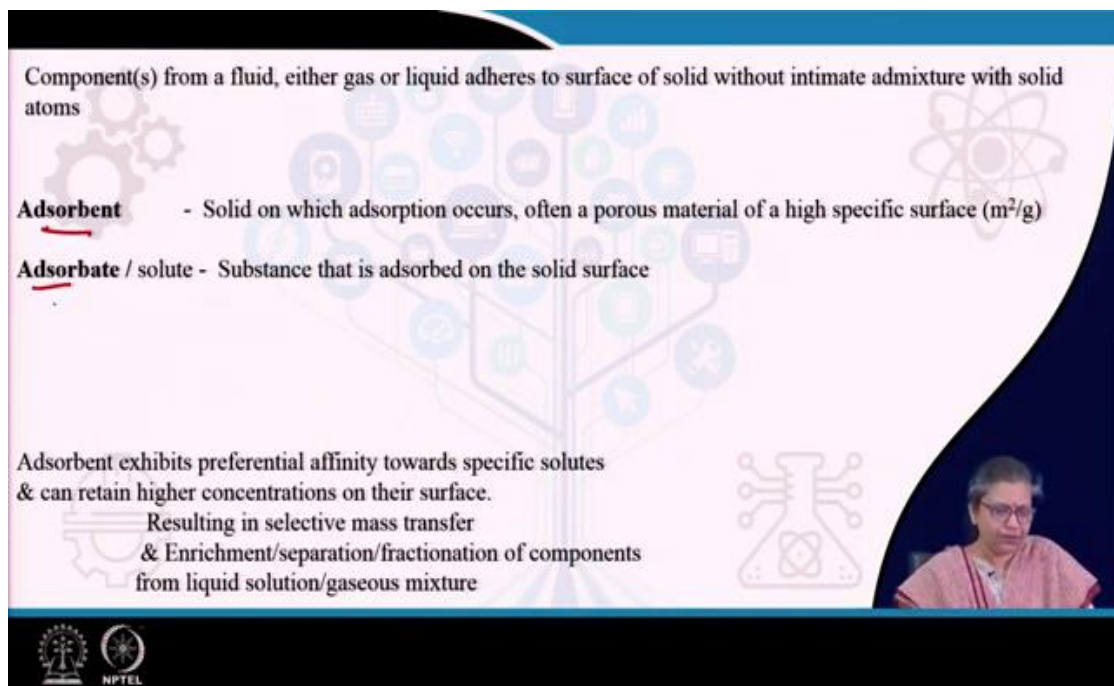


Principles and Practices of Process Equipment and Plant Design
Prof. Gargi Das
Department of Chemical Engineering
Indian Institute of Technology, Kharagpur

Module - 02
Lecture - 31
Adsorption

Well, hello everybody. After Distillation and Absorption, today we are going to discuss the process of Adsorption. As you all know the basics were discussed during the introduction part. You know that in adsorption, what do we have? We have the mass transfer in this case, either between gas and the solid or between a liquid and the solid.

(Refer Slide Time: 00:49)



Component(s) from a fluid, either gas or liquid adheres to surface of solid without intimate admixture with solid atoms

Adsorbent - Solid on which adsorption occurs, often a porous material of a high specific surface (m^2/g)

Adsorbate / solute - Substance that is adsorbed on the solid surface

Adsorbent exhibits preferential affinity towards specific solutes & can retain higher concentrations on their surface.
Resulting in selective mass transfer & Enrichment/separation/fractionation of components from liquid solution/gaseous mixture

The slide features a light blue background with faint icons of gears, a network diagram, and a molecular structure. In the bottom right corner, there is a small video inset of Prof. Gargi Das. The bottom of the slide contains the IIT Kharagpur logo and the NPTEL logo.

So, what do we do? The gas or the liquid, for example, the fluid it is brought in intimate contact with the solid and then these components among them some components on which the solids have got a preferential affinity. So, those components are more occluded on the surface of the solid. As a result of this preferential affinity towards some particular components of the fluid mixture, we get some sort of enrichment or separation or purification.

Now, it was already discussed and we will be different to these two terms during our entire discussion that is the adsorbent. The adsorbent is solid on which the adsorption occurs. Quite naturally, we know that adsorption is a surface phenomenon. So, if you have a larger surface area, then definitely adsorption is going to be better, and therefore, often we prefer a porous material of a very high specific surface area. The components which get occluded on the solid surface, they are referred to as the adsorbate.

Now, normally, what we find is that when adsorption occurs, there are different mechanisms by which the adsorption can occur.

