Downstream Processing
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Lecture - 13
Adsorption (Continued)

We have been talking about adsorption and we will continue on the same topic of adsorption; as I introduced in the previous class adsorption is a surface phenomenon.

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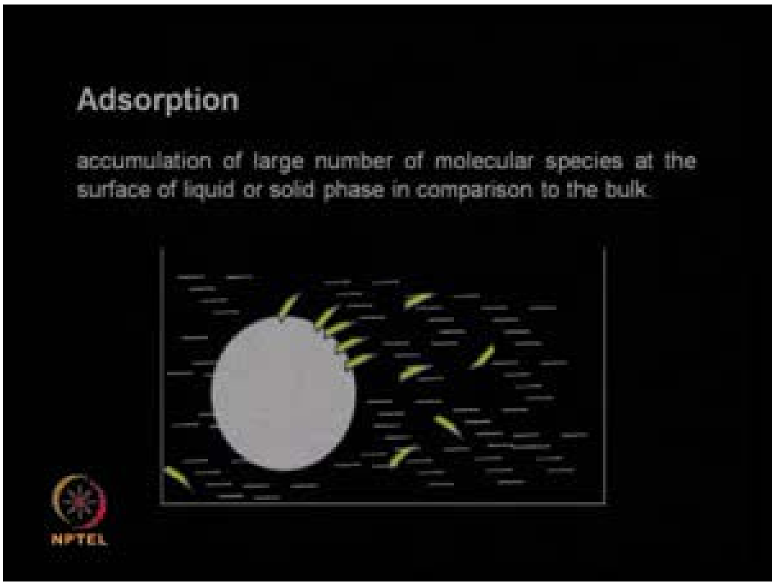

Adsorption

accumulation of large number of molecular species at the surface of liquid or solid phase in comparison to the bulk.

So, you can have a gas getting adsorbed on a surface; a solid surface or even a liquid in a solute can get adsorbed on a solid surface. So, it is a surface phenomenon and like adsorption where adsorption is a bulk phenomena. So, that is the main difference between adsorption and absorption; absorption is a b whereas adsorption is a d. So, in absorption a liquid gets the solute completely dissolved into it or adsorbed into it; whereas in adsorption the solute gets covered on a solid surface. So, there are different types of adsorption.

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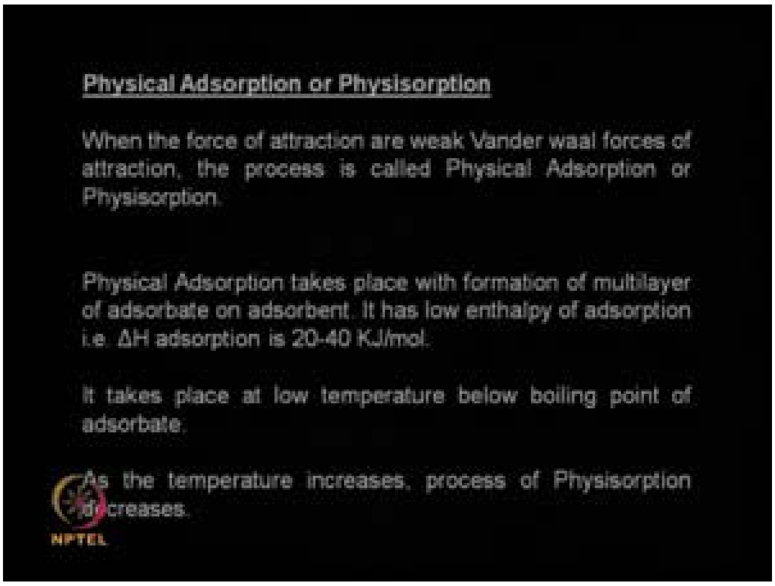

Physical Adsorption or Physisorption

When the force of attraction are weak Vander waal forces of attraction, the process is called Physical Adsorption or Physisorption.

Physical Adsorption takes place with formation of multilayer of adsorbate on adsorbent. It has low enthalpy of adsorption i.e. ΔH adsorption is 20-40 KJ/mol.

It takes place at low temperature below boiling point of adsorbate.

As the temperature increases, process of Physisorption decreases.

One is called the physisorption or physical adsorption, the other is called the chemisorption or chemical adsorption; both are different especially with respect to the energies involved, especially with respect to the forces that involved; that is the attractive forces between the solute and the surface. In the physisorption we have very weak forces mostly vanderwall forces of attraction. So, the energy is also low; if we see that delta H is of the order of 20 to 40 kilo joule per mole. And, it also takes place at low temperature that means below the boiling point of the adsorbate whereas as the temperature keeps increasing; the physisorption keeps decreasing.

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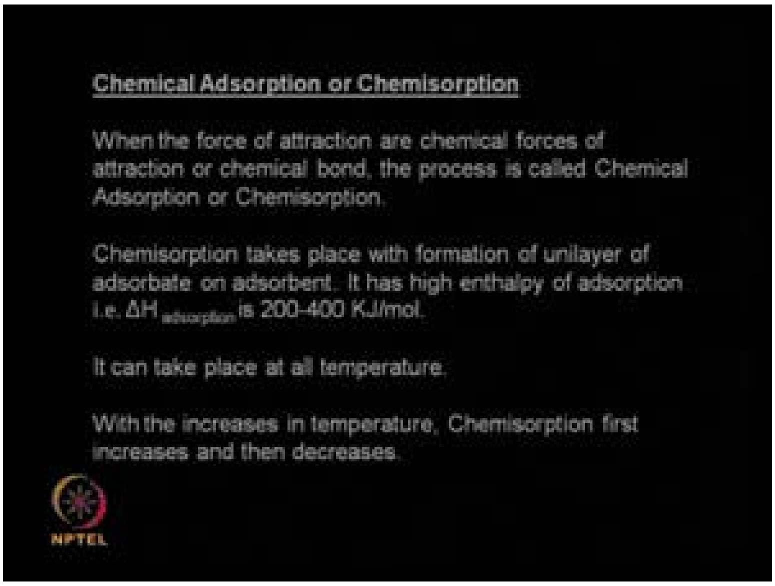

Chemical Adsorption or Chemisorption

When the force of attraction are chemical forces of attraction or chemical bond, the process is called Chemical Adsorption or Chemisorption.

Chemisorption takes place with formation of unilayer of adsorbate on adsorbent. It has high enthalpy of adsorption i.e. $\Delta H_{adsorption}$ is 200-400 KJ/mol.

It can take place at all temperature.

With the increases in temperature, Chemisorption first increases and then decreases.

Whereas on the contrary if we take chemisorption the forces of attractions are chemical forces; sometimes it can even form a chemical bond and that is why it is called a chemical adsorption or chemisorptions. And, delta H here is very high almost 200 to 400 kilo joule per mole. And, it can take place at all temperature that means the solute can be in the vapor form also an like in physisorption; where the solute is below the boiling point.

Here, when the temperature increases the chemisorption also will increase and then later on it will start decreasing. That means, the solute that got adsorbent surface getting dissolved. Generally, adsorption is always a thermodynamic equilibrium process that means you can have adsorption or you can have desorption; that is the reverse of the adsorption taking place from the surface of a catalyst or a metal or an inorganic material and so on and so on.

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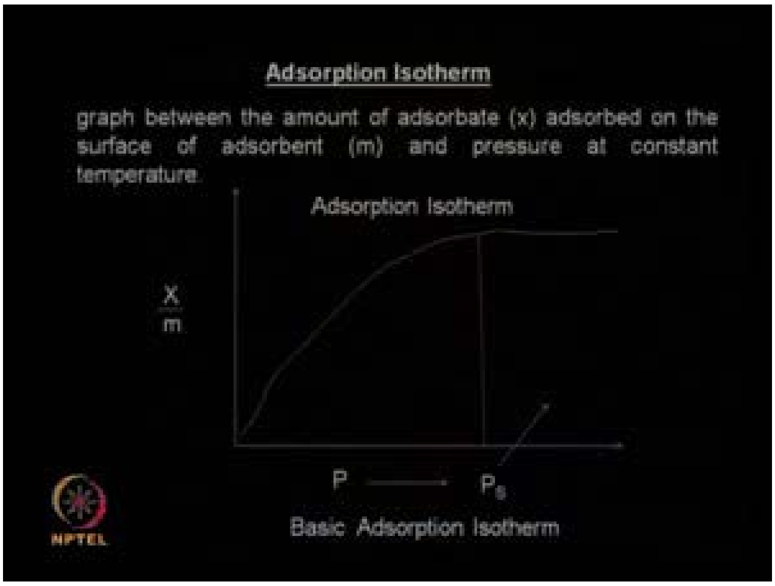

Adsorption Isotherm

graph between the amount of adsorbate (x) adsorbed on the surface of adsorbent (m) and pressure at constant temperature.

So, if you look at the typical adsorption isotherm on the x axis you have the pressure; and on the y axis you have the amount of adsorbate or the solute; that got adsorbed on a surface of the adsorbent of mass m. So, generally as the pressure increases the amount that is getting adsorbed per gram or kilogram or pound of the adsorbent will also increased. And, after sometime it get saturated that means further increasing pressure does not increase the amount of material or solute or adsorbate that got adsorbed. So, this is generally an isotherm that is carried out at a constant temperature.

So, if we change the temperature you may have a different curve but it will always follow the same pattern. It initial increase with pressure after that we get saturated; that is why here we call the saturated pressure region where you do not see many difference in the amount; that adsorb adsorbed even if you increase the pressure further and further. So, at different temperature you may have curves all exhibiting the same form.

