

Upstream LNG Technology
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Lecture – 33
Equilibrium fluid solid separation

Welcome. Today we shall be looking into the fluid solid separation, which is used for adsorption of liquids or gases on some adsorbents. So, today's lecture is on Equilibrium fluid solid separation.

(Refer Slide Time: 00:32)

What we shall learn

- ✓ Adsorption
- ✓ Types of Adsorption
- ✓ Adsorbent characteristics
- ✓ Desirable properties of adsorbents
- ✓ Factors affecting adsorption
- ✓ Adsorption equilibria
 - Adsorption isotherm
- ✓ Adsorption operation

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Now, in this particular lecture what we shall be learning? We shall be learning about adsorption, various types of adsorption, the characteristics of adsorption, the various desirable properties of adsorbents, then the factors which affects the adsorption separation, then adsorption equilibria, their representations through isotherms and lastly we shall look into some brief about the adsorption operation.

(Refer Slide Time: 00:58)

Adsorption

- ✓ The retention of one or more components of (solute) a mixture on a solid (adsorbent) surface .
 - A **solute** from fluid phase is adsorbed by an **adsorbent**.
 - Once adsorbed, the solute is called **adsorbate**.
 - Accumulation of the solutes generally occurs in layers.
- ✓ Accompanied by release of thermal energy (heat of adsorption).
- ✓ Adsorbent capacity or loading is the amount of adsorbate adsorbed by an adsorbent.



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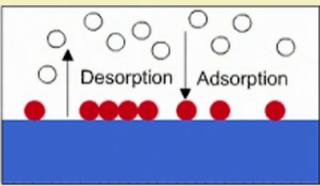


Now, first let us see what is adsorption. Adsorption is the attachment of a solute on a solid. Now the solute will can be from some liquid or it can be from some gas. The solute when it gets adsorbed its adds it is called adsorbate and the solid on which it gets adsorbed is called adsorbent. So, the accumulation of those solutes on the adsorbent happens generally in one or more than one layers.

(Refer Slide Time: 01:36)

Adsorption

- ✓ The retention of one or more components of (solute) a mixture on a solid (adsorbent) surface
- A **solute**
- Once ads
- Accumul: Adsorbate
- Adsorbent



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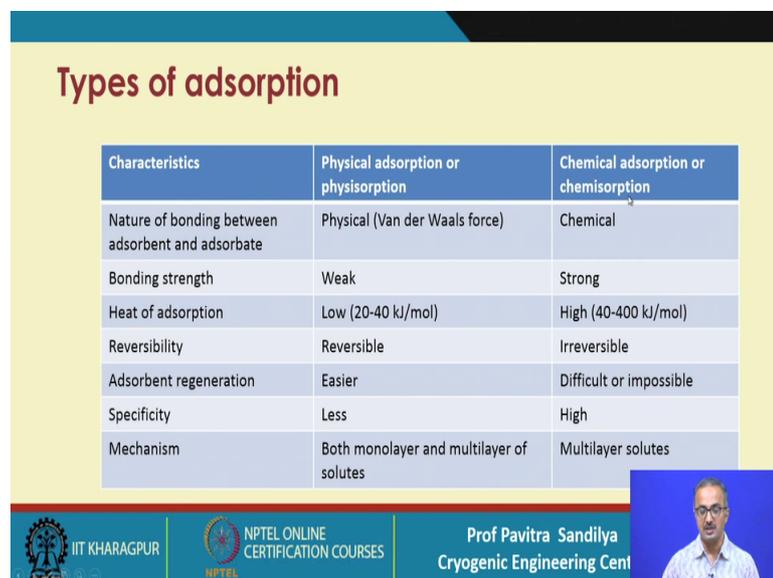


So, here is a pictorial representation of the adsorption, here we see there is a solid substrate this blue and this then we have the adsorbates given by the red balls and these

white balls are the solutes. So, these solutes are coming and sitting on the adsorbent and called adsorbate and some of these adsorbates can again go back to the fluid phase and that we call desorption.

Now, generally adsorption is accompanied by release of thermal energy; that means, there will be some kind of heating when adsorption goes on, and such kind of processes are called exothermic processes. So, adsorption is an exothermic process and we have some adsorbent capacity or what we call loading, this is the amount of adsorbate that gets adsorbed by unit mass of the adsorbent.

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The slide titled "Types of adsorption" compares physical adsorption (physisorption) and chemical adsorption (chemisorption). The table below summarizes the key differences between the two processes.

| Characteristics | Physical adsorption or physisorption | Chemical adsorption or chemisorption |
|---|--|--------------------------------------|
| Nature of bonding between adsorbent and adsorbate | Physical (Van der Waals force) | Chemical |
| Bonding strength | Weak | Strong |
| Heat of adsorption | Low (20-40 kJ/mol) | High (40-400 kJ/mol) |
| Reversibility | Reversible | Irreversible |
| Adsorbent regeneration | Easier | Difficult or impossible |
| Specificity | Less | High |
| Mechanism | Both monolayer and multilayer of solutes | Multilayer solutes |

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Here we show the two types of adsorption; one is the physical adsorption and another is the chemical adsorption. The physical adsorption in short is called physisorption while chemical adsorption in short is called chemisorption.

Now, here are the differences between these two types of adsorption; first based on the nature of bonding between the adsorbent and the adsorbate. In physisorption we have physical forces like Van Der Waal force which is a short range force; that means, only when the solute is very near to the adsorbent only then the adsorption is possible and in case of chemical adsorption, we have the chemical bonding that is there could be some kind of reaction between the solutes and the adsorbent.

In terms of bonding strength, the physisorption has weaker bonding because it is physical force whereas; in case of chemisorption due to the chemical force it is a much stronger bonding. In case for a heat of adsorption it is very low, that is about 20 to 40 kilo joules per kilo mole whereas, in case of chemisorption the heat of adsorption is higher this also means that we need more energy for desorption in case of chemical adsorption than in case of physical adsorption, and this is important when we think of regeneration of the adsorbents.

In terms of reversibility the physisorption is generally reversible, but chemisorption is generally irreversible; that means, the adsorbent can be used only once in case of chemisorption whereas, in case of physisorption the adsorbent may be reused a few times. Then the regeneration of the adsorbent is easier in case of physisorption than in case of chemisorptions. Then specificity means this is the this determines that how selective the adsorbent will be to a given solute.