(Refer Slide Time: 02:19)

Typical applications

<p>Liquid adsorption</p> <ul style="list-style-type: none"> - Adsorption of coloured matter from sugar solutions, & petroleum vegetable oil - Removal of objectionable taste and odour from potable water - Removal of grease from dry cleaning liquids - Removal of moisture dissolved in gasoline - Fractionation of mixtures of paraffinic and aromatic hydrocarbons 	<p>Gas adsorption</p> <ul style="list-style-type: none"> - Industrial drying/dehumidifying air and other gases - Removal of objectionable odours and impurities from industrial gases - Recovery of valuable solvent vapour from dilute gaseous mixtures - Fractionation of light hydrocarbons
---	---

In all applications, mixture to be separated is brought in contact with an insoluble solid and the preferential distribution of the adsorbate on the (solid) adsorbent leads to the desired separation

C | P

Generally, we find that the adsorption they have got a large number of applications, and primarily they are used for removal of colour, odour, or some sort of an objectionable taste from food materials or maybe from some sort of maybe separation of paraffinic and aromatic hydrocarbons.

A very important application for gas adsorption is your drying or dehumidifying of gases or maybe recovery of some particular very valuable solvent vapour from the dilute gaseous mixture. Quite naturally, we will go for this particular process, when

the relative volatilities are very less or if there is no suitable solvent to perform absorption or stripping, under these conditions we usually go for these processes.

As I have already mentioned, in all these applications the mixture from which the components have to be separated. Say we have a mixture of A + B and we would like to separate B. We have some particular solid adsorbent that has a greater affinity towards B as compared to A. So, naturally, when this particular mixture.

It is thoroughly mixed or it is brought in contact with this solid. Then this solid preferentially adsorbs B, and as a result of this particular adsorption. We get some sort of separation between A and B. Now, how much is it going to be absorbed? Again, in this particular case that is going to be governed by the equilibrium relationships.

You would be remembering that the equilibrium relationships. In this particular case, quite natural, it will be between the amount of adsorbate in the adsorbent which is usually you have shown as q and the concentration or the partial pressure of the adsorbate in the fluid mixture.

Generally, when it is a liquid solution, we express the composition in terms of concentration. When it is a gaseous mixture often in place of concentration, we prefer partial pressure. So, it can always be that it is c by p as a function of q or maybe q as a function of c or p . In any particular way, we can express it.


We have to remember adsorption. In this case, it is governed by the equilibrium adsorption isotherm which was discussed during our discussions on phase equilibrium. The best or the maximum possible adsorption that can occur is again governed by the phase equilibrium considerations or the equilibrium between the adsorbate concentration in the solid as well as in the fluid.

So, therefore, this is also a mass transfer, interface mass transfer which is governed by equilibrium considerations.

(Refer Slide Time: 05:23)

Adsorption Mechanisms	
Physisorption vs Chemisorption	
Physisorption	Chemisorption
Low enthalpy of adsorption (5–50 kJ/mol)	High enthalpy of adsorption (200–400 kJ/mol)
Reversible	Irreversible
Weak forces of attraction like van der Waals forces, hydrogen bonding, etc.	Chemical bonding involving orbital overlap and charge transfer
Multi-layer adsorption. BET isotherm used to model equilibrium.	Generally, monolayer adsorption Langmuir isotherm used to model equilibrium
Observed at low temperature (Higher temperature reduces surface coverage)	Observed at higher temperature
Not specific No surface reactions	Highly specific adsorbate-adsorbent pairs Surface reactions – dissociation, reconstruction catalysis possible

Surface condensation
Porous adsorbents
P.P
vap. fr.



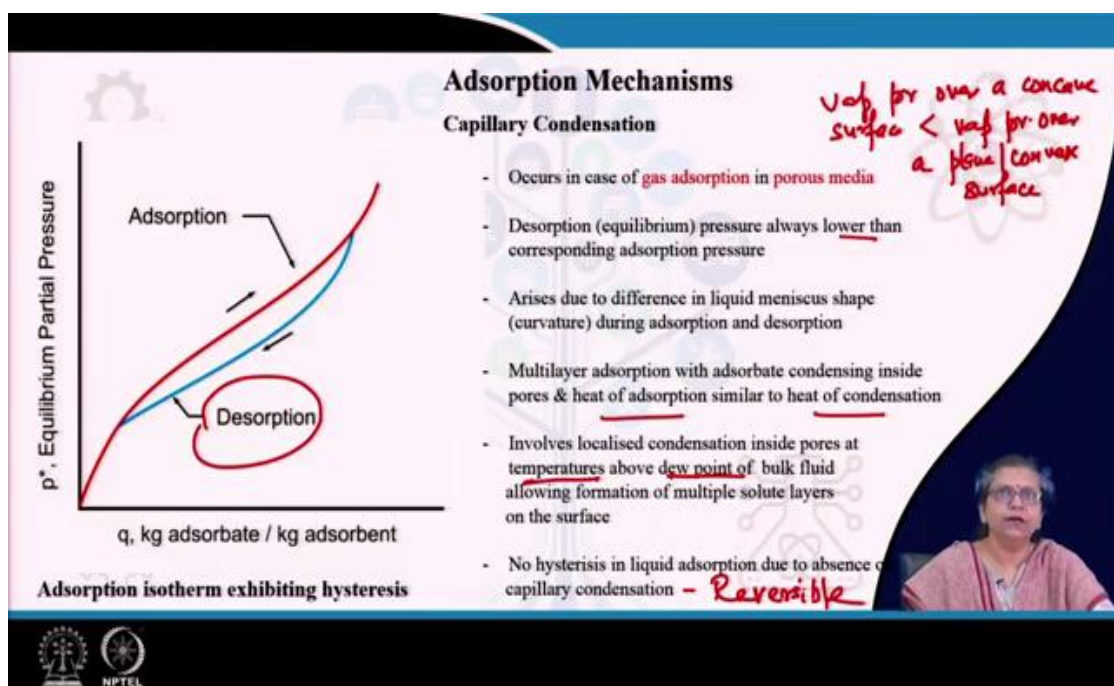
Now, how does adsorption take place? I understand there have been some basics of absorption taught to you in your mass transfer class. So, we know that there are primarily two ways by which the adsorbate is occluded or held to the surface of the adsorbent. There can either be a physical bond between them, a weak physical bond, like a van der Waals forces etc. There can also be a chemical bonding between them.