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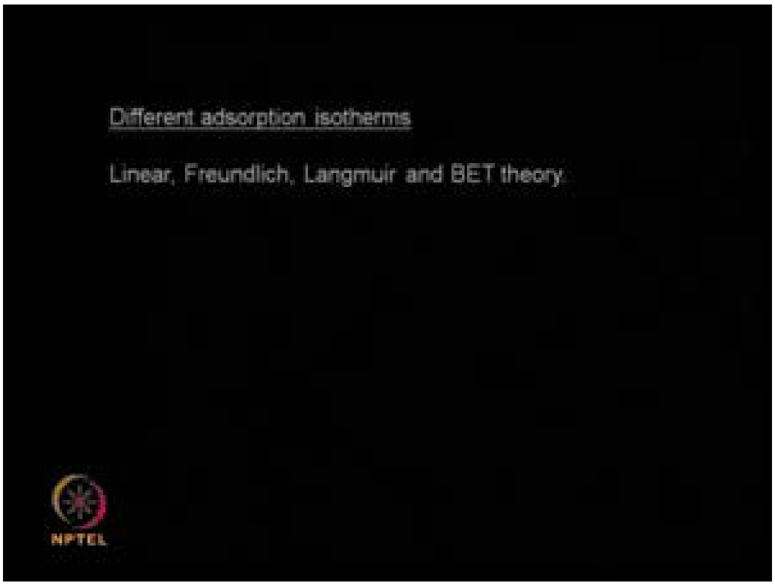

Different adsorption isotherms

Linear, Freundlich, Langmuir and BET theory

There are different types of adsorbtional isotherm. Generally, if we use a Linear adsorption isotherm or Freundlich or Langmuir and BET is also used a if you are talking about multilayer adsorption. And, these 3 adsorption isotherm which is generally consider as it as monomolecular layer.

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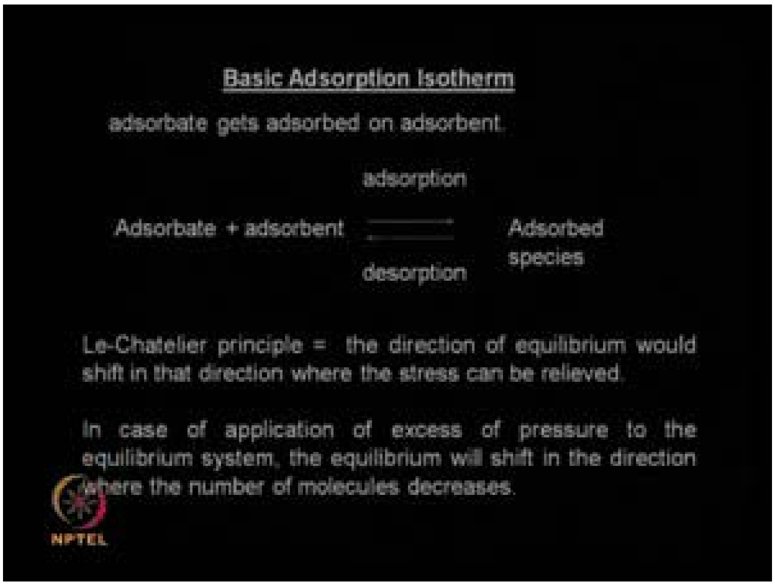

Basic Adsorption Isotherm

adsorbate gets adsorbed on adsorbent.

$$\text{Adsorbate + adsorbent} \underset{\text{desorption}}{\overset{\text{adsorption}}{\rightleftharpoons}} \text{Adsorbed species}$$

Le-Chatelier principle = the direction of equilibrium would shift in that direction where the stress can be relieved.

In case of application of excess of pressure to the equilibrium system, the equilibrium will shift in the direction where the number of molecules decreases.

So, the basic a relationship you have some adsorbate which is in the free form; it gets adsorbed on a adsorbent that is an adsorption process. So, you the adsorbed species; now the adsorbed species can desorbs. So, you have a vacant site available for some other adsorbate to get adsorbed. So, you have get a vacant site; so a vacant active site is necessary for the adsorption processes.

If we look at reactions like nickel catalyst hydrogenation; hydrogen has to get adsorbed on the surface of the nickel. If you have talking about some oxidation reactions on platinum catalyst; then the oxygen has to get adsorbed on the surface of the platinum before the reaction takes place and so on. So, the Lechatelier principle says the direction of equilibrium will always shift; so that the stress can be relieved.

So, if you have putting in pressure the direction of the processes will go from left to right. And, also if you look at left hand side you have 2 molecules and on the right side you have only 1 molecule. So, molecule always equilibrium will shift and the number of molecule also decrease. Because the adsorbate gets adsorbed at the adsorbent number of degrees of freedom also decreases. So, in based on all these principle we can see that the equilibrium will always shift from left to right.

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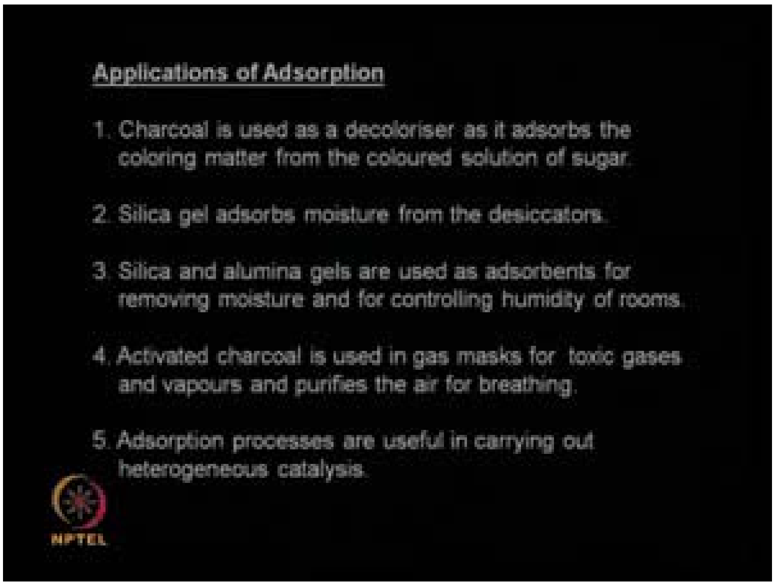

Applications of Adsorption

1. Charcoal is used as a decoloriser as it adsorbs the coloring matter from the coloured solution of sugar.
2. Silica gel adsorbs moisture from the desiccators.
3. Silica and alumina gels are used as adsorbents for removing moisture and for controlling humidity of rooms.
4. Activated charcoal is used in gas masks for toxic gases and vapours and purifies the air for breathing.
5. Adsorption processes are useful in carrying out heterogeneous catalysis.

Now, adsorption is the very important phenomena it is used in many places, it is used in a purifying air, removing toxic gases, it is used as gas mass, it is used as discoloring agent, in influence like sugar, influent silica gel which is used for removing moisture its as a desiccant in room purification system, alumina gels are also used. Then, we use something called realities. Realities are used in removing moisture; realities are used for many reactions, catalytic reactions. So, adsorption is very important phenomena and we come across it in many different processes actually.

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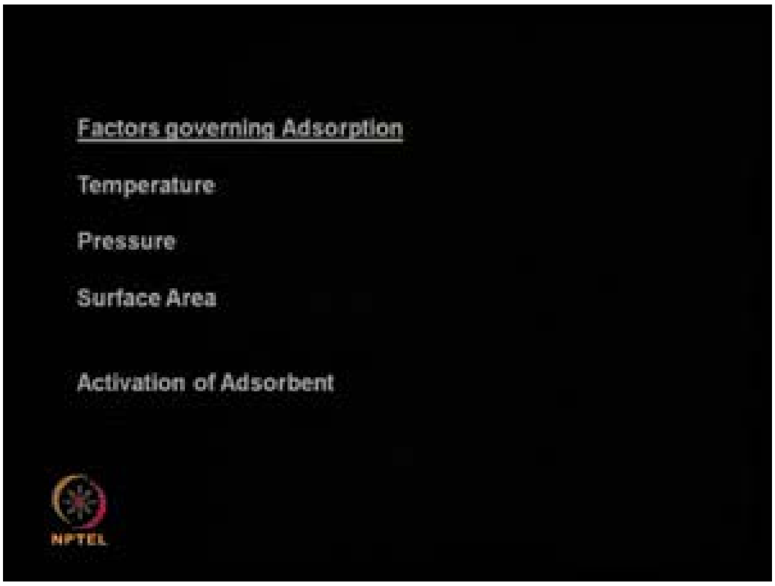

Factors governing Adsorption

Temperature

Pressure

Surface Area

Activation of Adsorbent

So, what are the factors that govern this particular adsorption, temperature, pressure, surface area, activation of adsorbent? So, all these have an effect and you will little bit try to understand the effect of each of this parameter ok. Temperature. For example, temperature has an effect an of the adsorption processes; as I talked about before especially on the chemical adsorption or chemisorptions there is a there are temperature effect on the process.

Similarly, pressure has an effect on the adsorption process and once the surface get saturated; after the saturation pressure we will not see any more adsorption taking place. Surface area more the surface area more is the adsorption; that is why you have activated charcoal which has several meter square of surface area per gram of the catalyst. So, very small amount of catalyst will have large surface area. So, higher the surface area higher is the adsorption.

So, for adsorption we will always use high surface area material; whether it is alumina or carbon or Zeolite or silica aluminates and so on. You will never use low surface area material here. Activation of the adsorbent you have to activate the surface. So, that adsorption can take place; some time we activate it by passing hydrogen, sometimes it activate by passing acid, sometimes we activate it by increasing the temperature and so on actually. So, there are different ways by which you activate. So, these are the factors which control the adsorption process.