So, we find that the physisorption is less specific whereas, the chemisorption is more specific and the mechanism of adsorption in case of physisorption is either monolayer or multilayer and in case of chemisorption it is generally multilayer.

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Absorption vs. Adsorption

| Absorption | Adsorption |
|--|--|
| Bulk phenomenon | Surface phenomenon |
| Surface tension force or inertial force is effective | Van der force is effective |
| Solutes distribute themselves throughout the bulk liquid (solvent) or solid phase. | Solutes attached themselves on the surface of the adsorbent. |

Adsorption + Absorption → Sorption


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Now, we know that we have some absorption and there is some adsorption, sometimes we confuse between these two.

So, here are some points based on which we can differentiate between adsorption and absorption. Now absorption is basically a bulk phenomenon; that means, the solute will go inside another liquid or solid phase and will be spread over in the whole phase.

Whereas in adsorption this is a surface phenomenon; that means, the solute will sit only when there is some surface available. The absorption is generally dictated by the surface tension force or inertial force whereas, in case of adsorption it is Van Der Waals force. Then the solute distributes themselves throughout the bulk liquid which we call solvent or a solid phase whereas, in case of adsorption, the solute attaches themselves to the surface of the adsorbent.

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| Absorption | Adsorption |
|---|--|
| Bulk phenomenon | Surface phenomenon |
| Surface tension force is effective | Surface tension force is not effective |
| Solute distributes throughout the bulk solid phase. | Solute attaches themselves on the adsorbent. |

Adsorption: Paint sticks on wall

Absorption: Sponge absorbs water

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Here is the pictorial representation that in case of absorption we find these blue colored balls are the solutes, which get spread over the whole solvent or the solid phase whereas, in case of adsorption they sit on the surface of the adsorbent. So, this is the mechanism you can see in our day-to-day life: a sponge absorbs water, and this we find then when we are painting the wall, the paint is sitting on the wall that is by adsorption.

Now when in some cases we cannot say that, specifically whether adsorption or absorption is there so, both these phenomena may occur together and then we call them absorption.

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| Major commercial applications | |
|---|--|
| Gas separation/purification | Liquid separation/purification |
| <ul style="list-style-type: none">• Separation of lighter normal or iso-paraffins from aromatics• Air separation (to produce N₂, O₂, Ar etc.)• Removal of CO, CH₄, N₂, NH₃ from hydrogen• Hydrocarbon removal from emissions• Sulphur removal from natural gas, hydrogen, liquefied petroleum gas• Dehydration of natural gas | <ul style="list-style-type: none">• Separation of heavier normal or iso-paraffins from aromatics• Separation of glucose and fructose• Deodorization of water• Water removal from organics• Colour removal from syrups, vegetable oils etc.• Sulphur removal from organics• Purification of fermentation products• Separation of detergent range olefins and paraffins |

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Now, here are some commercial applications of this adsorption. So, this adsorption is used both for gas separation or purification and a liquid separation or purification.

Here we find there are a most of applications, these are just some representative applications there are many more applications for adsorption, we find that the broad ones are like air separation to obtain nitrogen, oxygen, argon etcetera then for removal of carbon monoxide, methane, nitrogen ammonia from hydrogen. The hydrocarbon removal from emission gases, sulphur removals from natural gas, liquefied petroleum gas dehydration of natural gas and similarly we have many applications of liquid separation and purification by adsorption.

Here are some like deodorization of water, then from organic chemicals to remove water, then sulphur removal from organics purification of fermentation products etcetera.

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Major commercial adsorbents

| Adsorbent | Characteristics | Commercial uses | Strengths | Weaknesses |
|-------------------------------|---|--|---|--|
| Activated carbon | Hydrophobic surface, favours organics over air or water | Removal of organic pollutants from aqueous or gaseous effluents | Cheapest hydrophobic adsorbent, workhorse of pollution control | Difficult to regenerate if fouling occurs, may catch fire during air regeneration. |
| Carbon molecular sieve (CMS) | Separates on the basis of difference in intraparticle diffusivity | Production of N ₂ from air | The only practical adsorbent for selective adsorption of O ₂ over N ₂ | The only commercial application is in air separation |
| Silica gel | High capacity hydrophilic adsorbent | Drying of air and other gases | Higher capacity than zeolite molecular sieves (ZMS) | Not very effective if the moisture level has to be reduced to very low |
| Activated alumina | High capacity, hydrophilic adsorbent | Drying of gas streams | Higher capacity than ZMS | Not as effective as ZMS for the removal of moisture in traces |
| Zeolite molecular sieve (ZMS) | Hydrophilic surface, polar regular channels | Dehydration, air separation, separation of molecules based on size and shape | Separation of molecules based on both polarity and geometry | Lower adsorption capacity than many other adsorbents |
| Silicalite | Hydrophobic surface | Removal of organics from gas streams | Can be regenerated by burning more easily | Quite expensive |
| Polymer adsorbents | Styrene/divinyl benzene copolymer is most common | Removal of organics from gas streams | Less prone to fouling than activated carbon | Much more costly than activated carbon |

Reference :Keller GE. Adsorption: building upon a solid foundation. Chemical engineering progress. 1995.





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And in this table we find the various types of commercially available adsorbents, there are many adsorbents available and many are being developed here are some few representative ones, here we see activated carbon, carbon molecular sieves, silica gel, activated alumina, zeolite, molecular sieves, salicylate and polymer adsorbents.

This silica gel we may find in our day to day life very much like for example, when you go to purchase these water bottles at the shop, you will find that there is a small pouch kept inside the water bottle or in some case in sometimes you also find in some briefcases or boxes they have put some pouches these are nothing, but silica gel which are kept there to adsorb any kind of water present to avoid any kind of formation of any other microbes inside the vessel.

