Mass Transfer II

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Lecture No. # 31

In the previous lecture, we took up this new unit operation adsorption. And, towards the end of the lecture, we said that whether it is a batch experiment or the flow experiment on the loading or the solid phase concentration must be the same as in the two cases. In other words, if we do the batch experiment and if we have certain amount of solids in contact with liquid with certain concentrations, then, when the equilibrium is reached and we calculate how much is the equilibrium loading on the solid phase milligram per gram and then we do this flow experiment, where we have packed bed of these absorbents, we challenge, we bring in contact with the concentration level same as what we obtain in the final concentration in case of batch experiment. And then, we obtain the profile at the exit. We find the area under the curve uptake and then we find how much the loading milligram per gram that concentration must be same as two cases: batch or the flow experiment. So, that is a meaning of this equilibrium. It is only the time taken in two cases will be different. All it means rate will be different; time will be different. But, the final concentrations of the solid phase in equilibrium with the influent concentration or the final concentration of the aqua solutions or the solvent in the batch experiment; that too must be the same here as long as the temperature is fixed here.

We continue our discussion on that flow experiment and the batch experiments. And, we will also see how do we apply in the real industrial cases; what type of systems we need to have, because we must not forget that adsorption is limited by the capacity. Any adsorbents whether zeolites, charcoals, carbon nanofibers, carbon nanotubes have limited capacity; how much milligram per gram. At the end, when we are doing this experiment, the bed is saturated. One has to stop it and one has to regenerate it to make it fresh. So, industrially, how do we do it? We will also spend some time on that before we get into the mechanism; or, what is the mechanism of these adsorptions? what the different steps involve in adsorptions? Before we take up the example of this batch experiment, we do the flow experiment.

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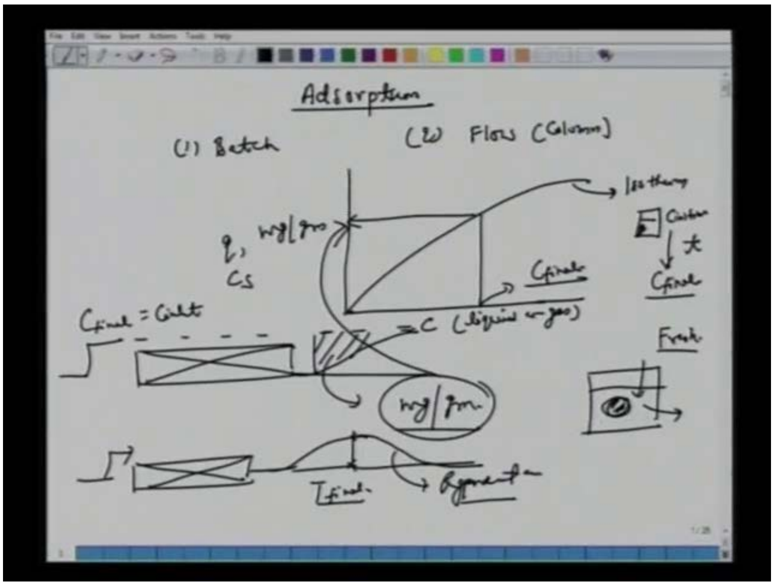

Let us continue our discussion on this adsorption. We say either we do the batch experiment or we do this flow experiment or what do we call column experiment; we should get the same result here. Given this concentrations in the solutions – liquid or gas phase, what is the loading here? Milligram per gram; we denoted by q or C s. So, this has some kind of equilibrium curve, which we call it isotherm. So, in case of batch experiment, this would be say C final. So, we started with some C initial and we have brought in contact with some solids; concentration will decrease after sometime t; and, this will become C final. Or, if we do this flow experiment, when we have this packed bed, we bring in contact with some C – let us say same C as C final here. So, this is same as C inlet. And, we monitor to the profile. Here we have this curve response. When the bed is saturated, this level is same as this level (Refer Slide Time: 03:56). Right now, the bed is saturated. So, the two levels increase. Then, we find this area under the curve; area gave up this curve; and, we calculate milligram per gram. This data must be the same as what we obtain here. So, that is the meaning of this equilibrium.

Now, the question is that suppose we have this flow experiment (Refer Slide Time: 04:18) and we are bringing in contact with some gas or liquid; now, the bed has saturated; let us say after certain time t final. Then, one has to stop this and one has to regenerate to make it fresh. So, this is the regeneration part of it. In the batch experiment also, when we have reached the final concentration and the solid is now saturated, one has to take out the solids or remove this fluid and bring fresh fluid to regenerate this. So, we have adsorptions and then we have desorptions; of course, it is reversible reactions. So, whenever you had adsorption, there is a reverse rate also. And, when we are regenerating it, there is an adsorption rate as well. But, in one case, adsorption rate is larger; in that case, desorption rate is larger. So, start with the fresh solvent; it will become fresh solid; it will become saturated. Regenerate to make it fresh again. So, industrially, how will you do it? Because we will have to stop adsorption here; so, generally, typically, industrially, we have two-bed system.

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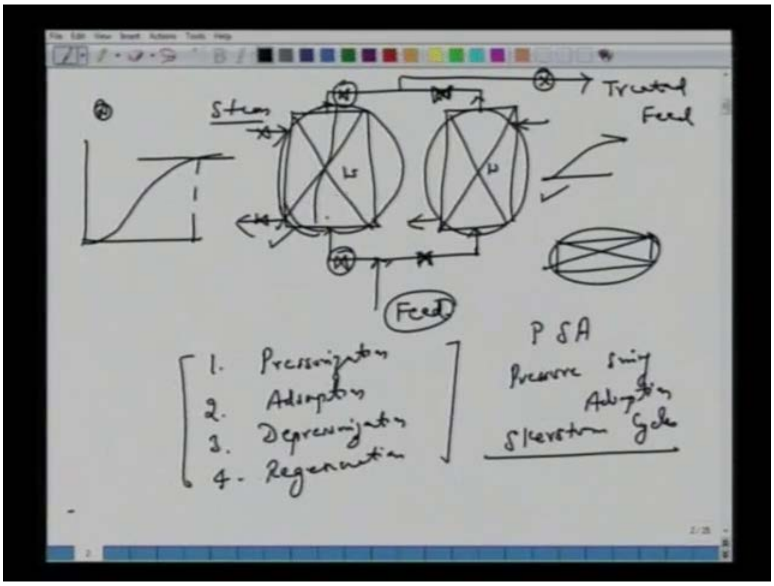

1. Pressurization
2. Adsorption
3. Depressurization
4. Regeneration

Just an introductory part here that how will you accomplish in industries. Suppose you have the feed. You have two beds here; you have put two valves. This is packed with adsorbents; this is also packed with adsorbents w amount, w amount. We take the output from here; we can put a valve and put a valve. And, this is the treated feed; and, this is the fresh feed. So, one time, this valve is closed; this valve is closed; and, entire feed goes through this. So, you monitor the exit concentrations here – this concentration here. When the bed becomes saturated, one has to stop this. Then, close this valve; close this valve; and, let the feed go through this to make the process continuous. But, when this bed is saturated, first bed is saturated, then one has to regenerate. So, maybe you will bring in some steam or some fresh fluid to regenerate this. So, that time you have regenerations. And, after some time when this bed is saturated, when this bed has reached a saturation level, then you will close this; you will close this. Feed will come to this.