Quite naturally, if there is a chemical bonding, it is going to be stronger. It is going to be irreversible. It will be associated with a higher enthalpy of adsorption. It is very natural. When it is a physics option or when the bond is much weaker, we will be having a lower enthalpy, it is going to be reversible, and in this case normally we get multilayer adsorption. While in the case of chemisorption, we get monolayer adsorption.

Now, apart from these two mechanisms, there is also a third mechanism, the third mechanism is known as surface condensation. Any idea under what condition this takes place? What does it mean? Now, during surface condensation what happens, takes place for gas phase adsorption. Surface condensation is observed only for porous adsorbents.

We do not get surface condensation for non-porous adsorbents, and even for adsorbents where the pore size is extremely narrow on the molecular scale, under that condition also we do not get it. Now, even for a porous adsorbent for when there is a very low relative vapour pressure, or in other words, when the partial pressure by the vapour pressure, when this is very low then for a porous adsorbent where the capillaries are not too narrow on the molecular scale under that condition more or less the adsorption mechanism is the same as that for a non-porous adsorbent. That adsorption occurs by physisorption or chemisorption as the case may be.

(Refer Slide Time: 07:57)



As we increase the pressure what happens? The moment we go to increase the pressure under that condition we find that the adsorbate gets adsorbed on the solid and then it goes into the pores and inside the pores the condensation occurs. Now and when the condensation occurs inside the pores, quite naturally the heat of adsorption becomes similar to the heat of condensation. This particular process is known as capillary condensation.

Can you tell me why this occurs? Now remember one thing, this occurs even when the temperature of the bulk fluid is above the dew point temperature. So, when the bulk fluid temperature is above the dew point. So, there are no chances of condensation in the gas phase, but when this particular gas is occluded inside the

pores, what happens? The moment, it goes inside the pores, we find that there is a curved meniscus inside of the liquid which is condensing inside the pores. You need to remember that the vapour pressure over the curved surface is different as compared to the vapour pressure over a planar surface.

More importantly, the vapour pressure over a concave surface, we find that the vapour pressure is less as compared to the vapour pressure over a plane or a convex surface. Inside the pores, we find that the liquid meniscus is actually concave.

As a result, we find that the vapour pressure inside the pore is less as compared to the vapour pressure in the bulk fluid. This results in the condensation of the vapour at a pressure lower than the vapour pressure of the same gas over a flat surface. Due to this lowering of the vapour pressure, due to the curvature of the liquid surface inside the pore, capillary condensation occurs.

