two are in equilibrium conditions and this can be related to the equilibrium isotherm relation depending on whether you choose a linear or a Langmuir type behavior. So, in the case of the linear behavior this would be simply equal to like k or in the case of Langmuir type it would be like 1 by some constant plus k multiplied with k. So, this model can be this convection dispersion model the solution to this model for a pulse input. So, typically the pulse input you know can be considered as something like this at time t is equal to 0. So where this m0 is the solute mass, A is the bed cross section and of course epsilon is this porosity of the bed and z represents the direct delta function.

So that is something is used for any pulse input. So the solution of that convection dispersion you know equation that an asymptotic solution of that convection dispersion model is obtained by Rice et al. And this solution suggest that you know the fluid

concentration or the concentration profile is distributed normally around a mean solute position, let us call that as z 0 something like, sorry solute front velocity multiplied with t is around that mean position along the z axis that this normal distribution profile is the solution of this concentration. So, let me write this concentration profile. So, this is how the concentration profile or this asymptotic solution if you are interested in how this asymptotic solution is reached which is something beyond the scope of this class.

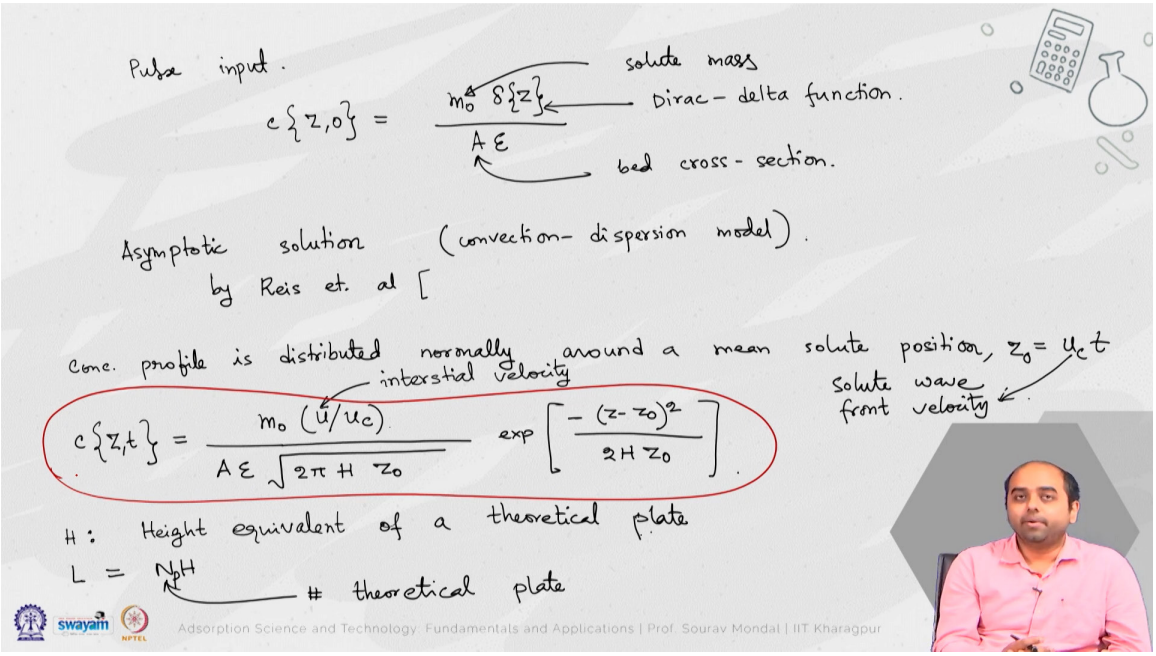


I suggest all of you to look into this reference article research article from Rice et al. And you can find out that how the solution is arrived of course this is here Z 0 represents the you know this mean position of this I mean related to this mean position of this solute. And in this case the u c represents the this you know solute wave front velocity and u represents the interstitial velocity of this mobile phase. Now, here this H represents the height equivalent of a theoretical plate, and you know this total length of the column is represented as N into H or Np into H where Np represents the number of theoretical plates. We will soon realize what does these you know represents or are helpful.

Now, this solution or this asymptotic solution that we see here is a Gaussian curve. And the chromatogram output that we get from high performance chromatographic analysis also follows you know normal distribution or a Gaussian curve. So, the properties of these two curve can be related to find out what would be the value of H the height equivalent, of a theoretical plate which is of course, a fictitious or a hypothetical you know quantity in this case, but that can be related to find out the number of theoretical plates and then we can see that how that can be related to find out the resolving power or

the resistance time etcetera. Now, if you try to look into this properties of the you know this bell curve. So this is like the normalized peak height.

So the peak value is like 1 in this case. And this is the time. So if I try to draw a curve something like this. So please note that any bell curve has two points of inflection. So this if you try to draw a transient at that two inflection points so this can be extended something like this at the top and here it can be extended something like little bit wider sorry something like this and at the other two points of inflection if you try to extend this will be something like this of course this has to be symmetric so please pardon my drawing this line is also not straight I should draw this properly this is important.