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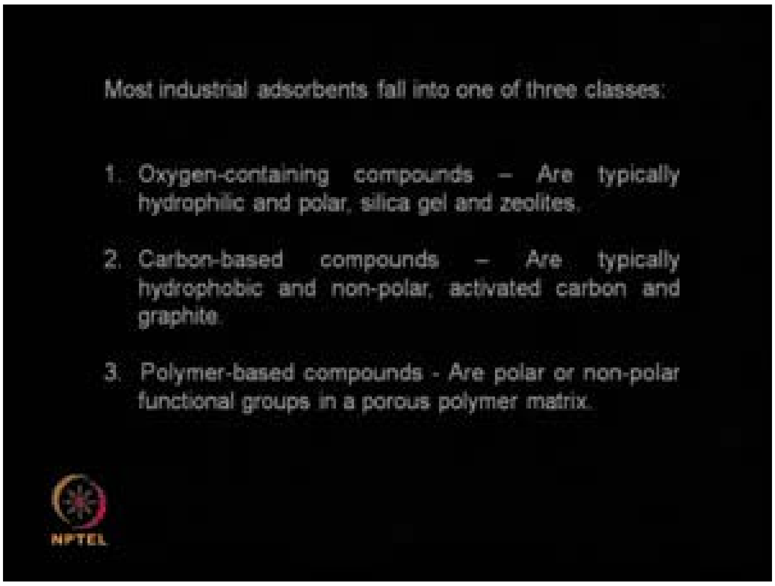

Most industrial adsorbents fall into one of three classes:

1. Oxygen-containing compounds – Are typically hydrophilic and polar, silica gel and zeolites.
2. Carbon-based compounds – Are typically hydrophobic and non-polar, activated carbon and graphite.
3. Polymer-based compounds - Are polar or non-polar functional groups in a porous polymer matrix.

So, most of the industrial adsorbent form into 3 categories; one is oxygen containing components that means generally they are hydrophilic material; they are polar like silica gels and Zeolites. Then, you have the carbon based material that means they are hydrophobic or non polar like your activated carbon graphite and so on. Third type is the polymer based material; the polymers act as a matrix especially if you look at the ion exchange type of adsorption, you have the cations an anions; hankered on to a polymer matrix. So, these are the 3 different types of adsorbent used in the industrial applications.

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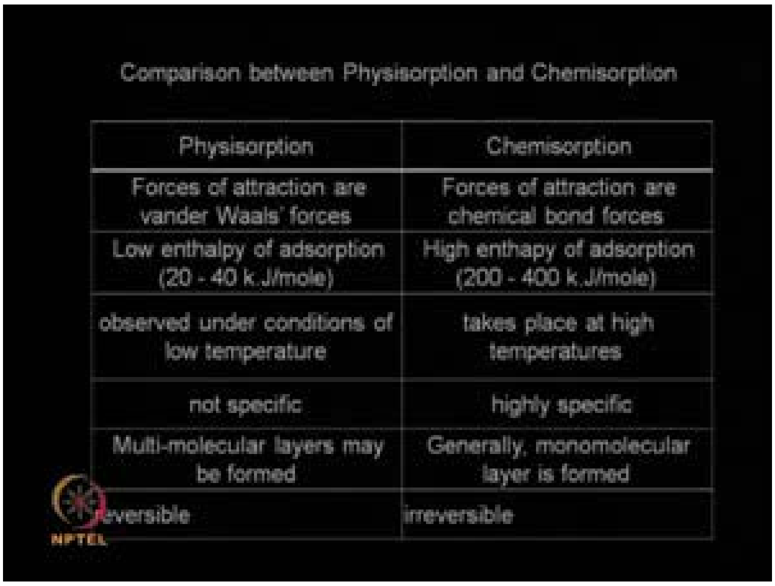

Comparison between Physisorption and Chemisorption

Physisorption	Chemisorption
Forces of attraction are vander Waals' forces	Forces of attraction are chemical bond forces
Low enthalpy of adsorption (20 - 40 k.J/mole)	High enthapy of adsorption (200 - 400 k.J/mole)
observed under conditions of low temperature	takes place at high temperatures
not specific	highly specific
Multi-molecular layers may be formed	Generally, monomolecular layer is formed
eversible	irreversible

So, we will look at some difference between the physisorption and chemisorption in fact stable explains those differences. Physisorption generally the forces of attraction are based on vanderwaals forces; chemisorption you have chemical bonds on chemical interactions is taking place.

So, this forces are weak, these forces are strong that is why the enthalpy of the adsorption processes also differs dramatically; if its physisorption or the chemisorptions. In the case of physisorption the enthalpy is of the order of 20 to 40 kilo joule per mole whereas in the chemisorption its 200 to 400 kilo joule per mole. Physisorption is generally adsorbed at low temperature that means below the boiling point of the solute; and it starts going down with the increasing temperature. That means, the physisorption processes goes down with increasing temperature.

Now, chemisorption if we take it takes place at high temperature that means the solute can be in the vapor form. And, the chemisorption takes place effectively. Physisorption is not very specific whereas chemisorption is highly specific. So, I can remove one single gas from a mixture of gases; that is the main adsorption of the chemisorption process. If you take physisorption generally you can have multilayer of the adsorbate on the surface at the adsorbent; whereas in the chemisorption generally it is a monomolecular layer. Physisorption is the reversible chemisorption is irreversible.

So, these are the difference between physisorption and chemisorptions. So, you can have the same solute or same adsorbate; adsorbing on the surface of the adsorbent either as a physisorption based processes or as a chemisorption based processes.

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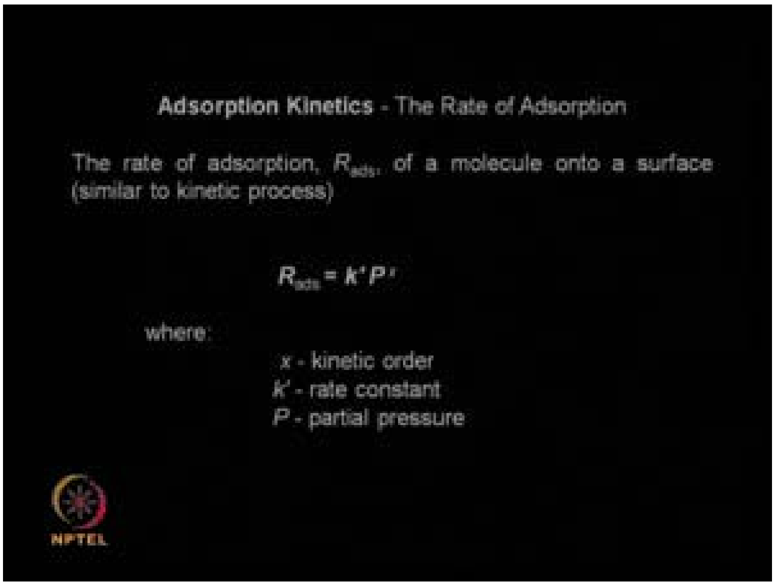

Adsorption Kinetics - The Rate of Adsorption

The rate of adsorption, R_{ads}, of a molecule onto a surface (similar to kinetic process)

$$R_{ads} = k' P^{x}$$

where:

x - kinetic order
k' - rate constant
P - partial pressure

So, if you look at the adsorption kinetics; you can look almost like a normal chemical kinetics. You have the rate of adsorption on the left hand side and there is a constant here; that is called the rate constant that is like chemical reaction we have a chemical rate constant; here also you have a rate constant. Then, we have P; P is the partial pressure of the solute which is getting adsorbed and x that is the exponent or kinetic order; see exactly like your chemical reaction. So, the rates; so adsorption of a molecule on a surface is directly proportional to the pressure raise to the power some exponent value.

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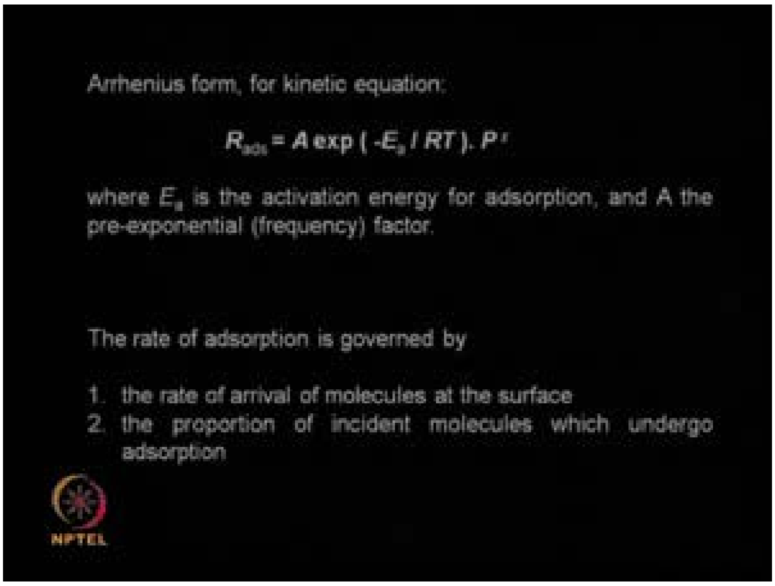

Arrhenius form, for kinetic equation:

$$R_{ads} = A \exp(-E_a / RT).P^x$$

where E_a is the activation energy for adsorption, and A the pre-exponential (frequency) factor.

The rate of adsorption is governed by

1. the rate of arrival of molecules at the surface
2. the proportion of incident molecules which undergo adsorption

Now, we can bring in Arrhenius term exactly like chemical kinetics; we can bring the Arrhenius term, we can bring in the pre exponential term as well or the frequency factor term. So, if we bring that we have the constant being replaced by A into exponent minus E a by R T multiplied by pressure raised to the power x. So, E is the activation energy for the adsorption processes, R is an your universal gas constant and T is the temperature; temperature in Kelvin and A is your pre exponential factor or pre frequency factor or collision factor. So, there are different names for A.

