Principles of downstream techniques in Bioprocess – a short course Prof. Mukesh Doble Department of Biotechnology Indian Institute of Technology, Madras Lecture – 9 Adsorption

Today am going to talk about downstream operation, it is called adsorption. So here you have a solid, that is called the adsorbent and then you have either liquid or a gas, where you have the solute or the adsorbate. So the adsorbate gets adsorbed on the solid adsorbent and that is what is called the adsorption phenomenon.

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As I said, so the solids get accumulated on to the surface and they start moving from the bulk and gets adsorbed on to the surface. So the solute could be in the liquid form or it could be in a gaseous form and the surface phenomenon.

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What is happening? So we have the adsorbate, that the material that is getting adsorbed and we have the adsorbent which adsorbs the adsorbate. So this type of adsorbent could be like silica gel, activated carbon, zeolites. So many different types of adsorbents are available nowadays in market and it can help. For example if I want to decolorize certain liquids after the fermentation, I can use an adsorption process, where the color, material, which use the color to the solution can get adsorbed. So you can get a very clear looking solution once we perform an adsorption.

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Now adsorption is an exothermic phenomenon that means when you perform this particular action, there will be a small heat that is going to get liberated. So the forces of attraction exist between the adsorbate and the adsorbents. Adsorbent is your solid, adsorbate is your solute, which could be gas or liquid and due to these forces of attraction heat is release okay.

So there are types of adsorption, that can take place and the forces of attraction involved here are like Vander Waal forces or it could be a chemical bond, also that could be a most stronger forces. So Vander Waal forces are something called non-bonded interaction, they are weak forces and the type of adsorption can be classified as physical or chemical, as you can see the name implies very clearly, physical will not have strong bond or permanent bond or a covalent bond formed, whereas in chemical adsorption there could be a bond formation.

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So two types of adsorption physisorption, it is a physical adsorption, chemisorption it is a chemiso chemical adsorption. So here you have Vander Waals forces here, it will be forming chemical bonds. The enthalpy is 20 to 40 kilo joule per mole here; we are talking almost 10 times more. This is generally adsorbed at more temperature, so if I keep increasing temperature physisorption is not favorable; this takes place at high temperature. This is not very specific.

This is very specific, you can have multiple layers of the adsorb adsorbent adsorbate formed on the adsorbents, whereas it is generally monomolecular layer. This is a reversible process and this is an irreversible process okay.

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So where do you use this type of adsorption charcoal? For example is used for decolorizing like I mentioned, you know especially you want to remove some color from liquid, then charcoal is very good ads adsorbents. Silica gel can adsorb moisture, so it is used in desiccators. Silica alumina gels are used for adsorb as adsorbent for controlling humidity of rooms. Activated charcoal is used in gas masks or removing toxic gases, sometimes even methane and So on actually.

So that it purifies the air, it can also be used for carrying out some heterogeneous type of reaction. If I am using oxidation or hydrogenation reaction using nickel or oxidation type of reactions or if I am using catalyst like platinum, hydrogenation and So on, there you come across adsorption. (Refer Slide Time: 04:35)

So what are the factors that govern adsorption? Temperature is a very very important factor, if you remember Le Chatleirs principles and if you assume the adsorption process like $A + S$ going to as that is the adsorbed material. A is your solute, S is your adsorbent, okay so low temperature favors the forward reaction, low temperature will favor the adsorption process okay. Pressure as I increase pressure, the adsorption goes up and then it will reach till saturation.

This is valid generally gaseous type of adsorption not for the liquid systems; pressure will not play much role in the liquid systems but for gaseous systems.

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Surface area if we increase surface area then adsorption also increases. Larger the surface area larger is the adsorption. How do you activate your adsorbent? We can break it into smaller pieces that is you can break the crystals. We can heat it to high temperature, we can was wash it with the acid. By doing all these we are increasing the activity of the adsorbents and thereby allowing it to adsorb more of the adsorbate.

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Different types of adsorption linear, Freundlich, Langmuir, these are the three types. We will look at them little bit in more detail and they are all governed by a theory call BET theory. Let us not go too much into that but these 3 types of adsorption takes place.