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Adsorbent characteristics

- ✓ Selectivity
 - Affinity between solutes and adsorbent
 - Intraparticle diffusion rate
 - Size of solute compared to the pore size of the adsorbent
- ✓ Adsorption capacity
 - Depends on affinity of adsorbent and specific surface area (surface area per unit mass of adsorbent).
- ✓ Porosity and pore-size distribution

| Pore classification | Pore Size range (nm) |
|---------------------|----------------------|
| micropore | <2 |
| mesopore | 2-50 |
| macropore | >50 |

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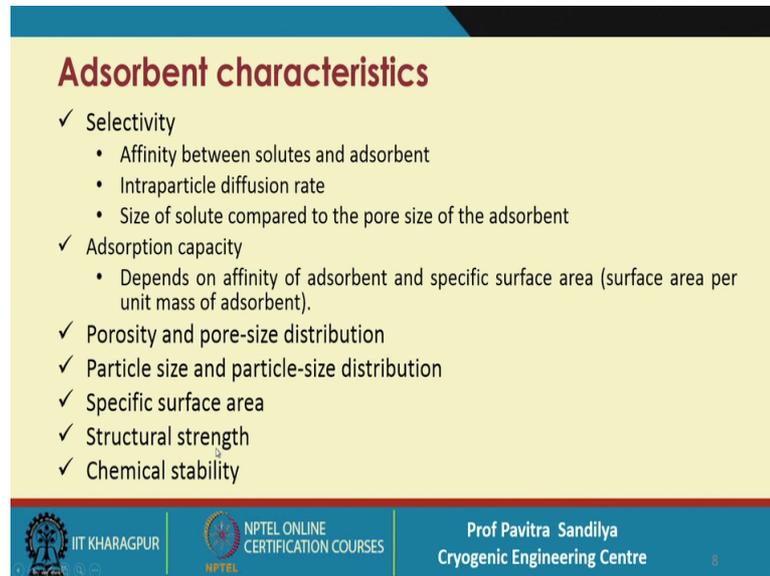
Now some of the characteristics which and therefore, adsorbents are selectivity. The selectivity means it will be attracted towards some particular solute and this is necessary for adsorption, if there is no affinity it will not be absorbed. Then there will be intra particle diffusion; that means, the there are various particles are there among the particles how one particle is diffusing through the other particles, and that will determine that how selectively that particle would be adsorbed by the adsorbent.

And then we have the size of the solute compared to the pore size, because if the pore size is smaller than the solute size the solute cannot enter inside the pores. So, it will be only on the surface of the adsorbent and these determine the selectivity of a particular solute on a given adsorbent. Then you have adsorption capacity, it means that how much loading we can have and this depends on the affinity as well as the specific surface area that is how much surface area is offered per unit mass of the adsorbent.

Then we have porosity and pore size distribution, it means that how porous the adsorbent is because if the adsorbent is non porous, then the inside of the adsorbent will not be available for adsorption. So, we need some porosity to increase the specific surface area, and pore size distribution means how uniform the pore sizes are if their pore sizes may be big and small. So, we want uniform pore sizes so, that we can be very specific about some particular type of solute.

And here depending on the pore sizes, we differentiate where the pores like we have micropores which means their sizes are less than 2 nanometer, mesopore their sizes are between 2 and 50 nanometer and macropore they are more than 50 nanometer.

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Adsorbent characteristics

- ✓ Selectivity
 - Affinity between solutes and adsorbent
 - Intraparticle diffusion rate
 - Size of solute compared to the pore size of the adsorbent
- ✓ Adsorption capacity
 - Depends on affinity of adsorbent and specific surface area (surface area per unit mass of adsorbent).
- ✓ Porosity and pore-size distribution
- ✓ Particle size and particle-size distribution
- ✓ Specific surface area
- ✓ Structural strength
- ✓ Chemical stability

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Other characteristics are the particle size and particle, size distribution if the bigger the particle the lesser the specific surface area the smaller the particle the more the specific surface area on the other hand if the particles are too small, then they will be packing too densely in a column and that will increase the pressure drop of the fluid passing through the adsorption bed.

So, we have to see that what kind of particle sizes we should be having in the adsorption bed. Then we have the specific surface area as I told you the surface area offered per unit mass of the adsorbent, the structural strength we want that the adsorbents must be enough mechanical stable so that they do not break up and get into powders, otherwise we shall be losing both their particle size as well as their porosity with which they were designed the adsorption was designed.

So, we want enough structural strength of the adsorbent particles so, that they do not get broken by the attrition during the actual operation. Then lastly we have chemical stability; that means, the adsorbent should not react with the process fluids otherwise it will lose its adsorption capacity.

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Desirable properties of adsorbents

- ✓ **High adsorption capacity at equilibrium.**
 - Lowers the required adsorbent volume, allowing for the use of smaller vessels with reduced capital expenditures and reduced heat input for regeneration.
- ✓ **High selectivity.**
 - Minimizes the undesirable removal of valuable components and reduces overall operating expenses.
- ✓ **Ease of regeneration.**
 - The relatively low regeneration temperature minimizes overall energy requirements and operating expenses.

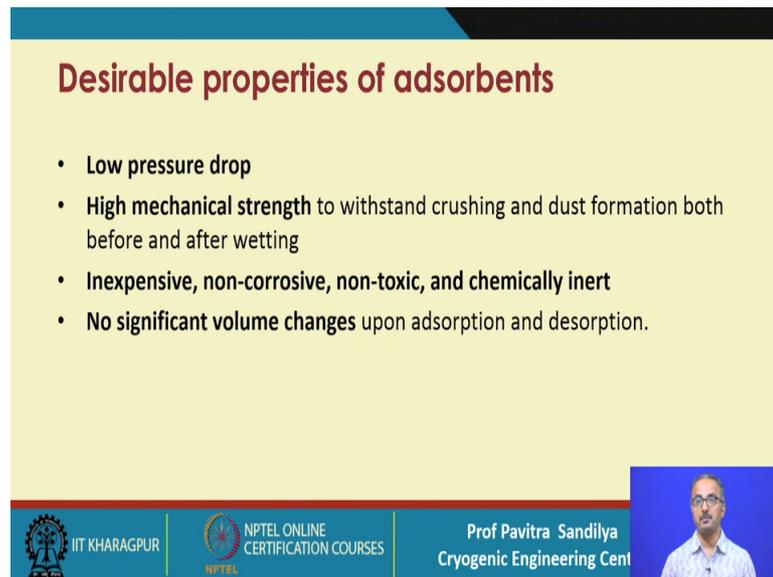
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So, desirable properties of adsorbents are that it should have a high capacity to adsorb at equilibrium, and if we have high capacity what will happen that we can lower the adsorbent volume and that will mean, that we need a smaller vessel and smaller vessel means, it will be having less capital cost.