Now, we will start regenerating this bed (Refer Slide Time: 07:04). So, this is the way the process is made continuous. And, this type of very typical cycles in which case you have some say pressurizations; or, it means before you start a bed, you bring it to a desired level pressure; then, you have adsorption. Then, after this bed is saturated, (( )) going to depressurize this and then one has to do regenerations. So, typically, these are the four steps we have. In a continuous cycle, we call it PSA (pressure swing adsorption). So, we swing the pressure between the two beds. Essentially, one bed is in operation; other bed is getting regenerated. When this bed is in operation, this bed is getting regenerated. And, the cycle is traditionally known as skarstrom cycle. So, for these codes, this is good enough – this type of introduction for your knowledge. We should know that how the process is continuously operated, because we said that adsorption is limited by the capacity. So, at one time this bed will get saturated; (Refer Slide Time: 08:25) one has to stop it and one has to regenerate it. So, in the way you will do it, you will have the two beds: one bed is in operation; other bed is getting regenerated.

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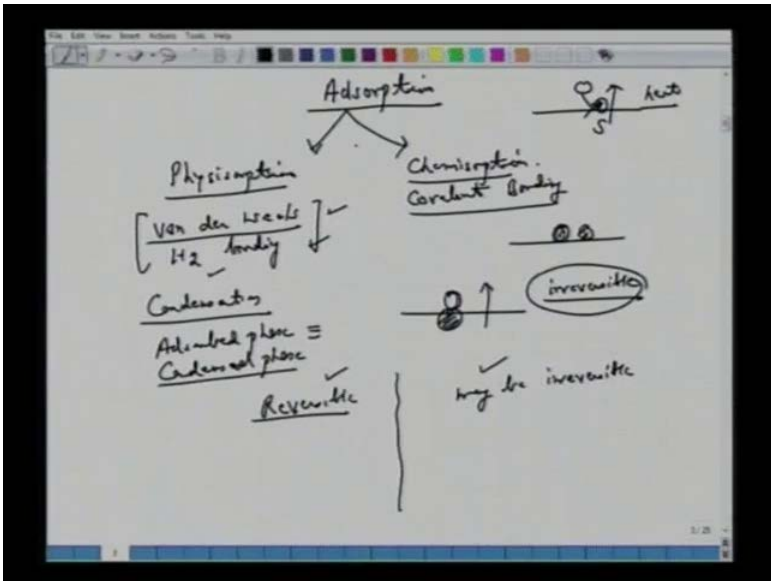

Now, we continue with this and we get into the mechanism of this adsorption; or, we would like to know what are the different steps involved in this adsorption. So, there are two different types of adsorption: one is called physisorption and one is called chemisorption. Again, in our discussion, we will be very limited to the extent that we are able to address mass transfer related problems. But, for your own benefit, we should know, we should understand at least the basic of this adsorption. So, when the molecules get adsorbed on the surface, they have either physisorptions or chemisorptions; all it means when you have physisorptions, there are bonds like van der waals. You must have heard in thermodynamics; you must have come across van der waal bonds; or, you have hydrogen bonding. So, these are weak bonds; or, it means when the molecules are adsorbed here, then one can regenerate. Say if we heat it, reverse the conditions, these molecules can be picked out. So, because they were bonded with the surface forces by van der pole, van der waal bonding or hydrogen bondings. So, that is adsorption. It is very similar to condensations. Essentially, this adsorb phase in this case – they are also after known as condensed phase. All it means the physical properties of the molecules, which are adsorbed here, say, sulfur dioxide or water, its physical properties, specific heat, latent heat, etcetera is very close to the condensed phase or the liquid phase.

Chemisorptions – here we have stronger than what bonding we had. Here we can have covalent bonding. So, in the molecules, which are getting adsorbed, now, it comes in contact with the surface molecules and they have this bonding say covalent bonding. And, if you want to regenerate, then it is possible that chemisorptions may be irreversible. So, very often, if you can go through certain kinetics books, let us say, by Smith, we will see a difference between adsorptions and chemisorptions. Adsorptions are physically reversible, because here the bondings between the two molecules are weak van der waal force or hydrogen bonding. In case of chemisorptions, mostly they are irreversible; or, if you want to regenerate the surface, then one has to have very aggressive regenerating conditions. And, when you have adsorptions… So, that is one aspect of our introduction. On this adsorption, the mechanism physisorptions or chemisorptions.

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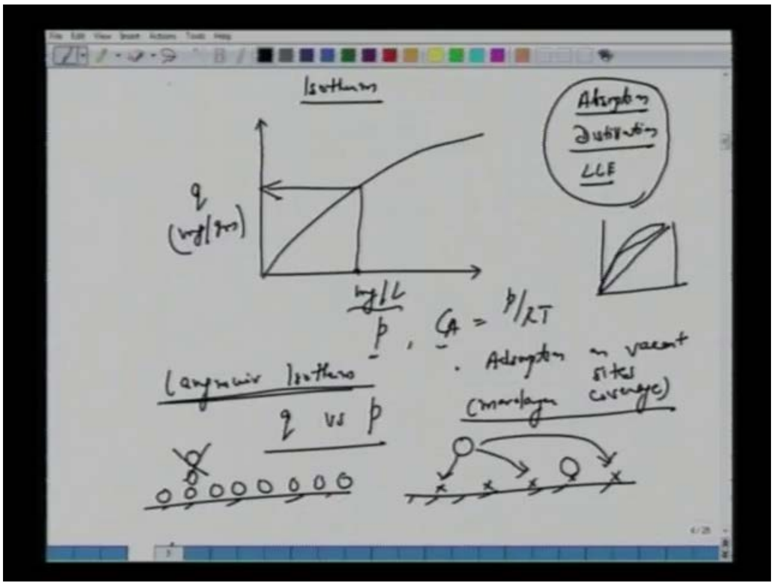

Another thing you would be interested and useful in our calculations is isotherm. So, we talked about this; that very similar to the different equilibrium curves like in case of adsorption, we have the solubility data. In case of distillations, we had this y versus x data; in case of extractions, we talked about LLE (equilibrium phase diagram). So, these are all equilibrium curves. So, similarly in case of adsorptions, we have very typically isotherms. Here where we plot q milligrams per gram of solid versus milligrams per liter of the liquid phase; or, if you have the gas phase, you would like to put the partial pressure of the liquid phase of the gas phase; or, you can also put certain concentrations here C A equal to p over RT. So, given this concentration in this liquid or gas phase, how much is the loading. And, there are different types of isotherms. Just like in case of adsorptions or distillations, we had different types of y versus x, y versus x like this. Similarly, here we have different types of isotherms.

