

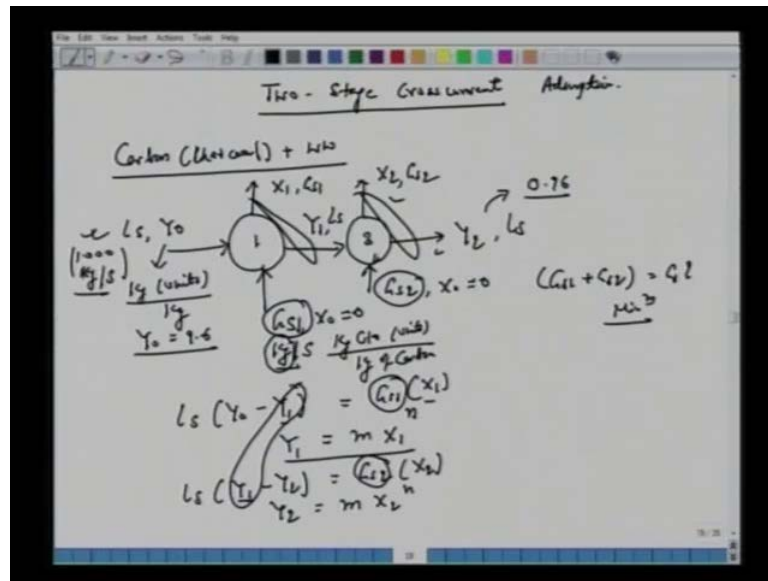
**Mass Transfer II**  
**Prof Nishith Verma**  
**Department of Chemical Engineering**  
**Indian Institute of Technology, Kanpur**

**Lecture No. # 33**

In the previous lecture, we took up an example on adsorption in single-stage and two-stage countercurrent stages. And, there we had an example of charcoal, carbon used to remove color from waste water. And there we showed the amount of adsorbents required in two stages is smaller than that required for single stage. And, that time also we said that if the number of stages are fixed, then to calculate or to determine the amount of charcoals or solids required for adsorption, one has to do some iterations. So, if you do graphically or you solve analytically, then there is some iterations required for this.

Today, in the example, we take the same system charcoal and color in waste water and we take up this example on two-stage crosscurrent. So, instead of countercurrent, now, we have two-stage crosscurrent. So, you have a feed brought in contact with charcoal; treat that feed; allow for the equilibrium to reach; take out to the feed; bring to the second stage. There again you treat with the fresh charcoal and determine how much amount you have at total required for this crosscurrent two-stage process. Here also, we will see that in some cases, we need to do **these** iterations to determine how much amount of charcoal is required. So, let us take this example on two-stage crosscurrent for charcoal and waste water system.

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We have this two-stage crosscurrent adsorption and we have this carbon or charcoal plus this waste water. So, what you will have is one stage here and the second stage; you have this feed say flow rate is  $L_s$  and  $Y_0$  is the amount of the weight fraction of color in this wastewater. So, generally,  $Y_0$  is said that we can have kg or certain units of color per kg of solutions. So, let us say that  $Y_0$  is given as 9.6. And,  $L_s$  – let us say we have 1000 kg of water to treat. So, again, here we can have 1000 kg or we can have 1000 kg per second. So, both are acceptable. All we are trying to say that if we work on batch, we have to do it twice. So, here are the basis is if we choose 1 second, and also we have this 1000 kg of water. So, now, we bring in contact with solid. So, we have  $G_s$  charcoal; let us say it is a fresh charcoal. So, zero concentrations. And, here also, we can have kg per second; we have kg per second. If we talk in terms of kg, how much kg of waste water; then, here also, we can have just kg alone of solid charcoal.

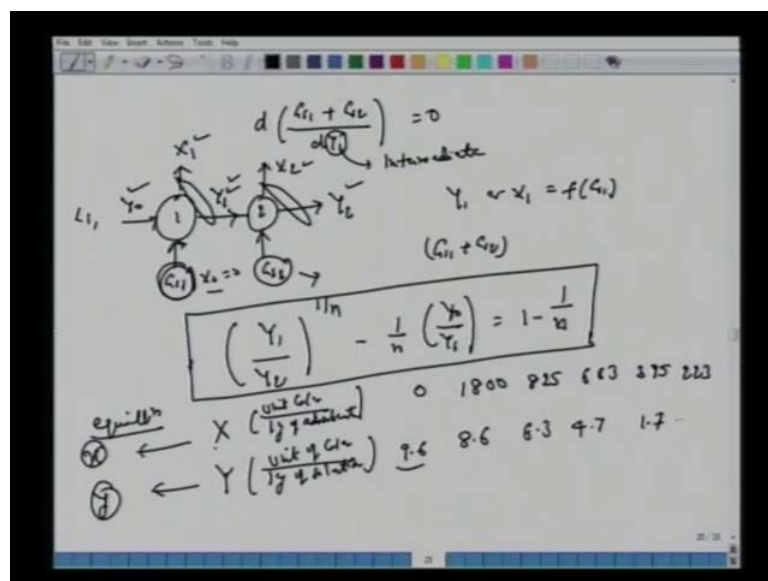
After treatment, this concentration is now  $Y_1$ . So, kg color of units per kg. And, here also, (Refer Slide Time: 03:56) this is kg of color for certain units per kg of carbon. So, after treatment, we have this  $X_1$ ; this is  $G_{s1}$ ;  $G_{s1}$  will remains same as this. Similarly,  $L_s$  will remain same as this; and here, we have this  $Y_2$ . So, we are working on solid free basis. And now, we bring in contact with again some different  $G_s$ ; maybe put  $G_{s2}$ ; we have  $G_{s1}$  here. This is also fresh carbon. And, after this, we have this  $X_2$ ; this is  $G_{s2}$ . Amount of solvent is  $L_s$ . The question asked here is that what is the

max optimum amount of charcoal required is. So, we have to optimize this minimum amount of charcoal required. So, this flow rate of G s 1 and G s 2 are not known.

We are assuming the ideal stages. So, X 1, Y 1 determined by the equilibrium; X 2, Y 2 determined by this equilibrium. Let us see again, we have 1000 kg per second of flow rates say solutions; waste water containing 9.6 units; we have been asked to reduce this unit to Y 2 as 0.96. So, one-tenth time deductions. So, this problem is the same as in the previous class, except now, we are working on two-stage crosscurrent. And, the question asked is that what is the amount of G s 1 and G s 2, so that total amount is minimum here. So, one can solve again analytically and graphically; let us write down the equations, which we have here L s Y 0 minus Y 1, so that the reduction in the color amount in waste water will be same as G s 1 and whatever it picks up – X 1 minus X 0, but X 0 is 0 here. So, we have G s 1 into X 1. And, Y 1 and X 1 are in equilibrium. So, they are determined by some isotherms. So, we can write Y 1 as equal to m X 1 to the power n or m X 1 here (Refer Slide Time: 06:11).

Similarly, we can write for the second stage L s Y 1 minus Y 2. So, reduction across the second stage should be equal to G s 2 X 2 minus X 0; X 0 is 0 here; and then, Y 2 and X 2 are on the equilibrium. So, Y 2 is equal to m X 2 to the power n. So, G s 1 is not known here; (Refer Slide Time: 06:36) G s 2 is not known here. Y 1 – you must notice that it is an intermediate here; it is an intermediate variable.