So, the rate of adsorption is given by this particular term. So, it looks exactly like your chemical kinetics and the rate of adsorption is governed by mainly 2 factors. So, the rate of arrival of molecule to the surface. So, you have molecule in the bulk and then you have the surface like a metallic surface or a oxide surface. So, the rate of at which these solutes or adsorbate or arrive at the surface of the adsorbent that is one term. And, then the proportion of the incident molecule which undergo adsorption.

So, just because they come near the surface or hit the surface it does not mean they get adsorbed. But there is always some proportion out of which the bulk of the molecule which come to the surface will get adsorbed. So, these there are 2 term. So, there is something called the sticking probability that will come into the picture.

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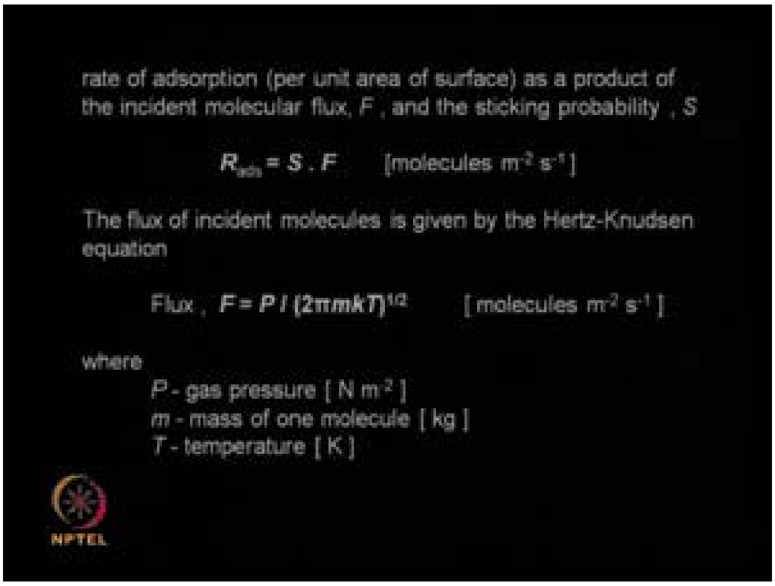

rate of adsorption (per unit area of surface) as a product of the incident molecular flux, *F*, and the sticking probability, *S*

$$R_{ads} = S \cdot F \quad \text{[molecules m}^{-2}\text{ s}^{-1}\text{]}$$

The flux of incident molecules is given by the Hertz-Knudsen equation

$$\text{Flux, } F = P / (2\pi m k T)^{1/2} \quad \text{[molecules m}^{-2}\text{ s}^{-1}\text{]}$$

where

P - gas pressure [N m^{-2}]
m - mass of one molecule [kg]
T - temperature [K]

So, the rate of adsorption per unit area of the surface. Because adsorption is always per area it is a product of incident molecule that is the flux and the sticking probability. That means, a molecule just because it hits the surface does not get stuck to the surface. So, there is always a probability. So, the sticking probability in just like any probability term it will vary between 0 and 1. So, the rate term we have it as number of molecules per meter square that is the surface.

And, because it is a rate term we have per second or per time something will come there actually. So, rate of adsorption is equal to the sticking probability into the flux. Now, if you have the flux of incident molecule it is given by the hertz Knudsen equation. So, the flux F is equal to P is your gas pressure divided by 2 pi m K T raised to the power half; T is your temperature in Kelvin; m is the mass of 1 molecule, K is your Boltzmann constant. So, this is the flux which can be substituted in these rate; so adsorption equation.

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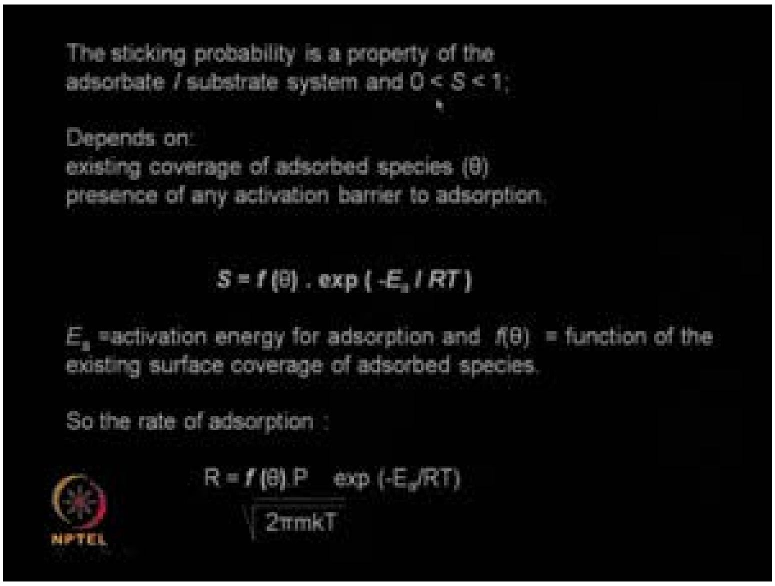

The sticking probability is a property of the adsorbate / substrate system and $0 < S < 1$;

Depends on:
existing coverage of adsorbed species (θ)
presence of any activation barrier to adsorption.

$$S = f(\theta) \cdot \exp(-E_a / RT)$$

E_a =activation energy for adsorption and $f(\theta)$ = function of the existing surface coverage of adsorbed species.

So the rate of adsorption :

$$R = \frac{f(\theta) P}{\sqrt{2\pi mkT}} \exp(-E_a/RT)$$

So, as we say the sticking probability because it is called an probability; it will always vary between 0 to 1. So, lower level it will be 0 that means nothing will get stuck and it can have the highest number as 1. That means, whatever comes and hits the surface of the adsorbent will get stuck. So, you can have either 0 or you can have 1. And, it depends on the existing coverage of the adsorbed species theta and presence of any activation barrier to adsorption. Because there is always certain barrier; the molecule has to overcome before it can get stuck to the surface. So, there it could be an activation barrier.

So, we can have a relationship like this sticking probability is equal to f of theta multiplied by exponent minus E a by R T; E a is your activation energy for the adsorption processes that is the activation barrier which I talked about before. And, f theta is a function of the existing surface coverage.

So, the sticking probability depends on the amount of surface coverage and presence of any activation barrier. So, that you have 2 terms; one is the function of the existing surface coverage; that is represented in the first term. And, this is the activation barrier which the molecule has to overcome.

So, that it can get adsorbed from a free state. So, the rate so adsorption if you put it all these term here we will end up with rate is equal to f theta into pressure exponent minus E a by R T divided by square root of 2 pi m K T. So, we see the rate of adsorption can be defined in terms of certain fundamental E a; E a is your activation barrier which the molecule has to overcome number 1; T that is the temperature at which your performing, P is the pressure of adsorption and f theta is the existing surface coverage. So, as surface coverage increases the rate of adsorption go down as the surface coverage is very low; the rate of adsorption will be very high. So, you see this equation for adsorption can be derived based on the Knudsen equation.

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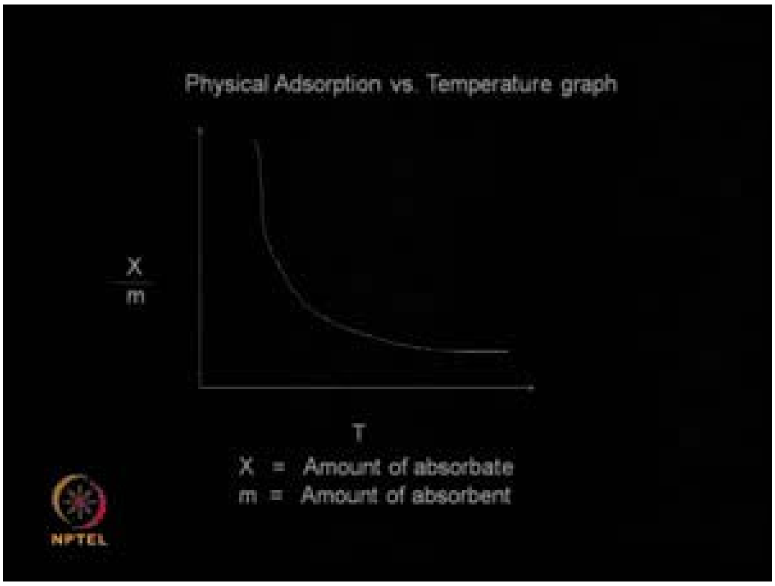

Physical Adsorption vs. Temperature graph

X = Amount of absorbate
m = Amount of absorbent

Physical adsorption as I said will be decreasing as you increasing the temperature because it is a very weak forces. And, its physisorption and it is generally happening below the boiling point of the solute. So, x by m; where x is the amount of adsorbate or solute which gets captured by the adsorbent divided by m is the amount of adsorbent. So, it goes down like that.

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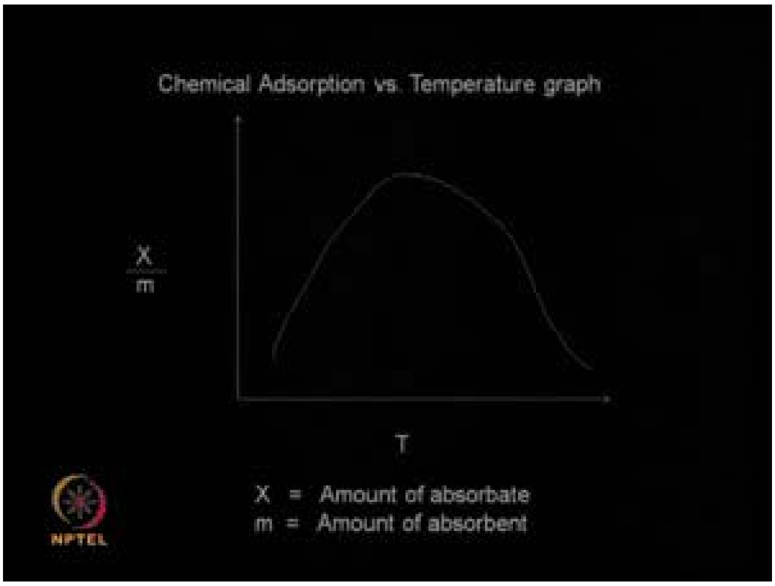

Chemical Adsorption vs. Temperature graph

X = Amount of absorbate
m = Amount of absorbent

So, if it is a chemical adsorption initially it will go up and then later it will fall down. So, initially as we increase temperature the amount adsorbed goes up; whereas later on as we keep increasing temperature the amount adsorbed goes down.

