Water and Wastewater Engineering

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Adsorption
Lecture # 34

Last class we were discussing about advanced wastewater treatment and we have seen what the need is for advanced wastewater treatment. If the wastewater is containing easily bio degradable organic matter then the secondary wastewater treatment processes will take care of almost all the pollutants. But we have seen that nowadays there are many non conventional pollutants and emerging pollutants present in the wastewater so these pollutants need not or may not be removed in the conventional secondary treatment.

So, if you want to discharge the effluent to existing water bodies and if you want to keep the quality of the water bodies intact then we have to further treat the wastewater. Moreover, nowadays instead of discharging the effluent coming out of the secondary treatment we are trying to reuse the wastewater because water scarcity is there and we want to protect the water bodies. So if you want to reuse the wastewater or the treated effluent from the wastewater treatment plants we have to give further treatment to achieve the water quality parameters based upon the beneficial use for which we are going to use the water.

We have discussed in detail how the membrane processes are working. We have seen in detail the micro filtration, ultra filtration and reverse osmosis, electro dialysis and dialysis. Today we will discuss in detail about adsorption, ion exchange, advanced chemical oxidation and distillation. Let us start with adsorption. What is this adsorption?

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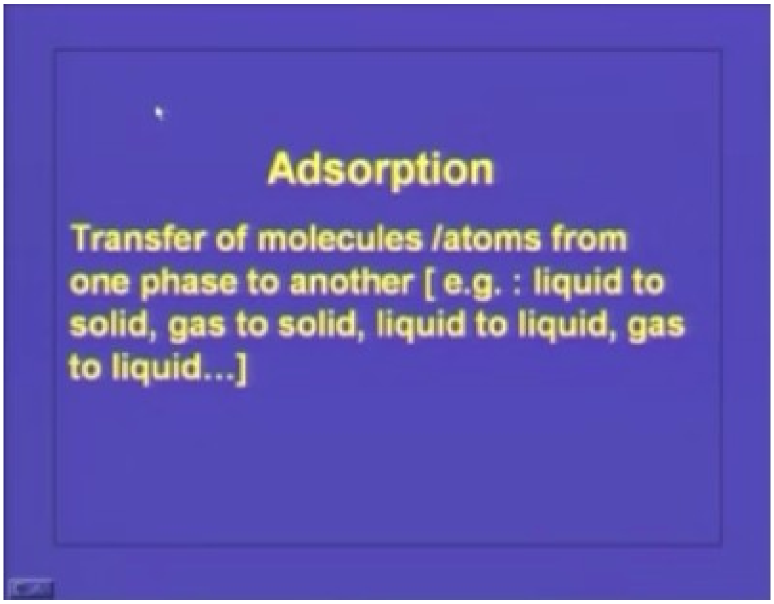

Adsorption

Transfer of molecules /atoms from one phase to another [e.g. : liquid to solid, gas to solid, liquid to liquid, gas to liquid...]

It is the transfer of molecules or atoms from one phase to another. Or for example we can tell that from liquid to solid or gas to solid or liquid to liquid or gas to liquid. Or in other words adsorption is a surface phenomena, the pollutant from one phase is getting concentrated on the surface of other matter or if the pollutant is present in the liquid. Whenever we talk about wastewater treatment the pollutants will be present in the liquid phase. So if you want to remove the pollutants from the liquid phase what we can do is add some solid and the pollutant is getting concentrated on the surface of the solid that is known as adsorption.

In the earlier days this adsorption was used for the treatment of polluted gases so they have developed all the theories based upon the gaseous pollutant treatment. But that same process can be effectively used for the wastewater treatment or the pollutant removal from water also. that is what I have already told. Adsorption was commonly used in gas phase and it can be effectively used for water and wastewater treatment and adsorption is a non selective process. That is the major disadvantage of this process.

What do you mean by non selective process? It is because it cannot select various pollutants, so depending upon the pollutant whatever is present in the wastewater everything will be getting adsorbed on the surface of the material so we cannot isolate each pollutant and get it removed just like in ion exchange process. In ion exchange process if we want to concentrate on a particular ion we can select the ion exchange resin in such a way that it is having affinity to only that ion or only that sort of ions. But in case of adsorption it is non selective, whatever pollutant is present will be adsorbed on the surface of the adsorbent so we will not be able to differentiate or separate the pollutants present in the wastewater. That is the major disadvantage of this adsorption process.

Now we will see what all are the terms commonly used in this adsorption process.

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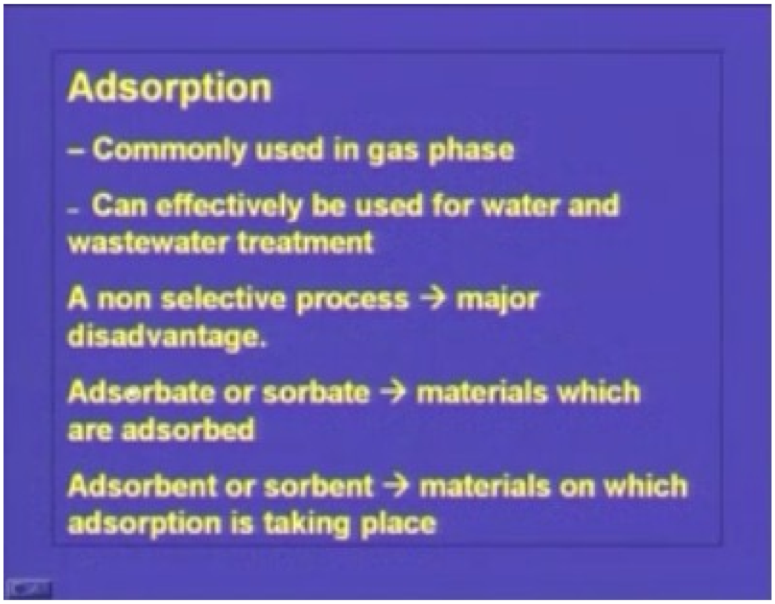

Adsorption

– Commonly used in gas phase

- Can effectively be used for water and wastewater treatment

A non selective process → major disadvantage.

Adserbate or sorbate → materials which are adsorbed

Adsorbent or sorbent → materials on which adsorption is taking place

The first one is adsorbate or sorbate. this is the material which is adsorbed or in other words the pollutant whatever is present in the liquid is getting adsorbed on some materials so that is known as adsorbate, the pollutant or the materials which are adsorbed and the other term is adsorbent or sorbent. It is the material on which adsorption is taking place.

For example, if you put a chalk piece in a ink bottle what will happen is the ink is getting adsorbed on the chalk piece so ink is known as the adsorbate and the chalk piece is known as the adsorbant. Therefore, the material on which the substances are getting adsorbed is adsorbent or sorbent and the material which is getting adsorbed it is known as adsorbate or sorbate.

Now we will see what are the different types of adsorption. If you have an adsorbent and an adsorbate the adsorbate is present in the solution and you are putting your adsorbent to that polluted water or solution. We also want to see whether the adsorption process is feasible or not.

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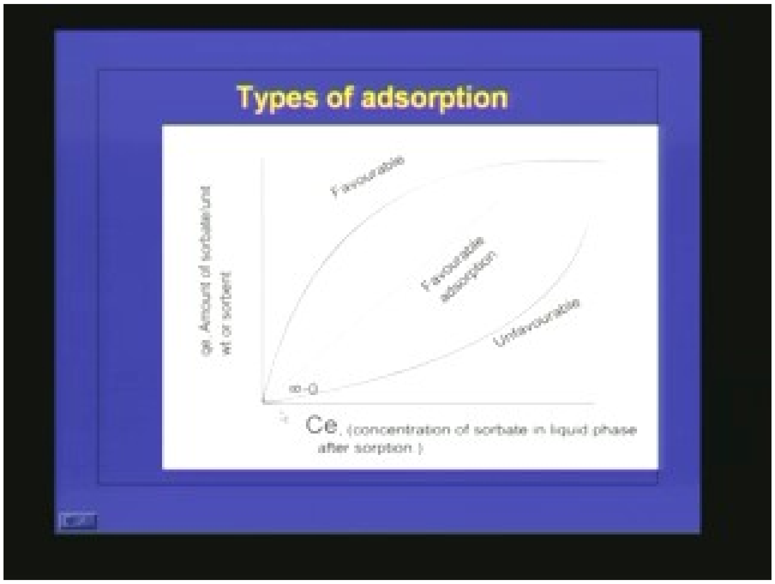
Types of adsorption

This is how we can find that out. The amount of sorbate per unit weight of sorbent is nothing but the amount of pollutant that has got adsborbed on the sorbate. So if you plot this versus the concentration of sorbate in liquid phase after adsorption whatever pollutant concentration is leftover in the wastewater will form a curve like this. So we will be getting either this type of a curve or this type of a curve (Refer Slide Time: 6:42) or this type of a curve. So if you get a curve like this we can say that it is a favorable adsorption. That means at very low concentration of pollutant whatever is leftover in the solution you will be getting a high concentration of pollutant on the solid phase or on the surface of the sorbent. That is known as a favorable adsorption.

But if you get a curve which is something like this that means even if you have a very high concentration of pollutant leftover in the liquid phase the pollutant concentration whatever is getting adsorbed on the sorbent or the solid phase is very less so it is not favorable or this type of adsorption is known as unfavorable adsorption. If you get a line like this (Refer Slide Time: 7:28) this is known as linear adsorption or linear adsorption. That means the amount of pollutant getting adsorbed on the sorbent is directly proportional to the concentration of the pollutant whatever is present in the liquid or in the solution. This is very very important because when we do the laboratory studies if you get a curve that is something like this then we can make sure that the pollutant cannot be removed effectively using adsorption process. But if you get something like this it is very clear that we can go for adsorption process for the treatment or removal of that particular pollutant.

Now we will see why this pollutant is getting adsorbed on the surface? We have seen that the pollutants are present in the liquid and we are introducing some other phase a solid phase into the liquid. So the pollutant whatever is present in the liquid has to migrate and get adsorbed or get attached to the solid phase so there should be some driving force otherwise it will not be coming to the solid phase.

For example, if the solute or the pollutant is highly soluble in water then definitely it will be having a tendency to remain in the solution. But if it is non soluble or very less soluble then what will happen is those molecules will be having a tendency to come out. So this type of solutes we can classify them as either lyophilic or lyophobic or hydrophilic or hydrophobic.