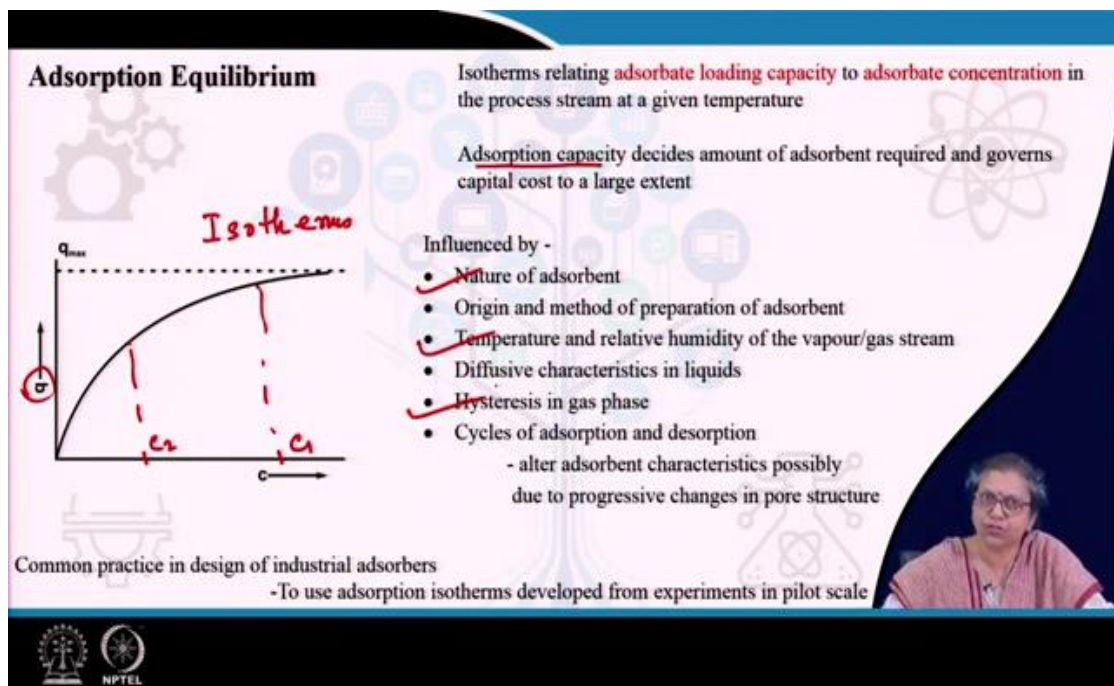
There are other very interesting phenomena associated with capillary condensation. This is also associated with the difference in the liquid meniscus shape during two particular processes is during adsorption and desorption. Adsorption means that when we start from a very low concentration, and then we keep on increasing the amount of the equilibrium partial pressure, and accordingly the amount of adsorption on the adsorbent that part also increases and we keep on going for higher and higher partial pressures.

Now, if we repeat the same experiment and try to generate the equilibrium data by lowering the partial pressure and the q correspondingly, or in other words, if we perform the process of desorption then we find that the equilibrium curve which is followed during desorption is different as compared to the equilibrium curve followed during adsorption. Every time, you will find that the desorption pressure will be always lower than the corresponding adsorption pressure as has been shown in this particular equilibrium curve.

This can also be attributed to the difference in the shape of the meniscus. Usually, during adsorption, we find the meniscus is either cylindrical or spherical, while during desorption the meniscus is always spherical. As a result, the equilibrium curve generated during adsorption is different and compared to the equilibrium curve generated during desorption.

Therefore, whenever gas phase adsorption occurs in the porous medium when the pores are not very small in the molecular scale, and the pressure is more or less moderate. We find the phenomena of hysteresis. This is not exhibited during liquid phase adsorption. As capillary condensation does not occur during liquid phase adsorption. As a result of which we find that liquid phase adsorption is more or less reversible.

(Refer Slide Time: 13:13)



Well, for every mass transfer operation, we have found that the equilibrium relationships are very important because they show that the maximum amount of mass transfer that occurs.

Definitely in this particular case, as I have shown you that if you are plotting q versus c . In other words, if you are plotting the adsorbate loading capacity as a function of adsorbate concentration in the process stream, generally these are plotted at a given temperature. Therefore, they are known as isotherms. These graphs are very important.

Because depending upon the isotherms, we know that for any particular absorption process, suppose we would like to reduce the concentration from particular c_2 the other

particular c_1 . Then, from this particular graph, once we generate, we know what will be the amount of q that will be required or rather what is the q that we have to provide.

From the q , we can find out what is the adsorption capacity or rather how much amount of adsorbent should be provided for any particular adsorption operation. Since the adsorbent is the primary cost that governs the capital cost to a significant extent.

So, therefore, the first thing like all mass transfer operations, we have to generate the adsorption equilibrium or the adsorption isotherms. We have already discussed the differential equations describing the isotherms and also the different curves etc. So, more or less, just had to recall. What are the main factors which influence the adsorption isotherm? Quite naturally, it is going to be influenced by the nature of the adsorbent. This is true for any particular mass transfer operation.