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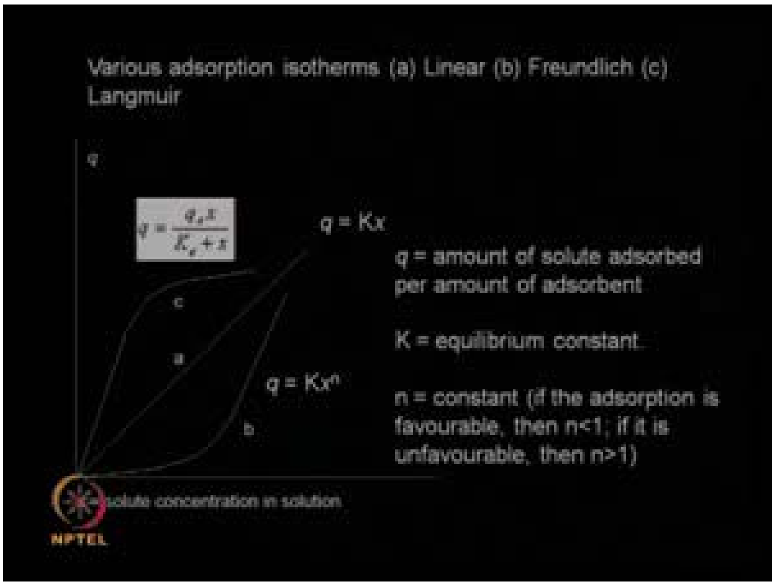

Various adsorption isotherms (a) Linear (b) Freundlich (c) Langmuir

q = amount of solute adsorbed per amount of adsorbent

K = equilibrium constant

n = constant (if the adsorption is favourable, then n<1; if it is unfavourable, then n>1)

Now, I introduced 3 types of adsorption isotherm; before let us spend more time on that will look at those equations. And, see what is happening the 3 types of adsorption is Linear, Freundlich and Langmuir. So, linear as the name implies is the linear relationship between the solute adsorbed and the concentration of the solute in the bulk phase. So, q is equal to K into x; q is the amount of solute adsorbed per amount adsorbent, x is the concentration of the solute in the bulk phase.

So, there is an equilibrium that is taking place between the x that is the concentration of solute in the bulk; and the concentration of the solute in the adsorbed phase and K is a equilibrium constant. So, this is called a linear relationship understand. So, according to this linear relationship as x increases q will keep on increasing.

So, if you look at the x axis hare the solute concentration in the solution and this is this amount of solute adsorbed per amount of adsorbent; it will keep on increasing in a linear fashion and will pass through the origin. So, that is called a linear relationship; generally it will not keep on increasing infinitely. Because after some time surface has to have some sort of a surface coverage and will prevent further adsorption.

But, at up to certain concentration of solute in the solution you will find rarely the relationship. And it becomes easy for you to perform certain calculation if you assume a linear relationship between q x. So, here q is the solute concentration adsorbed on the adsorbent and x is the solute concentration in the solution. So, there is a equilibrium between the solute in the adsorbed phase and in the bulk phase; and k is that equilibrium constant.

Now, let us look at another isotherm that is called Freundlich which is given by curve like this. So, here q equal to K x raise to power n; again you have the K which is equilibrium constant. But here the difference is you have a term called n; n can be greater than 1 or it can be less than 1. So, if n is less than 1 you can see adsorption is favorable; if it is greater than 1 we can say adsorption is not favorable. So, the graph will be like this or it may be in a different form depending upon the value of n. So, here I have drawn a graph for n is smaller than this.

So, Freundlich isotherm gives here non-linearity to the adsorption isotherm where the adsorption isotherm laids the solute concentration in adsorbent phase and in the bulk phase; q is what the solute concentration in the adsorbed phase. And, x the solute concentration in the bulk phase or in the solution phase.

Now, let us look at third adsorption isotherm that is given by the Langmuir isotherm. So, what happens here the solute concentration in the adsorbed phase increases as I solute concentration in the solution and after that it saturates, it platoes, it remains constant. That means, the number of sites available for adsorption of the adsorbate in the adsorbent reach a saturation; there are no more sites available. So, if you increase the concentration of the solute in the solution it will not get adsorbed; that is why it will sort out flatten out. So, initially it looks at the linear relation and after that it flattens out; you see that.

So, initially it is a linear an after that further increase in the solute concentration in the solution will not have any effect on the concentration of the solute found on the adsorbent. And, this equation is given like this q equal to q naught into x divided by some constant K plus x. So, if you look at this equation at very small x values this denominator we can neglect this x. So, you will have x only in the numerator. So, it will look like a linear relation between q and x.

So, at very low x values it is like a linear relation q is directly proportional to x; at very low x values. At very high x values if we neglect K that this x and this x will cancel. So, you will end of with the constant; that means at very large x values q will not depend on x. So, it is like a zero order reaction; that means very large x value your q will be constant in the zero order reaction. So, at very low x values when the x is very small; you will have q directly proportional to the x. So, q an x are related as a first order relationship here and at very large x values these x's will be cancel.

So, q will be a zero order relationship with respect to the x; that means increase in x will have no effect on q. So, this represents a first order relationship between q an x. And, this represent a zero order relationship with a respective q an x; this happens at very large values of x. Because your surface is getting saturated there are no more vacant sites available for the adsorbate to come and adsorbed on the surface of the adsorbent. And, this type of relationship is mostly more realistic when compared to your linear or Freundlich.

And, generally these relationship are reasonable at very low concentration of x. But at very large concentration of x I think I would say you can assume the relationship between q and x to follow a some sort of a Langmuir isotherm. But the most important assumption we need to remember in Langmuir is that it is a monolayer adsorption. That means, it is once the site occupied by one adsorbate you cannot have another adsorbate sticking on top of it. So, it is a monolayer adsorption process. So, that is the main assumption in the Langmuir as adsorption isotherm derivation.

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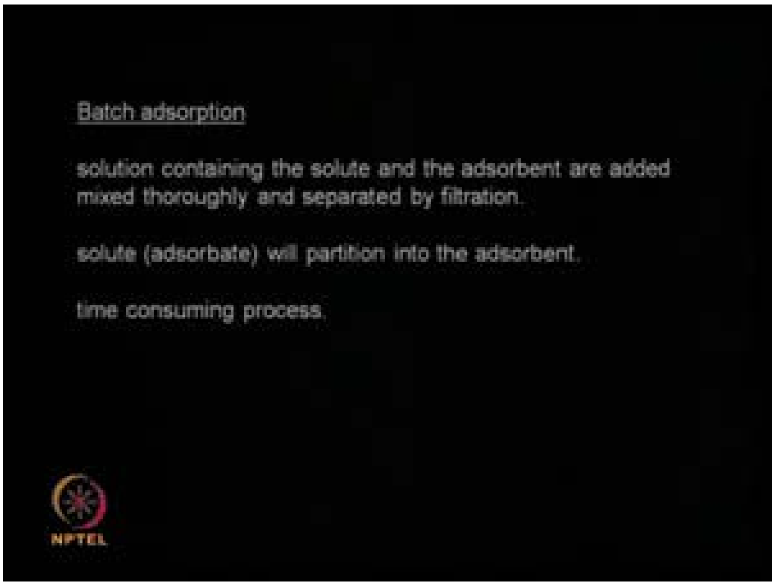

Batch adsorption

solution containing the solute and the adsorbent are added mixed thoroughly and separated by filtration.

solute (adsorbate) will partition into the adsorbent.

time consuming process.

Now, let us look at different type of adsorption process; how a chemical engineering will look at? Because a chemical engineer is to process type of approach and we will look at different types of process. You can have batch adsorption, you can have continues adsorption and so on. What happens in a batch adsorption? What you do you take adsorbent and then you add it to a solution containing the adsorbate or solute which you need to adsorb; mix them both thoroughly.

And, then let them reach an equilibrium you filter out the adsorbent. And, hopefully the solute would have got adsorbed in the adsorbent; the solute could be a toxic waste, unwanted chemical and so on or it could be a protein of urinaters or a metabolite of urinaters. So, in a batch processes what you do is you mix the adsorbent and this bulk solution; which contain your adsorbate mix it up thoroughly then filter it. And, then you have to be regenerate your adsorbent. So, that it can be again reused and then who do we regenerate if it is gases type of reaction; we can heat it up.

So, hopefully the adsorbate will get desorbed and the surface is available or you can use an activating agencies; sometimes you may use concentrated hydrochloric gas or you may use oxygen gas at high temperature. For example, if you are using oxygen at high temperature it will burn away the chemical or waste material that are adsorbed on the surface into C o 2; that way your surface will be again available for further adsorption or you can reduce the pressure.

So, that whatever has been adsorbed can get desorbed. So, these are the activation. So, in a batch processes you have 2 sets of operation; one is adsorption operation, other is the desorption operation where you are regenerating your adsorbent. And, now the adsorbent is available for further adsorption.