And if and also the heat needed for regeneration will also get reduced so that we shall be saving on the energy requirement. Then we have a high selectivity that if it is highly selectable then selective then what will happen that we shall be avoiding the impurities to be going with the actual products and that will also reduce the overall expense. And ease of regeneration; that means, we want that if that the after the adsorbent has been used for some time, it gets saturated and we should be able to reuse it and for reuse we want that the solutes which were earlier adsorbed should get removed easily so, that we spend less amount of energy for regeneration the adsorbent.

So, we want that regeneration should be easy and that will reduce both the operating cost as well as the energy cost.

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Desirable properties of adsorbents

- **Low pressure drop**
- **High mechanical strength** to withstand crushing and dust formation both before and after wetting
- **Inexpensive, non-corrosive, non-toxic, and chemically inert**
- **No significant volume changes** upon adsorption and desorption.

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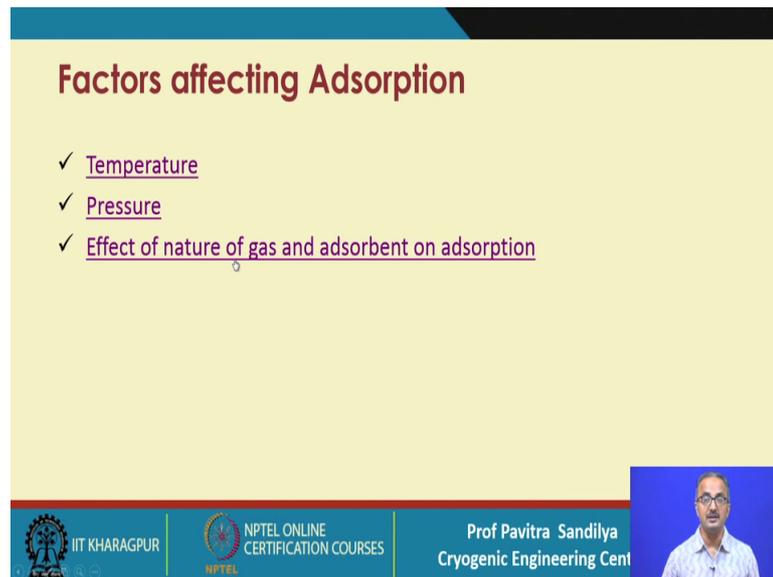
Then there should be low pressure drop, pressure drop means it translates into the pumping power or the compression power. So, we should have low pressure drop to the bed, then a high mechanical strength as I explained that they should not lead to any kind of dust formation by crushing and these should be inexpensive, non corrosive nontoxic and chemically inert.

And during their adsorption and desorption, there should not be any significant change in the volume otherwise we shall find that all the other properties like the specific surface area etcetera every the porosity, everything will get changed. So, we do not want any kind of volume change during this adsorption and desorption.

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Factors affecting Adsorption

- ✓ Temperature
- ✓ Pressure
- ✓ Effect of nature of gas and adsorbent on adsorption



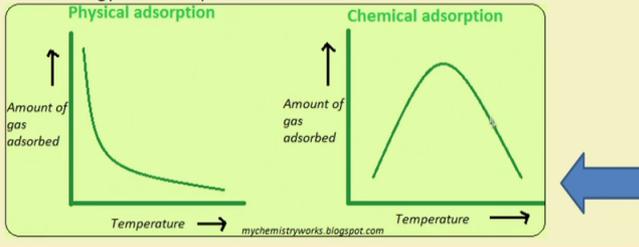
The slide features a yellow background with a blue header and footer. The title 'Factors affecting Adsorption' is in red. Below it, three bullet points are listed, each with a checkmark and underlined text. The footer contains logos for IIT Kharagpur, NPTEL, and the speaker's name and affiliation.

Now, what are the various factors which affect the adsorption? So, first factor is a temperature let us see how temperature affects.

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Temperature effect on adsorption

- ✓ Favored at low temperature.
- ✓ For chemisorption, initially higher temperature is needed to supply the activation energy for adsorption.



The slide features a yellow background with a blue header and footer. The title 'Temperature effect on adsorption' is in red. Below it, two bullet points are listed, each with a checkmark. The main content consists of two side-by-side graphs. The left graph is titled 'Physical adsorption' and shows a curve where the amount of gas adsorbed (y-axis) decreases as temperature (x-axis) increases. The right graph is titled 'Chemical adsorption' and shows a curve where the amount of gas adsorbed (y-axis) increases to a peak and then decreases as temperature (x-axis) increases. A blue arrow points from the right graph towards the left graph. The footer contains logos for IIT Kharagpur, NPTEL, and the speaker's name and affiliation.

Here are the temperature effects; we find that adsorption is favored at low temperature and this chemisorption and physisorption, so, different characteristics and dependency on the temperature. We find for physisorption we find that as we increase the temperature, we find the amount of gas adsorbed starts decreasing.

So, there is a continuous decrease in the amount of adsorption with increase in the temperature. Whereas, in case of chemical adsorption we find that initially the rate of adsorption increases and then after reaching some maximum, it starts decreasing. Now this behavior is because that initially we need some amount of activation energy for the chemical reaction to take place and that can happen only at higher temperature.

So, by when we initially the by raising the temperature, we are able to achieve the activation energy for chemical reaction chemical bond formation and once it has been done, then we find after further increase in temperature there is no more of adsorption and their adsorption start decreasing.

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Pressure effect on adsorption

- ✓ High pressure favors adsorption
- ✓ Pressure reduction causes desorption of already adsorbed species.

Temperature constant

Amount of gas adsorbed

Pressure

mychemistryworks.blogspot.com

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Next factor is the pressure the increase of pressure we find that the adsorption is favored at high pressure.