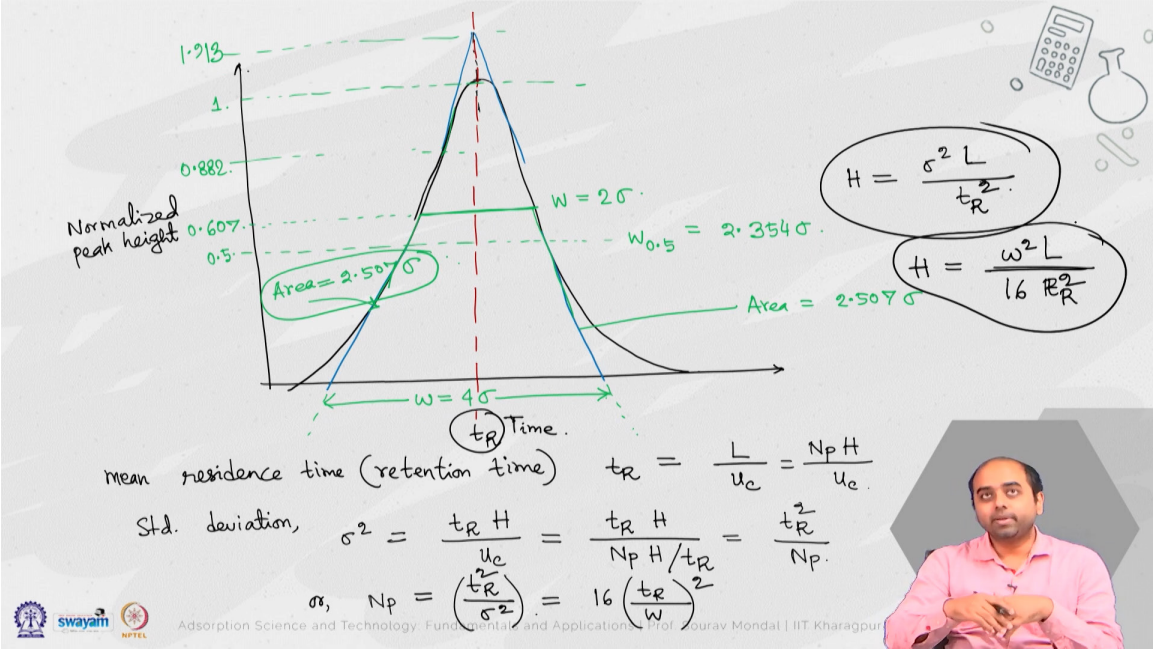
So, something like this all of you please realize that this is a this should be a symmetric drawing, but it is not symmetric at this in my sketch, but this is actually a symmetric you know curve. Now in this case. the height equivalent here is in this case it is 1 and where the 2 points of inflection does attach that is larger than this one. Now here in this case the width of this you know this extended inflection point is actually 4 times the standard deviation at the half height. at equivalent to half height, these are some properties which I am trying to write down here.

So, at this half height or 0.5 value, the width at 0.5 is 2.354 sigma and at the inflection point which is where the width is actually twice the value of the sigma from the base to

twice of this sigma. The value or the peak height in that case is 0.607. The inflection points at this stage at the top this is where the inflection point starts from the towards the bottom side and the top inflection point starts from a location 0.882 and they both of them converge at a position 1.213. Now, this area of this you know region with the inflection points this area is equal to 2.507 Cmax sigma. Of course Cmax in this case is I mean this is the relative concept. So, in this case for the this you know normalized sorry for this normalized you know this area. So, I will write it again where it is 2.507 times sigma is the area of this normalized curve which is extended with the inflection points. So, please note that this w represents the width at the base intercept and not essentially the extended portions of this Gaussian distribution.

Now, considering this overall shape of this Gaussian curve, the mean residence time which is this value here, this can also represents the you know this retention time or retention time is actually length divided by the solute wave front velocity. Now, of course, length can be represented by the number of theoretical plates and the height equivalent of each theoretical plates. The standard deviation sigma square is represented by this formula or this expression in this case and this directly comes from the analysis of the bell curve. Now of course, you can equate this u c in terms of N into H. So, u c can be so utilizing this idea that u c is tR into H and this divided by Np into H by tR.

So, this suggests that this is tR square by Np right or Np the number of theoretical plates can be represented as tR by sigma square sorry tR square by sigma square where sigma is the standard deviation and from the analysis of the this you know this bell curve we can say that this is nothing but equal to 16 times tR by the width of this region times the square of this retention time. So, from this you can also relate from this value of this Np one can back calculate out what would be the height of each theoretical plate. So, in that case the height equivalent H of each theoretical plate you can just substitute this expression of Np. So, that would be given from this value of this sigma square. So, this is sigma square L by tR square.