Now, one most common isotherm, which we should know for this course at least is Langmuir isotherm. You may have some experience or you must have come across in your kinetic class that the most common isotherms or the most common relationship given between q and the partial pressure in this gas phase. So, the main postulates of Langmuir isotherms, which we like to note down is – adsorption takes place on vacant sites; or, essentially, what we are trying to say is that we have monolayer coverage. So, it means, if it is the solid surface and there are certain sites here – active sites we talked about earlier in the previous lectures, the molecules, which are gas phase or liquid phase, will get adsorbed only on these sites (Refer Slide Time: 13:54). So, if some sites are already occupied with one molecule, then this molecule cannot come on this. So, this has to go to different sites. So, we have monolayer coverage. At the end, when entire surface is saturated, you will see or pictorially, one can describe this type of layer here (Refer Slide Time: 14:11). You do not have multi layers; that is not permissible in the case of Langmuir isotherms or Langmuir adsorptions. That is one.

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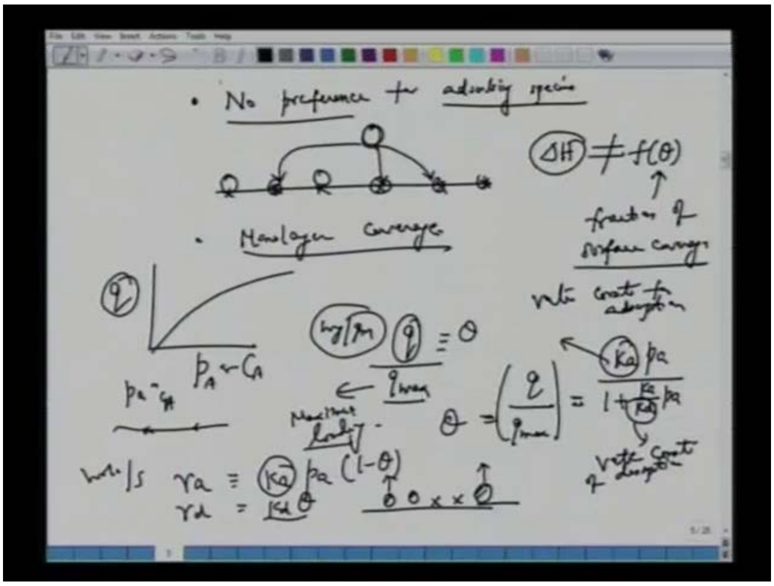

Second most common postulate of Langmuir isotherm is there is no preference for adsorbing species. Here the words what we are trying to say here that if these sites are vacant and let say some sites are occupied like this, like this, one species, which is in the gas phase or the liquid phase, probability of this molecule going to this site is as good as going to this site or this site. So, there is no preference for any adsorbing species for any type of sites here. And, the consequence of this is that heat of adsorptions – when the molecule adsorb, there is heat of adsorptions – could be positive or negative; could be exothermic or endothermic. All it means it does not depend upon the extent of surface coverage, f theta, is the fraction of surface coverage. So, the molecule, which comes here – for them it is a preference; there is no preference here. Heat of adsorption is constant. So, these are the main two postulates: one is the no preference for adsorbing species and another we say, it is monolayer coverage. And based on this, one can write down their rate expressions.

Ultimately, we are interested in finding a relation between q and partial pressure or C that are isotherms here. So, based on these two assumptions, one can show that we have a relation like this q or theta. So, this fraction surface coverage or q what we have – milligram per gram; theta would be q over q max – actual loading over the maximum loading. Sincerely, this q has been non-dimensionalized by q max. So, theta equal to q over q max; it has been shown. One can show; it is not difficult to show here; maybe you can go through certain books on kinetics to obtain a relation as k a p a over 1 plus k a over k d into p a. Here k is rate of adsorptions; k d is rate constant of desorption; and, we have k a as rate constant for adsorptions. So, one can make out that this relation has been obtained assuming that r a is the rate of adsorptions. In 1 second, how many moles get adsorbed depends upon first order kinetics like k a; how much is the partial pressure in the gas phase or concentration in the liquid phase and what are the sites, which are vacant – 1 minus theta. We said that it is monolayer coverage. Say if no sites are vacant, theta equal to 1; there is no rate of adsorptions. Rate of desorption is also a first order and depends upon theta. And here there is no preference for deserving molecules.

In other words, if we have situations like this – one site is vacant; another site is vacant; And, we have the species, which is adsorbed; the probability of this species getting adsorbed here is as good as probability of desorption of this species here (Refer Slide Time: 18:19). One molecule will see different types of forces here; then, this molecule here – there is no molecule here; it is a vacant site. So, we will expect that the rates should be different for this molecule and for this molecule. But, Langmuir isotherms or Langmuir adsorption assumes that which has depends upon how much is the surface coverage here. It is uniform for all the sites, k d into theta. So, when you (( )) these two, you will get these expressions.

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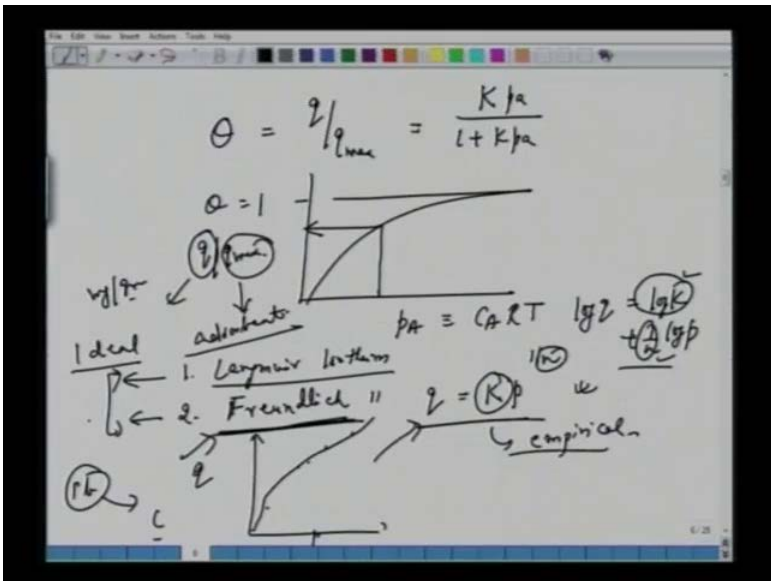

And, we have theta given as q over q max and this will be equal to k p a over 1 plus k p a. And then, we can plot this Langmuir isotherms; theta here will be 1; or, we are plotting q over q max. Here we have this partial pressure p A; you can also write as C A RT. So, given this partial pressure or concentrations, how much is loading here? q milligram per gram; q max will be the property of the adsorbent – what adsorbent we are using here; how many maximum sites are available. So, this type of information has to be given for us to do any calculations. So, that is one. We said this is a Langmuir isotherm or corresponding Langmuir adsorptions.