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So if I plot in the x-axis the solute concentration in the solution, we call it x, that is concentration of the adsorbate in the solution q sorry the q in the y-axis concentration of the solute in the adsorbate that is solid phase, huge the concentration of the solute in the adsorbent that is into the solid. x is the concentration of the solute in the solution okay then you can have 3 types of relationship. If it linearly vary like this, this is called linear adsorption isotherm. So q will be $=$ Kx.

K is a constant okay if we see, if we remember in your extraction, k we used to have $y=kk$ okay, k is called the partition coefficient so here that also a linear relationship. Here also when you have a linear adsorption relationship you will have $q= kx$. This is called a Langmuir adsorption relationship. So $q = q0$ $x /$ some capital $k + x$ okay. The q0 could be the maximum the adsorbate can adsorb on the adsorbent, maximum that can happen actually.

So that is why it is called q0, k is a constant here, so q =q0 x / k e + x here. So the graph will go up and the reach the saturation. The third type is called the freundlich, so the graph will be shooting up like this q =Kxn. Okay generally we do not find much of this actually. Generally we will find this and if we look at this graph at lower concentrations of the solute, this looks a linear at higher concentration of solute it is flat in mode.

So generally we find a linear relation at low concentration and at higher concentration the flattening out of this relationship or isotherm it is called. So we can see the x-axis is the solute concentration in the solution and y-axis is the amount of solute adsorbed per adsorbent okay. So the units are very different, q will have like grams of adsorbate on grams of adsorbent whereas in x it will be like grams of adsorbate per liter of the solution. That is how it will look like okay.

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So let us do a mass balance if there is a batch adsorption, so we have 2 steams coming in and 2 streams

going out. So we have a feed solution with the solute concentration xF and we have w amount of adsorbent added with concentration of solute as qF and then the solids go out w again. Now it has picked up some adsorbate, So it is q and your solution has lost some adsorbate, So it will be x which will be less than xF and the f is the concentration okay.

So we can do a mass balance $qF + f * f + xF f + qF$ w okay that is the amount of solute entering from these 2 streams, $q^*w + x^*f$ that is the amount of solute leaving out. So you have 2 streams through which the solute comes in, 2 streams through which the solute is going out and so x is the concentration of the solute in the feed, after it some of these solute got adsorbed by the adsorbent.

Okay So here again just like your extraction, if you are adding fresh adsorbent like in the extraction you are adding fresh solvent. So if you are adding fresh adsorbent qF will be zero. So you can have one term $xF = x * f by + qw$ okay that possible if you are adding fresh adsorbent here. Okay so this is the mass balance relationship for a single stage of batch adsorption.

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So if you plot that equation that is called the operating line okay, So on the y-axis as I said will be q and on the x-axis you will have the x and $q = qF + F$ by W^{*} xF - x that is the previous equation which I have shown you here know this equation, I am just rearranging it to bring q on the left hand side remaining things on the right hand side. So when you plot q verses x, you will get a straight line going down okay this is called the operating line and the equilibrium line could be the relationship between y and x. It could be $y = kx$ if it is a linear adsorption and So on actually. Okay. So this is called the operating line and the other one will be the equilibrium relationship okay.

So you can, if it is a linear you are going to have something like this $q = x Kx$, if you have going to have a Langmuir then you have $q = q0 x + capital K$ in $+ x$. If you are going to have a freundlich you will have $q=$ Kx raised to the power n. So the place where these two lines cut, that will be your the x and that will be your q, that is those are the concentrations of the solute in the liquid and the concentration of the solute in the solid, that is leaving the stage. Okay. So this is called the graphical method okay. (Refer Slide Time: 12:09)

Let us look at the small problem. If this is an usual mass balance equation because I want to calculate what should be the amount of adsorbent I should take, that is amount of solid, it could be silica gel or carbon or zeolite that I need to take okay and if I want to adsorb 90 % of whatever solute is entering. So the solute is entering here at a feed concentration okay 0.1 mg per litre and f is 1.2 litres. Now how much of w I require if I want to adsorb 90 % okay. Now am using fresh adsorbent, now qF sorry qF will be 0. So this term will be 0, so I take the mass balance equation okay and I know the xF so 10 % of the xF will be what is going out x.