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So, the question asked here is that what is the minimum amount of solid required. So, essentially, we are going to optimize this. We did it earlier in the previous lecture and  $Y_1$  equal to  $Y_0$  – we will set this to 0. So, why  $Y_1$ , because  $Y_1$  is the intermediate variable here. Again, go back to stage configuration. We have stage 1, stage 2; this is  $Y_1$ ; this is  $Y_0$ . This is  $G_{s1}$ ;  $X_0$  is 0; we have  $X_1$ . This is again  $X_0$ , but now, we have  $G_{s2}$ ; this is  $X_2$ ; and now, we have this  $Y_2$ . So, if we change by the amount of  $G_{s1}$ ,  $Y_0$  is fixed;  $L_s$  is fixed;  $X_0$  is fixed. And, we say that the two exit streams are in equilibrium. All it means that  $Y_1$  or  $X_1$  is a function of  $G_{s1}$ . So, once we change this  $G_{s1}$ ,  $Y_1$  will change;  $X_1$  will also change; they are in equilibrium here. But, once we fix  $Y_1$ ,  $Y_2$  is fixed first and these two are in equilibrium. So, we know  $X_2$ ; that means, the amount of  $G_{s2}$  is also fixed. So, essentially, one has to optimize the total amount –  $G_{s1}$  and  $G_{s2}$ ; should we take a very large amount in the beginning; should we take a small amount in the beginning. And, we did this exercise; we write down the two equations; eliminate  $L_s$  and  $G_s$ . And, we have only one variable left here, which is  $Y_1$  as an intermediate. If we differentiate, equate to 0, we have the conditions given as  $Y_1$  over  $Y_2$  raise to the power  $1/n$  minus  $1/n$   $Y_0$  over  $Y_1$  equals  $1/n$  minus  $1/n$ . This is equation we obtained in the previous class. So, we have this expression for this

Now, let us get back to our example. So, if you recall, we had the equilibrium curve; we did some calculations here. So, we would not repeat that. We will start from the same example of color in waste water and color in charcoals. So, if you recall, certain unit of color per kg of adsorbent, which is charcoal here. And, here we had some unit of color per kg of solutions. Again, when we use the solutions, actually, we should have been working on a small  $y$  as per the conventions and should have used small  $x$ . But, we said that it is a very dilute solutions; capital  $X$  is approximately same as small  $x$  and capital  $y$  is same as small  $y$ . So, we did this exercise in the previous class; we have now the numbers here – 1800, 825, 663, 395, 223. And, corresponding to this, we have 9.6. So, that is your starting material – 9.6. Then, we have 8.6. These are all equilibrium values 6.3, 4.3, 1.7; and, you have 0.7. So, these data are given to us. All we do – we substitute in this equation.

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$$\left(\frac{Y_1}{Y_2}\right)^{1/n} - \frac{1}{n} \left(\frac{Y_0}{Y_1}\right) = 1 - \frac{1}{n}$$

$$\left(\frac{Y_1}{0.96}\right)^{1/1.66} - \frac{1}{1.66} \left(\frac{9.6}{Y_1}\right) = 1 - \frac{1}{1.66} = 0.397$$

LHS:  $Y_1 = 3.3$  (kg/unit)  
 RHS:  $0.397$

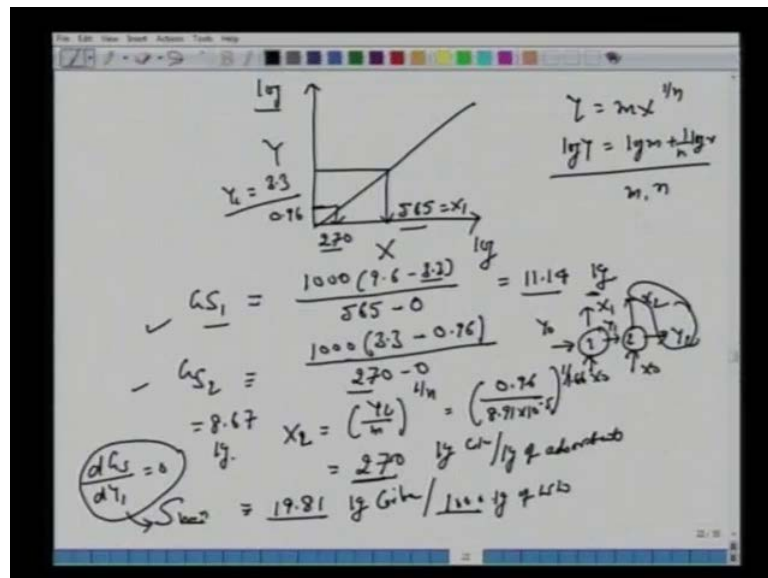
$$X_1 = \left(\frac{Y_1}{m}\right)^{1/n} = \left(\frac{3.3}{8.91 \times 10^{-5}}\right)^{1/1.66} = 565 \frac{\text{unit}}{\text{kg solution}} \equiv \text{solid phase concentration}$$

Let us rewrite down this equation –  $Y_1$  over  $Y_2$  raise to the power  $1$  over  $n$  minus  $1$  over  $n$   $Y_0$  over  $Y_1$  equals  $1$  over  $1$  minus  $1$  over  $n$ . And, if we recall, we had the slopes of  $y$   $m$ ;  $y$  equal to  $m$   $x$  to the power  $n$ ;  $n$  was obtained when we fitted this equilibrium curve on log-log scale. We obtained values of  $n$  as  $1.66$ . So, now, we can go back. And,  $m$  we can write down –  $8.91$  into  $10$  to the power minus  $5$ . So, now, we can put back here;  $Y_1$  is intermediate values; we are supposed to know about what we supposed to calculate from here –  $Y_1$ ;  $Y_2$  is the exit concentration of treated waste water, which is  $0.96$ . So, we are going to reduce from  $9.6$  to  $0.96$  minus  $1$  over  $n$ , which is  $1.66$ . Here we have  $1$  over  $1.66$ ;  $Y_0$  is  $9.6$ ; and,  $Y_1$  we are going to calculate; equals  $1$  minus  $1$  over  $1.66$ . So, you can see that  $Y_1$  has to be solved by some trial and error, by iteration; it is a non-linear equation. This number is check  $0.397$ . So, if we solve by some iterations, maybe left-hand side equals right-hand side; another very old technique to calculate this  $Y_1$ . You should get  $Y_1$  as  $3.3$  kg or some unit of color per kg of solution waste water. In fact, if you want to put the values of  $Y_1$  here –  $3.3$  over  $0.96$ , then we have raise  $1$  to the power  $1.16$ ; you will see that left-hand side and right-hand side are very close to  $0.397$ . So, you have to improve how much accuracy you want to solve this technique; or, maybe some numerical technique and make use of it. If you have taken some course on numerical methods, you can solve for this  $Y_1$ .