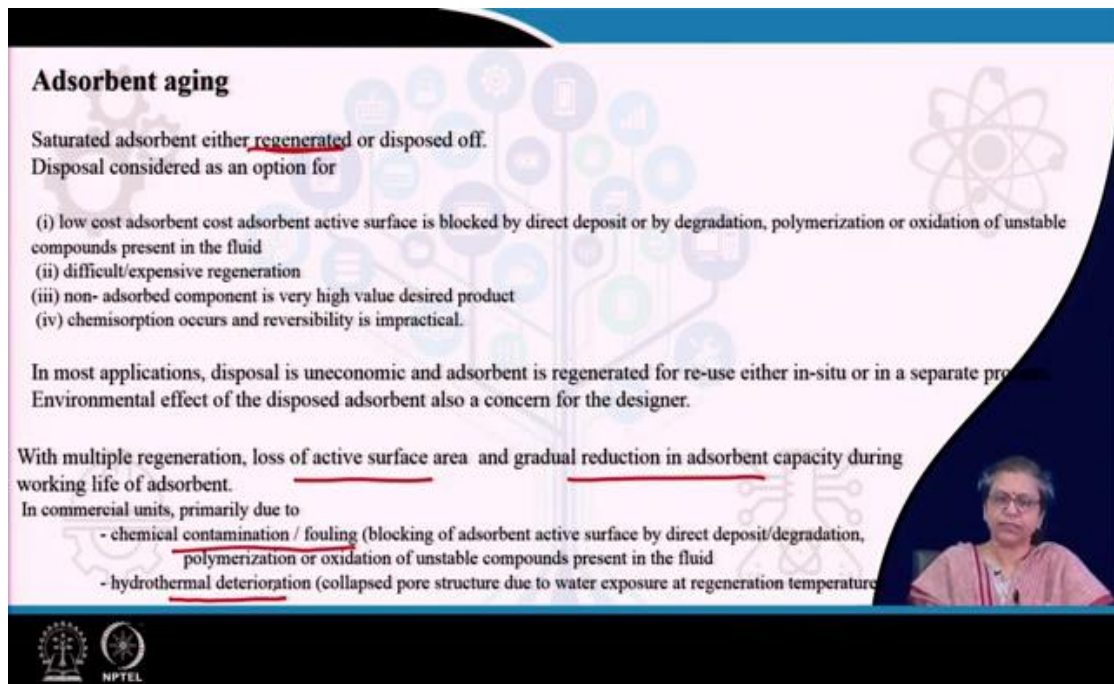
It is also going to depend upon the temperature and relative humidity of the vapour or the gas stream or also for the liquid stream. It is going to depend upon the temperature of the liquid. The other thing is, let us see the adsorbent how has been prepared. What is the source of the adsorbent? Those things also govern the structure, the molecular structure, the porosity of the adsorbent. So, therefore, this is also going to depend upon the origin and the method of preparation of the adsorbent inter.

For gas-phase, definitely, you have come to know that it is going to depend upon the hysteresis in the gas phase. For liquid phases, that the liquid has to diffuse into the adsorbent. So, the diffusive characteristics of the liquid are also going to influence this adsorption isotherm. We know that the diffusive characteristics of the liquid. They also depend on a large number of factors like temperature etc. There is one other very important thing on which this adsorption the equilibrium curve it depends.

Now, when you have an adsorbent and in that adsorbent when you are about where the adsorbate or the solute is being adsorbed, what happens? Naturally, there is more and more solute that is being adsorbed, again more and more solute will be absorbed. This continues till we reach the equilibrium concentration. Once we reach the equilibrium concentration, then no more adsorption is possible in this particular case.

Now, under that condition, what do you do? You just take the adsorbent and dispose of it.

(Refer Slide Time: 17:03)



Adsorbent aging

Saturated adsorbent either regenerated or disposed off.
Disposal considered as an option for

- (i) low cost adsorbent cost adsorbent active surface is blocked by direct deposit or by degradation, polymerization or oxidation of unstable compounds present in the fluid
- (ii) difficult/expensive regeneration
- (iii) non- adsorbed component is very high value desired product
- (iv) chemisorption occurs and reversibility is impractical.

In most applications, disposal is uneconomic and adsorbent is regenerated for re-use either in-situ or in a separate process. Environmental effect of the disposed adsorbent also a concern for the designer.

With multiple regeneration, loss of active surface area and gradual reduction in adsorbent capacity during working life of adsorbent.

In commercial units, primarily due to

- chemical contamination / fouling (blocking of adsorbent active surface by direct deposit/degradation, polymerization or oxidation of unstable compounds present in the fluid)
- hydrothermal deterioration (collapsed pore structure due to water exposure at regeneration temperature)

NPTEL

Under certain conditions, we dispose of it. Under what conditions do we perform the adsorption operation and simply dispose of it? When the adsorbent is a much more low cost under that particular condition, we would do this particular situation.

The other thing is when the regeneration method if we think of something when it is much more difficult, under that condition we would go for it. The non-adsorbed component may be of a much higher value. So, therefore, that is the desired product and that is much more expensive as compared to adsorbent. So, therefore, we do not bother about the adsorbent. We simply remove the undesirable components, and we dispose of them. We start working with the non-adsorbed component that we have done.

It can also happen that the chemist option is much stronger, as a result of which reversibility is difficult. So, under such particular conditions. what do we do? We dispose of it. But this is not an economic proposition and also there are environmental aspects of disposing of this used up adsorbent.

So, definitely for most of the cases, we do not go for disposing we go for regeneration. We would be regeneration is nothing, but dissolving the components which have been

adsorbed from the solid. So, we will be discussing since this desorption or regeneration is so very important. We are going to discuss the desorption mechanisms.

For the moment, you need to remember that whenever we go for this particular regeneration process. For with this repeated region adsorption and desorption, naturally what happens? There is some loss of the active surface area, and therefore, there is a gradual reduction in the adsorbent capacity during the entire working life of the adsorbent.

Quite naturally, why does it happen? It happens due to chemical contamination or fouling which is usually considered to be an irreversible process. There is also something like hydrothermal deterioration, where due to water exposure at the regeneration temperature, the pore structure is sort of, a collapsed pore structure occurs it is thought that this is reversible, but in practice, it is not completely reversible.

