Water and Wastewater Engineering

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Advanced Oxidation Processes

Lecture # 35

In last two classes we were discussing about advanced wastewater treatment.
We have seen the membrane processes as well as adsorption in detail. Yesterday we started with ion exchange process. Today we will continue on that. We will be discussing about ion exchange processes and other advanced wastewater treatment like advanced oxidation, distillation then today we will start on what is the theory of industrial wastewater treatment.

First we will see what is ion exchange. This we have discussed yesterday. 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 the solution in a chemically equivalent amount. That means here exchange of ions will be taking place. So one type of ions will be getting removed from the solution but equivalent amount or equivalent amount of ions will be coming from the resin that is why it is known as ion exchange process.

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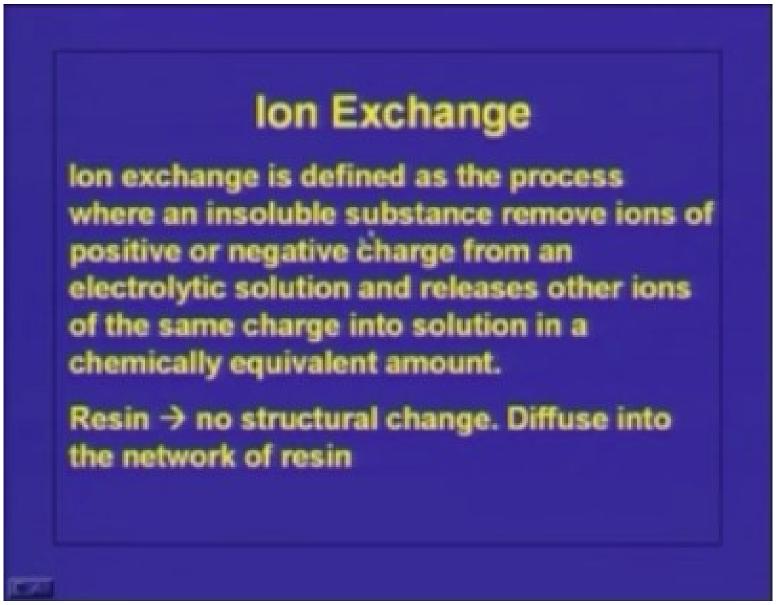

Ion Exchange

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

In the resin there will not be any structural change and whatever ions are present in the solution will be diffusing into the ion matrix. Therefore, if you want to write the equation of an ion exchange reaction we can write like this; n R into A to the power plus plus B power n plus. So this is the ion of interest in the solution we have to remove and this is the ion exchange resin, R is the anionic group attached to the ion exchange resin and A is the cation which is attached to the anionic group. And if ion exchange has to take place this B power n plus 1 should have more preference to this anionic group compared to A to the power plus. So what will happen? This B power n plus will replace A to the power plus so the charge neutralization should be there because this B is having n plus positive charge. So, instead of maintaining the charge neutralization what should happen is n ions of A to the power plus should come out that is what is written here; Rn minus into B power n plus plus n into A to the power plus.

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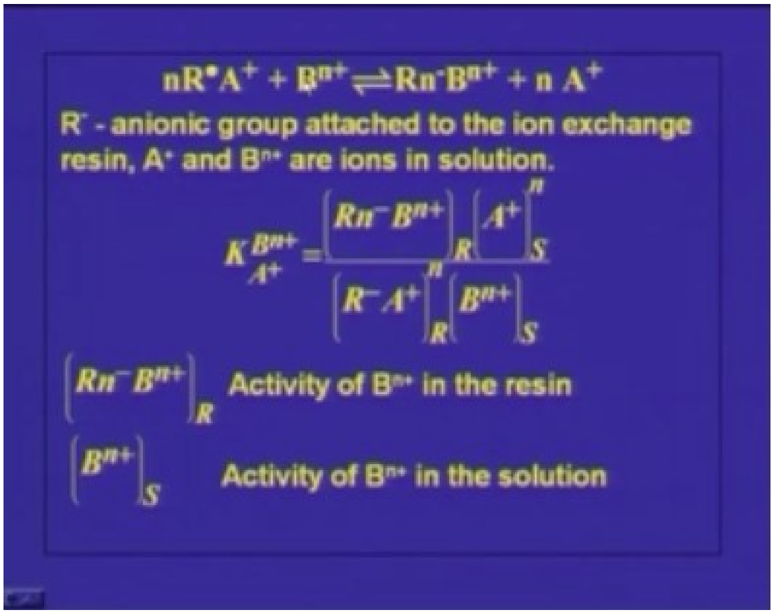

$$nR^{\bullet}A^{+} + B^{n+} \rightleftharpoons Rn^{-}B^{n+} + n\,A^{+}$$

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

So if you want to find out what is the selectivity coefficient or how much selectivity this B ion is having over A ion in the ion exchange resin then we can calculate that one using this expression so K B power n plus one over A to the power plus means selectivity of B over A, selectivity coefficient of B power n plus ion over A is equal to Rn minus 1 B power n plus 1 concentration in the resin into A to the power plus raise to n because n ions are coming out in the solution divided by R A to the power plus one raise to n because nR A to the power plus was involved in the reaction and B power n plus one in the solution. This is the expression to find out the selectivity coefficient.