Once we have this  $Y_1$ , we can go back and calculate  $X_1$ . So, again, let us draw very quickly. This schematics we have –  $1, 2$ ; this is  $X_1$  here (Refer Slide Time: 12:53) and

this is Y 1. This is y 2; this is X 2; this is X 0, X 0; both are 0. And, here we have this Y 0. So, Y 0 to Y 1 and Y 1 to Y 2; Y 1, X 1 are in equilibrium; Y 2, X 2 are in equilibrium; L s is known to us. We want to find out G s 1 and G s 2. To calculate G s 1, we have to make a balance around this; we have to determine this X 1. But, X 1 is in equilibrium with Y 1 or the two streams are in equilibrium. So, we can write X 1 as Y 1 to the power m raise to the power 1 over n. So, y 1 over m raise to the power 1 over n; y 1 we have calculated; 3.3 by iterations or by some numerical algorithms. m is the slope of isotherms – Freundlich isotherm, which we fitted in our previous example through the equilibrium curve 1 over 1.66. This – we should be able to obtain as 565. So, 565 units of color or kg of color per kg of carbon adsorbent. So, this is X 1 – solid phase concentrations in this living stream. It is a solid phase concentration; 565, which is in equilibrium with 3.3. In fact, if you go back to this (Refer Slide Time: 14:25) graph, which you have obtained with the slope of m, if you read Y 1 as 3.3, some values here, you should be able to read this number 565 directly from the graph.

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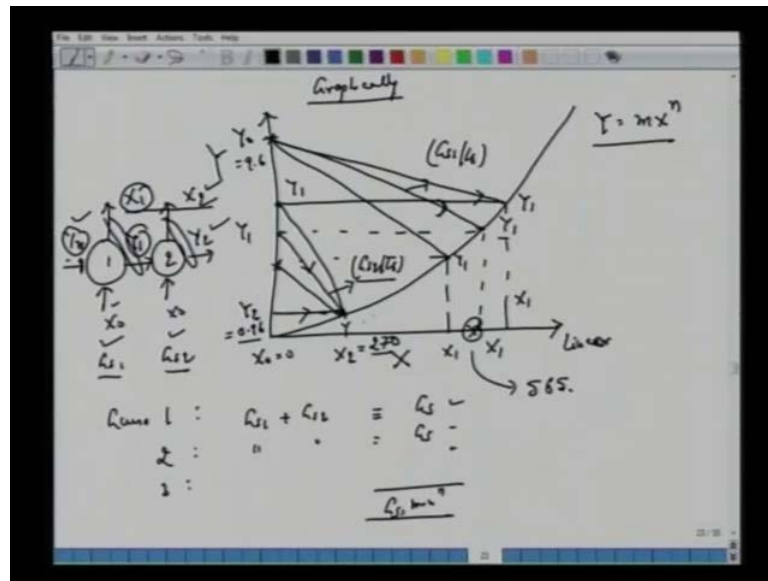


In other words if you have this Y, X on log-log scale, we have Y equal to m X to the power 1 over n; log Y equal to log m plus 1 over n log x. From this, we obtain the values of m and n. So, we have this Freundlich isotherm linear on log-log plot. Y 1 – we have just now calculated – 3.3; read from the graph. This should be equal to 565 or you can solve from the equations. Once we know the values of Y 1 here as 3.3 and 565 as X 1, we can make a balance, which we did earlier for the stage 1. X 1 will be equal to L s,

which is 1000. It contains 9.6. We have brought this minus **to** first stage – to 3.3. So, 1000 9.6 minus 3.3. And, the solid phase concentration has increased from 0 to 565. So, S 1 is 11.14 kg. Mind you – once we have S 1, we can determine S 2. S 2 is by the same method, you make a balance around the second stage – 1000 – this remains the same. Now, we are going to reduce from 3.3 to 0.96. So, that is why we said this Y 1 is an intermediate variable divided by **...**

Now, look at this – we should have 270 minus 0. So, what is this 270? Go back to this schematic – stage 1 and stage 2; X 0, X 0; we have Y 0; X 1 and Y 1 in equilibrium. Similarly, we have Y 2 and X 2 in equilibrium. So, if we know Y 2, which we know, here 0.96, we should say that we can go back to this curve. Let us see here – this is 0.96. Read from the graph; you should be able to read this number as 270. So, we have this number 270 and we have number this 565 (Refer Slide Time: 16:58). Alternatively, again, you go back to this number X 2 equal to Y 2 over m to the power 1 over n; Y 2 is 0.96. Slope of the curve we have obtained is 8.91 **into** 10 to the power of minus 5 raise to the power 1 over 1.66. This number will also be equal to 270 kg of color per kg of adsorbent. So, now, we have S 1 and we have calculated S 2. This number – if you put it here, you should get 8.67 kg here. So, the S min; why min, because we have differentiated to obtain Y 1; we obtain this min we had. So, this is actually G s 1 **above** previous nomenclature – d G s over d Y 1 equal to 0. So, this is what we set it here. So, we have S min. If S min is... So, if we calculate, add the two – 11.14 and 8.67; we have 19.81 kg of carbon per 1000 kg of waste water. So, that is the answer – 19.81 required for 1000 kg of waste water. Let us see how we can solve this graphically.

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If you want solve graphically... or, at least, you should be able to represent on the graph. So, we start here with Y versus X maybe on the linear scale, because operating line is linear on this linear scale. So, we have the same equilibrium curve. Now, we have Y equal to m X to the power n. Let us mark the points here. So, we know Y 0. So, again, let us focus on these two stages. We have Y 0, Y 1, Y 2; we have X 0, X 0; we have X 1; we have X 2. Two are in equilibrium; two are in equilibrium. Y 0 is known to us; Y 2 is known to us; X 0 is known to us; X 1, X 2; X 2 – we can find out from this equilibrium known to us. X 1 – not known to us nor Y 1 nor we have this value of G s 1 and G s 2. So, stage 1 – Y 0 and X 0 – two incoming streams. So, X 0 is 0 here. We know this; we can locate this coordinate here. And, at the end, we have this Y 2, which is 0.96. And, corresponding to this Y 2, we had this calculated X 2, which was 270. So, we can mark this point here. This is X 2 and this is Y 2. Y 2 equals 0.96 and Y 0 equal to 9.6; X 2 is 270; we read from here.