So, naturally, with every cycle of adsorption-desorption, there is some degeneration of the adsorbent capacity. Therefore, it is also very important that the adsorbent that you are using whether it is fresh or whether it has undergone different cycles of adsorption and desorption, with every cycle the characteristics are going to change because of the progressive changes in the pore structure.

So, therefore, it is quite evident that if you have generated the isotherm say for fresh activated charcoal this is not going to hold after the charcoal has gone through say 3 or 4 cycles of adsorption and desorption.

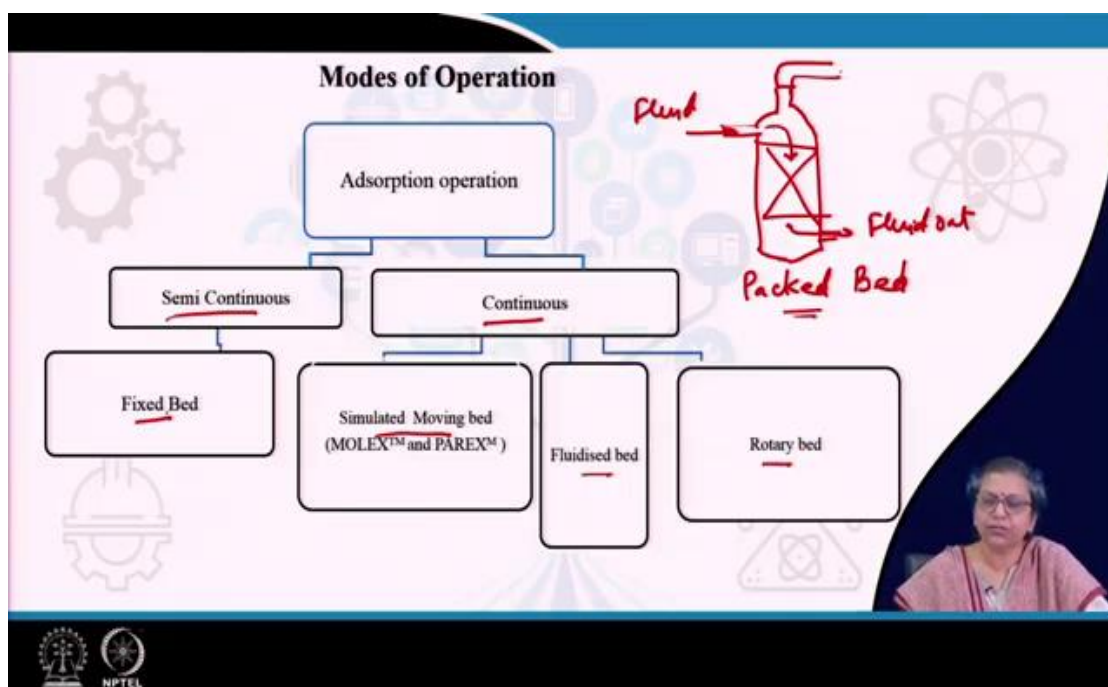
Why I am telling you so much about the factors which are influencing the adsorption equilibrium? Just to emphasize to you that due to this. Unlike solubility or vapour liquid equilibrium data, there is very less published reliable data that you can use for the design of adsorbers. Even if some data may be on gas-phase adsorption on fresh adsorbents, in liquid phase absorption there is still lesser data.

So, therefore, whenever you have to go for the design of industrial adsorbers, usually what is the conventional practice that is done? Conventional practices just before the design, experiments are performed in pilot scale to develop the adsorption isotherms with the adsorbent which will be used along with the adsorbate which has to be

adsorbed under the conditions which are close or which mimic the actual process conditions.

So, under the actual process conditions with the actual feed stream that we are going to use and the adsorbent that we are going to use. Experiments are performed to develop these isotherms, and then from the experimental data, we generate the isotherms. These are used for the design of adsorber beds.

(Refer Slide Time: 22:03)



So, therefore, more or less you have understood what is adsorption, what are the mechanisms of adsorption. Since this is a mass transfer operation, so the adsorption equilibrium what are the important parts, those things you have understood.

Now, just like all mass transfer operations, that the two phases have to be brought in contact, and then the mass transfer occurs. Just like the other mass transfer operations, the adsorption operation can also be continuous. But here we have another unique feature, we can have a semi-continuous mode of operation.

In the semi-continuous mode, what do you have? You have a packed bed through this particular packed bed the fluid is introduced through this particular packed bed. It goes through the packing remains, the packing is stationary, it does not move. The

fluid moves through the packing and then the fluid depleted from the adsorbate that comes out from here.

So, in this case, since it is only the fluid moving, the solid is in the form for a packed bed it is stationary, therefore, this is known as a semi-continuous mode of operation. Although the contact is continuous, it is a semi-continuous mode of operation. These generally take place in a packed bed. They are known as packed bed adsorption. Packed bed adsorption is the oldest and the conventional method of adsorption. We will be discussing packed bed adsorption in detail.