It is just similar to the chemical equilibrium. How we will find out the chemical equilibrium constant. It is nothing but the product of the concentration of the product divided by the product of the concentration of the reactant so that is exactly what we are doing here so another term which is constantly used in ion exchange process is selectivity quotient or it is also known as separation factor, we have already seen this yesterday.

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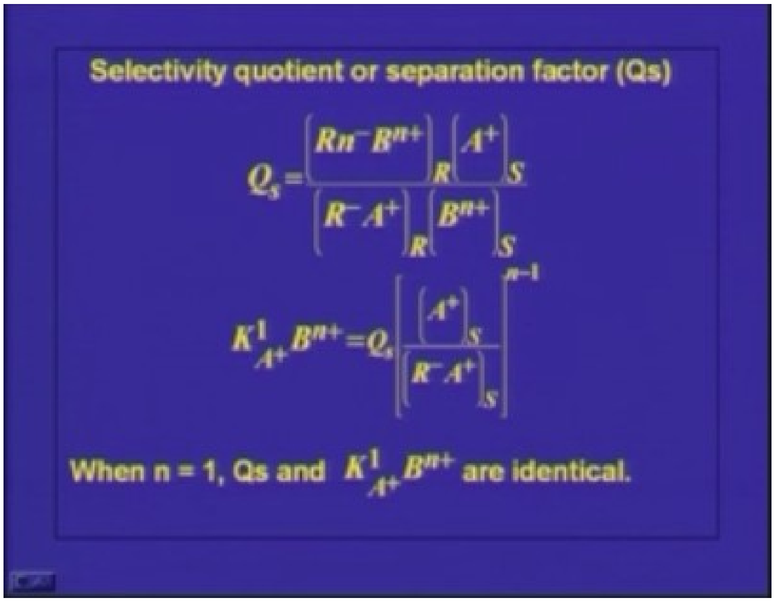

Selectivity quotient or separation factor (Qs)

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

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

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

Usually it is represented as Qs, it is similar to the selectivity coefficient, the only thing is here we are considering only ion of each cation so here we are writing like this; Rn minus B power n plus in the resin into A to the power plus in the solution. We are not taking the number of ions into consideration divided by R A to the power plus in the resin by B power n plus in solution. Or if you want to make a equation which shows the relationship between the selectivity coefficient and selectivity quotient then we can write like this; selectivity coefficient is equal to Qs into A to the power plus solution by A to the power plus in the resin raised to n minus 1 because 1 is taken care of here and n ions of A to the power plus is involved in the reaction so if you multiply this Qs by this ratio raise to n minus 1 then we will be getting the activity coefficient and if n is equal to 1 Qs and this activity coefficient are identical. this Qs is a very very important term because by seeing the Qs we can make out whether the ion exchange is feasible or possible or not.

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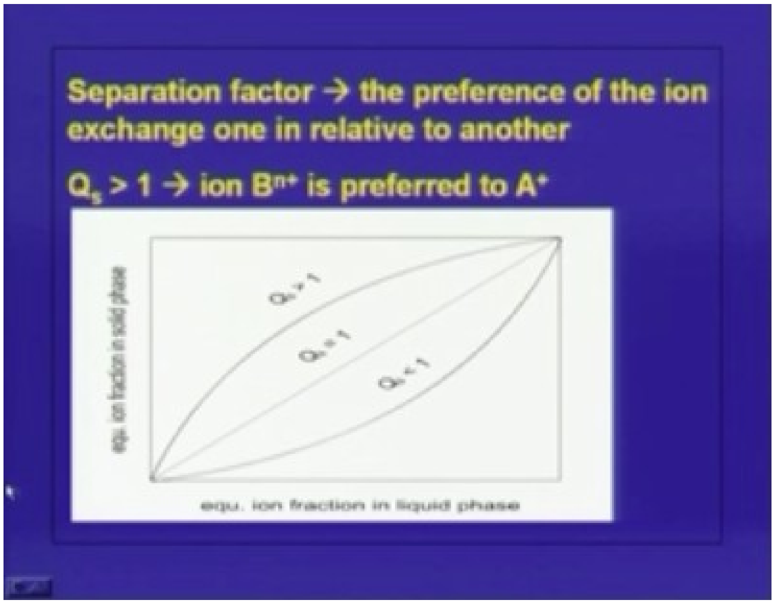