So, in case of both physisorption and chemisorptions, as we increase the pressure we find that the amount of the solute adsorb also start increasing and in this case we are keeping the temperature constant. Next is the effect of the nature of the gas and the adsorbent.

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Adsorption equilibria

- ✓ Determines the maximum amount of solutes that may be adsorbed on the adsorbent (saturated capacity of an adsorbent) at a given set of operating conditions.
- ✓ Dictated by temperature and pressure.



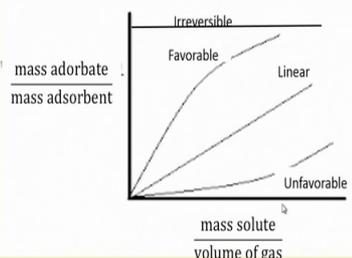
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In this case we find that the nature of the gas impacts in a way that it affects.

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Effect of nature of gas and adsorbent on adsorption

- ✓ Nature of gas:
 - Easily liquefiable gases also get adsorbed easily by physisorption.
 - Chemisorption occurs only if the gas can bond chemically with the adsorbent.
- ✓ Nature of adsorbent:
 - Higher surface area and higher porosity of adsorbent increases adsorption.



$\frac{\text{mass adsorbate}}{\text{mass adsorbent}}$

$\frac{\text{mass solute}}{\text{volume of gas}}$

Irreversible
Favorable
Linear
Unfavorable



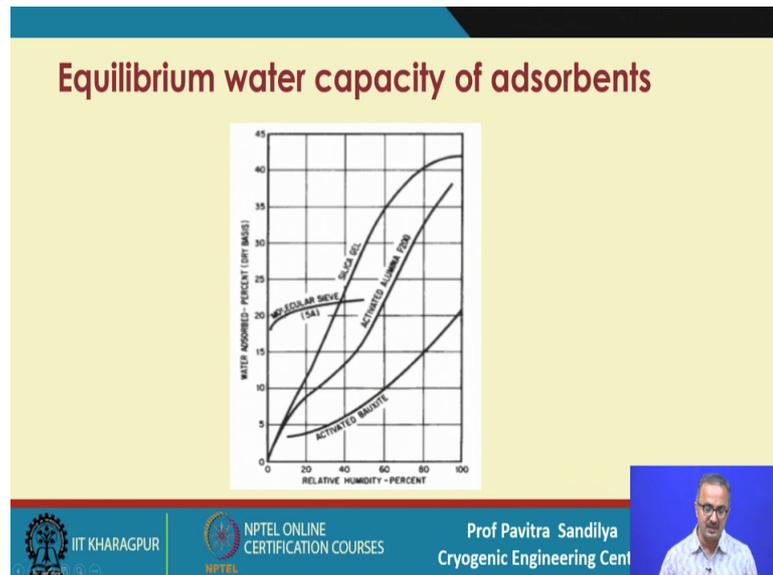
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The adsorption a way that those gases which can get liquefied easily have been found also could to get adsorbed easily because liquefaction is one way of deposition of the solutes on some surface.

So, any gas which is which can be liquefied easily can also get adsorbed easily, and chemisorption occurs only if the gas can bond chemically with the adsorbent and nature of adsorbent means the adsorbent should have high surface area and high porosity for

higher adsorption. And here we see in this particular graph that on the x axis we are having the solute concentration, on the y axis we have the adsorbent loading, and we find that depending on the type of the solute and the particular adsorbent, we have having different types of adsorption characteristics about which we shall be learning later.

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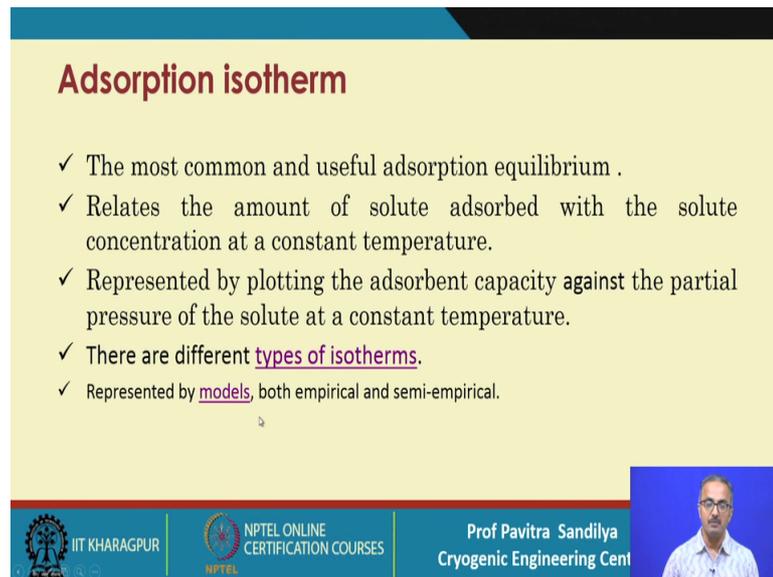


And here in this particular graph we show that how that all water gets adsorbed on different types of adsorbents. Here we have different adsorbents which are represented by different curves; first we have activated bauxite, then activated alumina, silica gel and molecular sieve. So, water can be adsorbed in any of these adsorbents and we find that all of them are showing different characteristics; in this case we find that for a higher concentration of water, silica gel shows the best performance.

Whereas in case of the lower concentration of water, we find molecular sieve is showing very good performance. So, these are the curves which are generated experimentally to select a given adsorbent for adsorbing some particular solute. After learning the factors now we come to the adsorption equilibria. Now water at the equilibria? They determine the maximum amount of solutes that may be adsorb under some given operating conditions decided by the temperature and the pressure.

So, what is the maximum amount that can be adsorbed that is given by the adsorption equilibria.

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Adsorption isotherm

- ✓ The most common and useful adsorption equilibrium .
- ✓ Relates the amount of solute adsorbed with the solute concentration at a constant temperature.
- ✓ Represented by plotting the adsorbent capacity against the partial pressure of the solute at a constant temperature.
- ✓ There are different **types of isotherms**.
- ✓ Represented by **models**, both empirical and semi-empirical.

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And there are various ways of representing the equilibria, one of the most common ways is the adsorption isotherm. As a name signifies that it is related to the constant temperature isotherm that is constant temperature and at constant temperature we try to relate the amount of solute adsorbed with the solute concentration in the fluid.