Lyophilic means the solute which likes the solvents so that is lyophilic on liquid likely. Lophobic is the solute which dislikes the solvent or liquid disliking solutes. So if the solute is liquid disliking then what will happen is as soon as it gets some opportunity it will be having a tendency to come out of this one. Similarly if the solute is some pollutant and the solvent is water then we can call it as hydrophilic or hydrophobic. Hydrophobic substances are the ones which is having less solubility in water or they are water disliking molecules. So if the molecules are water disliking then what will happen is if the solution of that pollutant is existing then all the molecules will be coming to the top surface of the liquid or they will be trying to escape from the liquid at the earliest.

So if you introduce some other medium to that one then it wants to jump from the liquid phase or from the water so they will be immediately getting attached to some other phase. So, one of the driving forces for this adsorption is the water liking or water disliking nature of the pollutants. But when we talk about the non conventional pollutants or the complex organic molecules they may be having water disliking path and water liking path. That means hydrophilic components and hydrophobic components. The hydrophilic components will be always staying inside the water and hydrophobic molecules will be coming out of the water surface. So when we put some solid media to the water then the hydrophobic substances or hydrophobic group of that molecule will be getting attached to the solid media. That is one of the driving forces. This is what I have written here.

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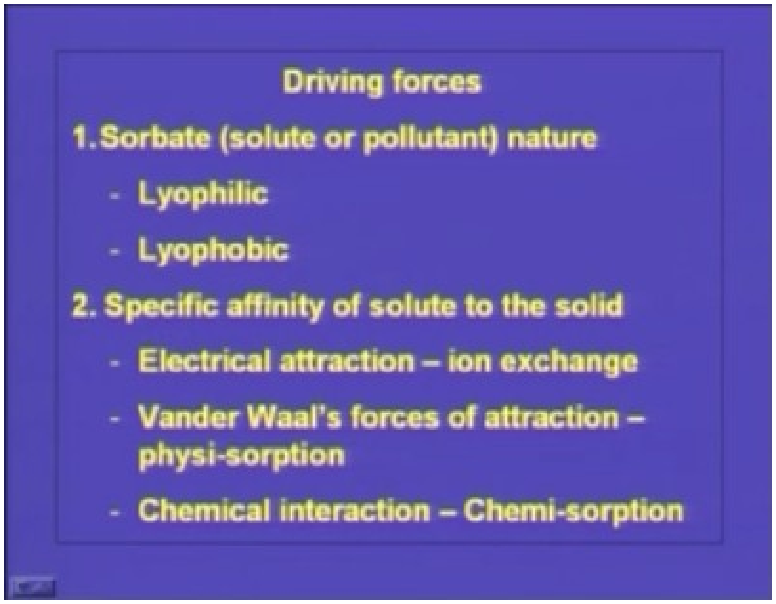

Driving forces

1. Sorbate (solute or pollutant) nature
   - Lyophilic
   - Lyophobic
2. Specific affinity of solute to the solid
   - Electrical attraction – ion exchange
   - Vander Waal's forces of attraction – physi-sorption
   - Chemical interaction – Chemi-sorption

Driving forces:

One is the sorbent nature or the solute or the pollutant’s nature that is lyophilic and lyophobic. Lyphilic is nothing but liquid liking and lyophobic is liquid disliking and hydrophilic is water liking and hydrophobic is water disliking. So if the sorbate or the pollutant is water disliking it will be having a tendency to come out of the water at the earliest or whenever there is a chance it will be trying to come out of the water that is one of the driving forces for adsorption. So it is very easy to remove the pollutant if they are hydrophobic in nature by adsorption.

Now, the second driving force is the specific affinity of the solute to the solid. This specific affinity can be either by electrical attraction. For example, some ions are present in the pollutant or the pollutant is in the ionic form in the liquid some other ions are present in the sorbent or the adsorbent or the material where the pollutant is getting settled. So what will happen is whatever ions present in the solution as pollutant will be having more affinity to the solid than the ions already present there so what will happen is this more affinity ions will be coming out of the liquid and going and getting attached to the solid media and corresponding amount of ions from the solid media or the adsorbent will be coming out. That is one type of electro static attraction. This is what is known as ion exchange.

The major reason for adsorption is one ion is exchanged with the other ion and the third one is Vander Waal’s forces of attraction. When the molecules are in very close vicinity to the adsorbent the attractive forces will be acting between the adsorbent and the adsorbate so because of that one the pollutant will be getting attracted to the sorbent or the adsorbent and will be sitting there. This is known as the adsorption due to Vander Waal’s forces or we can call this adsorption as physi-sorption or physical sorption. The reason is the energy of adsorption will be very very less in case of physical sorption because solute or the pollutant is going and sitting on the adsorbent because of the weak Vander Waal’s forces or because of the concentration gradient.

If the concentration gradient is there more solutes will be present in the liquid and more and more contact will be there between the adsorbent and adsorbate. So if you release the concentration gradient then whatever is sitting there because of this less energy attractive force and because of the reversal of concentration gradient it can come out. That is what is known as the physi-sorption which is due to the Vander Waal’s forces of attraction.

The next one is chemical interaction. There will be some functional group available on the adsorbent which will be having some affinity to the pollutant or the pollutant is able to undergo some chemical reaction in the functional group whatever is present in the adsorbent so what will happen is two components will be reacting and forming a bond so that is having high energy. Hence, that type of an adsorption is known as chemi-sorption. Here the reversibility of the chemi-sorption is very difficult or if you want to reverse it we have to add some other chemical which can react with this compound and release the pollutant from that one.

We have seen what all are the driving forces. I will explain once again. One is the solute nature, depending on whether it is hydrophobic or hydrophilic. So if hydrophobic it will be having more affinity to adsorb on solid media. The other one is the forces between the adsorbent and adsorbate, it can be electrostatic attraction. That means it can be by ion exchange. One ion of the pollutant is getting exchanged between other ion whatever is present in the adsorbent. And the second one is Vander Waal's forces of attraction. That means when the adsorbent and adsorbate are coming in very close vicinity the attractive force will be predominant and because of that one the ions will be migrating to the solid media.

The last one is chemical sorption. Here what is happening is the pollutant will be having some chemical reaction between a specific group on the adsorbent so because of the chemical reaction some bond will be created or generated and it will be going and sitting there. So compared to physical sorption the energy of adsorption is very high in case of chemi-sorption. So, if you want to reverse the adsorption physical sorption is very very easy whereas chemi-sorption is very difficult so we have to add some other chemicals which is having high affinity to that functional group on the adsorbent compared to the pollutant then only we can reverse the adsorption which is due to the chemi-sorption.

Now we will see the adsorption isotherm. We have the pollutant and we have some adsorbent and we are adding the adsorbent to the pollutant or pollutant containing liquid so what will happen is the pollutant will be going and getting adsorbed on the adsorbent. And at the same time because of the change in concentration gradient more and more pollutant will be going and sitting on the adsorbent. So, after some time the concentration of the pollutant on the solid phase will be much more compared to the liquid phase and there will be a tendency to the pollutant molecule to transfer from the solid phase to liquid phase. That means at the same time forward reaction and backward reaction will be taking place, at the same time adsorption and desorption will be taking place where finally the system will be reaching equilibrium. What is that equilibrium? The amount of pollutant what is getting adsorbed will be equal to the pollutant what is getting desorbed that is the adsorption equilibrium.

We can represent this adsorption equilibrium schematically like this:

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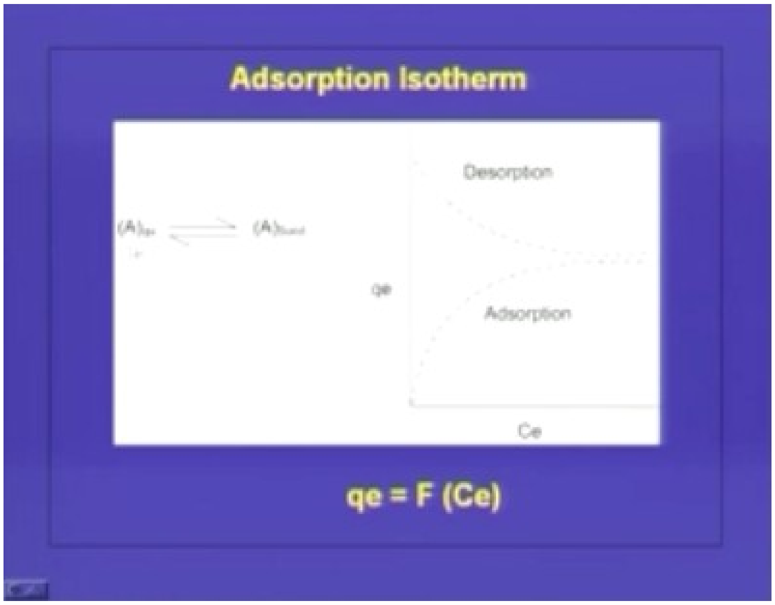

You have the pollutant A in the aqueous phase and we have the pollutant A in the solid phase so from the aqueous phase the pollutant can come to the solid phase so this is the forward reaction and the same time we know that with respect to time the concentration of the pollutant the solid phase will be very high and the concentration in the liquid phase will be less so whatever pollutant has got adsorbed on the solid phase will be migrating to the liquid phase so forward reaction and backward reaction will be taking place simultaneously.

So at equilibrium what will happen if you plot qe, qe is the amount of pollutant adsorbed on the sorbant or adsorbent, it is the unit weight of the adsorbent and Ce is the concentration of the pollutant left over in the aqueous phase. As the concentration on the solid phase is initially less so this will keep on increasing (Refer Slide Time: 18:50) and afterwards it will be almost reaching a saturation level and at the same time what will happen is whatever desorption is already present there will be coming out so both these rates will be remaining a constant at this place. Or at equilibrium what will happen is this is the amount of pollutant adsorbed on the sorbent per unit weight and this will be the equilibrium concentration or the pollutant concentration left over in the liquid phase. This is very very important because this is the maximum pollutant recovery we can achieve in this case.