Separation factor → the preference of the ion exchange one in relative to another

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

If Qs is greater than one we will be getting line like this or the ion exchange process can be expressed like this. This is the equivalents of fraction in solid phase (Refer Slide Time: 6:15) and this is the equivalents of ion fraction in liquid phase. So this shows that more ions are getting concentrated on the liquid phase and if Qs is 1 that means it is a linear variation and Qs is less than one it is unfavorable ion exchange. That means the cation whatever already exists in the ion exchange resin is having more selectivity over the ion whatever is present in the liquid. So we will take a common example.

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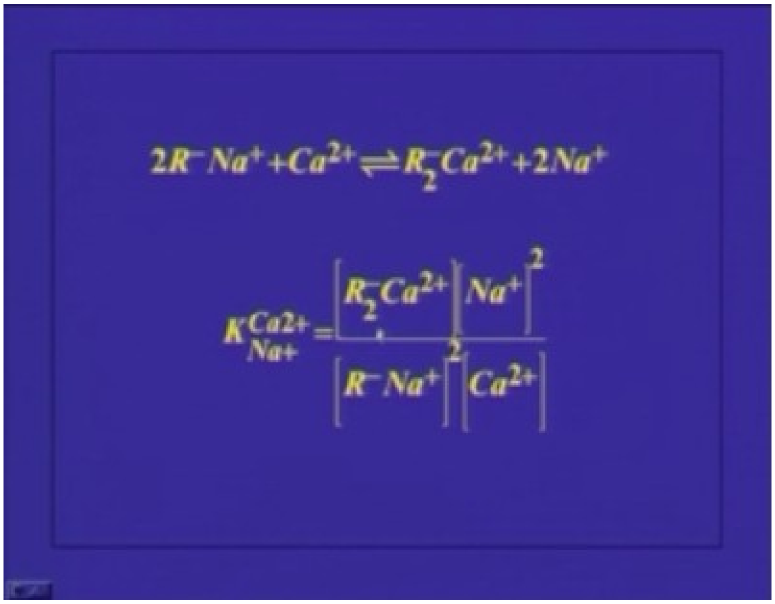

$$2R^-Na^+ + Ca^{2+} \rightleftharpoons R_2^-Ca^{2+} + 2Na^+$$

$$K^{Ca2+}_{Na+} = \frac{\left[R_2^-Ca^{2+}\right]\left[Na^+\right]^2}{\left[R^-Na^+\right]^2\left[Ca^{2+}\right]}$$

If you have a resin with sodium ions on that one and we want to use this resin for the removal of calcium so the chemical equation we can write like this 2R NA to the power plus because calcium is having a valency of 2 and sodium is having a valency of 1 so if you want to exchange calcium ions then definitely there should be two molecules of this R Na then only the exchange process can take place that is why the reaction is coming like this so 2R NA to the power plus plus Ca power 2plus will give you R_2 Ca power 2plus plus 2Na. So if you want to find out the selectivity coefficient of calcium over sodium then we can get it like this; R_2 Ca to the power 2plus concentration into Na raised to 2 because 2 ions are coming out by R NA to the power plus raised to two because two molecules are present here into Ca power 2plus. So if this is greater than 1 that means the ion is having more preference on calcium ions than sodium ions that means calcium ions can easily be removed from the solution.

Now we will see how the affinity of ions for a resin can be generalized because many different types of ions will be present in the wastewater. Especially when we talk about the wastewater coming from the industries in the process they will be using different inorganic salts. So definitely when it is in the solution different types of cations and anions will be present. We are interested in removing a particular ion or a group of ions and we don’t want to remove all the ions. So how can we decide which ion exchange resin can do that one or which ion will be removed more? Hence, these are the points which will tell you which is having more affinity. Ions of high valence are preferred over ions of low valence. This is very very important.

If you have a ion with three valency and an ion of two valency and an ion of one valency the ion with three valence will be preferred over two valence then the single valence ion will be taken up so that is what this shows. Fe power 3plus will be having more preference over Mg power 2plus over NA to the power plus. Similarly anions are also phosphate it is having three valence, it is having more preference over sulphate and sulphate is having more preference over nitrate which is a single valent ion. So this preference increases with a decrease in the total ionic concentration of the solution. For example we have seen that Fe power 3plus is having more preference over NA to the power plus but if Fe power 3plus concentration is very very less compared to NA to the power plus then what will happen is because of the concentration gradient NA to the power plus will be getting attached more. This is also a very important point.