And we shall see how we can get these things and these adsorption isotherms are obtained by plotting the adsorbent capacity against the partial pressure of the solute this partial pressure is nothing, but a way to denote the concentration of a solute in a fluid. So, when we plot the adsorbent loading with the partial pressure at a constant temperature, we get the adsorption isotherm.

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Basic types of adsorption isotherm

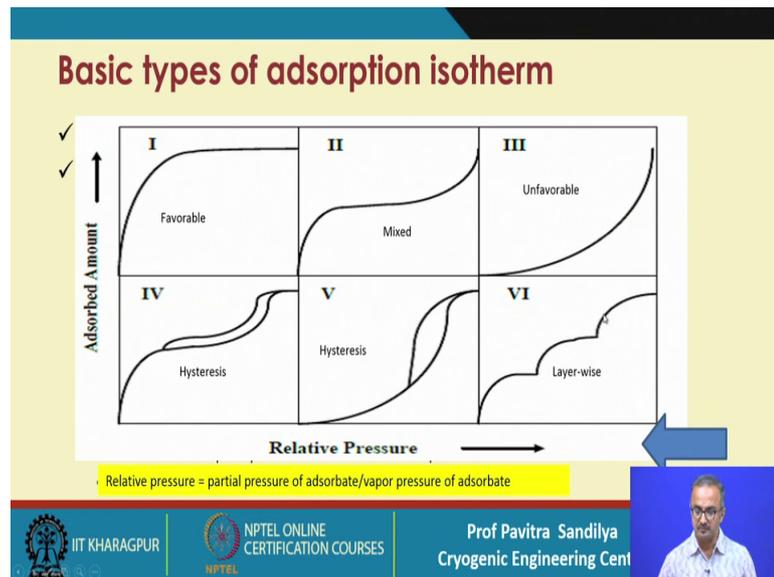
- ✓ Many shapes are possible depending on the forces involved.
- ✓ Brauner empirical classification into following types:
 - Type I – Favorable adsorption:
 - Due to monolayer formation.
 - High adsorbate loading at low solute concentrations
 - Type II – Mixed adsorption:
 - Monolayer adsorption followed by multilayer condensation
 - Type III – Unfavorable adsorption:
 - Stronger adsorbate-adsorbate interactions than adsorbate-adsorbent interactions.
 - Types IV and V – Hysteresis
 - Due to capillary condensation in the mesopores
 - Type VI – Multilayer adsorption-condensation

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There are various types of actions possible and we show a few basic types of isotherms and these isotherms can have different types of shapes, a browner proposed some of this isotherms we classified this isotherms into few groups.

We shall be checking those groups, and they have been grouped in different types Type I, Type II, Type 111, Type IV, Type V and Type VI, these are named as favorable adsorption, mixed adsorption, unfavorable adsorption hysteresis and multilayer and these are characterized by the number of layers formed on the adsorbent and the type of loading characteristics they show by virtue of this number of layers formed.

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So, here we were see that how they are represented pictorially. So, we find this is a favorable unfavorable isotherm by favorable, because we find that the amount adsorbed becomes very high for a small change in the solute concentration and this is mixed because, here we find initially it is favorable and then it goes to unfavorable, and this is totally unfavorable and here we have hysteresis; hysteresis comes because during the adsorption some solid particles may enter which we call capillary condensation.

So, due to this capillary condensation the solute particles enters the adsorbent adsorbents and while we are trying to regenerate it, they may not be able to come out of the adsorbent body, due to not enough force to take to dissolve themselves from the solid that network, inside the adsorbent particles. So, that is why we obtain hysteresis in case of this adsorption and regeneration.

And next we have layer wise type six layer wise, in this time we say that the adsorption goes on in layers after layers. So, each of these are representing the formation of different layers. Next all these isotherms can be modeled by various manners and some of these models are either empirical or they are semi empirical and these are some of the models.

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Commonly used isotherm models

- ✓ Freundlich isotherm (empirical)
- ✓ Langmuir isotherm (semi-empirical)
- ✓ BET isotherm (semi-empirical)

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So, these are some of the models which are very common otherwise in literature you will find there are many other isotherms proposed by different workers.

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Freundlich Isotherm

- ✓ Assumes formation of mono-layer on adsorbent surface.
- ✓ Works well at low pressure, but not at higher pressures.

$$q = kp^{1/n}$$

- q : Adsorbate loading
- p : Partial pressure of the solute being adsorbed
- k and n : empirical constants
 - Depend on the nature of the solid and adsorbate, and on the temperature.

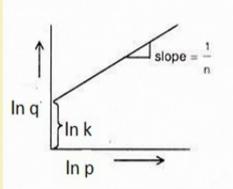
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So, one is Freundlich Isotherm, which is given by this particular expression q is the adsorbate loading and p is the partial pressure, k and n are some kind of parameters and this assumes that there is mono layer formation on the adsorbent surface. So, our intention is to figure out the value of this k and n from the adsorbent data.

(Refer Slide Time: 22:39)

Freundlich Isotherm

- ✓ Taking logarithm on both the sides we get,
$$\ln q = \ln k + \frac{1}{n} \ln p$$
- ✓ Plotting $\ln q$ against $\ln p$, a straight line may be fitted. Values of n and k may be obtained from the slope and intercept of this straight line.



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So, what we do to get the value of k and n we take the log on both sides, and now we find that $\log q$ becomes a linear function of $\log p$; that means, if we plot $\log q$ versus $\log p$ and put make a regression analysis on the experimental data, to plot a straight line then we will find the slope of the straight line is $1/n$ whereas the intercept is $\log k$.

So, this way we can find out the value of the k and n and then we using the k and n we can predict the adsorbate loading for different solute concentrations, for that particular adsorbent solute pair under different conditions. Similarly we go to the another type of isotherm this also be popular Langmuir isotherm.

(Refer Slide Time: 23:29)

Langmuir Isotherm

$$q = \frac{ap}{1 + bp}$$
$$\frac{p}{q} = \frac{1}{a} + \left(\frac{b}{a}\right)p$$

- ✓ The parameters a and b can be obtained from slope and intercept by fitting a straight line to p/q vs. p plot.
- ✓ Langmuir isotherm works better at higher pressures.