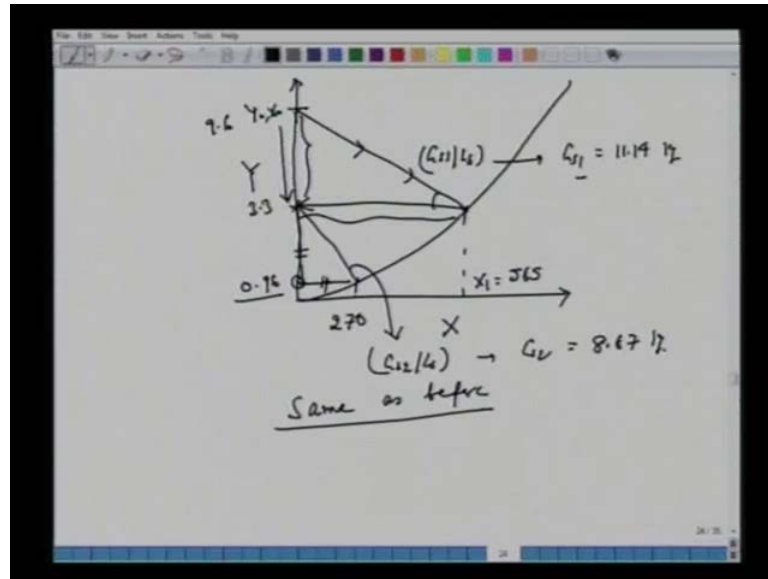
Now, how do we get G s 1, G s 2 and Y 1. We do not know the slope; or, crosscurrent is a negative slope of G s 1 over L s. So, all it means it is quite iterations. So, let us take arbitrarily, curve like this; that means, we have assumed certain slope or we have assumed certain amount of solid. So, essentially, we have G s 1 L s; minus of this negative slope here. And, when we (( )) this, that is, Y 0. This is brought down to Y 1. So, this would be the values of the Y 1 here; corresponding to which, you will get X 1. But, Y iterations, because now, if we know Y 1, which we know here say with this first



guess, then if you connect this  $Y_1$ , now,  $Y_1$  is brought in contact with  $X_0$  again, now, we get the final concentration of  $Y_2$ . This line will be now fixed. Also, try to understand what we are saying here that we do not know the amount of  $G_{s1}$ . So, we assume a value of  $G_{s1}$ , we reach this  $y_1$ . So, this stream starting from  $Y_0$  is brought down to  $Y_1$ . So,  $Y_0, X_0$  enter and they leave at  $X_1, Y_1$  in equilibrium. Now,  $Y_1, X_0$  equal to 0; again, they reenter second stage and leave as  $Y_2$  and  $X_2$ . This point is already fixed, (Refer Slide Time: 22:04) because this is 0.96; so, in this 270, this line is fixed. Once we know  $Y_1$ , we can connect with this. So, now, we have from the slope; now, we know  $G_{s2}$  over  $L_s$ . So, we calculate  $G_{s1}$  plus  $G_{s2}$  in case 1. So, calculate this; get the amount here; total amount –  $G_s$ .

Take another slope. Suppose I choose the slope; that means, it is a new value of  $Y_1$ ; or, it is a new value of  $Y_1$  here. But, once  $Y_1$  is here, now, we have new values of  $G_{s2}$  over  $L_{s2}$ . This will give you different values.  $G_{s1}, G_{s2}$  as different values; choose another case here; this is  $Y_1$  again. This  $Y_1$  is in equilibrium with  $X_1$ ; this is also with  $X_1$ ; new values of  $X_1$ . So, we know new  $Y_1$ . Once this  $Y_1$  is known, we connect with this; we have now different values of  $G_{s2}$ . So, one has to make this guess here and see which weight it falls, which number gives you the best on minimum amount of  $G_{s\min}$ . And, if you do this exercise graphically as... So, you have to take several of this; you must be able to convince yourself that you are getting the same numbers; maybe this is  $X_1$ , which should be equal to 565 and ... So, this is  $X_1$ ; and, what  $Y_1$  you will get here? This is 0.96 corresponding to this 565. This number will be 3.3; same as before.

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So, let us redraw this curve again assuming that we have reached right guess, right values, which gives you minimum amount of solvent or charcoals, solid. So, we have this equilibrium curve; we start with  $Y_0$ ,  $X_0$  we have this number. So, this stream gets... So, stream concentration. Now, waste water decreases till we have this equilibrium concentration, exit concentrations, which is  $X_1$ .  $X_1$  is 565 corresponding to which we have now 3.3. So, this  $Y_0$  was 9.6; we have brought down 9.6 to 3.3; we have to get down to 0.96. So, this number is fixed here – 0.96. And corresponding to this, this value is fixed to 270. So, all you do – connect this; get this  $G_{s1}$  from the slope of  $G_{s1}$  over  $L_s$ . If you calculate, you should get  $G_{s1}$  as 11.14 kg. And, from this slope,  $G_{s2}$  over  $L_s$ ; if you calculate  $G_{s2}$ , we should be able to get 8.67 kg; or, look at from this, slope of this curve is  $\tan \theta$ ; this divide by this number here. So,  $G_{s1}$  over  $L_s$ ;  $L_s$  is nothing but this by this. From this also, we can get  $G_{s1}$ .

And similarly, for this, (Refer Slide Time: 25:23) here we have 3.3, say, 0.96. So, this segment divided by this segment; 2.72. From this also, we can get  $G_{s2}$  over  $L_s$  to obtain the same answer as before. So, what we have obtained here is we have the same message; either we solve analytically or we solve graphically, there is an iteration required. And, this always happens when the number of stages are fixed. So, if you have told that we have been given two stages, three stages, four stages, then calculate the amount of charcoal required; or, amount of solid required for the treatment of the feet. Then, one requires iterations; whether it is a crosscurrent or it is a countercurrent. However, if

solvent or the amount of solid is given – solid phase concentrations, then how many stages are required that should be a straight forward?

For example, you can go back to this if you are told that this amount of  $G_{s1}$  is given; the amount of solid is also given for the second stage; how many stages are required when we start from here; this was stage 1; then, you have stage 2. So, if the solvent is given, the amount of solid is given to us, solution is given to us; then, the slope we can find out; there is no iteration required. We can come to this equilibrium curve and calculate this intermediate numbers; then, we know the second slope  $G_{s2}$  over  $L_s$ ; we can get this number here, which is  $Y_2$  equal to 0.96. So, whenever we have this question of phrasing the problem, one has to understand and one has to be careful both mathematically, analytically; there will be iterations if stages are given and the amount of solid is asked to determine here. So, these are the three examples we have chosen on adsorptions – stage wise; and, here we are saying that two leaving streams: solid and liquid; they are in equilibrium.

What we do now next is batch adsorptions. So, when we say that we have calculated this isotherm, you must have recalled that we did very small like experiment; **we had took a beaker**; take some waste water; what solutions we have? Add adsorbents; we have adsorbents, adsorbate and a small batch beaker. Allow for the equilibrium to reach maybe 10 hours, 24 hours. Then, calculate the concentration in this solution phase. Take that difference; the difference will tell you how much amount has gone on the solid. So, given the final concentration, what is the amount in the solid that will give you the equilibrium curve? What we want to know – how long will it take? So, there are certain processes, which are also batch, especially, the waste water treatment; or, in pharmaceutical industries, you have certain small amount of feed, which you want to clean, purify by adding certain solids. In that case, it is a batch absorption and one would be interested to know how long will it take to bring down one concentration level from one to another; maybe the final concentration is in equilibrium. So, that type of small exercise we should be able to do **in** this lecture.

One thing again, if you recall, we talked about these adsorbents – different type of adsorbents. One is porous; one is non-porous. Not many people will like to work on non-porous, because it has a small **bd** area; small surface area. So, it has a small number of sites. Everybody would prefer in general to have large amount of **bd** areas, so that you

have very good number of sites. And, for a small amount of adsorbents, you can remove very large amount of adsorbent. So, again, from the mass transfer point of view or whatever you have learned in this course, if you take a solid adsorbent, bring in contact with this some solutions feed, then what are the rates involved.