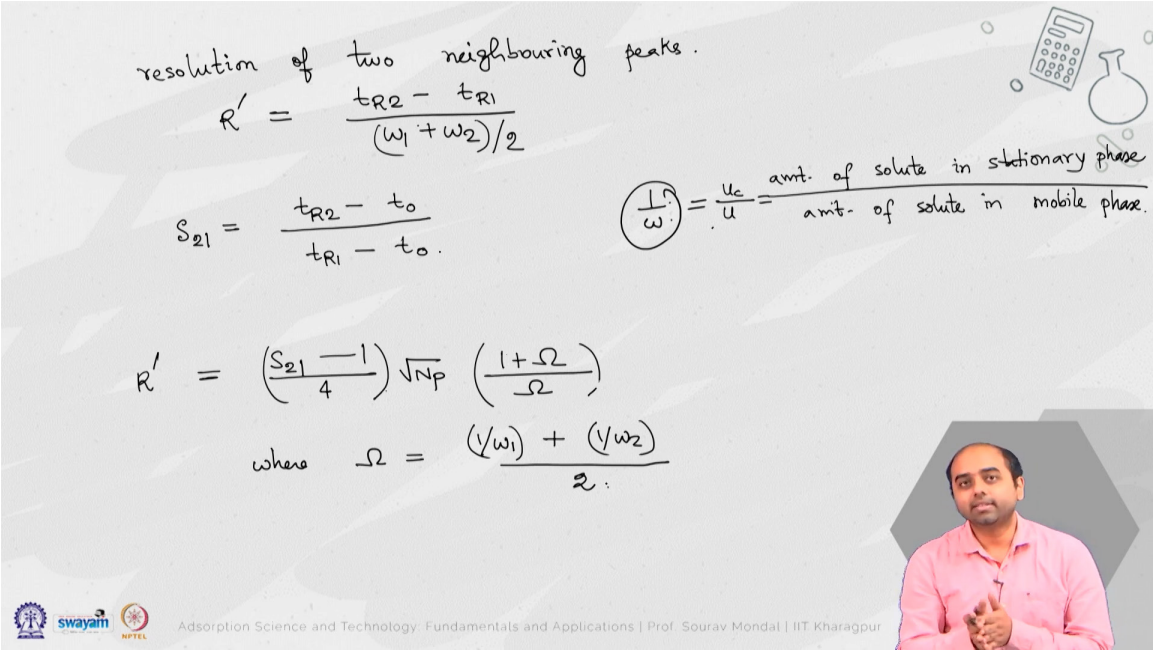


So, the height equivalent can be found out. So, of course, L can be, I can substitute. So, this is the formula from the this relation of this Np. So, So, once you I think all of you realize that once you find out your number of theoretical plates you can use this expression to substitute into your relation of this sigma square here to find out what would be the value of H as a function of u c or the height equivalent of each theoretical plate can also be found out. from the you know this overall length of this column which is something that I have already written h is equal to sigma square.

So, for a particular length of this column, this height can be found out from the knowledge of the standard deviation. Of course, sigma square can be reduced with respect to the width. So, it can be like width square length by 16 times tR square. So, now this height equivalent is a very important characteristic as well as the number of equivalent is also very a number of equivalent plates that is needed for this calculation is also very important and that defines the resolution or the resolving power of this you know chromatogram. So, the resolution of two neighboring peaks, two neighboring peaks are prime is represented as the difference of the retention time divided by the average width of this both of these peak areas or the peak width at the base.

Now, typically this selectivity S21 is defined as the, something like this is something which we already have discussed with respect to a reference value. This adsorption you

know this ratio of the amount that is present in the adsorbate to the adsorbent phase sorry to the fluid phase. So, this the ratio of this amount of solute in stationary phase to amount of the solute in mobile phase. This can be represented by u c by u essentially. So, let us call this as a constant omega or w or 1 by omega or 1 by alpha whatever.



So, typically 1 by omega is like u by uc but one can also write this as alpha or omega whatever this ratio. So, in these terms the resolving power can also be written down as number of theoretical plates plus this quantity, where this is the average of, let us see if I am trying to discuss this for between two species. So, this is the average of these two amounts or the fraction of the solutes present in the you know stationary phase with respect to the fraction of the solute that is present in the mobile phase it can be related to this quantities. So, this is like the you know resolving power that is related to the number equivalent of the this number equivalent of the theoretical plates for this chromatogram or this chromatographic system or this separation. So, I hope all of you understood the background of how the resolution or the resolving power can be worked out in a chromatographic system based on the calculation of the number of theoretical plates and the height equivalent of each theoretical plates.

And this also helps in designing the column length or fixing the velocity within this column because this parameter omega represents nothing but the you know the fraction of the fluid velocity with respect to the solute wave front velocity. So, that is how the resolving power of the resolution higher is the resolution better is the you know separation between these two solutes. So, in the next two classes of this week we will be

talking about some problems related to this chromatography and chromatographic operations. Thank you I hope all of you found this useful lecture.