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x = 0.1 * 0.1 \text{ m}g/ltr = 0.01
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xF * F + qF * W = x * F + q *W
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0.1 * 1.2 + 0 = 0.01 * 1.2 + q *W
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q = K * x
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q = 1.0 10^{.5} * 0.01
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0.1 * 1.2 = 0.01 * 1.2 + 1.0 10^{.5} * 0.01 *W
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So I will take the mass balance equation like $xF^*F + qF^*w = x^*F + q^*W$ okay. qF is 0 because am using fresh adsorbent. So x=xF is the feed that is 0.1 f is my feed quantity 1.2 90 % adsorbed. So remaining 10 % is what is coming here okay here 0.01 and $q = k$ x because I have said it is a linear adsorption equation k is given here so $q = Kx$. So instead of q here I can put kx okay and I know the x value here. So I calculate W, I end up with 108 grams. So I need 108 grams to recover 90 % of my adsorbate okay where I say it is a linear adsorption relation I have given F and I have given the W. (Refer Slide Time: 14:11)

Okay now let us look at another problem. I have a feed 1.2 litres that is f containing so much of protein. Okay that is my xF, am adding 80 cc of an adsorbent okay and I am saying it will adsorb maximum is so much moles of protein. Okay. It follows a Langmuir relationship. So you know Langmuir relationship right q=q0 x by capital $k + x k$ is given here q0 is given here because am saying maximum. So q0 is given here k is given here okay so simple. $q = q \max x / k + x$. q max is given this, k is given here and then I use a mass balance again, w^{*}q, now again I am using fresh adsorbent.

So my concentration of solute in the feed is in the adsorbent is 0. So I can adjust put them together I can calculate okay, what will be the concentration of the solute in the solution leaving. Simple. Okay it is quite an useful relationship using just the mass balance.

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Now I can have 2 stages of adsorption just like 2 stages of extraction. So each time am adding some amount of adsorbent and its fresh adsorbent that is why I have put here $qF = 0$, you can see this right. So my feed is coming here at 1 litre and the concentration of the solute is 0.1grams per cc. So some solute gets adsorbed, so same thing goes into the next one, some solute gets adsorbed. So I want to know what is the final concentration and I want to know what is the overall efficiency of adsorption okay.

So first one I do a mass balance I know the relationship and I can calculate the x1 right that is 42.8 % okay. So percentage of recovery is 42.8 % recovery, okay, now that that concentration goes here and again am adding fresh adsorbent again, I use the same mass balance equation I calculate x2 and again I calculate the overall efficiency of recovery okay. So x2 is this, x1 is this and xF is 0.1. So 0.1 it goes down to 0.057 then it goes down to 0.0326. So the overall recovery is 67 %.

So as you can see just like extraction when I move from one stage to another, this is cross flow type because every time I am adding fresh w okay fresh adsorbent improving the adsorption to fort from 42 to 67%

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Okay now I have done something interesting. So I do not add fresh, I add fresh only in the second absorber and I take this and put it there slightly complicated. So only here I am having w fresh. So qF is 0 but here qF is not zero whatever it has picked up here in the second stage is coming here, okay. So calculations are slightly tricky. So I use this same mass balance but I will have 2 equations. Then I simultaneously I will solve for q2 okay and q1 okay and I get very interesting.

So overall x1 comes out we point 0.75 x2 comes out to be 0.043. So overall recovery is 56 %. So I want to compare this with the previous problem.

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In the previous problem I am adding fresh w in both that means, totally I have added 50 cc of adsorbent and I got a recovery of 67 % but when I take the adsorbent from second adsorber and put it back into

that fast that means, am not adding fresh 25.

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What happens my adsorption efficiency is 56 %, so from 67 it has come down to 56 % but I have used only 25 cc okay. The same 25 only am using in the first. Whereas in the previous one I have used 50 cc of adsorbent, so see I have reduced the adsorbent by half and instead of 65 I have come down to about 57 % okay. So if the cost of the adsorbent is very high I would have saved quite a lot of cost okay, I would have reduced the cost into half.

So this is very very important. The previous example is almost like a cross flow okay, cross flow where I am every time adding fresh adsorbent but as whereas in this particular example am taking the adsorbent from the second stage putting it into the first stage. So this is like a counter-current adsorption just like counter-current extraction. In the previous class I talked about cross flow extraction, counter-current extraction, same thing here but the advantage as you can see is tremendous.

Am able to reduce the amount of adsorbent by half and but my efficiency has gone down little bit. So it has come down to 57 whereas in the other case it was if I add 25 cc fresh in each I get about 65 okay. So that is the advantage of doing a counter-current operation okay.