The second most common you will find is Freundlich isotherms. And, this is more of empirical equations, where you have q given as some constant into partial pressure over 1 over n. So, this type of situation occurs when you say you are doing some experiment – batch experiments and you have the data like q and different concentration or partial pressure. So, one can fit certain line here to obtain this k; and, it is mostly empirical. Langmuir isotherm is another extreme case, very ideal situations. And, for all systems, most of the commercial or industrial systems between adsorbent and adsorbed, we have Freundlich type of equations – q equal to K into p to the power 1 over n. One has to determine from the experiment, what is the value q and n. If we take a log, one can show that log q as log k plus we have 1 over n into log p. So, from here also, intercept and the slope – you have done this exercise before – one can obtain k and n for that type of system here. So, these are the two most common: Langmuir and Freundlich isotherms we are going to use in our case as well for different say liquid systems, certain dyes, certain colors. They follow this Freundlich isotherm or certain metal ions in aqua systems when you bring in contact with say charcoals – they also follow this Freundlich isotherms. So, these are the two most common. We are going to follow this in this course.

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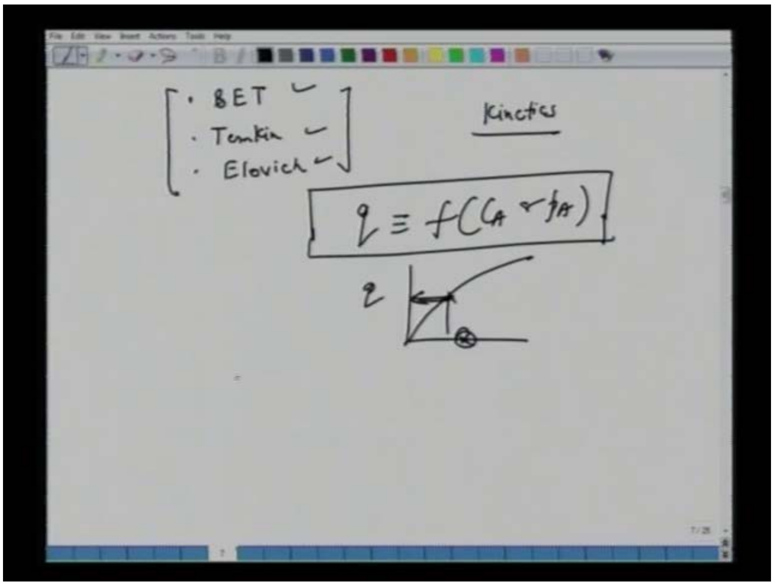

There are several types of isotherms, which just for your knowledge – one is the BET isotherms; one is Temkin; one is Elovich. So, out of interest, you can go through any books on kinetics to be familiar with different types of isotherms. All these isotherms give relations between q and a function of concentrations or the partial pressure; thus, the idea of thermodynamics. Langmuir, Freundlich sips BET, Temkin, Elovich. Ultimately, we like to know that given so much concentration in liquid phase or gas phase, how much is the loading; what does the thermodynamic say there; what q we will get in equilibrium. Once we have this, then we can do all our calculations.

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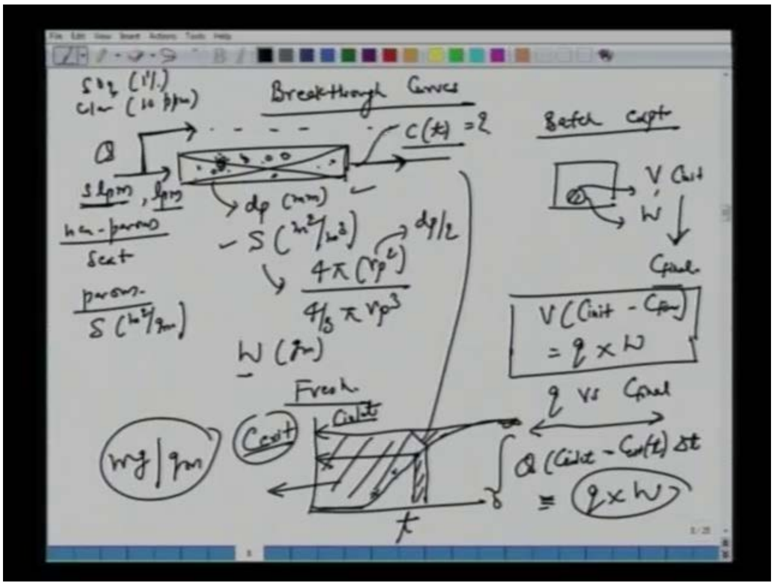

Now, what we do, we take another topic here, which is breakthrough curves. So, this is another introduction. We will skip most of the mathematical calculations to obtain these breakthrough curves. So, what we are discussing here, first, we had batch experiment; if we recall, most simplest experiment is a batch experiment. You take some fixed amount of V solutions, certain concentrations C initial; bring in contact with adsorbent, certain amount of w. Let the things get adsorbed, solute get adsorbed. You have final. You do this material balance – V C initial minus C final equal to how much is the loading into w, so that we have a relation experimental data, q versus C final. So, that is equilibrium. And, we said that same situations; same data we can also obtain if we do the column experiment. So, we take the adsorbents packed here. So, let us say, we have for simplicity, spherical pellets, adsorbents of diametral, let us say, d p millimeter; let us say it is non-porous. We talked about this earlier also that we can have non-porous adsorbent. So, essentially, we have all external surface area. We can also have very large porous charcoals, zeolites. So, we have a very large amount of area here – meter square per gram.

For the simple case, let us say these are non-porous. So, we have d p; we have S – external surface area per cubic meter volume. So, what we are talking is, let us say, 4 pi r p square over 4 by 3 pi r p cube; where r p is the radius of the particles. So, we know this d p; we know this external surface area. Let us say we have put certain w gram or kilo gram of this adsorbent. Now, to begin with, adsorbents are fresh. So, it does not contain any solute. We bring in contact with a continuous flow of Q say standard liter per minute of gas or liquid per minute of certain liquid. So, we have the gas or the liquid passing through this at certain rate Q; and, it is a pure Q, pure solvent. So, there is no solute. All these adsorbents are also fresh. Then, at a certain time, we inject, we bring in some step input there. So, we bring in contact with certain impurities say color in liquid or certain gas in this air sulfur dioxide, S O 2 – 1 percent; or, let us say we have certain color, dye in liquid say 10 ppm. So, we bring in contact with this.

And now, what we want to monitor is the exit. So, here we are interested in knowing what will happen, what is the response of this exit concentration. So, qualitatively, you should be able to make out that this response here – for a long time, you will see we want to plot t and we want to plot C exit; see for a long time, you will not see any concentrations here, because one, the fluid will take some time to reach here; that is the residence time. But, even then, when the fluid goes through this phase adsorbent, some solute will be getting adsorbed here. Only after a long time when the bed starts getting saturated, you will see the concentration level at the exit, will start increasing. And after a long time, then it will reach C exit. C exit will be same as C inlet. Now, we can say that the entire bed is saturated. So, the response will be like this (Refer Slide Time: 26:39). This level will increase same as this inlet concentration. Now, the entire bed is saturated.