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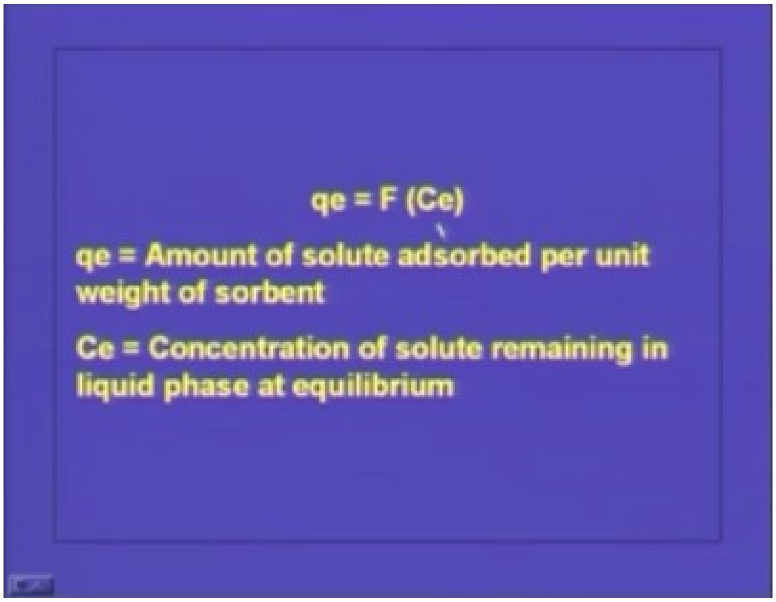

qe = F (Ce)

qe = Amount of solute adsorbed per unit weight of sorbent

Ce = Concentration of solute remaining in liquid phase at equilibrium

Or we can write it in the other way qe the specific adsorption capacity or the pollutant adsorbed per unit weight of the adsorbent, qe is a function of Ce. Ce is the equilibrium concentration of the pollutant in the liquid that is what I have written here; qe is equal to amount of solute adsorbed per unit weight of the sorbent and Ce is the concentration of the solute remaining in the liquid phase at equilibrium. So, as Ce increases qe will be increasing and after some time it will be reaching the equilibrium value or whatever be the Ce value it will be independent of this Ce value or we can see that here it is of first order reaction and here it is a mixed order reaction and afterwards it is coming to a zero order reaction. That means qe is independent of Ce. But in initial stages qe is directly proportional to Ce as I have written here qe is a function of Ce.

Now we will see what isotherm is. Isotherm is a functional expression for the quantity of adsorption with concentration of solute at a constant temperature which is called as adsorption isotherm. That means if you find out what is the amount of pollutant adsorbed on the adsorbent at a constant temperature so we can get the adsorption isotherm. So if you plot the adsorption isotherm that means qe versus Ce we can get either this type of a curve or we can get this type of a curve. This shows how the adsorption is taking place.

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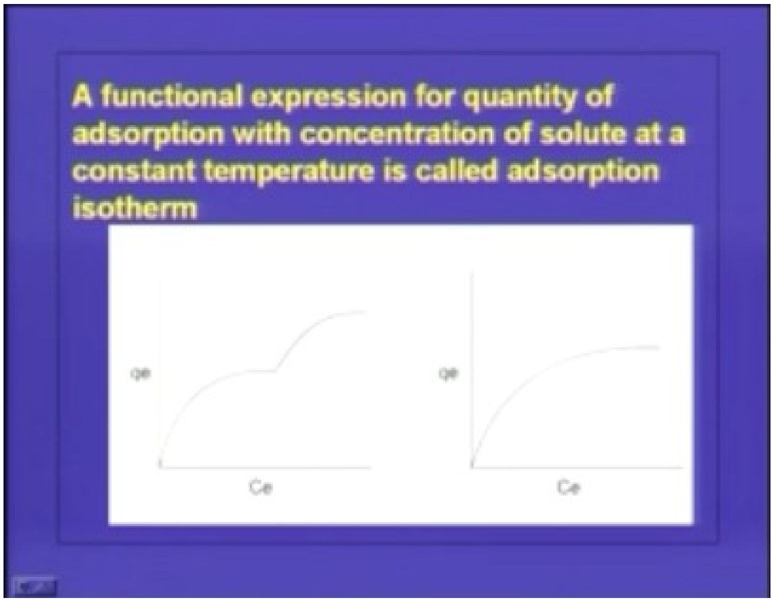

A functional expression for quantity of adsorption with concentration of solute at a constant temperature is called adsorption isotherm

Here, only a single layer adsorption is taking place. Here we can see that the single layer is getting completed and again another layer of pollutant is going and sitting on the adsorbent. So this is an isotherm of multilayer adsorption and this is for a mono layer adsorption (Refer Slide Time: 21:47). So there are different models available for these adsorption isotherms. The most commonly used ones are Langmuir isotherm, Freundlich isotherm and BET isotherm. These models are adsorption isotherm models. Let us look at each one of them in detail. First we will discuss about Langmuir isotherm.

In Langmuir isotherm the assumptions are the adsorption is monolayer. That means the pollutant or the solute can go and sit on the adsorbent only as a single layer. That means no molecule can sit one over the other or the pollutant will be just finishing a single layer. That is one of the major assumptions of Langmuir isotherm. If this single layer has to be formed what has to be there is the adsorption energy should be uniform throughout the surface area or your pollutant will be having uniform adsorption or attractive force or uniform preference to all the sides of the adsorbent. That is what is known as the constant adsorption energy. The third assumption is once the molecule is going and sitting on the adsorbent there will not be any transmigration of the solute. Or once it goes and gets attached it will be sitting there permanently. Hence, those are the three assumptions of Langmuir isotherm.

Once again I will tell, it is a mono layer adsorption and second one is it assumes adsorption energy is uniform throughout and third one is once it is adsorbed the solute will not be going through any transmigrational movement. So if you assume that one and if you plot 1 by qe that means qe is the specific adsorption capacity versus 1 by Ce where Ce is the equilibrium concentration then you will be getting a curve like this so this intercept will be giving you 1 by Qmax so this Qmax is nothing but the maximum specific adsorption capacity. Or this will give you the amount of solutes that can go and sit on the adsorbent which will be forming a complete single layer or complete monolayer over the adsorbent. That is a significance of this Qmax.

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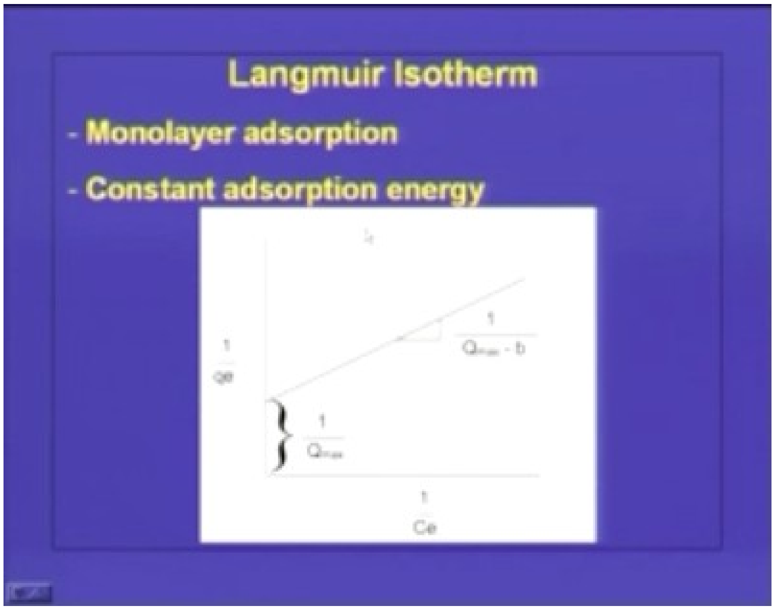

Langmuir Isotherm

- Monolayer adsorption
- Constant adsorption energy

I will explain that one in detail here. So in Langmuir isotherm this is the equation: qe is equal to Qmax into b into Ce by 1 plus b into Ce. Once again qe is equal to Qmax into b into Ce by 1 plus b into Ce where b is the energy or net enthalpy of adsorption or b is proportional to e raise to minus delta H by RT where delta H is the enthalpy of the system the total energy of the system and T is the temperature at degree K and R is the universal gas constant and this Qmax is nothing but the maximum specific adsorption capacity.

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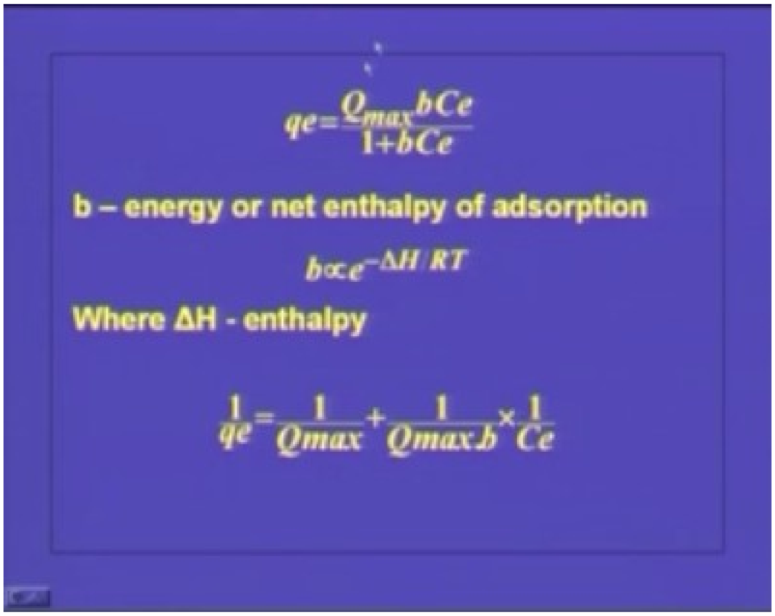

$$qe=\frac{Q_{max}bCe}{1+bCe}$$

b – energy or net enthalpy of adsorption

$$b\propto e^{-\Delta H/RT}$$

Where ΔH - enthalpy

$$\frac{1}{qe}=\frac{1}{Qmax}+\frac{1}{Qmax.b}\times\frac{1}{Ce}$$

The unit will be weight by weight and Ce is the equilibrium concentration of the solute in the liquid or if you want to linearize this one we can write like this 1 by qe is equal to 1 by Qmax plus 1 by Qmax into b into 1 by Ce so this equation is in the form of y is equal to mx plus c so c is this 1 by Qmax and m is 1 by Qmax into b that's what I have shown here. So if you plot that equation 1 by qe versus 1 by Ce the slope will give you 1 by Qmax into b and the intercept will be giving you 1 by Qmax. So we get two equations so from this one we can find out what is the Qmax value and what is the b value. The b value will tell you how strong the solute is adsorbed to the solvent and Qmax will give you what is the maximum adsorption capacity.