But it is also important for you to remember that continuous modes of operation are gaining increasing importance in modern times. Particularly simulated moving beds, where the MOLEX and the PAREX, two are the recently developed simulators that are widely used for simulating moving beds. We also have fluidized beds, and we have rotary beds. We will not be discussing these operations in detail. We will primarily be concentrating our attention on fixed-bed adsorption.

(Refer Slide Time: 24:49)

Packed Bed Adsorption

Commonly vertical cylindrical vessels to ensure symmetric fluid distribution
Opted for $Q < 1.2 \text{ m}^3/\text{sec}$.
Usually fluid flow in vertical direction
Vertically upflow during vapor phase adsorption to accommodate bed expansion
Downflow operation for liquid streams

To ensure proper flow distribution, adequate plenum space above and below packed bed/employing perforated baffle plates and inlet and outlet nozzle placed symmetrically.
Bed supported either by
(i) series of grids and screens where the screen for each upper layer has a progressively smaller opening to prevent passage of adsorbent and the screen of each lower layer has a higher mechanical strength
(ii) graded system of particles arranged from larger to smaller size
eg, typical bed for water treatment may use filter blocks at the bottom covered by smaller sized particles (commonly ceramic and gravels) and have sand as the uppermost layer.

Channeling is minimized

Diagram labels: Inlet, Liquid phase, Gas phase, Sand, Ceramic, Filter blocks, Effluent, Equal zone, Active zone, T2, C1, C2

Video inset: A woman speaking.

NPTEL

So, as I have told you that in the fixed bed adsorption more or less, we have packed bed adsorption. Usually, we take up vertical cylinders for this particular case. In this particular; when we take up the vertical cylinder usually it ensures the symmetric fluid

distribution. Particularly, when the flow rate is less than $1.2 \text{ m}^3/\text{S}$. We opt for this vertical cylindrical vessel, where the fluid flow is also in a vertical direction.

Normally, when we have a gas phase adsorption, for a gas phase or a vapour phase adsorption the fluid flow occurs in the up-flow direction, and when we have liquid phase adsorption. Then under that condition, the fluid flow occurs in the downflow mode. Naturally, for something it is very important is that we would like to avoid channelling this is quite known to you.

So, therefore, just to ensure the proper flow distribution adequate plenum spaces are left above and below the packed bed or else some perforated baffles baffle plates etcetera are used, inlet and outlet nozzles are placed symmetrically to ensure that flow distribution is proper and channelling is minimized. This is something very important because we would like to utilize the entire bed properly.

When the adsorption operation is occurring, we would not like the adsorbent to be taken away with the gas phase or to be carried away with the liquid phase. So, the bed is usually supported by several grids and over the grid, the screens are placed. So, therefore, we can have a layered sort of arrangement where for each upper layer quite naturally the opening has will be progressively smaller.

So, when we have the grid and the screen arrangement, and the screens have got progressively lower and lower of openings, as we go to upper and upper layers. What does it do? It prevents the passage of the adsorbent.

So, therefore, as we go for higher and higher screens, the screens are fitted with smaller openings. As we go down, we find that the screen of each lower layer has got a higher mechanical strength. Quite naturally because it has to support a greater weight of the adsorbent.

Usually, what do we have? Over and above this particular adsorbent, we have some larger size particles. Usually say ceramic particles or something. It not only keeps the bed in place but through these ceramic particles etc. The pressure drop definitely when we have larger particles, the interfacial area decreases, but along with that, the pressure drop is also less.

We can also have a graded system of particles which where they are arranged from a larger to a smaller size. For example, for water treatment, what we can do? At the bottom, we can use a filter. We can use at the bottom, we can use some filter blocks and above the filter blocks. We might have your ceramic or gravel particles and above this, we can have sand particles.

So, therefore, we are having 3 types of adsorbents in this particular case. For such a case, they are arranged in order of size. The larger size particles at the bottom, and then with progressively smaller and smaller sizes. This we adopt when we take up multiple adsorbents for adsorption. But when we have a single type of adsorbent, generally the adsorbent is placed between two layers of inert material of larger sizes to keep the bed in position.

Such that the and also to allow for some amount of bed expansion when the gas phase is flowing. But the expansion should not be so much that the particles are moving out from the bed. So, in this particular way, the packed bed adsorption is arranged.

Now, when we are discussing the packed bed, there is something very important that you have to think about. What is that? We find that whenever say suppose the, say suppose the liquid phase is entering. What happens? The liquid phase has got some particular initial concentration of the solute here. When the liquid phase say this is a packed bed when the liquid phase says entering from here it has a concentration of say c_i .

So, what happens? This is a packed bed. So, initially, when it comes, it comes in contact with the initial layer of the adsorbent bed and mass transfer occurs here. After this, the mass transfer occurs within a very short layer, and within this layer, the concentration drops from the initial concentration to the equilibrium concentration which will be very less.