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Now let us look at continuous stirred tank adsorber. So generally your adsorbent is inside the solids they are suspended in a agitator, so you are adding a fresh feed containing some solute xF, it gets adsorbed and then it goes out and then which will have a concentration of x. So this is continuously it can happen until your adsorbent gets totally saturated at that point, you may have to stop the adsorption process and try to either drain everything and then add fresh adsorbents or add some chemical which will activate your adsorber. So this is the continuous... Okay.

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So the equations are much more complicated. You do not get scared by this. So on the left hand side we have how the concentration of the adsorbate changes with time dx/dt. v is the volume, e is called the voidage of the reactor, I mean sorry of the adsorber. So 1 - E will be the amount of solids present. 1 - E * v is the amount of solid present, $E * v$ is the amount of liquid present inside the tank, $F * xF$ is the

amount of solute that is entering, F^*x is the amount of solute that is leaving okay. xF is large, x is small because some adsorption has taken place okay then r adsorption is the rate of adsorption per volume of tank okay.

So you have input, you have output through, the flow and the liquid loses some solute on to the adsorbent. So this is the mass balance for the solute. So r adsorption we can put different equations we can put Langmuir, we can put freundlich, we can put linear or whatever if you like okay.

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Now another thing that you need to consider is some sort of a mass transfer that is taking place right because there is a the solute has to move from the solution bulk and come to the surface of you solid adsorbent. So there is a mass transfer kL a. kL is the mass transfer coefficient, a is the surface area of a adsorbent per tank volume, X is the concentration of the solute in the bulk liquid, X^* is the concentration of the solute which will be in equilibrium with the adsorbent okay.

Now this X $*$ and q are related like this q for a linear relation q =Kx $*$. So I can put here instead of x $*$ q by k. So there are two equations, one differential equation and one equation for r adsorption. (Refer Slide Time: 22:48)

So we can solve it and we can end up with this type of relation as a function of time. We can see okay how these things change okay so $q / KxF =1$ - and So on actually. Okay. - sigma 1t - sigma 2t where sigma 12 are given like this and the b is given like this that is b of here is given like this. So you do not get scared of this. So what this relationship gives you is, how q varies with respect to time. This is okay how q varies with respect to time k, k is the equilibrium constant for the linear constant, xF is the amount of solute that is entering in the feed liquid okay and so on actually.

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Let us not get scared but how q will build up like that because as the adsorbent keeps taking in solute or the adsorbate of the function of time, the concentration of the solute will go up and then finally reach the saturation and if you look at the liquid side, that is xF - x it will keep going down and finally it will reach the saturation. So after this, there is no adsorption going to take place where I need to stop my adsorption process and then I need to replace the adsorbent with the fresh adsorbent, otherwise its of no use.

So generally by this time the adsorption process is stopped and then they have to either reactivate the adsorbent or charge with the fresh adsorbent that is what is done actually okay.

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You can also have a tubular adsorption that means the adsorbent is packed in a cube and the fluid containing the solute or the adsorbate is charged inside okay as a function of time. So here it gets adsorbed here and the product will come out here in the liquid. So initially this is the fresh okay fresh adsorbent .So this every solute that is entering will get adsorbed. So you will not see any solute or adsorbate in the ff fluid that is leaving.

So after some time it will start coming out and coming out that means by that time your adsorbent is totally saturated. So this after some time it takes off, so this time is called breakthrough is called breakthrough curve because initially the adsorbent is very fresh. So all the solutes get completely adsorbed but as it gets saturated after sometime the adsorbent has no power to capture the solute. So the solute that is entering starts coming out and then finally it comes out fully.

Okay so this is called a breakthrough curve and this is the equation and this partial differential equation, where we have time here, we have z is the distance along this length and so the concentration of the solute varies as a function of length, as well as the x as well as the time. Okay. So x is the time as well as x is a function of z here.

So let us not bother too much about this relation but will think about this breakthrough. So if you look again look at the equation more in detail this is called accumulation term, this is due to flow this is due to diffusion and this is due transport of the solute from the liquid phase to the solid adsorbent. So this is how the equation is broken down lets again not bother.