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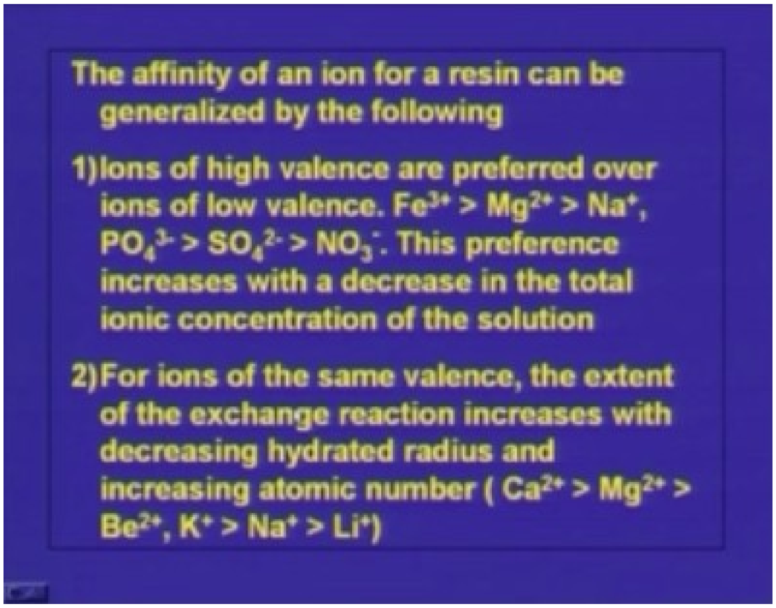

The affinity of an ion for a resin can be generalized by the following

1) Ions of high valence are preferred over ions of low valence. $Fe^{3+} > Mg^{2+} > Na^{+}$, $PO_4^{3-} > SO_4^{2-} > NO_3^{-}$. This preference increases with a decrease in the total ionic concentration of the solution

2) For ions of the same valence, the extent of the exchange reaction increases with decreasing hydrated radius and increasing atomic number ($Ca^{2+} > Mg^{2+} > Be^{2+}$, $K^{+} > Na^{+} > Li^{+}$)

The second one is for ions of same valence. The extent of the exchange reaction increases with decreasing hydrated radius and increasing atomic number. So this is also very important. If the valency is the same then if the ion which is having the less hydrated radius and more atomic number it will be preferred.

For example, if you have calcium, magnesium and berilium we know that all these three ions are having a valency of 2 plus, so which will be preferred over the other. Calcium will be having more preference over magnesium and magnesium will be having more preference on berilium. Similarly if you take the case of potassium, sodium and lithium, lithium is coming first in the periodic table then sodium then potassium so potassium is having high atomic number so K power plus will be preferred over Na and Na will be preferred over lithium.

Similarly, for a solution with high total ionic concentration the extent of ion exchange reactions follows no general rule and is often reversed. For example, if you have a single valent ion and a trivalent ion or a divalent ion so from the dilute solutions we can easily remove the divalent ion with the exchange of single valent ion but if you put another solution which is having very high ionic strength then what happens is the preference may reverse. This principle is used for the regeneration of ion exchange resins.

For example, if you want to use some resin especially the zeolite resin and so on for hardness removal the calcium ions and magnesium ions will be getting removed and once the ion exchange resin is saturated if you want to regenerate that ion then we have to pour sodium chloride solution with high concentration. That means some 10 to 20 percentage sodium chloride solution if you pass then the calcium and magnesium ions will be thrown away from the ion exchange resin and sodium will be occupying the place. That is what is written here.

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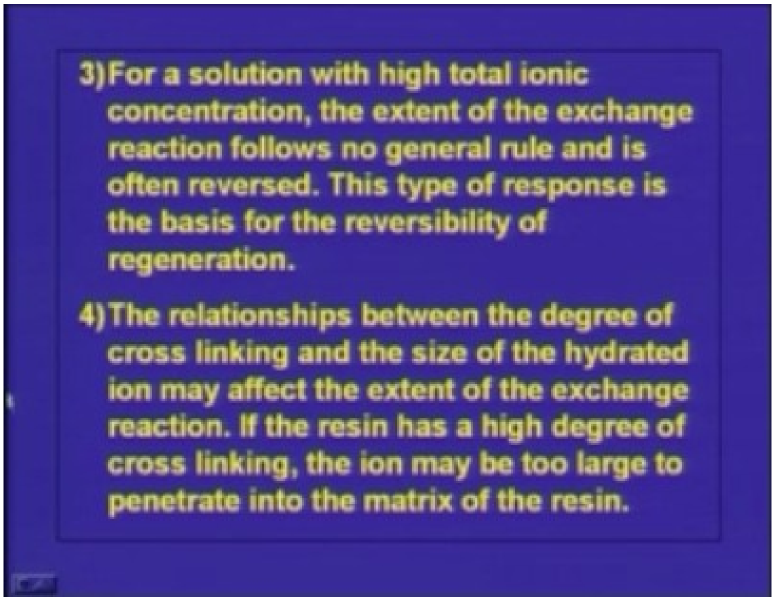