If there is a flow or you can have a **steady**, there is a Reynolds number. Given the Reynolds number, there will be a film mass transfer coefficients. So, that is one rate. At what rate this solute or the color is transferred from the feed to the solid surface; so, that is one rate. Once it gets on to the solid surface, then it has to diffuse inside the pores, because this is porous adsorbent charcoals; very large **b t** areas; 2000 meters square per gram or 3000 meters square per gram. So, then, the solute has to diffuse inside the pores. So, that is the second rate; rate of diffusion; knudsen diffusion; pore diffusion. We have talked about those earlier. And then, once it diffuses inside, then it has to adsorb and desorb on the solid surface inside the pores. So, you have the third rate, which is the rate of adsorption and rate of desorption. So, whenever you have three rates in series, again, you should inspect and see which rate controls. This also we have discussed when we talked about the two film resistance.

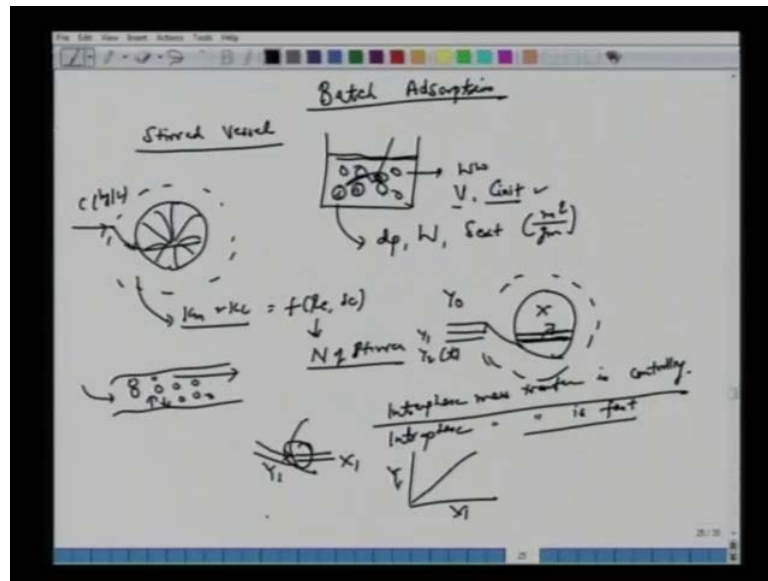
Whenever we have two resistances in series, then one which is very smaller controls the entire mass transfer rate. So, here you have three rates. One rate is rate for mass transfers in the bulk solid; we call it interphase mass transfer. Then, you have the pore diffusion inside color **diffuses**. So, we have interphase mass transfer. Then, once it reaches on the wall, then it **adsorbs, desorbs**; you have third rate – rate of adsorption; rate of desorption; first order second order given by Langmuir kinetics or Freundlich kinetics, some arbitrarily kinetics, etcetera. So, in that case, now, what happens, one is a good practice to make an estimate that which one is controlling. If all three of them have the same order of magnitudes, then all of them have to be taken into **the according** into solutions. But, if one of them is much smaller than the other two, then you can say that the process or overall adsorption is controlled by that rate and the rest of the two steps are in equilibrium. So, in case of poly porous solid, it is very common that always most of the rates are determined by the poor deficiencies or at least by the rate of adsorption, desorption. Bulk phase from the solutions to the solid surface – generally, we have very large Reynolds number; **whether** you have a stirring or you have some tubular coated – some tubes you have coated with the solid adsorbents or we have packed bed, generally,

we have very large flow rates. So, interphase mass transfer is never controlled; it is always very large; or, at least, the user can choose a very high Reynolds number; that situation never occur.

But, then as far as mathematics is concerned, if we recall from our previous lecture also when we wrote down the equations, then the second stages or when we have the pore diffusions or when we have rate of adsorption, desorption, then mathematically, it is very difficult to solve; you have a set of partial differential equations; set of ordinary differential equations. Unfortunately, in the real world, you have rates determined by pore diffusions or by adsorption, desorptions; very rarely it happens that rate is controlled by the interphase mass transfer. But, we have to solve the set of pdes by some programming or some different numerical algorithms. But, in today's lecture, just for the sake of continuity, we assume that rate of adsorption, desorption is controlled by interphase mass transfers. So, that means, **we will neglect; we will say that** inside the solid surface, you have very fast kinetics; or, diffusion rate is very large. So, as soon as the solute comes inside, it diffuse inside; there is no concentration profile inside. Remember – whenever there is resistance, there is a drop. So, we are saying that all drops occur outside the solid surface; not inside. So, inside there is no concentration gradient; there is only one concentration – we call it  $X$ . And, when it adsorbs and desorbs, then also it is very fast kinetics. So, whatever we have concentrations in the liquid phase or gas phase, outside the solid surface, we assume that the solid phase concentration is also in equilibrium given by this isotherm.

So, it is a very simplified case, but for this undergraduate level, we have to do this exercise. We assume that it is the interphase, which is controlling. In the real world of questions, it is other way round, but then solving a set of equations becomes very cumbersome. So, let us get back to start this new topic for this adsorption, which is batch adsorption.

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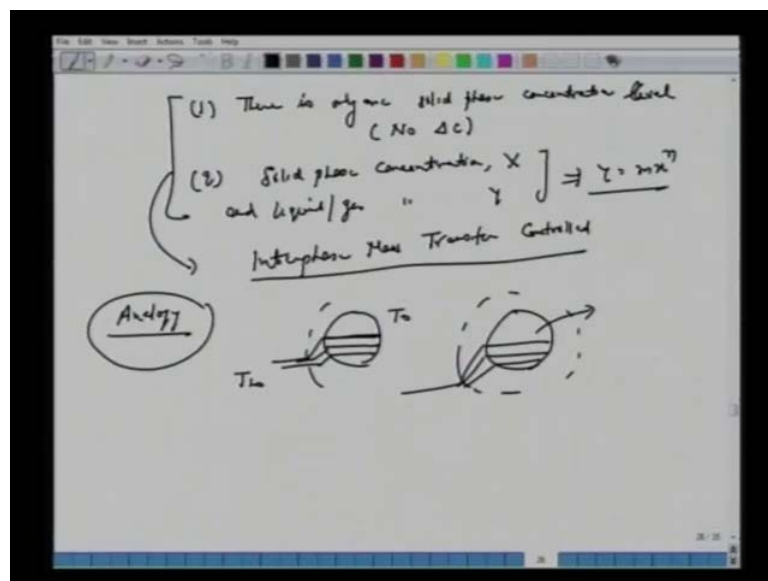


We start with this batch adsorption. What we are talking here is stirred vessel. So, we have a beaker; let us say certain waste water, certain volume,  $c$  initial concentrations, maybe color, maybe some benzene, zilene, talene and we have the solids, charcoals here or adsorbents. And, what we do here is stirring. So, there is a little bit of stirring here also, so that concentration inside it is well mixed; but, now, to the extent that mass transfer coefficients inter phase is very large. So, let us get back to this; we have volume, certain  $c$  initial concentrations; we have certain adsorbents here. Let us say particle size is  $d_p$ ; total weight is  $W$ . We know, its external surface area – we can call it meter square per gram. This is known to us.