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So initially the concentration of the solute coming out of the tubular adsorber will be 0 because your solute is fresh. It is adsorbing everything but after sometime it start coming out and finally everything comes out. So this is called the breakthrough time tb and this is called te exhaustion time okay complete breakthrough happens here. So this is very important breakthrough curve because you have to stop your adsorption as soon as you see some solute coming out

And then you have to recharge your tubular adsorber either put in fresh adsorber or activate it by passing some chemical to it actually. So this breakthrough curve is very very important breakthrough time is also very very important.

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So there are some relationship, this portion is called the equilibrium zone and this portion is called the adsorption zone. There are some relationship which relates equilibrium zone and the adsorption zone. (Refer Slide Time: 27:57)

Let us not bother about how they are derived but this is how there is a relationship the fraction of the bed which is loaded when there is a breakthrough is given by 1 - delta t, that means the exhaustion time - breakthrough time / 2 times breakthrough time. So the fraction of the bed is used up loaded when the breakthrough happens is 1 - te - td / 2tB. Let us not bother too much how the relationship is derived. So the adsorption zone, so this is the equilibrium zone and the equilibrium zone and this is the adsorption zone okay.

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I can use to calculate the equilibrium I can use to calculate the fraction of the bed used for this particular problem. So solute is coming at 1.3 mg per litre length is so much, epsilon is so much, fluid is coming out, k is given by 38, breakthrough is given by 6.4 hours, exhaustion time is 10 hours. So theta it is fraction of the bed is given by 1 - 10 - 6.4 / 2 times 6.4 right? That is what we do. (Refer Slide Time: 29:12)

Ok this is the equilibrium time and this is the adsorption zone. So at fraction of zone used 1 - delta t/2tB that is 72. So 72% of the bed is is totally consumed when the breakthrough happens, you would

like to have much larger and larger. So that most of the bed is used up okay. Then how do you calculate the adsorption zone, as I said this is the adsorption zone, this is the equilibrium zone. So we can calculate from this relationship, 1.3 is the flow, 10 power 6 is the exhaustion time, 6 .4 is the breakthrough time / 6.4.

So adsorption zone is 0.73 okay and 1.3 is the total length so 1.3 - 0.73 is 0.57 which is the equilibrium zone. So 0.7 0.57 is the equilibrium and 1.3, 0.57 is the equilibrium and 0.57 is the adsorption zone okay. So together it makes the 1.3 meters actually. So the relationship for calculating the adsorption zone relationship for calculating equilibrium zone is given here actually okay.

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Okay so the okay, so feed of 1.2 litres contains so much of solute that needs to be adsorbed with 20cc of fresh adsorbent. So Freundlich relationship $q = 32$ x raised to the power 1/3. So we can plot that. That will called the equilibrium here the operating line is your mass balance. So wherever they cut that will give you the x, in the amount of x in the x-axis and here it will give you the q in the y-axis. So this is called the graphical method.

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The pressure drop also we can calculate because if we have packed adsorber, you are going to pump in certain liquid here or a gas here and it has to overcome this entire bed okay. So the pressure drop will be sufficient to overcome the entire bed. So that it liquid or gas flows on the other side. So the length of the bed has an effect on the pressure drop, the velocity has a effect on the pressure drop and the diameter of the tube also will have the effect on the pressure drop.

So especially when we are talking about um packed bed adsorbers, we need to consider the pressure drop also unlike the agitated adsorber or a single batch stage adsorber. So today we talked about different types of adsorbers the batch adsorption, tubular adsorption, packed bed adsorber and stirred tank adsorber. The last 2 are continuous systems whereas the first one batch is a batch system. When using mass balance I told how to calculate the various important parameters like how much adsorbent I will require given the amount of adsorbent.

What will be the efficiency of adsorption if a multistage cross flow systems, how many stages I will require if it is counter-current system. What will be the efficiency of the adsorption and so on actually. So just by using the mass balance equations, we are able to do all these calculations and its extremely powerful and one interesting thing which we saw is the entire logic, the mass balance calculations, the cross flow, counter-current, all these they look very similar to liquid-liquid extraction.

So there are lot of similarities. So the partition coefficient k in the liquid-liquid extraction is same as the linear k in the linear adsorption isotherm. So you can see there are similarities between the stage operation of a liquid-liquid extraction with respect to a single stage adsorption you unit operation.

Thank you very much