The second one is Freundlich isotherm. For Langmuir isotherm we have seen all the assumptions namely monolayer, uniform adsorption energy and no transmigrational movement. But in Freundlich isotherm it is assuming heterogenous surface energies. We know that the adsorbent will be having many many functional groups and depending upon the pollutant each functional group will be having different energy or different preference to the pollutant. We cannot assume a uniform energy in all the cases unless the adsorbent is having uniform or same type of functional group throughout. So in most of the cases especially in natural systems if you use soil or some natural materials as adsorbent then what will happen is it will be having many many functional group on the surface of the adsorbent and each functional group will be having different energy of attraction or energy of adsorption. So in such cases it is always better to go for this Freundlich isotherm because Freundlich isotherm considers heterogeneous surface energies. Hence for the Freundlich isotherm we can write the equation like this:

qe is equal to kf into Ce raise to 1 by n.

So qe is the amount of pollutant or amount of solute adsorbed per unit weight of the adsorbent and Kf is the capacity factor the milligram of sorbate adsorbed per gram of adsorbent and the unit of this Kf will be milligram per gram into litres per milligram by 1 by n and because of this 1 by n this also will be 1 by n and n is a constant indicating the intensity of adsorption

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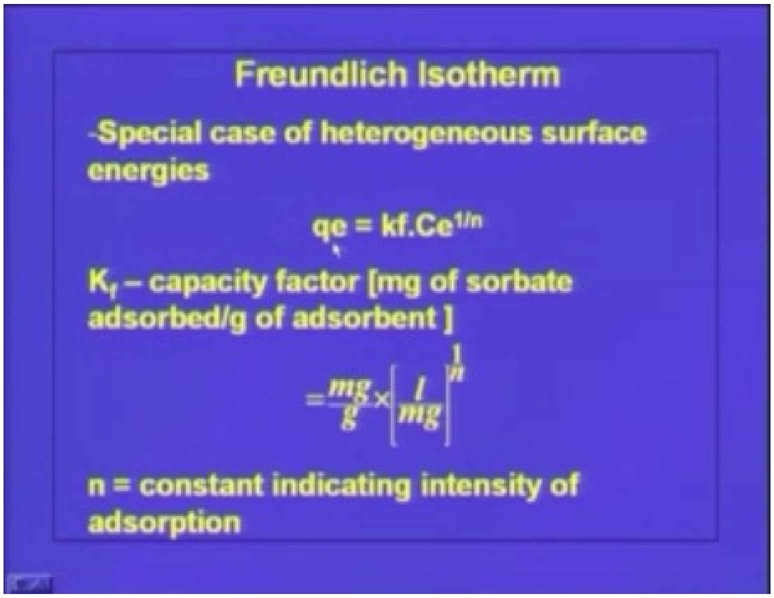

Freundlich Isotherm

-Special case of heterogeneous surface energies

$$qe = kf.Ce^{1/n}$$

K_f – capacity factor [mg of sorbate adsorbed/g of adsorbent]

$$= \frac{mg}{g} \times \left[\frac{l}{mg}\right]^{\frac{1}{n}}$$

n = constant indicating intensity of adsorption

This n can be 1 then it is a linear adsorption or it can be any integer or any decimal number so that will be telling you what is the intensity of adsorption. Therefore, if you linearise the Freundlich isotherm we can take the logarithm on both sides of this equation so what we will be getting is log qe or ln qe is equal to ln Kf plus 1 by n ln Ce so if you plot that one you will be getting a curve like this. This is (Refer Slide Time: 28:28) lnqe in y axis and lnCe in x axis so if you plot that one the intercept will be lnKf this is the Kf value and the slope will be 1 by n so we can find out what is the adsorbent capacity and what is the intensity of adsorption and Kf is proportional to RT n b into e raise to delta H by delta T and this is somewhat similar to the Langmuir isotherm or lnqe is equal to lnKf plus 1 by n into lnCe.

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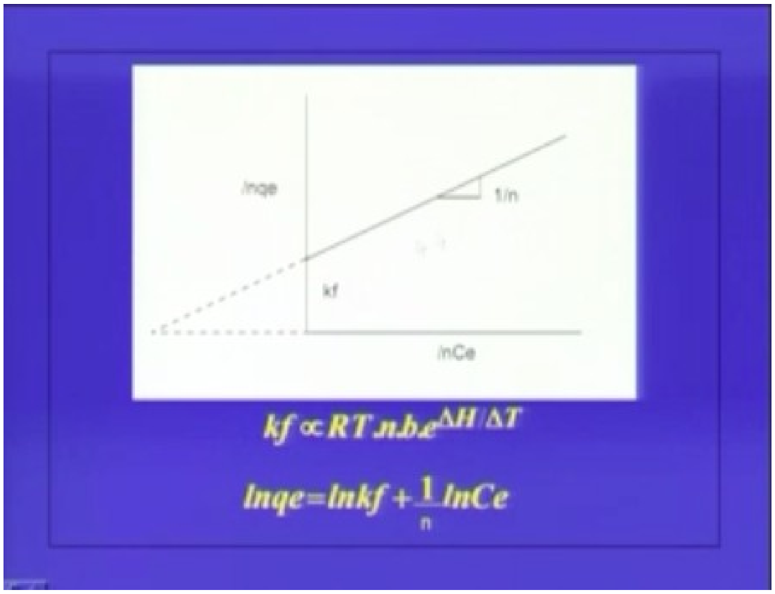

$$kf \propto RT.n.b.e^{\Delta H/\Delta T}$$

$$lnqe = lnkf + \frac{1}{n} lnCe$$

The next one is BET isotherm. BET isotherm is a short form of Brunar Emmet Teller. These are the three Scientists who have developed this isotherm model that is why it is known as BET isotherm. BET isotherm is a special case of Langmuir isotherm. In Langmuir isotherm we are assuming that only monolayer adsorption is taking place. But in BET isotherm once the monolayer adsorption or monolayer is completed the adsorbent will be going and sitting on the adsorbent again so another layer will be starting so that is why it is known as a multilayer adsorption.

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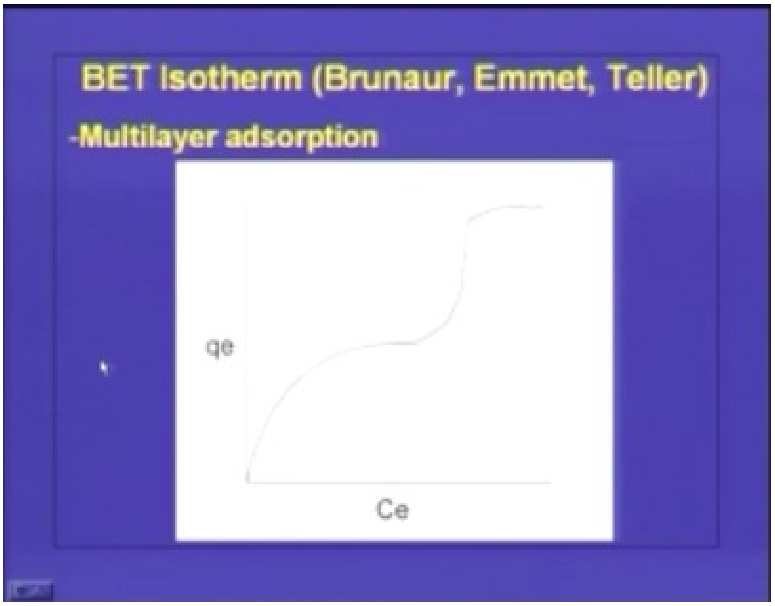

BET Isotherm (Brunaur, Emmet, Teller)

-Multilayer adsorption

We can see here this is the qe and this is the Ce so up to here it is going like this that means at this stage the first layer is completed and again it will be raising and the second layer will be forming so that is the multilayer adsorption, it is a special case of Langmuir isotherm

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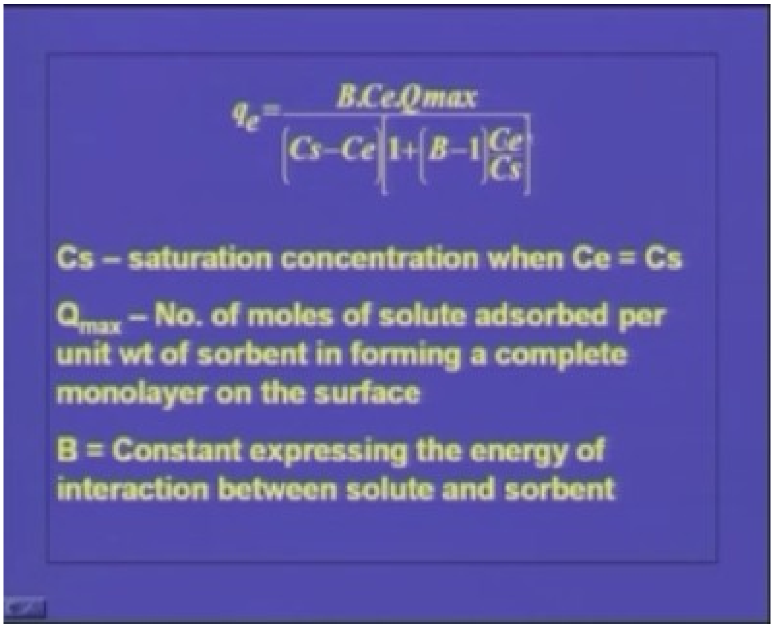

$$q_e = \frac{B.Ce.Qmax}{(Cs - Ce)\left[1 + (B-1)\frac{Ce}{Cs}\right]}$$

Cs – saturation concentration when Ce = Cs

Q_{max} – No. of moles of solute adsorbed per unit wt of sorbent in forming a complete monolayer on the surface

B = Constant expressing the energy of interaction between solute and sorbent

Hence if you want to write the expression for the BET isotherm we can write like this qe is equal to B into Ce into Qmax by Cs minus Ce into 1 plus B minus 1 into Ce minus Cs. We have seen what this Qmax is. Now we will see what is this Cs. Cs is nothing but the saturation concentration when Ce is equal to Cs and Qmax is the number of moles of solute adsorbed per unit weight of sorbent in forming a complete monolayer on the surface. This we have seen in Langmuir isotherm and B is a constant expressing the energy of interaction between the solute and the sorbent so this B is almost the same as the ‘b’ we have seen in the Langmuir isotherm.