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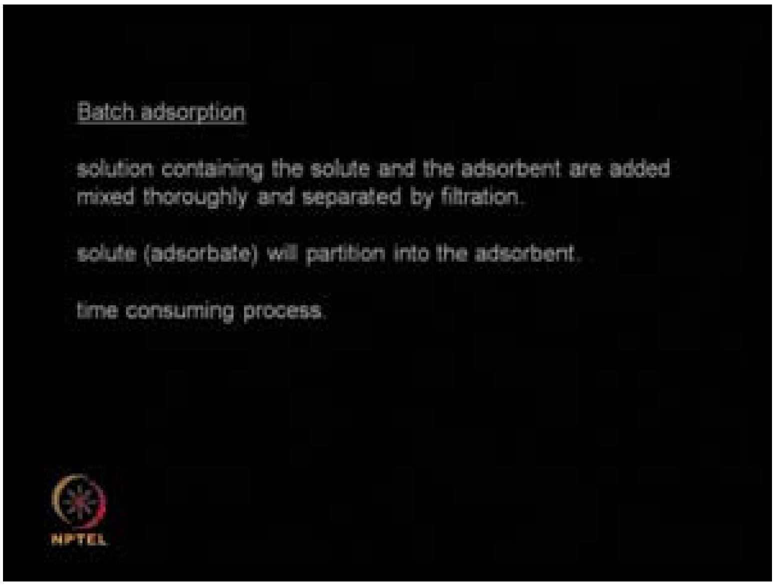

Batch adsorption

solution containing the solute and the adsorbent are added mixed thoroughly and separated by filtration.

solute (adsorbate) will partition into the adsorbent.

time consuming process.

So, when you mix the adsorbent into the bulk your solute gets partitioned between the adsorbed and the adsorbent or in the bulk that your K; the constant value that com comes into the picture actually. So, this process is bit slow; it is a time consuming because it is need to do the adsorption. And, then it will do the desorption regeneration again you go back to the first step. So, it is a slow processes and time consuming.

Batch process is always slow and time consuming but it is very easy. Because you just need a vessel; you take your solution which contains your solute that needs to be adsorbed; you add your adsorbent mix it. And, then you take it to another filter or another vessel where your separating; you know what than you can take it. Then, third vessel where your regenerating your adsorbent and again bring it back to the first vessel. So, that is how you keep doing this operation; it is a manual operation. Because you need to mix them, remove them, filter them, regenerate, again mix them and so on.

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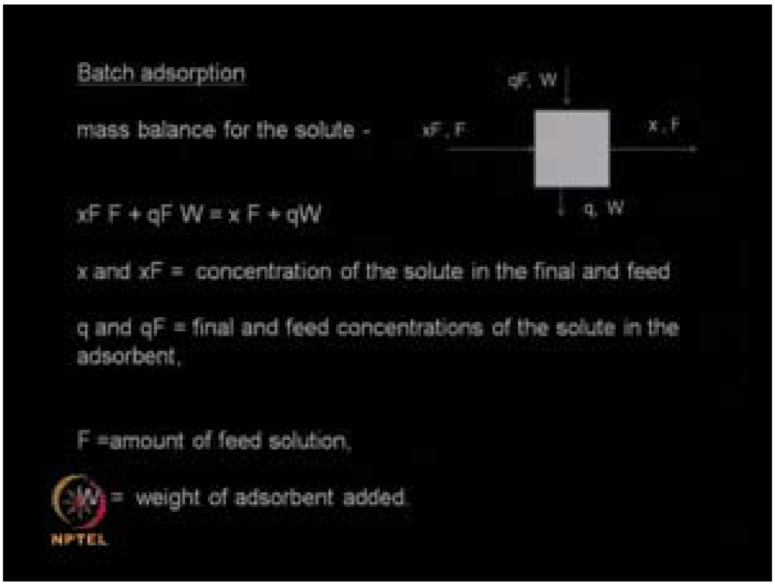

Batch adsorption

mass balance for the solute -

$xF F + qF W = x F + qW$

x and xF = concentration of the solute in the final and feed

q and qF = final and feed concentrations of the solute in the adsorbent,

F =amount of feed solution,

W = weight of adsorbent added.

Let us look at the mass balance in the batch adsorption process. Suppose if I want to design a adsorption system I need to know how much adsorbent I need to take to remove certain percentage of toxic metabolite or a solute? So, I need to decide on that or if I know I am going to add certain amount of adsorbent how much of this solute will get removed? So, if I want to do both these type of calculations all I need to do is the mass balance. The concept principle is very simple just do a mass balance for the solute that is all. So, here we have a stage you are adding a feed solution which contains x F concentration of the solute that needs to be adsorbed; then your adding the adsorbent that is the solid.

So, imagine your F is a liquid and W is a solid; the solid may contain certain concentration of adsorbate; if you are adding a fresh adsorbent then of course q F will be 0. But if you are using a old adsorbent it may contain a some of the adsorbate present here. So, there are 2 inputs and there are 2 outputs; the one output is your bulk solution F. So, the same amount of F that is entering is living but the concentration of the solute or the adsorbate here would have decreased; because some of the adsorbate have been adsorbed.

So, if you look at the W that is your adsorbent the amount will be the same W here and W there; but it would have picked up some solute. So, here q will be greater than q F whereas here x will be less than x F. Because some of the solute or the adsorbate has been transferred to the adsorbent. So, there are 2 inputs, 2 outputs; so what do we do. We take a concentration of solute in here, plus concentration of solute, in here that should be equal to concentration of solute out in the stream plus concentration of solute out in the stream.

So, there are 2 inputs 2 outputs and this what the equation represents x F into F is the amount of solute coming in through this stream and q f into w that is the amount of solute living in this stream; this stream this should be equal to x F that is amount of solute leaving in this stream and q W that is the amount of solute leaving in this stream. This stream is because of the adsorbent and this stream these two stream are the because of the solution or bulk liquid which contains your adsorbate.

So, the bulk liquid is loosing some adsorbate which is taken up by the adsorbent that is what this equation is. So, here x F is your concentration of your solute in the feed, q F is the concentration in the solute in the adsorbent, x is the concentration in the solute that living the feed; and q is the concentration of the solute in the adsorbent that is living the stage. So, this is the single stage mass balance. So, knowing certain terms we can calculate the amount.

So, F is the quantity or the amount of the feed solution it could be in liters per minute or liter cube per minute or cc per minute. And, W is the weight of the adsorbent that is getting added could be in grams, kilograms, micrograms. So, this for the units please note the units of x and q should be corresponding that. So, if you have F in liters; so x will have micrograms and grams or kilograms per liter. So, if W is in kg or grams then your q will be concentration per gram or kg. So, that they all match the units have to match; because F is in volume you will have x will have a denominator volume term. And, if w is in weight q will have a denominator weight term.

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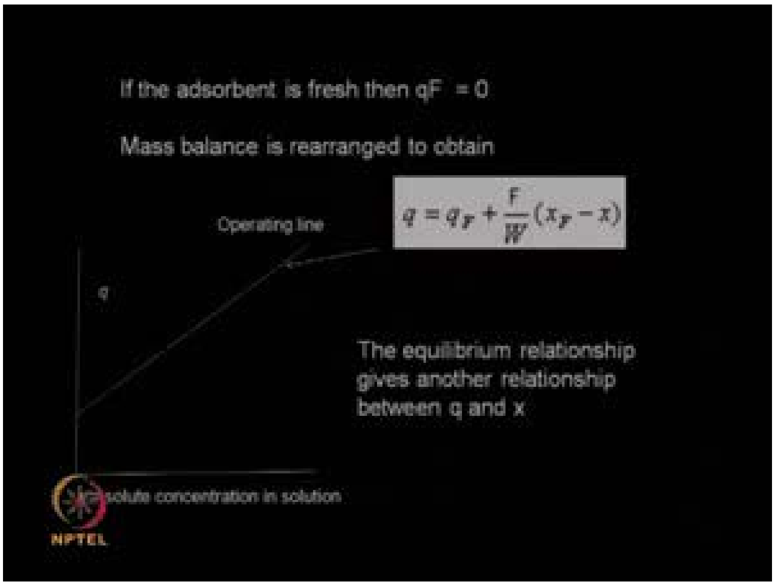

If the adsorbent is fresh then qF = 0

Mass balance is rearranged to obtain

$$q = q_F + \frac{F}{W}(x_F - x)$$

The equilibrium relationship gives another relationship between q and x

So, we can rearrange this equation mass balance equation to get q equal to q F plus F divided by W multiplied by x F minus x. So, x F is the concentration of the solute in the feed solution, x is the concentration of the solute that is living in the solution of floret F, and W is your amount of adsorbent and q F is the initial amount of a solute present in your adsorbent; and q is the amount of solute that is present in the adsorbent that is living the stage.

Generally, q F is 0 if I am taking a fresh adsorbent there are many solute present. So, I can neglect this term F term and q will be equal to F by W into x F minus x this is called the operating line. Because if I plot a of graph where x axis is x, x is the solute concentration in the solution and y axis is q, q is the concentration of the adsorbate in the adsorbent. Then, this will be a straight line this equation and this is called the operating line.