One can calculate experiments. So, these are the data. One can calculate this area under the curve (Refer Slide Time: 26:52). From here, we can find out how much is the loading; how much amount has been adsorbed by material balance. This also we did in the earlier class. Take this response here; at a time of del t, how much is C exit; make a material balance; Q is constant; C inlet minus C exit, which is a function of time t del t. If you can integrate 0 to infinite time, you can find out how much amount has been adsorbed. So, material balance – inlet minus outlet. This must be same as your capacity, which you want to calculate – q into w. With the proper units, you can get also this q as a function of this C inlet or C exit. Next time you do different concentrations, you will get different q's. This is the way we can also generate isotherms.

What we are interested here is trying to understand this response. So, this response is nothing but what we call breakthrough curve, which is the topic here. What are the mechanisms? What are the factors, which you govern to obtain certain characteristics of this modelling profile?

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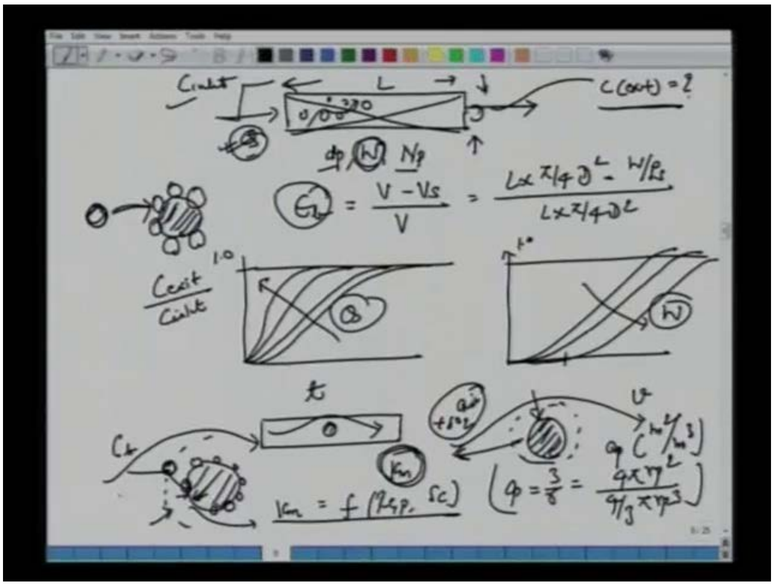

And, what we will do in this course, we will like to skip certain very regress mathematical; we will take very simple cases here. So, let us get back to this problem here – packed bed; certain diameter among this adsorbent; certain amount; we also know how much is the number of these particles, which we have put it here of each size w, so that we can calculate bed porosity. So, what is bed porosity? Total volume say the length is L; diameter of this column is D. So, V minus V of the total solids divided by V. V is nothing but L into pi by 4 D square; V S – total weight is w. Let us say the solid density is rho s. So, this is the total volume of the solid; bulk density of this rho is solid. Then, we have L pi by 4 D square. We know essentially how we have packed what is the bed porosity here; empty spaces between that solids through which this gas flows from one direction to another directions. So, here we have this Q, flow rates; we have certain C inlet; and, we are trying to obtain this breakthrough curve, which is C exit.

We are also assuming that the solids are non-porous, which means whatever solid gets in; whatever gas phase, species, sulfur dioxide, ammonia or say color, dye in this liquid – when they reach here, they get adsorbed on the external surfaces only. There are no pores inside. So, we would like to obtain how we can mathematically obtain this response if these quantities are known – flow rates, C inlet, diameter, w etceteras or the geometry of the column and the geometry of this sphere here.

Before that, let us do certain qualitative assessment here. What we will expect if we want to plot say C exit and say ratios C inlet just non-dimensionalized so that we have 1 here (Refer Slide Time: 30:33). So, if we have say certain response like this at certain conditions of Q; now, let us say if you increase the flow rate say Q 1 to Q 2, you should expect that the curve will go like this. The response will appear at the inlet. So, we should expect this type of response with increasing Q. Similarly, what happens if you have a response? Now, we increase w amount of this adsorbent keeping the liquid or gas flow rate same. In that case, if you increase the w, you should expect that the response will not be delayed, because you have lot of amount of adsorbents going to adsorb a lot. So, the response of the exit concentration at the outlet will be increasing. So, this is 1 here and this would be w. So, similarly, one can do a lot of exercise here if you know how to solve this set of equations, which we are going to put it here.

Let us start with this – what we have mechanistically? We have column like this say one adsorbent like this; (Refer Slide Time: 31:45) liquid goes pass like this; now, the gas goes pass like this. So, we have a sphere solid and the flow is like this. Corresponding to this Q, let us say the velocity is v here. We know the surface area of this; we know the weight; we know the diameter. So, we know this a p – meter square or surface area over cubic meter volume. So, for a sphere, this is nothing but 4 pi r p square over 4 by 3 by r p q. So, a p is nothing but 3 over r.

Now, when bulk air containing this sulfur dioxide travels pass the solid or water containing certain ppm, certain amounts of color, dye, certain metals – lead or fluoride, arsenic, they go pass these solid adsorbents like charcoals, zeolites. Then, there will be a mass transfer. So, I recall your knowledge from the first few lectures; they will be k m, film resistance represented by… Qualitatively, one can say what the resistance in terms of mass transfer coefficients is. So, pictorially, what we are saying here that we have the solid say non-porous – no pores inside; and then, there is a concentration profile. So, we have this (Refer Slide Time: 33:20) C, which is bulk; and then, it stops decreases because of this resistance – mass transfer resistance given by this mass transfer coefficients, which recalls – should be a function of Reynolds number and Schmidt number. So, first lectures three-four lectures, which we addressed in the mass transfer, can again be applied here. So, we have the C p, then this species mole, certain molecule or sulfur dioxide.

Now, it reaches solid surface. Now, when it reaches, there will be adsorptions; solid is fixed; this molecule now gets adsorbed. We do not worry whether it is getting adsorbed by physisorption or chemisorptions. So, there is an adsorption of certain rates there. So, from the bulk, essentially, certain amount is getting lost here; it is a flux.

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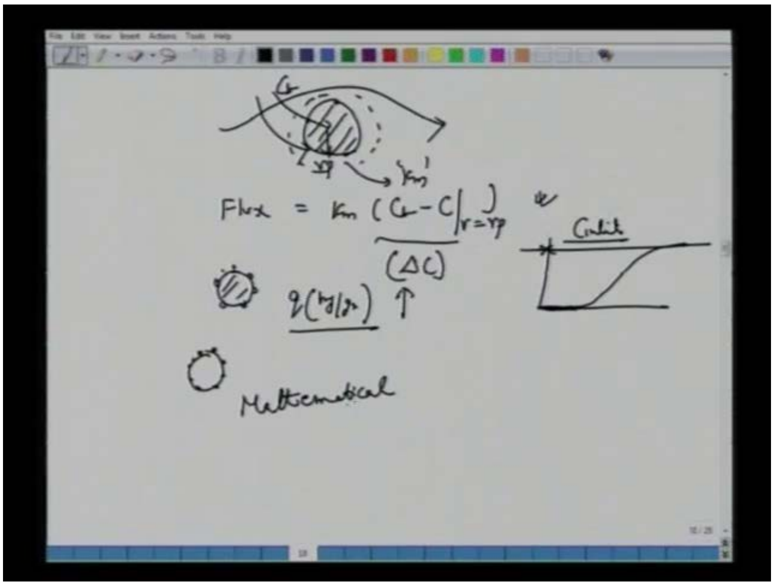

What is this flux? This is a solid here; liquid goes or gas goes pass like this. There is a mass transfer coefficient, k m. So, there is a flux towards the solid surface is nothing but k m into C bulk minus the concentrations at the surface C at r equal to r p. So, this is r p here. So, there is del C, concentration drop across this, because of this resistance. So, that is the flux here. And because of this flux, which arrives here, now, the solid is getting adsorbed. So, there is a certain rate at which the solid phase concentrations q milligram per gram of this solid increases. So, the bulk phase – there is a decrease and the solid phase – there is an increase. This is how we are getting a response here. But, lot of time you do not see any exit concentrations; why, because solid surfaces were adsorbing species. Till solid start getting saturated, the surfaces on more sites are left. So, then we have these saturations; and, all the exit concentrations have reached inlet concentrations. So, this is the physical (( )) fixed representations, which we will like to represent by mathematics here, mathematical representations.