So if you want to linearise this equation we can write like this; 1 by qe into Ce by Cs minus Ce is equal to B minus 1 by BQmax into Ce by Cs plus 1 by BQmax. So if you plot the equation like this, in the x axis you put Ce by Cs where C is the equilibrium concentration and this is the saturation concentration and in the y axis it is Ce by Cs minus Ce into 1 by qe so you will be getting a line like this and in the intercept it is nothing but 1 by BQmax and this one is B minus 1 by BQmax so you will be having two equations and two unknowns so we can find out what is the B value and what is the Qmax value.

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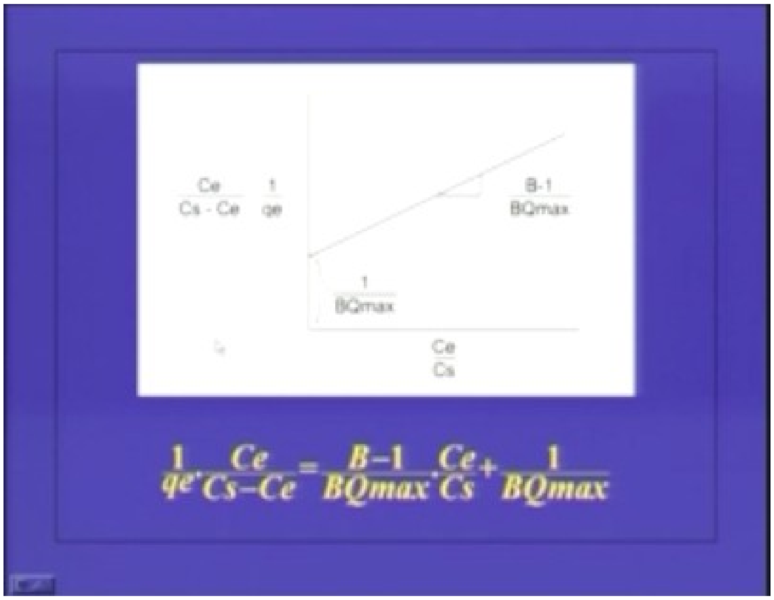

$$\frac{1}{qe}\cdot\frac{Ce}{Cs-Ce}=\frac{B-1}{BQmax}\cdot\frac{Ce}{Cs}+\frac{1}{BQmax}$$

This is the BET isotherm, it is almost similar to the Langmuir isotherm except here multilayer is permitted whereas in Langmuir isotherm only single layer of adsorption is permitted.

Before going to the type of adsorbents let us see what all are the factors that affect the adsorption. The major factor that affects the adsorption is the surface area. We have seen that adsorption is a surface phenomena so if you give more and more surface area definitely the adsorption will be more that is why if you can decrease the size of the adsorbent the adsorption capacity will be very very high.

The second parameter is the pH of the system. If the pH is low hydrogen ions concentration will be very very high and if the pH is very high hydroxil ions concentration will be very very high. So depending upon the pollutant nature either of this H plus ions or OH minus ions will be competing for the adsorption sides so pH is also very very important in adsorption.

The third one is nature of the pollutant. That we have discussed in detail. If the pollutant is hydrophilic or highly soluble in water adsorption will be difficult compared to some substances which are hydrophobic.

The other one is the temperature. We know that the solutes are going and sitting on the adsorbent because of some energy. Another thing is we have seen that the energy is proportional to delta H. So, if the temperature is more definitely the enthalpy of the system will be more so you will be getting a better adsorption.

The major process involved in adsorption is; the first one is migration of the pollutant from the liquid phase to the solid phase. Thus when you take the solid phase there will be a thin liquid film over the adsorbent so the pollutant has to pass through the thin liquid film and it has to go to the adsorbent and the pollutant has to enter through the pore space of the adsorbent then it has to undergo the chemical reaction and sit there. Therefore in adsorption there are three main processes that are involved. One is the film diffusion from the bulk liquid to the solid phase.

Second one is the pore diffusion. That means in the adsorbent itself there will be pores so it has to diffuse through the pores otherwise only the surface of the adsorbent will be available for the adsorption process and third one is the chemical reaction or adsorption reaction. Any one of these steps can be the rate limiting steps. That means the speed of that step will be very less compared to the other two processes. That is known as the rate limiting step. There are various ways by which we can find out which is the rate limiting step and we can overcome that one by certain means.

Now we will see the various types of adsorbents commonly used in water and wastewater treatment. Whenever we talk about the adsorbents the most commonly used one is activated carbon. Activated carbon is very commonly used not only for wastewater and water treatment but it is also commonly used in gaseous pollutant removal also. For activated carbon we can use either the granular form or powdered activated carbon. If you go for powdered activated carbon definitely the surface area will be very very high so naturally the adsorption will be very high if you go for powdered activated carbon. But there are some associated problems. If it is in the powdered form solid liquid separation will be very very difficult so again we have to go for energy intensive solid liquid separation process.

Therefore, in most of the cases what will happen is, people will go for granular activated carbon adsorption using fixed beds. So what you can do is you make a column of this adsorbent and allow the polluted water to pass through that one so the pollutant will be getting adsorbed on the activated carbon and the liquid will be coming out so there is no need for a solid liquid separation process because the solid is staying there as such. But if you use powdered activated carbon what will happen is all the pollutants will be getting adsorbed to the powdered activated carbon but the powder will be in the mixed form in the liquid so either we have to go for coagulation flocculation and settling or centrifugation. This will be increasing the cost of treatment.

Second one is silica based adsorbent. This is also commonly used. And another one is synthetic polymeric compounds and activated alumina is also being commonly used for removing anions like fluoride, oxinic etc from water and another one is biosorbents.

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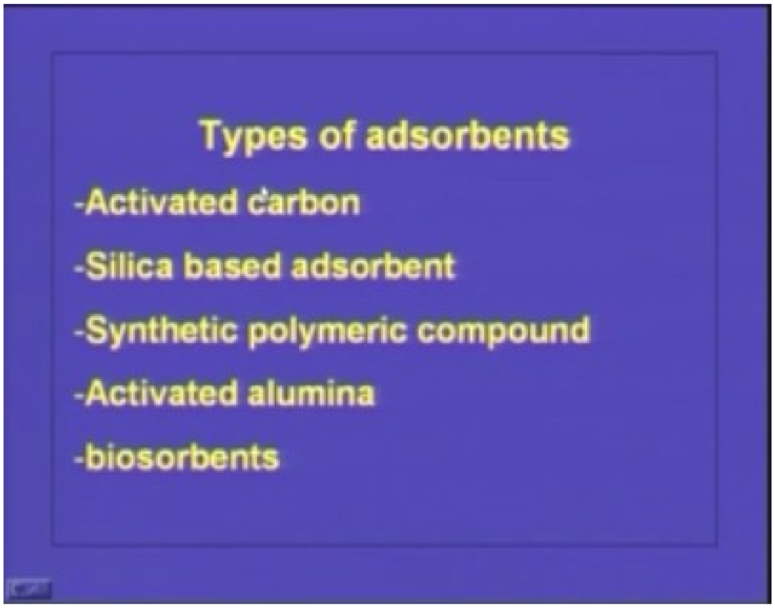

Types of adsorbents

-Activated carbon

-Silica based adsorbent

-Synthetic polymeric compound

-Activated alumina

-biosorbents

Biosorbents are the adsorbents which is developed from biological means either they are dead ones or living ones and it is reported that these biosorbents are having very high adsorption capacity for many pollutant especially the heavy metals.

Now we will see the rate limiting step. This I have already mentioned. The rate limiting steps can be either film diffusion or pore diffusion or chemical reaction.

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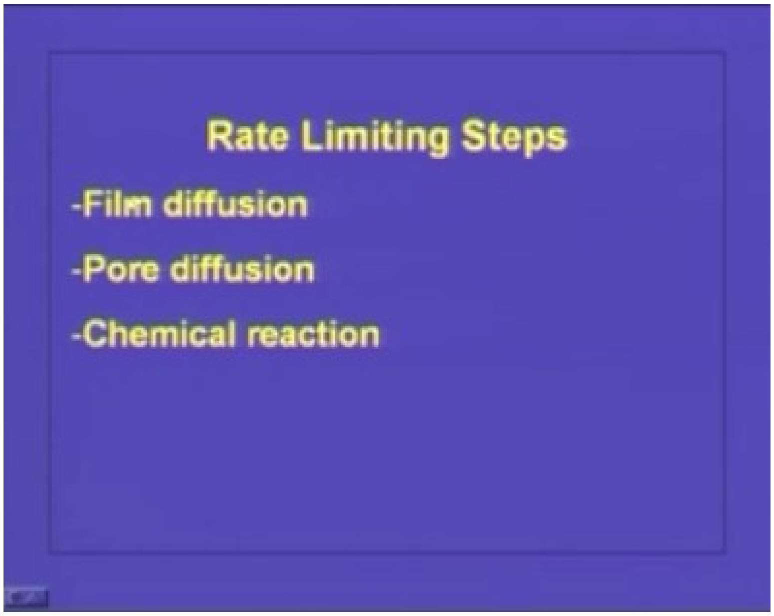

Rate Limiting Steps

-Film diffusion

-Pore diffusion

-Chemical reaction

Film diffusion means the time or the process by which solute is coursing over the thin film of the liquid surrounded on the adsorbent that is the film diffusion. So if you want to reduce the film diffusion rate then we have to give high turbulence. If the turbulence is high definitely the liquid film thickness above the adsorbent will be very very less. If you can increase the turbulence in the system the film diffusion step can be or the time required for the film diffusion can be cut down. Now, the pore diffusion is depending upon the pores of the adsorbent as well as the molecular size of the pollutant. If the molecular size of the pollutant is more than the pore size of the adsorbent then it will take more time to pass through that one. That is pore diffusion and chemical reaction.

So most of the time, either this film diffusion or the pore diffusion will be the rate limiting step. Till now we were talking about the adsorption but there is another term which is known as absorption. What is the difference between this adsorption and absorption? Adsorption is a physical or it is a surface phenomena where the pollutant is getting concentrated on the surface of the solid as far as wastewater treatment is concerned. But in case of absorption what is happening is the solute or the pollutant will be getting into the solid particle or other liquid particle and there will be a molecular level attraction. It is not only the surface phenomena so that is known as absorption.