This solid adsorbent (Refer Slide Time: 32:10) – if we look at slightly magnified, maybe they are porous. But, we are saying that diffusion inside is very fast. In other words, if we draw schematically, we are saying that if this is the bulk phase concentration, say,  $c$  milligrams per liter of color in this liquid, then all drops occur inside this film. So, this is given by  $K_m$  or  $K_l$  mass transfer coefficients, which is a function of Reynolds number. Smith number – we have done it before. This Reynolds number will be based on the rpm of this stirrer. So, somewhat... So, essentially, all drops occur in this. And inside, there is no drop here. So, if we look at one pore, the reality is that this species get inside and then they adsorb and desorb at the wall at certain rates. But, we are saying that this is very fast kinetics; there is no gradient here.

At any time if we look at these adsorbents and you have the solutions surrounded by the solutions, (Refer Slide Time: 36:16) what you have here is to start say this concentration is  $Y_0$  here and it is a fresh adsorbent. So, there is no concentration here. After some time, this concentration will drop and this will increase solid. But, look at this – there is only one concentration here  $X$ . So, there is no concentration drop here; why, because we are saying that interphase mass transfer is controlling pore diffusion or intraphase is fast; intraphase mass transfer is fast. What diffusion resistance is smaller here. So, with the time, this concentration will drop, color will change in the waste water from  $Y_0$  to  $Y_1$  to  $Y_2$ ; all function of time and this concentration will increase. But, if you increase, there is only one concentration level here. And, at the solid surface, whatever concentrations we have here say  $Y_1$ , then we have corresponding this  $X_1$ , but  $Y_1$ ,  $X_1$  are given by this isotherm. So, next time if it is  $Y_2$ , its concentration has increased to  $X_2$ ; we have another isotherm here. So, every time, liquid phase is in equilibrium with the solid surface.

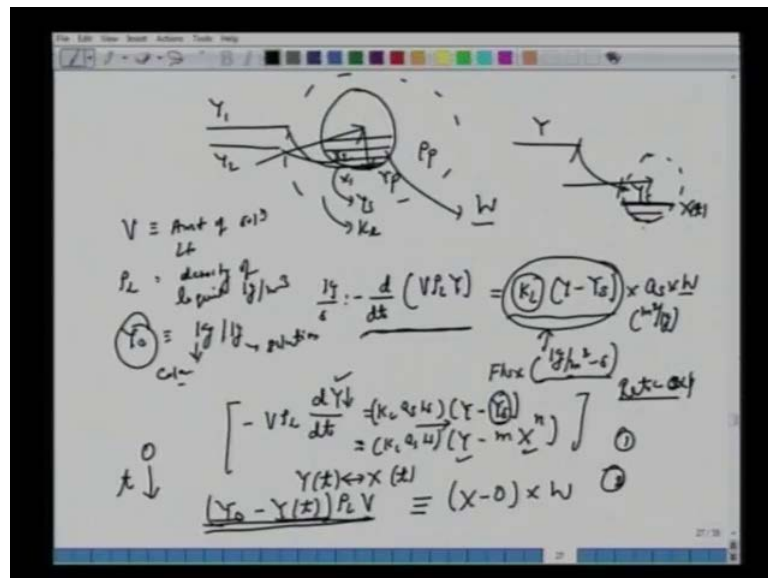
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This exercise or assumptions have two consequences: one – there is only one solid phase concentration level; no concentration gradient inside. And, number two – solid phase concentration – solid phase concentration, which is  $X$  and liquid in the case or maybe gas phase concentration,  $Y$  are given by this equilibrium –  $Y$  equal to  $m X$  to the power  $n$ , say, Freundlich isotherm. So, these are the consequences of the assumptions that this is interphase mass transfer control. So, with this assumption in our understanding, now, we

can make some calculations. Just for one more analogy, if we recall, we may have done in heat and mass transfer or just heat transfer. When we take a solid hot say solid temperature say  $t_0$  and immerse in cold water,  $T_w$ , if thermal conductivity of this metal is very large, then you will experience the same thing; the temperature will be uniform here. And, whatever drop occurs, that drop will occur across this film here. Similarly, a solid surface can also be heated. In that case and if it is say  $r_n$ , copper, very high thermal conductivity, **one temperature, one temperature, and one temperature**, all temperature gradients will be appearing only in this film transfer, which is a liquid transfer. So, this is the same analogy we are making here for this solid adsorption also. So, that is our physical understanding.

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Now, we can set up; we can make some calculations. So, let us draw this is schematic; say we have solid; say the radius is  $r_p$ , charcoal; particle density is let us say it is  $\rho_p$ , it is immersed in waste water. So, there is a film mass transfer coefficient  $K_L$ . We have certain concentration level  $Y$ , which changes with time. So, to begin with, this is fresh;  $Y$  and  $X$ . Then, it decreases and this level will increase here. So, this is  $Y_1$ ; we can write it  $X_1$ ; and, we have  $Y_2$ ; we have this  $X_2$ . And, inside, there is no concentration. So, it is all one gradient here. So, let us see how we can make this balance here.

We have – let us say  $V$  is the amount of solution. It is a batch – certain liter let us say. And,  $\rho_L$  is the density of the liquid. So, kg per cubic meter; let us say  $Y_0$  is the kg per



kg. So, this is solution; (Refer Slide Time: 41:20) and, here you have this certain impurity; let us say again it is this color. At what rate this color changes? You have  $d$  by  $d t$   $V$ , volume into  $\rho L$  into this  $Y$ . So, this is kg per second in one second; so much concentration of this water or waste water, which changes; it decreases; so, minus sign here. Why does it decrease? Because there is a mass transfer into this. How does mass transfer takes place? It is because of interphase mass transfer. So, there is  $K L$ , mass transfer coefficients; there is  $Y$  minus  $Y$  surface,  $Y_s$ . So, this  $Y_s$  is say at the surface at any time. So, we have  $Y$ ; it drops to this  $Y_s$ .

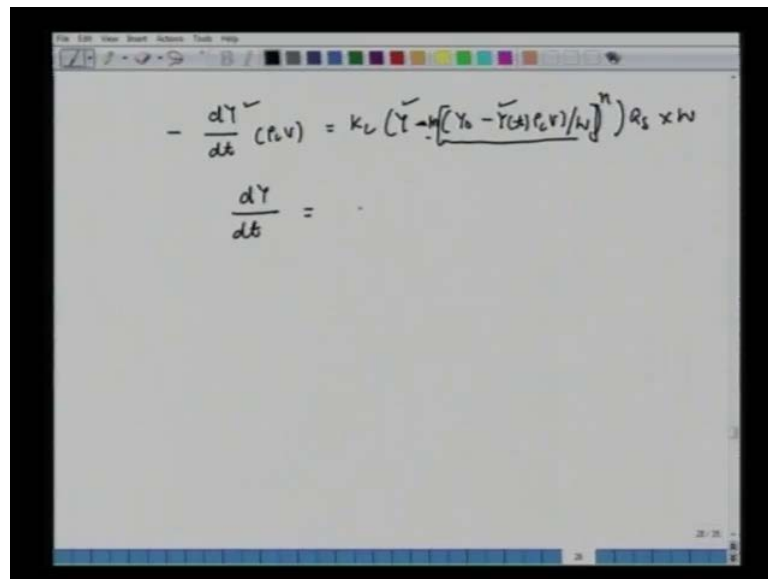
Now, before we write some other terms, let us see that what we have here. This  $K L Y$  minus  $Y X$ ; you must recall this is flux. So, let us say we have chosen this value of  $K X$ , so that the flux is kg meter square per second. Recall – earlier we used to use moles per meters square per second. So, here in case of adsorption, we are working on kg per second. So, the flux is kg meter square per second multiplied by this  $a_s$ . So, what is a  $s$ ?  $a_s$  is the external surface meter square per kg. So, this is the meter square flux (Refer Slide Time: 42:53). So, we are talking of this flux across this. So, meter square per kg multiplied by this  $W$ . What is the weight of this solid surface? This is  $W$  kg. So, see that is in kg per second, how much kg per second of colored is lost? Whatever is lost here, it is gained or it is transferred across the film to this solid surface. So, we have the flux kg per meter square per second multiplied by meter square per kg multiplied by  $W$  to make it kg per second. So, that is the solute balance.