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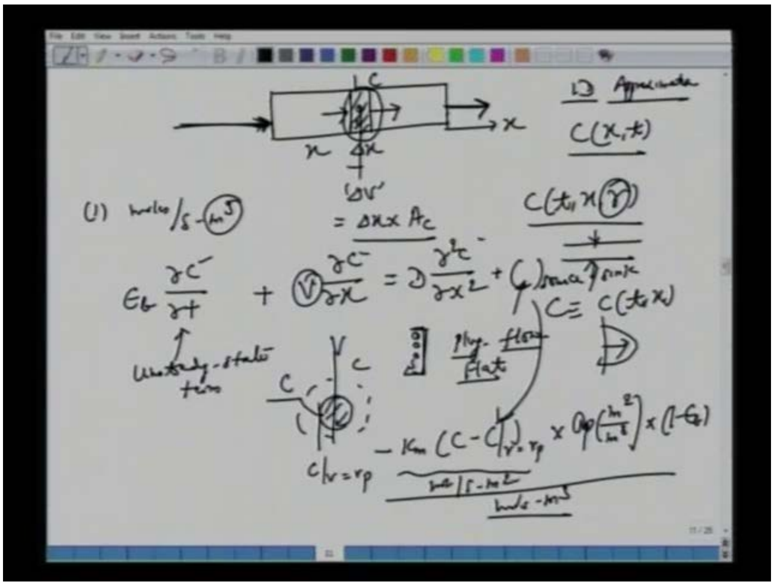

Let us redraw on this column for the last time and set up the governing equations. We have this packed bed. So, what we will do? We will set up certain governing equations – very simple governing equations; let us see at a distance of x. So, this is x here; x directions. Let us take very small, thin volume or the width say del x. So, what we are assuming here that this is 1D – one dimension. So, concentration profile here at any location at x; if it is C here, C is just a function of x and time. So, it is called 1D approximations or 1D model. In principle, this C concentration should be a function of time, x, as well as r – radius. But, we are assuming that this column is very thin; a small column in compression to the length or certain operating conditions, we assume that C is not a function of r; C is just a function of t and x.

Now, we are going to make a species balance. So, what this del x strip? Let us make a balance of moles in 1 second per cubic meter of this control volume del V. So, this del V is nothing but del x into the cross-sectional area of this column. So, in 1 second in one cubic meter, how much moles get in, how much mole gets out? Why there is a difference? Because there are solids here; it is getting adsorbed. So, certain species are getting lost, getting adsorbed at this solid surface. So, if you recall, some species balance we have done earlier also; continuity we wrote is species balance, where we can write epsilon b, which is bed porosity – del C by del t. So, the first term is unsteady-state term; then, there will be convective term – v del C over del x; there will be a diffusion term or dispersal term – del square C over del x square. So, let us say that V is a constant. So, we have a velocity profile, which is more like a plug flow. In empty tube, we will expect that this would be a laminar profile; it is a solid surface. So, it is a very good assumption to assume that the velocity profile is of flat. So, V del C by del x. Notice there is no r term here; plus or minus there should be one more term; that is the term of source or sink. So, we talked about this solid surface.

There is mass transfer coefficient; there is a drop here. So, what is this term here? (Refer Slide Time: 39:16) This minus k m flux C – so, this location, let us say, concentration is C here minus C at r equal to r p. So, now we are talking of concentrations at these locations C at r equal to r p. And, this C here is a bulk phase concentration. So, minus k m C minus C r p is a flux – moles per second per meter square. We have talked about this earlier – the basic mass transfer. So, moles per second per meter square; this meter square is the external surface area. And, here we are writing moles per second per cubic meter of this control volume. That means multiply this by a p surface area per cubic meter of particle volumes. And then, if you multiply it by 1 minus bed porosity, you will get this term as moles per second per cubic meter of the bed volume; so, going from particle volume to this bed volume.

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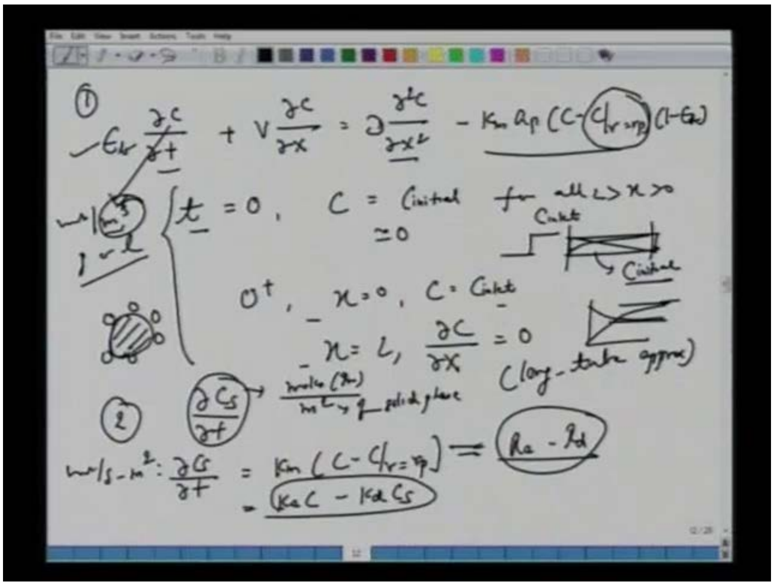

Now, we can write this full equation as epsilon b – del C by del t plus V del C by del x equal to D del square C by del x square minus k m a p C minus C at r equal to r p multiplied by 1 minus epsilon b. Notice – it is the first order time. So, we require a condition here t equal to 0; C is C initial; maybe it is very small; fresh bed is all fresh here; it is for all, x greater than 0 and less than L. So, for all length, the bed is fresh. This what it means; or, some C initial concentrations – very small concentrations. And, at 0 plus, at x equal to 0, now, we have C equal to C inlet. So, we have brought in contact with C inlet. So, it is a second order; we need two conditions: one condition is x equal to 0; C equal to C inlet; and, x equal to L. We require one more condition. And generally, one condition, which is very common and more realistic also – del C by del x equal to 0. So, we are saying that there is no gradient at the exit; it is like this – long tube approximations; like this – all variables; (Refer Slide Time: 41:54) they have reached asymptotically flat here. So, this is del C by del x equal to 0; no gradient conditions; or, it is also known as long-tube approximations.