But in most of the cases it is very difficult to separate the adsorption process and the absorption process so usually the term sorption is used. Sorption will represent both the adsorption as well as absorption. And in the same definition instead of adsorbate we use it as sorbate that means the one which is getting adsorbed or absorbed and similarly sorbent is the one which is adsorbing or absorbing. So when you see the term sorbtion, sorbent or sorption it is nothing but a combination of adsorption and absorption because in such cases we won’t be able to distinguish between these two terms.

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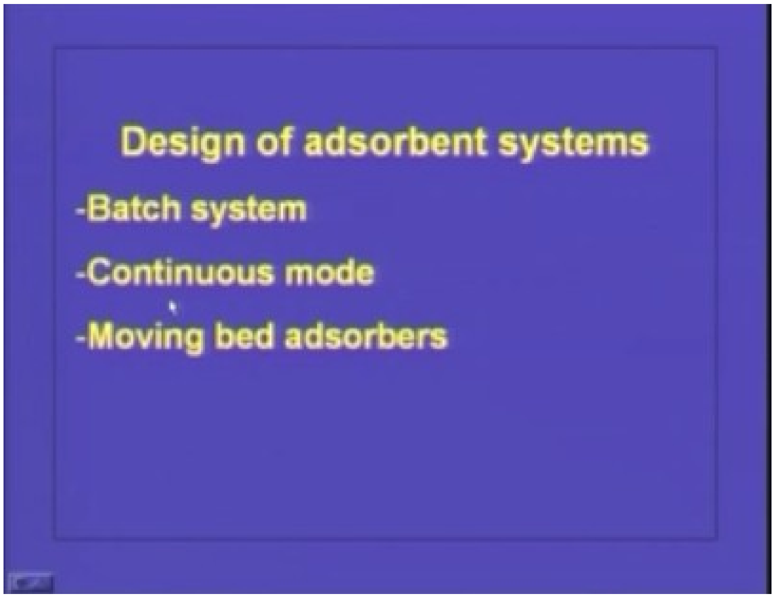

Design of adsorbent systems

-Batch system

-Continuous mode

-Moving bed adsorbers

Now we will see how to design this sorbtion systems or adsorbent system. Either we can go for a batch system or a continuous mode or moving bed adsorbers.

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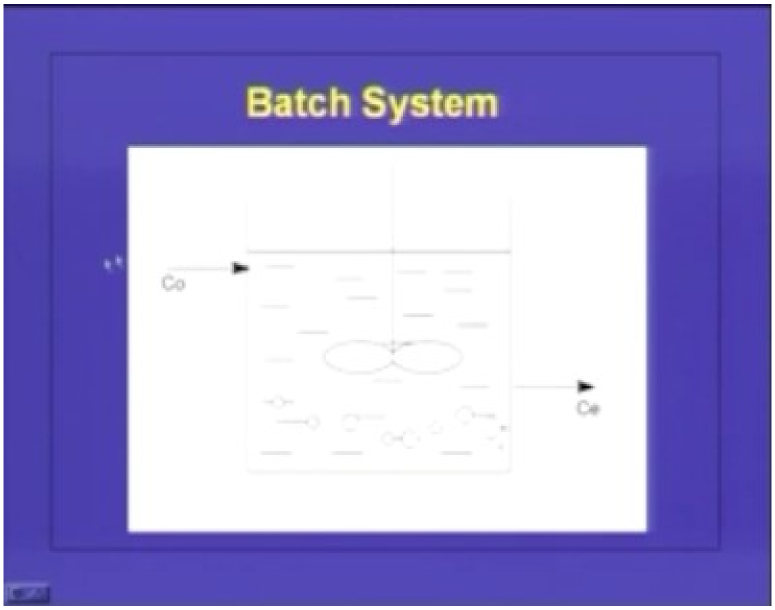

This is a batch system. here you have a reactor, you know what a reactor is, you have the contaminated water or the polluted water or wastewater and the polluted water we are allowing it to enter into the system, it is having a concentration of Co and these are your adsorbents (Refer Slide Time: 40:50) as you can see here and you are stirring the system so that there will be good contact between the adsorbent and the adsorbate, the pollutant whatever is present in the liquid medium. So what will happen is with respect to time the pollutant or the sorbate will be getting adsorbed or the sorbent and after some time most of the pollutants will be getting adsorbed here and we will be getting an effluent. The concentration of the pollutant is Ce so this is a batch system. You give enough reaction time here and afterwards you can take the clean water outside. This is known as a batch system.

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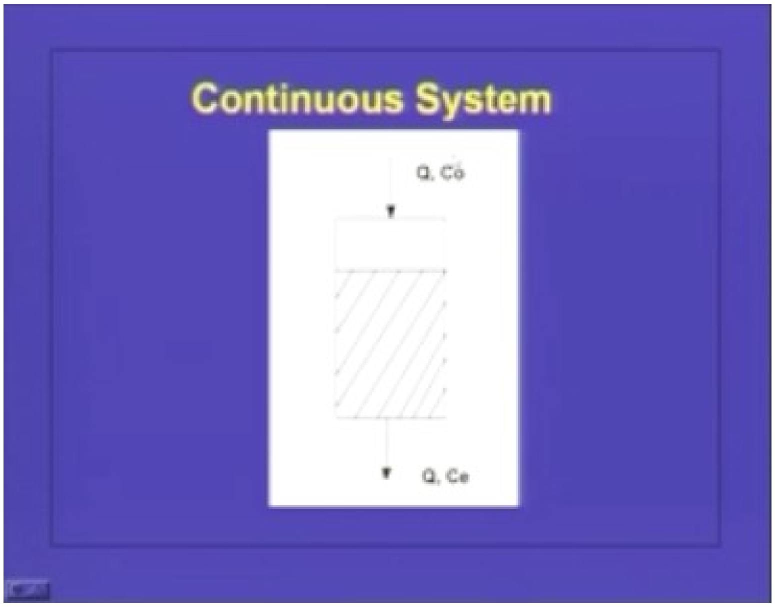

Continuous System

This is a continuous system. Here what is happening is you will be having a column it is filled with the adsorbent and the polluted water is going like this, Q is the flow rate and C0 is the pollutant concentration and the water is coming out, here Q is the flow rate it is the same flow because nothing is getting conserved here so whatever is going in it is coming out in the same rate but only thing is the pollutant concentration is changing from C0 to Ce so whatever the C0 minus Ce is getting adsorbed here so this is the continuous system.

Therefore the adsorbent column will be able to remove the pollutant for quite some time and afterwards what will happen is this Ce value will be gradually increasing and it will be reaching almost equal to C0 value. That is what I have represented here. This curve is known as the breakthrough curve (Refer Slide Time: 42:25). So if you plot Ce by C0 Ce is the effluent concentration of the pollutant or pollutant concentration in the effluent whatever is coming from that column and C0 is the initial concentration of the pollutant or the concentration of the pollutant whatever is entering in the column so definitely Ce by C0 the maximum value will be one because when Ce is equal to C0 we will be getting a value 1 and here we can put either time that means what time it is (adsorbent column) taking to remove or we can put it as throughput volume. So we know the Q and we know the time so we will be able to find out what is the total volume of treated water coming out of the column so this x axis can be either time or throughput volume.

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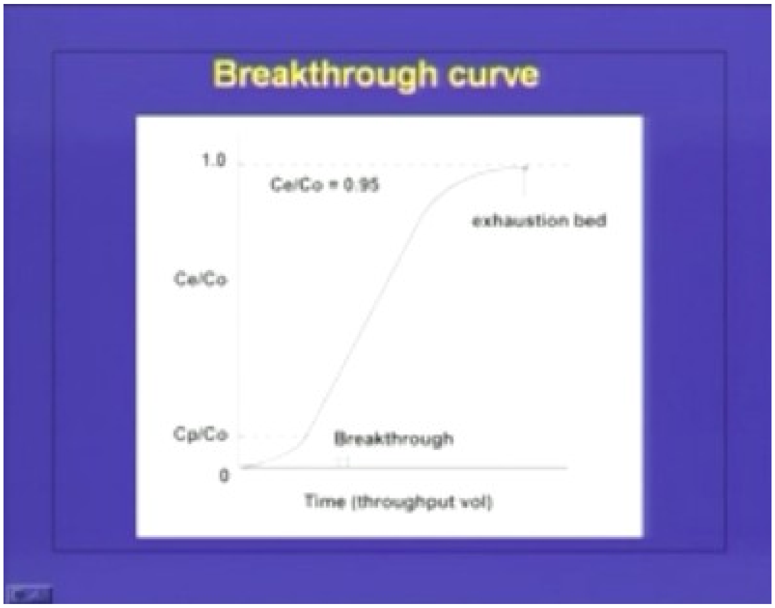
Breakthrough curve

Therefore, if you plot Ce by C0 versus time or throughput volume you will be getting a typical curve like this in any adsorption system so this point Cp by C0 is known as breakthrough point so this Cp is the permitted pollutant concentration because we know that for a particular case for example if you want to use the water for drinking purpose and you have some heavy metal for example you have chromium present in the system so we know that the chromium concentration permitted in drinking water is 0.05 milligram per litre and you are using an adsorption system for the removal so the Cp value permitted here is only 0.5 milligram per litre but your C0 value may be one milligram, two milligram depending upon the water or the wastewater characteristics.

This is the breakthrough curve (Refer Slide Time: 44:15) that means up to here whatever is coming is meeting the standards but your column will be still having a left over capacity so it will be increasing it will be removing some of the pollutants but the effluent pollutant concentration will keep on increasing. Afterwards what will happen is the effluent concentration will be remaining as a constant. Theoretically it should be one but in most of the cases it will reach a value around Ce by C0 is equal to 0.095 which is known as the exhaust concentration. That means after that the bed is not having any capacity to remove any pollutant. So this is the typical breakthrough curve. By seeing through the breakthrough curve we can make out how the adsorbent is going to behave. Sometimes it will be a very sharp curve like this, sometimes it can be like this so depending upon the curve nature we can make out what type of adsorption it is and what is the rate of adsorption etc.

Whenever we go for a fixed bed adsorber how can we find out the depth of the bed required for adsorption? We know that the pollutant is entering into the top of the adsorption column or if it is in the (……. 45:26) it will be entering in the bottom of the adsorption column so the pollutant will be coming in contact with the adsorbents present in the column and the pollutant will get removed. but if you take a thin layer in the top that layer may not be able to remove all the pollutants so the first layer will be removing some of the pollutants and slowly it will be coming and after reaching a particular depth the pollutant concentration will be zero and once that layer is exhausted that layer will be coming down and down and the entire column will be getting exhausted. That’s what I have represented here.