Now, we can write as  $V \rho L$  **is** constant. So, we have minus  $d$  of  $Y$  over  $d t$  equals  $K L a_s W$ . Let us put it together here. And, we have  $Y$  minus  $Y_s$ . What is  $Y_s$ ?  $Y_s$  is surface phase concentration or concentration of solutions near this solid surface or at this solid surface. And, we said that because of the assumptions, there everything is controlled by this interphase mass transfer. And, the kinetics are faster here whether it is diffusion kinetics or **pore** diffusion kinetics.  $Y_s$  is in equilibrium with this  $X$  – solid phase concentration. So, we have let us say  $X$  here. So,  $Y$  equal to we can write  $m X$  to the power  $n$ . So, now, we have  $Y$  and  $X$ . So, one equation; but, both  $Y$  is a function of time and  $X$  – solid phase concentration is also a function of time here. So, one has to eliminate this; or, one can also make the total balance. At any instance, say we are starting with  $Y_0$ . So, at any time, if the concentration is  $Y$ , that means,  $Y_0$  minus  $Y t$ . So much **kg per color...** kg of color per amount of per kg of this solution has been transferred or has been

moved to this solid phase. So,  $Y_0$  minus  $Y_t$  multiplied by say  $\rho_L$  into  $V$ . So, this is a total amount, which has been transferred from 0 to this  $t$  time. And, where it has gone? This is gone into solid. And, solid phase initially was  $X$ ; right now it is  $X$  mole fractions kg per kg; initially, maybe it was 0;  $X$  minus 0 into  $W$ . So, this is the second equations. So, this is the rate.

It is the rate expressions. In one second, at any time, what is the rate at which this  $Y$ , this waste water concentration decreases. Why does it decrease? Because there is a transfer flux and we are saying that the **solid surface**; the two phases are in equilibrium. So,  $Y$  is equal to  $m \times X$  to the power  $n$ . But, what is  $X$ ?  $X$  is nothing but starting from 0; at any time, this  $X$  is solid phase concentration. How this concentration has increased from 0 to this? (Refer Slide Time: 46:02) Over a time of  $t$ , 0 to  $t$ , the concentration has come down from  $Y_0$  initial values to any time  $Y_t$  to make the balance. Concentration of this has increased from 0 to  $X$ ; you have  $X$  minus 0 into  $W$ .

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$$-\frac{dY}{dt} (\rho_L V) = k_L (Y - m(X - \frac{Y_0 \rho_L V}{W}))^n \rho_s \times W$$

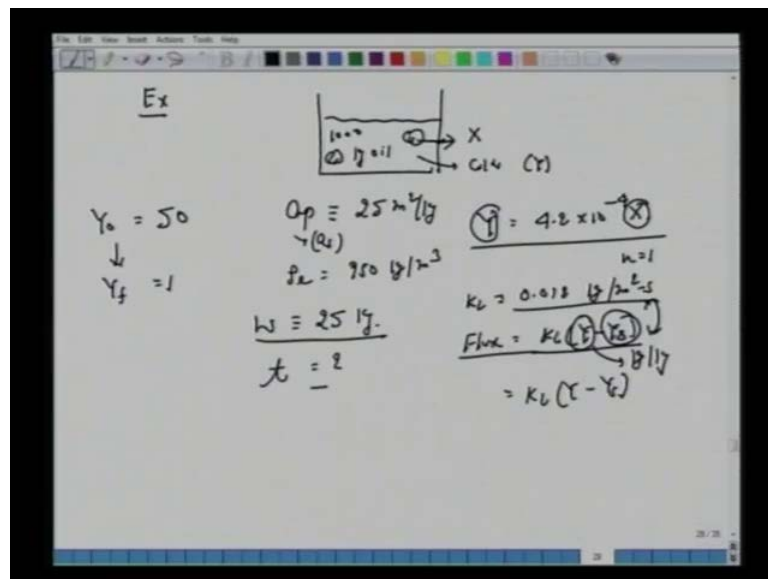
$$\frac{dY}{dt} = .$$

So, two – if you put together, now, we can set up this equation –  $dY$  by  $dt$ ; all  $d$  have  $\rho_L$  into  $V$  on the left-hand side;  $K_L Y$  minus – now, we have  $Y_0$ . So, we are replacing now  $X - Y$  minus or  $Y_s$ .  $Y_s$  was in terms of  $m$  into  $X$ . So, now, we have  $Y_0$  minus  $Y_t$   $\rho_L V$  over  $W$ . And, you have here say  $m \times X$ . So, you have  $m$ . Entire thing raise to the power  $1$  over  $n$ . So,  $Y$  minus  $m$ . And, here you have this everything –  $X$  to the power  $n$ . So, everything should put raise to the power  $n$  into we have this – a  $s$  – we have this  $W$ .

So, essentially, now, we have  $Y$ . We can write down this expression as  $dY$  by  $dt$  equals some  $a$   $Y$  minus  $C$ .

And then, (Refer Slide Time: 47:34) one can integrate with  $\int \frac{dy}{ay - c} = \frac{1}{a} \ln|ay - c| + \text{const}$ ; we can put this  $t$  here. Starting with  $0$  time, how long will it take reach this  $0$  and  $t$  here. And, we have  $Y_0$  and we have this  $Y_t$  here. So, we can have these calculations, these integrations here to calculate how long will it take to reach this concentration say  $Y_0$ ; and,  $Y_t$  is equal to maybe  $Y_{\text{final}}$ ;  $t$  equal to total time here. So, this balance; this equation; we can immediately apply.

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Let us take a very small example here. So, this example – we have the same – say this waste water. Let us say this is kg; certain kg of oil. So, 1000 kg of oil – it has certain color; say fraction is  $Y$  here. Bring in contact with the solid – some charcoal. So, this is  $X$  phase here. Let us see we have the equilibrium,  $Y$  is equal to  $4.2 \times 10^{-4}$  minus  $4X$ . So, essentially,  $n$  equal to  $1$  for our simplicity. So, kg of color per kg of solid phase; and, here we have kg of color per kg of this oil phase.