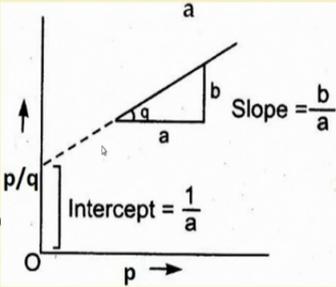
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Which is semi empirical and this isotherm is given by this particular equation this can be derived also theoretically to some extent with some assumptions without going into derivation; we see this is the nature of isotherm and we if we rearrange this isotherm in this fashion, we again find that p by q becomes a linear function of p .

(Refer Slide Time: 23:54)

Langmuir Isotherm



- ✓ The parameters a and b can be obtained from slope and intercept by fitting a straight line to p/q vs. p plot.



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So, if we plot p by q versus p like this we again we can do regression to fit a linear curve through these experimental points, we find that this slope of this line will be b by a and the intercept will be 1 by a from this we can figure out the value of a and b for the

Langmuir isotherm and Langmuir isotherm; has been found to work better at higher pressures.

(Refer Slide Time: 24:28)

BET (Brunauer, Emmett, and Teller) Isotherm

$$\frac{P}{v(p^{\text{sat}} - p)} = \frac{1}{v_m Z} + \left(\frac{Z - 1}{v_m Z}\right) \frac{p}{p^{\text{sat}}}$$

where v : the volume, reduced to standard conditions of gas (or vapor) adsorbed at system pressure P and T per unit mass of the adsorbent
 p : the partial pressure of adsorbate
 T : the temperature
 p^{sat} : the vapor pressure of the adsorbate at temperature T
 v_m : the volume of gas (or vapor), reduced to standard conditions, adsorbed when the surface is covered with a unimolecular layer
 Z : A constant at any given temperature.

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Next we come to another isotherm that is BET isotherm, this is also semi empirical the name it is derived from the name of names of three scientists Brunauer Emmett and Teller and this is the particular type of isotherm equation they are proposed in this equation we have p as the pressure, p^{sat} as the saturation pressure of vapor pressure and v is the volume reduced to a standard conditions for per unit mass of the adsorbent; that means, volume of the solute adsorbed per unit mass of the adsorbent that is the adsorbent loading.

But loading we defined in terms of mass of solute in this case we are define in terms of volume of solute, and then we have the v_m as the volume of gas reduced to a standard conditions when the surface is covered with a unimolecular layer, and Z is the is the constant given at any given temperature.

(Refer Slide Time: 25:25)

BET isotherm

- ✓ The constant c is approximately given by

$$Z = \exp[(\varepsilon_a - \varepsilon_l)/RT]$$

where ε_a : The enthalpy of adsorption of the first adsorbed layer due to interaction between the surface and the gas, and
 ε_l : The enthalpy of liquefaction (or condensation) of the gas (or vapor).



So, many of these parameters have to be found experimentally and Z is given in terms of some enthalpy of adsorption and enthalpy of liquefaction or condensation.

(Refer Slide Time: 25:38)

BET isotherm

- ✓ When only n layers of gas can be adsorbed on a surface, BET isotherm is modified as

$$v = \frac{[v_m z (p/p^{sat})] [1 - (n+1)(p/p^{sat})^n + n(p/p^{sat})^{n+1}]}{[1 - (p/p^{sat})] [1 + (z-1)(p/p^{sat}) - z(p/p^{sat})^{n+1}]}$$

- ✓ The two BET isotherm equations yield similar result for $n > 4$ when the gas pressure is less than $0.4 p^{sat}$.
- ✓ For larger values of n , the two results become identical.



So, these are the parameters which we need to estimate the loading, and this is another expression for the bet isotherm itself, but this assumes n layers of the solids getting formed on the adsorbent. So, this is also very popular and the previous one was for monolayer this is for n number of layers and these two bet isotherm equations yield

similar result for n more than 4, when the gas pressure is less than 0.4r into p sat that is 40 percent of the saturation pressure.

(Refer Slide Time: 26:13)

Gas Adsorption Parameters for BET Relationship

| Adsorbent | Adsorbed gas | Temperature (K) | v_m (m ³ /kg) | ϵ_a (kJ/kg) | ϵ_1 (kJ/kg) | $(\epsilon_a - \epsilon_1)$ (kJ/kg) |
|------------------------------------|------------------|-----------------|----------------------------|----------------------|----------------------|-------------------------------------|
| Silica gel | N ₂ | 90.1 | 0.127 | 300.054 | 181.429 | 118.626 |
| Silica gel | N ₂ | 77.3 | 0.135 | 305.869 | 198.408 | 107.461 |
| Silica gel | A | 90.1 | 0.122 | 424.030 | 361.693 | 62.337 |
| Silica gel | O ₂ | 90.1 | 0.132 | 289.354 | 212.596 | 76.758 |
| Silica gel | CO | 90.1 | 0.132 | 345.876 | 200.269 | 145.607 |
| Silica gel | CO ₂ | 195 | 0.102 | 700.126 | 573.126 | 127.000 |
| Charcoal | H ₂ O | 282.8 | 0.185 | 2326.011 | 2477.190 | -151.179 |
| Charcoal | H ₂ O | 257.8 | 0.185 | 2581.860 | 2581.860 | 0.0 |
| Charcoal | N ₂ | 77.3 | 0.182 | 287.494 | 198.408 | 89.086 |
| Charcoal | N ₂ | 90.1 | 0.173 | 279.818 | 181.428 | 98.390 |
| Charcoal | A | 77.3 | 0.216 | 491.949 | 421.006 | 70.943 |
| Charcoal | A | 90.1 | 0.216 | 440.079 | 361.693 | 78.386 |
| Charcoal | O ₂ | 90.1 | 0.235 | 262.605 | 212.596 | 50.009 |
| Charcoal | CO | 90.1 | 0.180 | 273.538 | 200.269 | 73.269 |
| Cr ₂ O ₃ gel | N ₂ | 90.1 | 0.0505 | 291.680 | 181.428 | 110.252 |

Now these are this is the table from which we can get the various parameter values the v_m , epsilon, epsilon 1 etcetera for different types of adsorbent solute combinations like here we have silica gel nitrogen silica gel nitrogen for different temperatures. So, with temperature difference also we find the these values of the parameters also change. So, we have silica gel carbon dioxide, charcoal argon then charcoal carbon monoxide. So, this is the table which can be used as a two estimate the salute loading from the BET isotherm.