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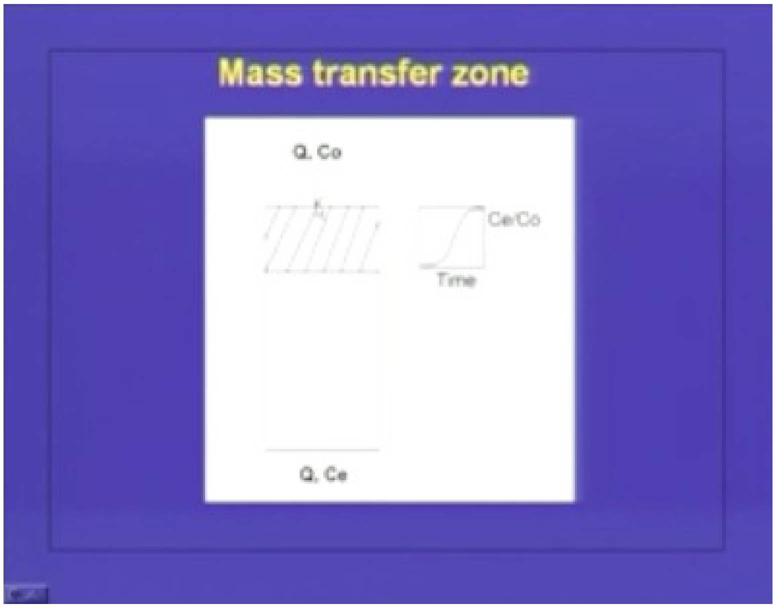

Mass transfer zone

This is your adsorption column. The pollutant is coming here. So if you take a thin layer like this the C0 may not be becoming zero so some of the pollutant will be getting adsorbed here but as it passes here say this much of depth so the C0 will be here and if you see the pollutant concentration may be almost 0 or almost approaching zero concentration. That means this much of depth is necessary to remove the pollutant completely from the flowing liquid. This is known as mass transfer zone or the primary adsorption zone.

So whenever we design a column or a fixed bed absorbent column the bed depth should be more than the primary adsorption zone depth. If you want to provide this much of depth then you will not be able to remove the pollutant completely at any time. This is very very important. This depth can be found out from batch studies in the laboratory and that information can be used for the design of the continuous columns. Now we will see how to design adsorption column.

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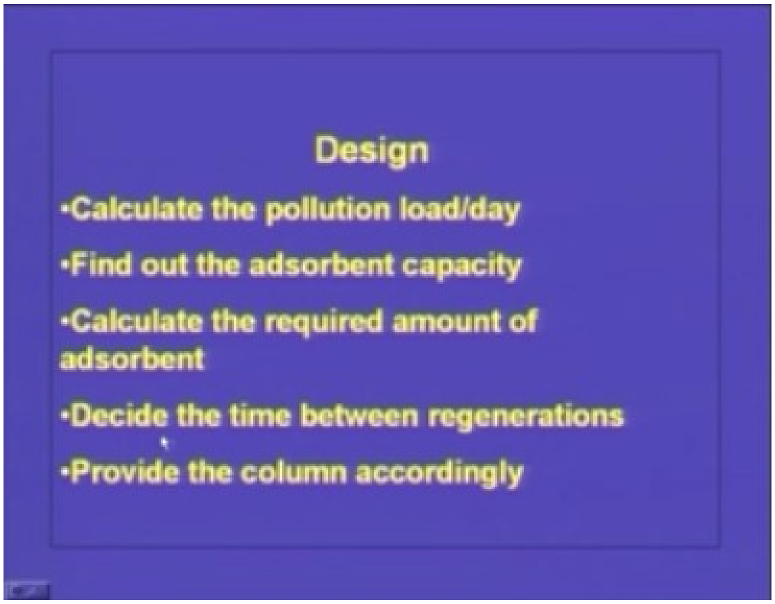

Design

- Calculate the pollution load/day
- Find out the adsorbent capacity
- Calculate the required amount of adsorbent
- Decide the time between regenerations
- Provide the column accordingly

First we want to know the total amount of pollutant coming to the system so we calculate the pollutant load per day and second one is find out the adsorbent capacity so for this one we can use either Freundlich isotherm or Langmuir isotherm or BET isotherm. What we have to do is we have to conduct laboratory studies and see which model the adsorption of that particular pollutant is following, whether it is following Langmuir isotherm or Freundlich isotherm or BET isotherm so depending on that one we can find out what is the adsorbent capacity.

Then the third step is calculate the required amount of adsorbent. We know what the total pollutant load per day is and we know what the adsorbent capacity is so we can calculate the required amount of adsorbent that is total pollutant load divided by the adsorbent capacity so you will be getting the amount of adsorbent needed per day.

The fourth step is to decide the time between regenerations because once the adsorption capacity is completely exhausted we cannot just throw away the adsorbent. If you just throw away the adsorbent your treatment cost will be so high so we have to regenerate the adsorbent that means you use some chemical reagents to wash the adsorbent so that whatever pollutant is sitting on the adsorbent will be coming out and the bed will be free to remove more and more pollutant that is known as the regeneration. You decide the time that you can provide between regenerations and depending upon this time provide the column depth accordingly. This is all about adsorption.

We have seen the different forces, what are the different types of adsorption, what all are the factors affecting and how can we design an adsorption system. The next process is ion exchange. Ion exchange is defined as the process where an insoluble substance removes ions of positive or negative charge from an electrolytic solution and releases other ions of the same charge into the solution in a chemically equivalent amount. Once again I will explain.

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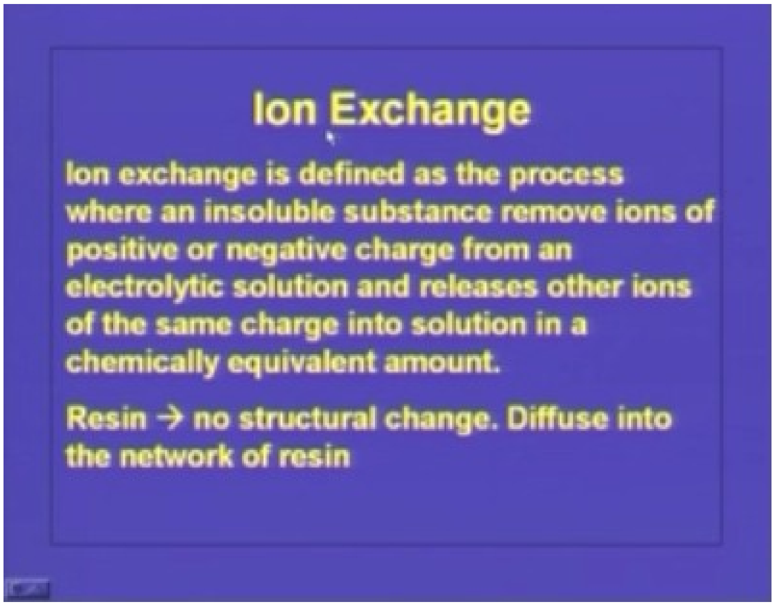

Ion Exchange

Ion exchange is defined as the process where an insoluble substance remove ions of positive or negative charge from an electrolytic solution and releases other ions of the same charge into solution in a chemically equivalent amount.

Resin → no structural change. Diffuse into the network of resin

Ion exchange is defined as the process where an insoluble substance removes ions of positive or negative charge from an electrolytic solution and releases other ions of the same charge into the solution in a chemically equivalent amount. That means here in ion exchange you will be having some substance and it will be having some ions present in that one and your solution will be having other ions.

Please remember that it is possible only for electrolytic solution or ionic solution. If you have some organic matter which is non ionizable we cannot use ion exchange process for the removal of the pollutant. Here what happens is some ions are present in the liquid and some ions are present in a substance in the solid form. So once we put the solid form or the solid into the liquid then what will happen is the ions whatever is present in the solid will be having less affinity to that solid matrix compared to the ions what is present in the liquid. So what will happen this ions whatever is present in the solid will be going to the liquid and same amount of ions will be coming to the solid media. That is known as ion exchange where exactly one ion is exchanged for the other ion.

Therefore, whenever we go for ion exchange process the total dissolved solids concentration the treated water will be remaining the same if you calculate the total dissolved solids concentration in terms of milli equivalents per litre. If 1 milli equivalent of the pollutant is coming to the adsorbent the same amount or the same 1 milli equivalent ions whatever is present in the ion exchange resin will be going to the liquid so there will not be any net change in total dissolved concentration if it is expressed in terms of milli equivalents. But if you express in terms of milli grams per litre there will be some change because the molecular weight of the compounds will be different. so after this ion exchange resin is the solid on which the ions are located and the exchange is taking place so there will not be any structural change in the resin and these ions will diffusing into the network of the resin. So, if you want to express it in terms of equations we can write like this;

nRA plus plus Bn plus is equal to Rn minus into Bn plus plus n into A plus.