Let us say we have a  $p$  – surface area of charcoal as  $25 \text{ m}^2/\text{kg}$ . This  $a$   $p$  is same as we have used nomenclature maybe a  $s$ ;  $\rho_L$  – all densities –  $950 \text{ kg/m}^3$ . Let us say we have  $K_L$  as  $0.012 \text{ kg/m}^2 \cdot \text{s}$ . Look at this unit of this. All it means we have the flux given as this  $K_L$  into  $Y$  minus  $Y_s$ . So, this is kg per kg – one in the bulk phase and one is in the solid phase. So, we have  $K_L$  kg per

meter square per second and we have this dimensionless quantity here. So, K L is given 0.012. You have to be careful what unit is given for K L, so that you can write this flux. So, this flux is kg per meter square per second; same as this unit of K L here. Amount of W, adsorbent, which is taken here, is let us say 25 kg. Question is how long will it take to reduce the concentration level starting from  $Y_0 = 50$  to  $Y_f = 1$ ? So, this is all 50 kg per kg or unit per kg starting from  $Y_0$  to  $Y_f$ .

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The image shows a whiteboard with handwritten mathematical work. At the top, the differential equation is written as:
$$-\frac{d}{dt}(1000 \times Y) = \frac{K_L(Y - Y_s)}{1/2 \times 10^{-5}} \times a_p \left(\frac{m^4}{19}\right) \times W(Y)$$
Below this, it is simplified to:
$$-\frac{dY}{dt} = 625 \times 0.012 (Y - mX) \times 4.2 \times 10^{-4}$$
A small diagram of a tank with a stirrer and a scale is drawn on the left. The relationship  $Y = mX$  is noted. The initial condition  $Y_0 = 50$  and final condition  $Y_f = 1$  are used to derive:
$$\frac{(Y_0 - Y) \times 1000}{0.01} = X \times 10 \times 25$$
This leads to  $Y = mX$  and  $X = Y/m$ . The differential equation is then integrated:
$$\int_{50}^1 \frac{dY}{1.01687 - 0.84} = 7.5 \int_{0}^t dt \rightarrow t = 12 \text{ min}$$

Everything is given here; you can start from the fresh balance very quickly – d over dt 1000 kg – already we have – this into Y; this will be equal to K L Y minus Y s. So, this is the flux, which is kg per meter square per second – multiplied by a p, which is meter square per kg solid – into W kg here. So, this is the total balance here. All you do – you just put everything together here; you must obtain this as 625 into 0.012 Y minus Y s; and, Y s we write as m into X. So, what is this m? m is also given as 4.2 into 10 to the power minus 4 here. So, all these values are given here; K L – this is 0.02 here. a p – weight was 25 kg; a p – we have 25. So, 25 into 25 is 625 0.02; we have 1000 here. And, this number is 0.02 4.2 into 10 to the power of minus 4 here. So, with these calculations, now, again we need to replace this X. So, we have  $Y_0$  minus  $Y$  – starting here into 1000 equal to X into W – 25 kg.

Starting from time equal to t equal to 0, concentration has come down to Y – so much into 1000 kg of oil we had; so much kg has been transferred to make the concentration of

the solid phase raise from 0 to X in 25 kgs. So, all we do – we replace X in terms of all these known quantities here.  $dy$  by  $dt$  – this will be equal to – multiplied by this is  $7.5 Y$  minus  $4.2$  into  $10$  to the power minus  $4$ ; X is now  $50$ . So, this is  $50$  minus  $Y - 25$ ;  $1000$  by  $25$  – we have now  $40$ . No raise to the power  $1$  over  $n$  here. So, we have this. Simplify further – say  $7.5 \cdot 1.0168 Y$  minus  $0.84$ . You bring it down –  $dY$  over  $1.0168 Y$  minus  $0.84$ . And, here you bring this  $dt$  in this way –  $7.5$  – integrate  $0$  to  $t$ . And, here the concentration goes from  $50$  to  $1$  with the minus signs. Calculate  $t$  equal to approximately  $12$  minutes. So, we got the answer that it takes  $12$  minutes for this solid phase concentrations to build up from  $0$  to this X, (Refer Slide Time: 53:37) which have replaced. Now, you can go back and once we know the values of this Y here, the last concentrations, we say that it has to drop from  $50$  to  $1$ . So, corresponding to this  $1$ , we can write down  $Y$  equal to  $m X$ ; again X is  $1$  over  $m$ . So, whatever we have here, solid phase concentration rises from  $0$  to corresponding to this X here when the water concentration decreases from  $50$  to  $1$ ; and, it takes  $12$  minutes. Notice that this is the first order here. So, to reduce  $50$  to  $0$  or any value, very small values, it will take very long time.

All we can plot it here (Refer Slide Time: 54:19). It is the first order starting from Y  $0$  to a very small quantity. So, this example – we have chosen on batch absorptions. So, we qualify by saying that all resistances are negligible; and, it is only interphase resistance, which is predominant. So, diffusion resistance in interphase mass transfer is significantly higher. Why it is higher? Recall our previous lecture – Reynolds number is poor; maybe stirring rate is poor; flow rate is small. So, all resistance occurs across the film around this solid surface. Inside, there is no resistance or resistance is negligible; kinetic is very fast here. So, we have only **1 X** concentrations; and, this concentration increases; waste water decreases. And, all the time, at the solid surface, liquid phase or the solution phase concentrations is in equilibrium or solid phase is in equilibrium with this solution phase. So, with that approximation, it seems we can solve it analytically; otherwise, if you allow for finite rate inside by pore diffusion or by rate of adsorption, desorption, the things become more complicated. So, that maybe will be learning at higher graduate levels, where you set up this odes, partial differential equations; then, make use of certain numerical method to this kind of predictions here. For us for the third year levels, this kind of simple example for batch adsorption is good enough.

Let us sum up today's lecture. So far, we had four lectures on adsorptions. We started with very basic of adsorbents, **characterization** of adsorbents. So, we talked about **bt** area; **pore size** distributions; then, we talked about thermodynamics, isotherms – Langmuir isotherms, Freundlich isotherms; then, we said the process could be two: one is stage wise and one is column wise. In stage wise, we talked of one stage – single stage; then, multi-stage cross flow. And then, we had this countercurrent phase stage. So, these are the stage wise operations; where you say that the two leaving streams are in equilibrium. We can also have the rate processes. And, one very small example we took it in today's lecture, where we say that we have the rate whether rate is controlled by this interphase.

Now, when we meet the next time, then we take up our study on the packed bed column. So, our approach is similar to the previous example, previous unit operations on absorptions, where we have this continuous packed bed column, unlike extractions, where we had stage wise. So, adsorption can also take place in batch, where you have packed bed like this example; or, you can have a column, where there is continuously flow there. So, we have column packed with certain adsorbents – could be porous; could be non-porous; bring in contact with certain solutions, solvent or gas phase, liquid phase, which we want to treat and then monitor the exit concentrations. So, over a period of time, let us say, the concentration will be very small. Slowly it will pick up till this bed becomes saturated. Once it becomes saturated, one has to stop it and one has to regenerate it. So, this is the end of today's lecture. We will see you the next time.