Mathematically, now, we can say that problem is well defined here; concentrations – one condition for time; two conditions for x. However, you notice that we do not know C equal to r at r p. So, we have a solid surface. What is the concentration right here at r equal to r p in the bulk phase, in the liquid or the gas phase? So, this is equation one (Refer Slide Time: 42:30). And, equation 2 – that means now, we are talking of this solid phase concentrations – del C s over del t. This C is moles per cubic meter of gas or liquid. Here we are talking of del C s moles; or, this could be gram – just like here it could be gram – per meter square of solid phase. So, now, we are making a balance on this solid phase, because certain species now are getting adsorbed. So, whatever flux gets into this, that is same as del C s by del t, is now, k m C minus C at r equal to r p. So, it is moles per second per meter square. And, this will also be equal to some rate of adsorptions minus rate of desorptions. So, we were talking about all those isotherms – Langmuir isotherms, Freundlich isotherms, etcetera; we have this type of situations. Most common would be for rate of adsorptions – say first order adsorptions and we have first order desorptions. This would be the most simplest of these.

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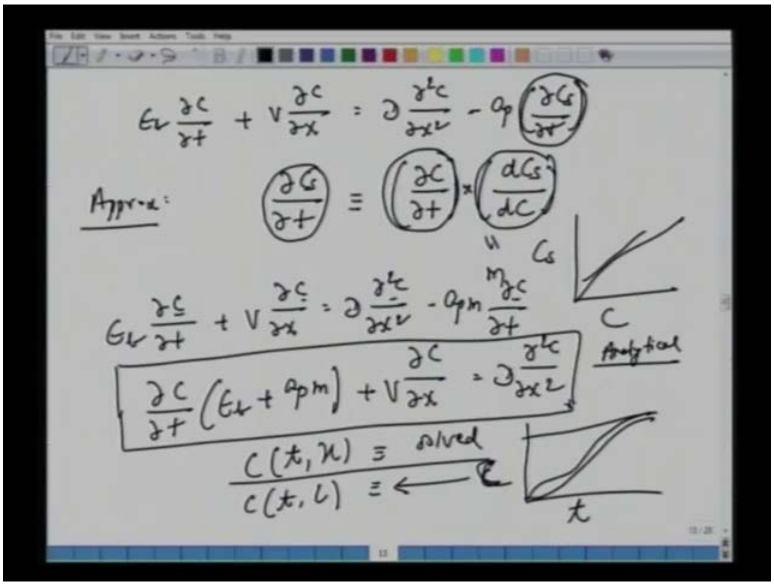

$$\epsilon_b \frac{\partial c}{\partial t} + V\frac{\partial c}{\partial x} = D\frac{\partial^2 c}{\partial x^2} - a_p\left(\frac{\partial C_s}{\partial t}\right)$$

Appr-x:

$$\frac{\partial C_s}{\partial t} \equiv \left(\frac{\partial c}{\partial t}\right)\times\left(\frac{dC_s}{dc}\right) = m$$

$$\epsilon_b \frac{\partial c}{\partial t} + V\frac{\partial c}{\partial x} = D\frac{\partial^2 c}{\partial x^2} - a_p m\frac{\partial c}{\partial t}$$

$$\boxed{\frac{\partial c}{\partial t}(\epsilon_b + a_p m) + V\frac{\partial c}{\partial x} = D\frac{\partial^2 c}{\partial x^2}}$$

$$C(t,x) \equiv \text{solved}$$

$$C(t,L) \equiv \leftarrow C$$

Going back to this first equation, we can write epsilon b del C by del t plus V del C by del x equal to this dispersion term or diffusion term; and, here you have the flux. Now, that flux is nothing but at what rate solid phase concentration changes. Notice – this is the flux we had equated to the flux as well as to this rate of adsorption and desorptions. So, the only thing here is that what is this del C s by del t? What is the best way the one most simplest model, which is used is cos I steady state; where we say that change in the surface concentrations is proportional to this gas phase or liquid phase concentrations. So, this is equal to del C by del t into d C s by d c. So, this is an approximation here; otherwise, one more we will have to solve with the previous expression, which we wrote. But, one best common simplest assumption would be the del C s by del t – rate of change of the solid phase concentrations equals gas phase or liquid phase concentrations multiplied by d C s over d c. So, mathematically, notice – this term d C s by d C is nothing but slope of these isotherms. So, this is equal to m.

Now, we can write our equations – epsilon b over del C by del t plus V del C over del x equal to D del square C over del x square minus a p into m del C by del t. So, now, notice – we have just one variable C; C everywhere. That means, we can write del c by del t epsilon b plus a p into m plus V del C over del x equal to D del square C over del x square. And, those conditions remain same as what we had earlier for time and for x. You can box this; this is the governing equation. If we solve numerically or analytically, mind you there are some analytical solutions available for this type of partial differential equations. If you solve, now, we will get an expression for C in terms of t and x. So, this can be solved here.

Essentially, when you have these expressions, you can have C, t and l; and, we can plot or we can predict even this t, C exit concentrations, which is nothing but C, t at l like this, (Refer Slide Time: 46:47) but the response curve for different conditions for varying x and y. Then, the species absorb on the solid. So, there was second part. Then, we got into this mechanism aspect that adsorptions could be physisorptions, could be chemisorptions; full sides are equivalent. So, we have one heat of adsorptions – first order adsorptions; first order desorptions. So, we have certain expressions.

Mathematically, one can obtain the expressions in terms of the loading and the concentrations. And, we said that we all we can also have very common Freundlich type of isotherms, which is very common; and, we are going to use in this course. So, idea is that our experimental data has to be correlated by certain equations, mathematical representations, which is like Langmuir isotherms or Freundlich isotherms or different types of isotherms, which have been reported. We did not get into details; out of your interest, you can go into some text book on kinetics, let us say, by Smith, etcetera to get a feel of it.

And, the last part of today’s lecture was mathematical representation of this breakthrough profiles, which means if we have a column and column geometries known to us – length and diameter, we have packed it with certain adsorbents; we know the property of the absorbents; how much amount; what is the size; what is the bulk density we can get the bed porosity, etcetera. We will like to mathematically predict what this column experiment is, what the column response is, because we will have certain experimental data, which has to be fitted by this response here – C versus t. And, to do this, one has to write down certain conservation equations, species balance, which we have done earlier also. So, the one simplest or approximated model would be 1 D model, in which we neglect the concentration profiles in the radial directions. So, we take balance over del x; we write down the species balance, material in, material out; at what rate material is getting adsorbed here. So, we had one equation for the bulk phase, one equation for the solid phase.