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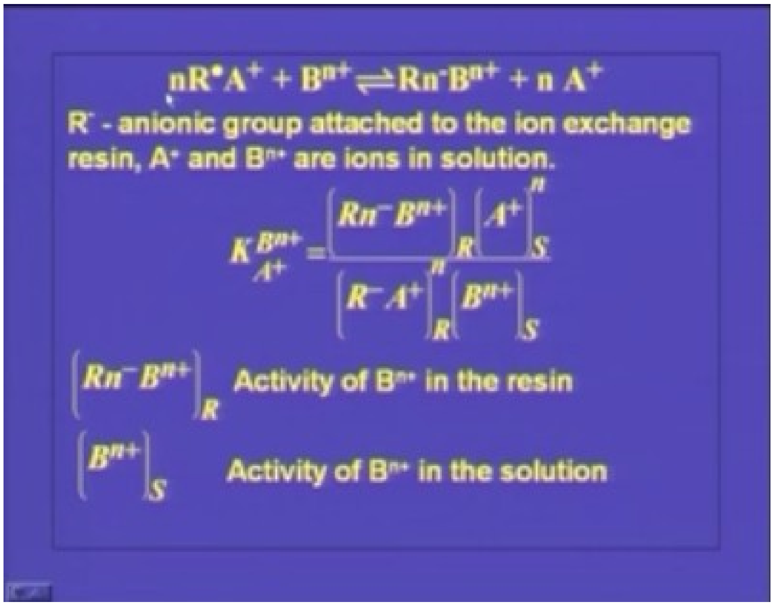

$$nR^{\bullet}A^{+} + B^{n+} \rightleftharpoons Rn^{-}B^{n+} + n\,A^{+}$$

R^{-} - anionic group attached to the ion exchange resin, A^{+} and B^{n+} are ions in solution.

$$K_{A^{+}}^{B^{n+}} = \frac{\left(Rn^{-}B^{n+}\right)_R \left(A^{+}\right)_S^{n}}{\left(R^{-}A^{+}\right)_R^{n} \left(B^{n+}\right)_S}$$

$\left(Rn^{-}B^{n+}\right)_R$ Activity of B^{n+} in the resin

$\left(B^{n+}\right)_S$ Activity of B^{n+} in the solution

Therefore, what is happening is nR minus A plus that means R is the anionic group which is attached to the solid matrix and A plus is the cation which is getting attached to this anionic group so this is the resin whatever is present in the system so it is having an anionic group and a cation sitting here and Bn plus (Refer Slide Time: 52:55) is the cation present in the solution or this is your solute on which you want to remove. so in ion exchange what is happening is the A plus is getting removed and Bn plus is coming so there should be that electro or the charged balance so if you want to replace this Bn plus with A plus so nA plus should be going out because the charge should be the same. So this A is having only monovalent or it is a monovalent ion but it is a multi valent ion with charge of n. So if you want to take one Bn plus ion we have to release nA plus ions that is why the reaction is coming like this; Rn Rn minus this is the anionic group into Bn plus plus n into A plus.

A and B are the ions in the solution or if you want to write down the coefficient or activity, this (Refer Slide Time: 53:58) is the coefficient of ion exchange KBn plus with A plus that means A is replaced by Bn plus so the coefficient of that one is equal to Rn minus into Bn plus that means the product of the reaction by the reactants. This is the product of the reaction and this is the reactants so product of the products by product of the reactants is the equilibrium constant. We have seen this one in any chemical equation and that is what is written here.

It is this concentration multiplied by this concentration divided by this concentration multiplied by this concentration. That means what is the concentration of Bn plus in the resin into what is the concentration of A plus in the solution by what is the concentration of A plus in the resin by what is the concentration of Bn plus in the solution. So Rn minus Bn plus resin means activity of Bn plus in the resin and Bn plus 1 and S means the activity of Bn plus in the solution. That means some Bn plus ions will be in the resin and some will be in the solution similarly for A plus some will be in the solution and some will be in the resin so if Bn plus 1 is more in the resin that means this resin is having more affinity to this B compared to A and vice versa.

That means if more A plus is sitting in the resin after the ion exchange also then A is having more affinity to the resin than B so B cannot be removed effectively by ion exchange, this is the coefficient. Or K Bn plus by A plus is known as the coefficient.

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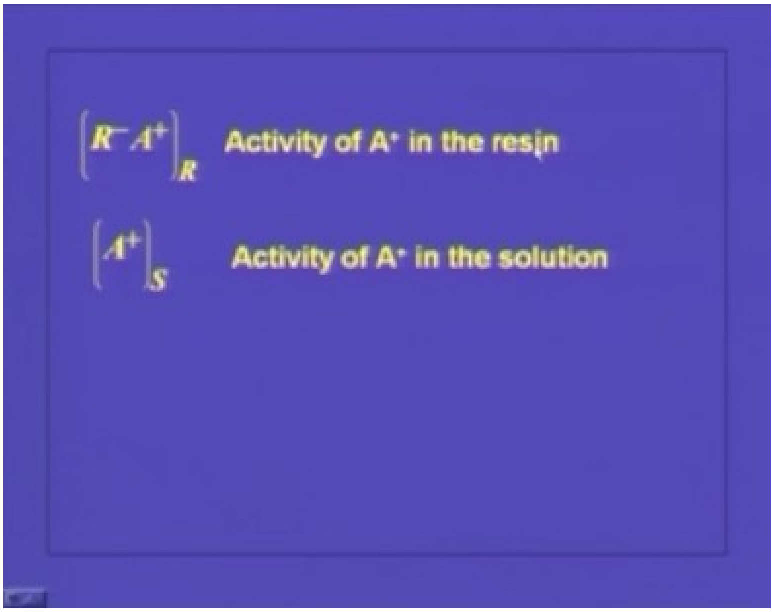

$\left(R^- A^+\right)_R$ Activity of A^+ in the resin

$\left(A^+\right)_S$ Activity of A^+ in the solution

And here it is R A plus R activity of A in the resin and this S is activity of A in the solution. So another term we can use is the selectivity quotient or separation factor which is represented by Qs so that is nothing but Rn Bn plus into A plus divided by R A plus into Bn plus. Earlier we have seen that if the valency or the charge is not same for one ion we have to send n ions of A plus. So the reaction constant or this equilibrium constant or the coefficient will be coming like this (Refer Slide Time: 56:36) the n term will be coming here and the n term will be coming here but whenever we talk about the selectivity quotient it is for the mono ion exchange, one ion is going there and one ion is coming here or the selectivity quotient and the quotient are same when n is equal to 1 or Qs and K dash A plus Bn plus are identical. This is this is known as the separation factor or the selectivity quotient.

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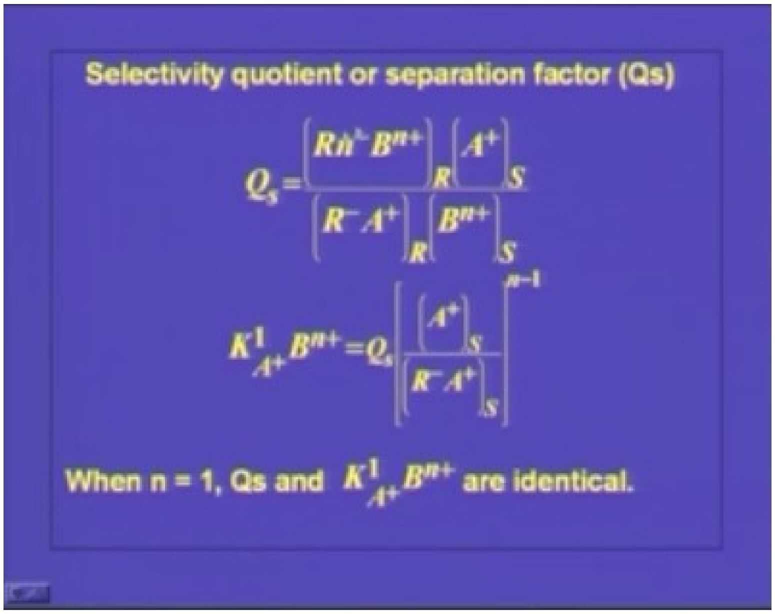

Selectivity quotient or separation factor (Qs)

$$Q_s = \frac{\left(R_n^- B^{n+}\right)_R \left(A^+\right)_S}{\left(R^- A^+\right)_R \left(B^{n+}\right)_S}$$

$$K^1_{A^+} B^{n+} = Q_s \left[\frac{\left(A^+\right)_S}{\left(R^- A^+\right)_S} \right]^{n-1}$$

When n = 1, Qs and $K^1_{A^+} B^{n+}$ are identical.

Therefore by using the selectivity quotient we can see whether ion exchange is feasible or non feasible. If Qs is greater than 1 we can remove the pollutant using ion exchange. If Qs is equal to 1 it will be coming like this. That means the ion exchange is linear with the concentration of the pollutant in the solution and if Qs is less than one it is an unfavorable ion exchange. That means the ion whatever is sitting on ion exchange will be having more affinity to the resin than the ion of interest or the ion whatever is present in the solution. Or if this is the case it will be very very difficult to remove the pollutant from the solution.

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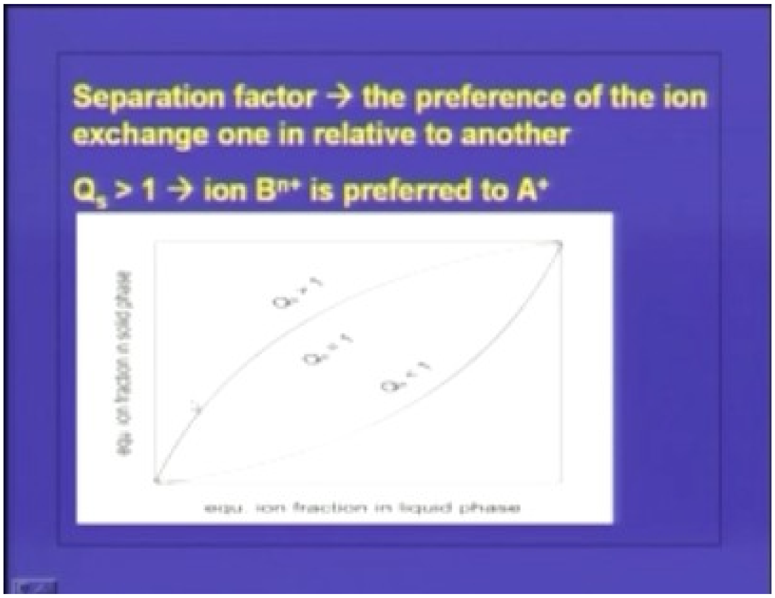

Separation factor → the preference of the ion exchange one in relative to another

$Q_s > 1$ → ion B^{n+} is preferred to A^+

Till now we will see what we have discussed so far and remaining portion of this ion exchange we will discuss in detail in the next class. Today we were discussing basically about the adsorption and we have seen adsorption is a phase transfer process. That means the pollutant from one phase is getting concentrated on the other phase and this is basically because of the solute nature as well as the sorbent nature.

If the solute is hydrophobic then it will be removed at a faster rate. The other forces responsible are electrostatic force, Vander Waal’s force and chemical forces. And we have seen that adsorption is a non selective process. It will be adsorbing all pollutant concentrations that is a major disadvantage of adsorption but adsorption process is very commonly used in water and wastewater treatment. And the most commonly used adsorbent is activated carbon and we can use activated alumina, biosorbents etc from this process and we were discussing about ion exchange. We have seen the major difference between adsorption and ion exchange. The remaining portion of ion exchange we will discuss in the next class.