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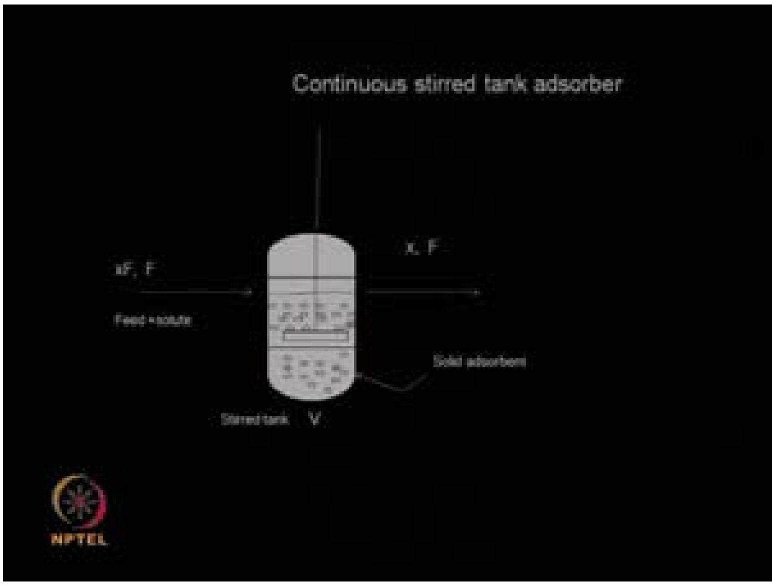

Continuous stirred tank adsorber

So, if we take continues stirred tank; so far we looked at the batch process. So, in the batch process what we are going to tell is in a batch process you have 2 streams entering a stage; one of the stream contains you are the bit solution where the solute is present or the adsorbate is present. Then, we have another stream where you have the adsorbent which may or may not contain the solute; when you bring both of them together mix them thoroughly.

Let them re allow it to reach the equilibrium and separate them using a filter. We are using a filter because we assume that adsorbent is a solid like a activated charcoal or it could be Zeolites or it could be a silica gel or it be silica alumina and so on. So, by separating it out you the solute has transferred from the bulk solution into the adsorbent. So, we do a mass balance of the solute present in 4 streams.

What are the first streams; the stream one is the feed solution, stream two is the fresh or used adsorbent that is added stream, three is the bulk solution that is living. So, it has lost some adsorbate to the adsorbent and stream 4 is the adsorbent that collected after filtration. So, some of the adsorbate has moved or got transferred from the bulk solution to the adsorbent. So, that is how a batch processes work. So, what I can do? Suppose if my adsorption efficiency is not 100 percent I have achieved 60 or 70 percent.

Now, I take the solution take it to another vessel; where again I add some adsorbent, again I do adsorption processes and again I remove some of the solute. So, I may have multistage adsorption taking place be 1, 2, 3 stages. So, I will do in the adsorption where I add the solid then I will do the filtration. Then, again I will do an adsorption process where I may add some more solid and again I will do filtration. So, you may have more than 1 stage that is possible actually. So, that you remove as much of the solute or the adsorbate possible from the bulk solution.

And, especially if you are interested if it could if it is in a environmental type of situation where you do not want toxin present at all in your water living. Then, you do this operation many times until the concentration of the toxin comes down PPB or even very small or negligible or if there is a situation where you would like to recover a protein interest.

So, you do not want any of the protein to go away with the bulk solution you may carry out this adsorption stage 2, stage 3 and many stages until whatever protein is present in your bulk solution has been totally adsorbed. So, that is how you do in a batch process. Now, let us look at a continuous process where as the name implies the adsorption process is continuous.

So, in a continuous process what can happen you may add your feed solution or the bulk solution continuously. This feed solution may contain your solute or adsorbate at a concentration of x F. Now, you have tank containing your solid which is the adsorbent like it may have the activated carbon inside or the Zeolites inside. So, the solution comes in they get mix thoroughly here; because there is a residence time here the solute gets adsorbed in the by the adsorbent.

So, the solution that is leaving will have the concentration of the solute x; here x will be less than x F. So, during that residence inside the solute gets transferred from bulk phase to the solid phase. So, there is always a residence time in this process. And, what is the residence time we can calculate the residence time if I know the volume of the tank and also the feed solution.

So, if I do V divided by F that gives you the residence time of the solution inside the vessel adsorbed as you call it adsorbent. The most important thing is the solution that is living the tank should not carry the adsorbent as well. So, generally you will have a filter unit present here. So, that the solids are retained and kept inside your vessel and they do not get transferred and travel with the liquid that is leaving the tank. So, this is how a continues stirred tank adsorber works.

So, you can adjust your residence time; so that the adsorption is efficient or there is a equilibrium that will be reached between the solution that is leaving the vessel with the solids that are present inside the vessel. So, what are the advantages, disadvantages with a continuous adsorbent? We can continuously process a some fluid that is one advantage but one disadvantage as we keep on mixing the solids may start breaking down into smaller particle.

And, they may start traveling and leaving the adsorber with the fluid stream or the exist stream. So, that could be a disadvantage in that. You assume that the liquid that is entering reaches the equilibrium with the solids that are present inside. So, residence time has to be sufficient. So, that they reach a equilibrium; so you need to keep those that also in mind actually. So, let we can also do a mass balance for the continuous stirred tank adsorber as well.

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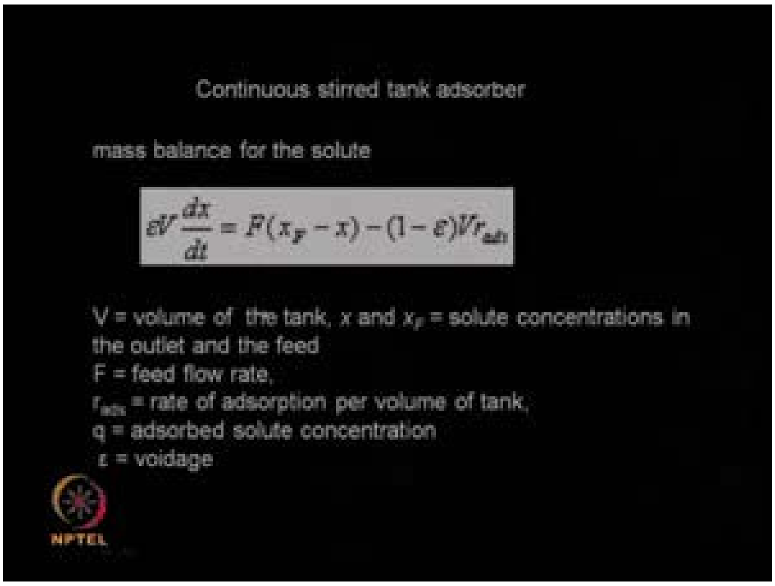

Continuous stirred tank adsorber

mass balance for the solute

$$\varepsilon V \frac{dx}{dt} = F(x_F - x) - (1-\varepsilon) V r_{ads}$$

V = volume of the tank, x and x_F = solute concentrations in the outlet and the feed
F = feed flow rate,
r_{ads} = rate of adsorption per volume of tank,
q = adsorbed solute concentration
ε = voidage

So, what are the things happening in a continuous stirred tank adsorber? There is a feed entering that is the bulk solution that entering which contains your solute x F is the concentration of the solute in the feed, x is the concentration of the solute living. So, F, x F minus x is the concentration difference which has been taken up. Now, this minus 1 minus epsilon v are adsorbed; this the amount of solute that gets transferred to the adsorbent; where here epsilon is wide age. So, V is the volume of the vessel, r is the rate of adsorption process. So, this is the mass balance on the right hand side this should be equal to the accumulation.

So, here we are talking about the input minus output minus amount getting adsorbed from the liquid phase into the solid phase. So, this is the input minus output leaving the vessel that is material coming into the vessel material leaving the vessel minus the material that is getting transferred from the liquid phase to the solid phase; this should be equal to the amount that is getting accumulate inside the vessel. So, what is accumulated inside the vessel?

So, epsilon into V this is the amount of the liquid present inside the vessel multiplied by d x by d t where x is the concentration of the solute in bulk inside the vessel. So, this is the amount accumulation e into V d x by d t; this is the amount of the solute entering the vessel because of the flow of the fluid. And, this is the amount that is leaving the vessel because flow of the liquid flowing out. And, this is the amount that is getting adsorbed from the solution phase or the bulk phase to the adsorbent phase.

So, epsilon is the wide age. So, e epsilon into V gives you the amount of liquid present inside the reactor or the adsorber 1 minus epsilon into V tells you the amount of the liquid that is epsilon V 1 minus V into V gives you the amount of solids present in the vessel. So, epsilon into V tells you the amount of liquid present in the vessel 1 minus epsilon into V tells you the amount of solids present in the vessel. So, this is called the mass balance entire mass balance. And, if want to solve this particular equation we need to have some initial condition right.

So, initially the vessel will not have any solute present inside; at time equal to 0 your solute with the solutions starts flowing inside. So, whatever adsorbed initially at time equal to 0 will be 0. And, then slowly there will be a buildup of solute inside the vessel as well as in the exit stream. So, we can solve this first order differential equation.

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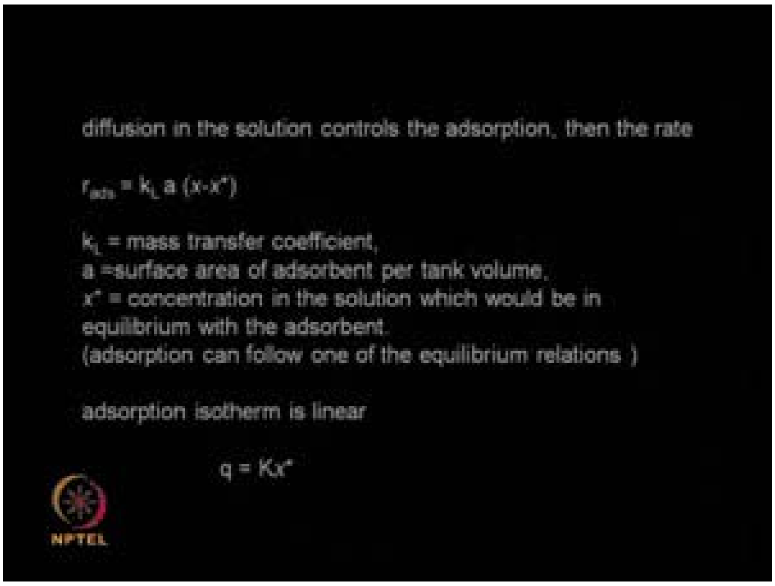

diffusion in the solution controls the adsorption, then the rate

$r_{ads} = k_L a (x - x^*)$

k_L = mass transfer coefficient,
a =surface area of adsorbent per tank volume,
x^* = concentration in the solution which would be in equilibrium with the adsorbent.
(adsorption can follow one of the equilibrium relations)

adsorption isotherm is linear

$$q = Kx^*$$

And, by doing that we will be able to calculate what is the effect of time on the concentration; that is x, that is the concentration of the solute that is leaving the vessel. So, in order to do that we need to still consider many other terms. For example, we need to have an equation for the r adsorbed. So, we assume mass transfer type of relationship; all chemical engineers will know what is mass transfer. So, it is a very common term because you are going to have the solute present in the liquid phase moving into the a solid phase.