So, therefore, after this the fluid which is flowing after this for that fluid we find it is relatively free of the adsorbed component. So, therefore, we find that the fluid which is flowing from there is the material that has to be adsorbed that gets adsorbed within a thin layer at the beginning.

And after that, the fluid is relatively free from the adsorbate it flows down and exits the absorber column. So, therefore, the effluent that comes out is relatively free of the adsorbed substance.

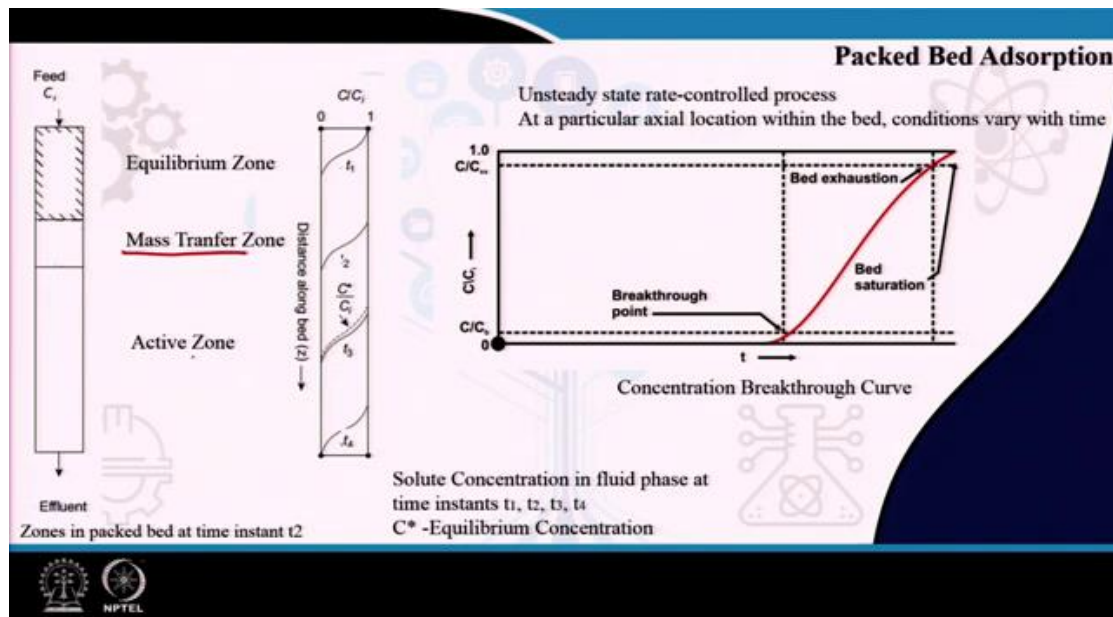
Now, after sometimes what happens? After some time, we find that in this particular zone where adsorption was occurring that that zone gets saturated. That means, the entire zone has reached an equilibrium concentration of c_e , and no mass transfer occurs in this particular zone. In other words, this zone becomes an equilibrium zone.

Then what happens? Mass transfer starts occurring over a zone just below this particular zone. Now, we find that the mass transfer occurs in a zone that is just below the equilibrium zone. Here mass transfer occurs in this particular case the concentration falls from near c_i to c_e , and after that of course, the effluent is more or less free of the adsorbed material it flows out.

So, therefore, as long as this mass transfer zone, it is there, it is quite away from the exit section. We find that subsequently as time proceeds this mass transfer zone. It gradually travels downwards. As it travels downwards, there is it leaves behind an equilibrium zone where no mass transfer is occurring or that zone it is not available for mass transfer.

This particular mass transfer zone, empty zone as it is called. This is followed by a zone where mass transfer does not occur, but it is ready for mass transfer. It is known as the active zone. The effluent which comes out that has got a very low concentration of the adsorbent.

(Refer Slide Time: 33:11)



So, at any particular point of time or any particular instant of time or maybe at any particular axial location, what do we find? At any particular axial location, we find that initially, we have the mass transfer taking place. The mass transfer takes place as long as the concentration difference is away from the equilibrium considerations.

This goes on as long as equilibrium is not reached. Moment equilibrium is reached, we find that mass transfer no longer occurs there, and the mass transfer zone has shifted to slightly lower or rather slightly after this particular portion.

So, at any instant of time, if you look at the adsorber bed, you find that the bed comprises of 3 zones. What are the 3 zones? There will be an equilibrium zone, where mass transfer has already occurred. It is no more available for mass transfer. And mass transfer will be occurring at a zone, just after the equilibrium zone. This is known as the mass transfer zone. Beyond the mass transfer zone, there will be an active zone, where mass transfer has not started, but it is capable of mass transfer.

So, with this, I will be ending this particular lecture. We will be starting up with this particular unsteady-state operation of the packed bed adsorption. We will be discussing the different concepts like the breakthrough point, the bed saturation bed, adsorption. Then, we will be discussing the details of a packed bed adsorber. Thank you very much.