(Refer Slide Time: 26:53)

Multicomponent adsorption equilibrium

- ✓ More than one component get adsorbed simultaneously.
- ✓ A Langmuir-Freundlich combined model may be used.
- ✓ For the adsorption of i -ith component

$$q_i = q_{im} \frac{b_i p_i^{n_i}}{1 + b_1 p_1^{n_1} + b_2 p_2^{n_2} + \dots + b_i p_i^{n_i} + \dots}$$

Where p_i : partial pressure of component i



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Now, we go to multi component adsorption, in this case we mean that when more than one components are getting adsorbed and in this we just modify the Langmuir Freundlich in this way that, we put this in the loading of the i th component when there are all the components have the tendency to get adsorbed and we put this in terms of this equation. This is we find that the combination of the both Langmuir and Freundlich and this you know this n_1 n_2 etcetera and the b_1 b_2 etcetera may be estimated from some experimental data.

(Refer Slide Time: 27:30)

Adsorption operation

- ✓ Thermal Swing Adsorption (TSA)
 - Adsorption at lower (near-ambient) temperature
 - Desorption at higher temperature
 - Used only for both liquid and gas purification
- ✓ Pressure Swing Adsorption (PSA)
 - Adsorption at higher than atmospheric pressure
 - Desorption at atmospheric pressure
 - Used only for gas separation or purification
- ✓ Vacuum Swing Adsorption (VSA)
 - Adsorption at atmospheric pressure
 - Desorption at lower than atmospheric pressure
 - Used only for gas separation or purification



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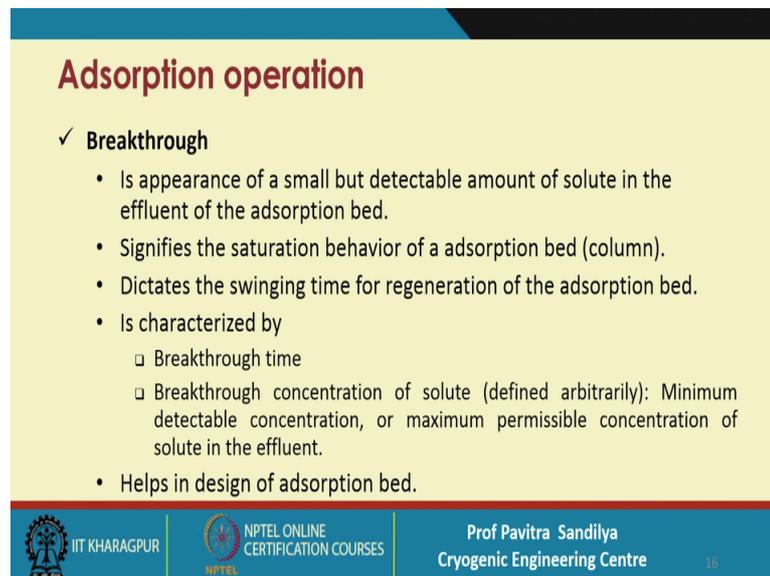
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Next we come to the adsorption operation, in this operation we have different ways of operating a carrying out the adsorption, we have thermal swing adsorption, we have pressure swing adsorption and we have vacuum swing adsorption, and these have been differentiated by the way the adsorbents are regenerated. In case of TSA we find that the regeneration is done by increasing or heating the adsorbent. The in case of PSA the regeneration is done by lowering the pressure of the adsorbent, in the VSA also we lower the pressure.

The difference between PSA and TSA are that, in case of PSA adsorption is done at a pressure higher than atmospheric whereas, desorption is done at a pressure at atmospheric pressure whereas, in case of VSA adsorption is done at atmospheric pressure. Whereas, regeneration or desorption is done at a pressure lower than atmospheric that is vacuum pressure. So, that is why the name VSA and then we have a very important parameter breakthrough.

(Refer Slide Time: 28:35)



Adsorption operation

- ✓ **Breakthrough**
 - Is appearance of a small but detectable amount of solute in the effluent of the adsorption bed.
 - Signifies the saturation behavior of a adsorption bed (column).
 - Dictates the swinging time for regeneration of the adsorption bed.
 - Is characterized by
 - Breakthrough time
 - Breakthrough concentration of solute (defined arbitrarily): Minimum detectable concentration, or maximum permissible concentration of solute in the effluent.
 - Helps in design of adsorption bed.

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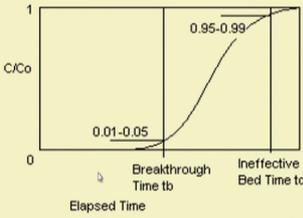
This breakthrough signifies that how long we can carry out the adsorption process when we are when we see that the solute concentration the or the concentration of the impurity in the outlet increases some user specified value then we have to stop the adsorption operation.

So, we keep monitoring the exit concentration of the impurity in the process fluid, and when we find that the impurity level has increased some specified value then we have to stop this operation and take the bed for regeneration.

(Refer Slide Time: 29:08)

Breakthrough curve

- ✓ Is a plot between the effluent solute concentration and time of treatment.
- ✓ The bed is not generally taken to complete saturation.
- ✓ The spread of the curve depends on the effectiveness of adsorption.



C : Concentration of the solute at the inlet of adsorption column
 C_0 : Concentration of the solute at the outlet of adsorption column

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And this is how we plot this breakthrough curves on this we have the time and on this we have the normalized concentration of the impurity. And we find that these kind of thing that initially there is no impurity and slowly the impurity level increases, and we define some breakthrough time, which is taken as the time to have about 1 to 5 percent of the concentration of the impurity in the exit.

So, we want that some the impurities must go out and the desirable solute must be retained inside the bed. So, as soon as we find that the desirable solutes starts coming out of the bed we have to stop adsorption and we have to take the bed for regeneration. So, this way we are able to generate this breakthrough curve.

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