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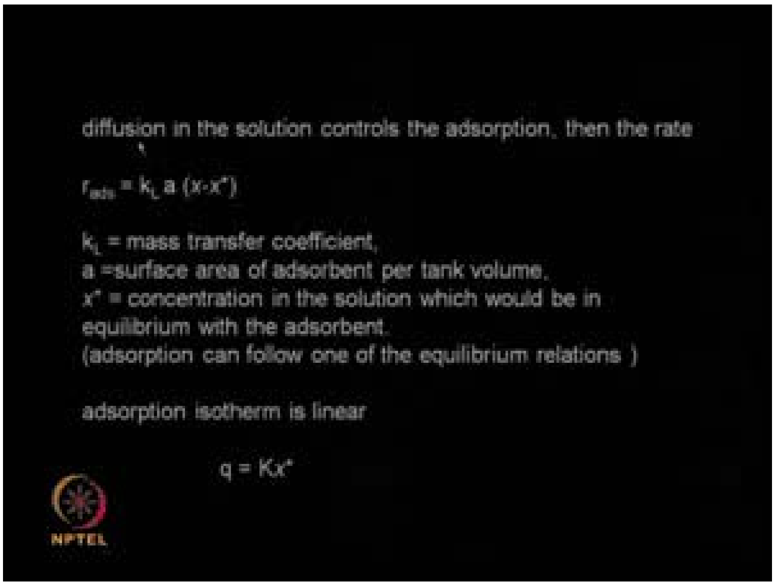

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So, we can have a term like this where r adsorbed is equal to k L into a into x minus x star. So, k L is the mass transfer coefficient, a is the surface area of adsorbent per tank volume, x minus x star where x star is the concentration of the solution which should be in equilibrium with the adsorbent; this is the driving force and this is the area and this is some constant.

So, these 3 terms gives you rate of adsorption and if it is the linear adsorption isotherm like as we saw before q can be is equal to k into x star. So, we can instead of x star put it as q by K here. So, here instead of r adsorption we can write this particular equation and instead of x star we can write it as q by K. So, once you have these terms included into our first order differential equation it becomes very simple for one to solve.

Let us not go into the solution of these first order differential equation but if you solve this first order differential equation.

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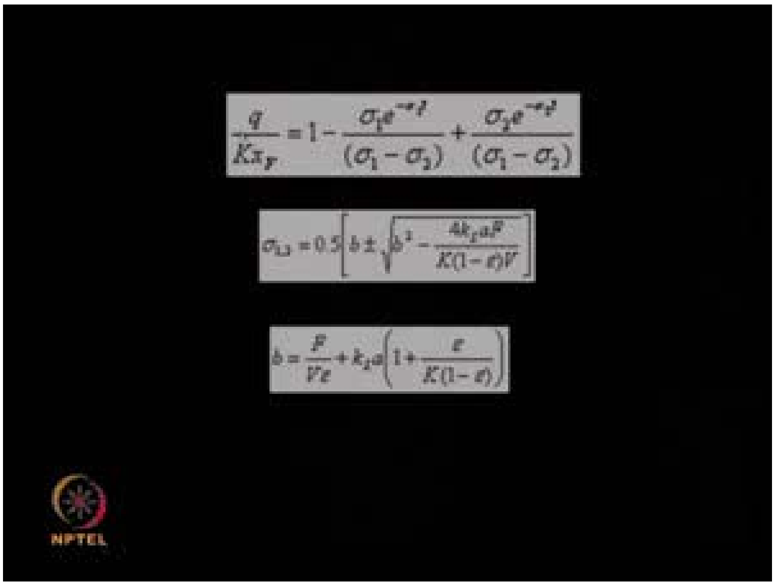

$$\frac{q}{Kx_F} = 1 - \frac{\sigma_2 e^{-\sigma_1 t}}{(\sigma_1 - \sigma_2)} + \frac{\sigma_1 e^{-\sigma_2 t}}{(\sigma_1 - \sigma_2)}$$

$$\sigma_{1,2} = 0.5\left[b \pm \sqrt{b^2 - \frac{4k_L aF}{K(1-\varepsilon)V}}\right]$$

$$b = \frac{F}{V\varepsilon} + k_L a\left(1 + \frac{\varepsilon}{K(1-\varepsilon)}\right)$$

You will end up with the equation of this form q by K x F is equal to 1 minus there is a e raised to the power minus sigma 1 t; there is e raised to the power sigma 2 t. So, e power minus t will always have an exponential type of decaying function actually where sigma 1 and sigma 2 is given by this particular equation and b present inside this equation is given by this.

So, you can see here simple quite a relationship which connects the q that is the amount of solute that gets adsorbed on to the surface as a function of time; with all the basic parameters like fluorites, the volume of the tank, the wide age factor, the K which is the partition between these liquid and solid phase, k L is the mass transfer coefficient, a is the interfacial area and so on actually. So, you have all the basic design terms relating between a t the time and the q. So, how will be the relationship will look like?

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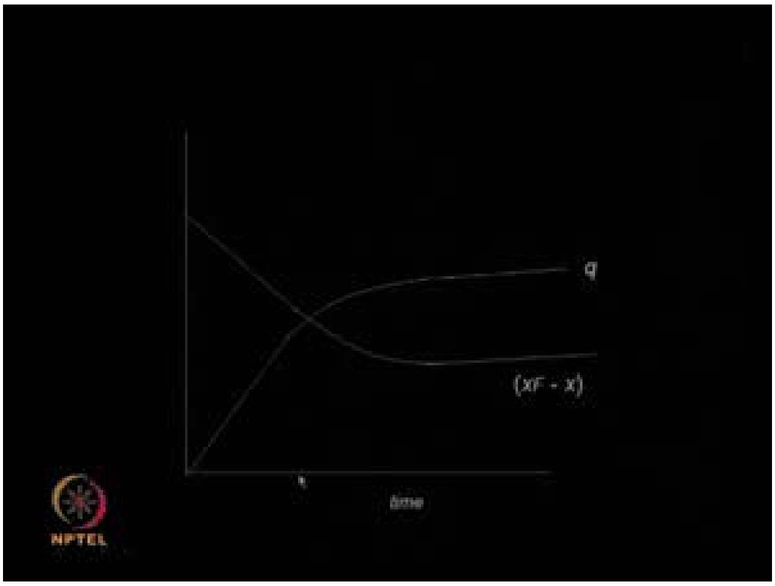

So, as the time increases initially q will go up because initially you have fresh adsorb adsorbent present inside your tank. So, as time increases the value of q will start from 0 and then go up and get saturated. So, after that you will not be able to allow the same adsorbent to adsorb any more fresh solute or adsorbate. So, what do you have to do we need to stop the process and regenerate your adsorbent or we need to add fresh adsorbent and so on actually.

So, again as time increases the x of minus x initially at time equal to 0; it will be here. And, then it will be start going down and it will reach a Plato here. So, after some time your adsorbent gets fully saturated with the adsorbate. So, as I said we need to do some further regeneration of the a adsorbent or we need to add fresh adsorbent. So, these are the 2 different ways by which you can increase the adsorption of the solute. So, we looked at 2 different types of operating conditions; one is the batch type of adsorption, other one is the continuous type of adsorption.

In the batch type what you do? We take a the adsorbent that is the fresh adsorbent or used adsorbent it is a solid then mix it up thoroughly with your bulk solution which contains your adsorbate; and then you filter it. So, by doing this you have transferred some of the solute or adsorbate present in the bulk to the adsorbent.

So, once you have transferred you can desorb and again regenerate your adsorbent. And, again put it back for further recycle; whereas in your continuous process what we do? You have a stirred vessel; you have the adsorbent present all the time inside the liquid flows in. And, the solute that is present and the adsorbate that is present gets adsorbed. So, when in liquid goes out the concentration of the solute going out will be much less than concentration of the solute that is inside the vessel. So, how did we model it? Here, we have something like a first differential equation.

So, input minus output minus the amount adsorbed will be equal to the accumulation. So, this is very standard mass balance relationship. So, by taking that by assuming that the rate of adsorption follows a mass transfer type of process. And, if we assume a linear relationship we can have a numbly we can have a analytical solution for the adsorption process as function of time. But if you have a non-linear relationship for a adsorption isotherm like a Langmuir type of model; then you will not be able to get a simple analytical solution.

But, you need to use some sort of numerical package to solve this entire differential equation. Because it becomes slightly a non-linear type of differential equation rather than a linear type of differential equation. But it can be solved using a math lab or any other differential equation solver type of package. So, we can get a relationship between the rate of adsorption process depending upon the flow rate into the stirred tank as well as the volume of the stirred tank. So, we can manipulate and we can change the adsorption process.

Thank you.