For the solid phase, there can be made some approximations – steady state – we said that the rate at which concentration change in the gas phase, the same rate or same proportion rate we have the change in the surface phase. Based on that we approximated the two equations with just one equation; we brought slope of the isotherms m, which we know from our thermodynamic experiment, thermodynamic data. Then, we can say that mathematically, now, we can solve these equations with a given initial conditions and with the conditions on x. From this, if you can solve by say some certain mathematical softwares like say mathcad or say certain fortran nag library or c libraries, one can solve this partial differential equation. In the literature, it has been solved analytical also. So, we do have analytical solutions for 1 D model; in which, you have time dependence and x dependence. So, that solution is also available so that we can predict your response in column experiments as very simple for non-porous.

The problem becomes more complicated when you have a porous materials. In that case, now, you have adsorbents, which have very large pores inside. And then, you can imagine that earlier we wrote two equations: one for the bulk phase; one for the external solid. Now, we will also have to write a balance for inside the porous. So, things become quite complicated for this course – third year level course – mass transfer. We skip the mathematical detail part of it. Just out of your knowledge, now, we have to write down one more species balance inside the solids; and, one has to solve set of partial differential equations.

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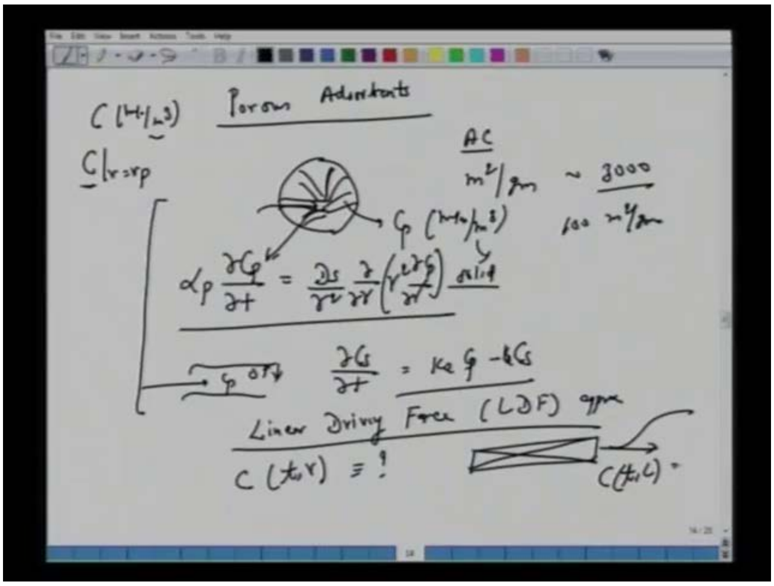

Generally, one makes some approximation; again, very well-known approximation is LDF (linear driving force) approximations. So, just note down this approximation here. When we have this porous adsorbents – so, now, we are saying that there are porous. Now, we talked of say activated charcoals – very large pores inside; surface area is some meter square per gram of the order of say even 3000 meter square per gram. Zeolites may be like 100 meter square per gram. So, essentially, these are the ports these are the conduits. So, in this case, one has to also write down the species balance inside. And, that you can imagine this would be another complexity here say del C p by del t. So, now, we are writing of C p moles per cubic meter of solid phase. Remember – first, we had C moles per cubic meter of gas or the liquid phase, bulk phase; then, we said that there is C at r equal to rp, solid external phase.

Now, we are talking of C p, which is inside this force here (Refer Slide Time: 51:55). So, inside, there is no convection. We have just pure diffusion; we have spherical geometries. If you have spherical beats here, r square del C p over del r. So, that is one model for this. So, now, one has to solve all these three equations together. Now, we have these pores – C p inside; species now, again adsorb and desorb; we have certain rate here – del C s by del t will be equal to K a C p, for example, first order adsorptions and second order desorptions. So, things are quite getting complex here mathematically. One approximation very often made is linear driving force approximations or LDF approximations. So, based on these approximations, one can still solve for C as a function of t and r in a column here. So, we will have packed bed column. Essentially, one can predict this C at what time and at what length.

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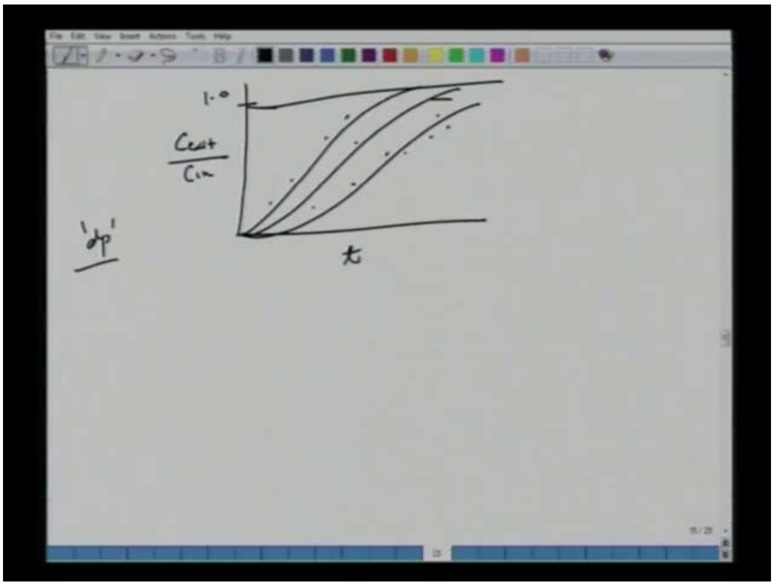

The idea of all these mathematical treatment is that we can predict C exit over C in for different time for different conditions, for varying flow rates or varying amount of D or varying particles size, etcetera. One can do this kind of model predictions and see how one can fit the data here, experimental data.

In today's lecture, we had some mathematical approximations or mathematical treatment for flow in a packed bed of porous as well as non-porous adsorbents. In general, most of the adsorbents are porous very large (( )) areas, so that it has a very large capacity. But, mathematical treatment is quite aggressive. We said that we are going to make a lot of approximations here. One very simple approximation is that when we assume that the flow is ideal, no dispersions. So, that type of mathematical treatment we are going to address in the next lecture; how do we get a very good estimate or approximate estimate of this response curve so that we can find out how long will it take for a solid to get saturated. At least this we should be able to address.

Then, we will take up the examples of this thermodynamic and the operating line; the way we have the treatment for the extractions, where we bring two liquids in contact. Here we bring liquid in contact with the solid; we will find out how many stages we require to achieve certain degree of separations; or, how much is the amount of adsorbent is required in a packed bed column. So, here also we have the same situations. We can have stage-wise adsorptions or we can have the packed bed columns. So, stage wise –

one, we have uniform mix like CSTR in kinetics we have done; we take the solvent; bring in contact with the solids; bed gets saturated; take out that solvent; bring into the fresh solvent; tend to the next stage; or, we can have a packed column; put all those three in a continuous; and then, we have a continuous flow of this. So, that is more like industrial applications where we have waste water, which we want to treat or we have the gaseous effluent, which we want to treat. So, we have a continuous column process. Instead of stage wise, generally, if you have say pharmaceutical industries, where they have handled very small amount or batch amount, there we do that type of experiment or we do that type of testing there. So, the next lecture when we meet, we take up our topics on batch adsorber and the continuous adsorber.