3) For a solution with high total ionic concentration, the extent of the exchange reaction follows no general rule and is often reversed. This type of response is the basis for the reversibility of regeneration.

4) The relationships between the degree of cross linking and the size of the hydrated ion may affect the extent of the exchange reaction. If the resin has a high degree of cross linking, the ion may be too large to penetrate into the matrix of the resin.

The fourth point is the relationship between the degree of cross linking and the size of the hydrated ion may affect the extent of the exchange reaction. If the resin has a high degree of cross linking the ion may be too large to penetrate into the matrix of the resin so the cross linking of the matrix of the resin is also very very important. If the pore size is very small then what will happen is the ions with large hydrated radius may not be able to penetrate through the pores of the resin or the matrix of the resin so in that way also we can segregate the ions and remove the ion that is not needed.

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Now we will see what all are the advantages and disadvantages of choosing ion exchange process.

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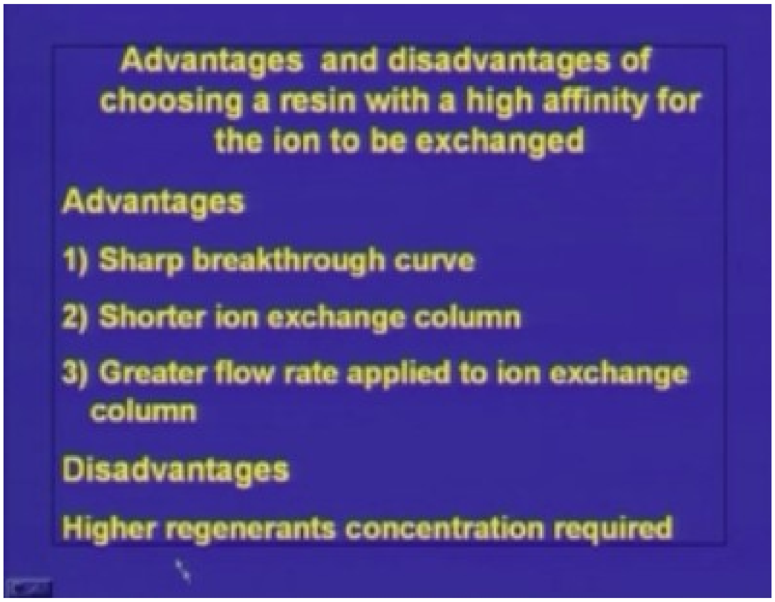

Advantages and disadvantages of choosing a resin with a high affinity for the ion to be exchanged

Advantages

1) Sharp breakthrough curve

2) Shorter ion exchange column

3) Greater flow rate applied to ion exchange column

Disadvantages

Higher regenerants concentration required

If you go for a high affinity for the ion to be exchanged then you will be getting a sharp breakthrough curve then a shorter ion exchange column because the ions in solution will be having very high preference over the ions whatever is sitting on the resin so a shorter ion exchange column can remove the ions in the solution and greater flow rate can be applied to the ion exchange column. These are the advantages if you choose a resin with a high affinity for the ion to be exchanged.

- Harp breakthrough curve
- Shorter ion exchange
- Greater flow rate applied to the ion exchange column

The disadvantage is higher regenerants concentration is required. This is because the ions which is exchanged is having very very high affinity to the resin compared to the ion whatever was already existing in the resin. So, if you want to replace the ions or if you want to regenerate the resins then what we have to do is we have to give very high concentration gradient then only it can push out the ions whatever is exchanged.

Now we will see what all are the different types of ion exchange resins. The ion exchange resins can be divided into two major categories. One is cation exchange resin and another one is anion exchange resin. The name itself explains what it means. The cation exchange resin can be divided into two categories. One is strong acid exchange resins and another one is weak acid exchange resins. In anion exchange resins also there is strong base exchange resins and weak base exchange resins. So once again the major classification is cation exchange resin and anion exchange resin. Again in cation exchange resin strong acid exchange resins are there and weak acid exchange resins are there.

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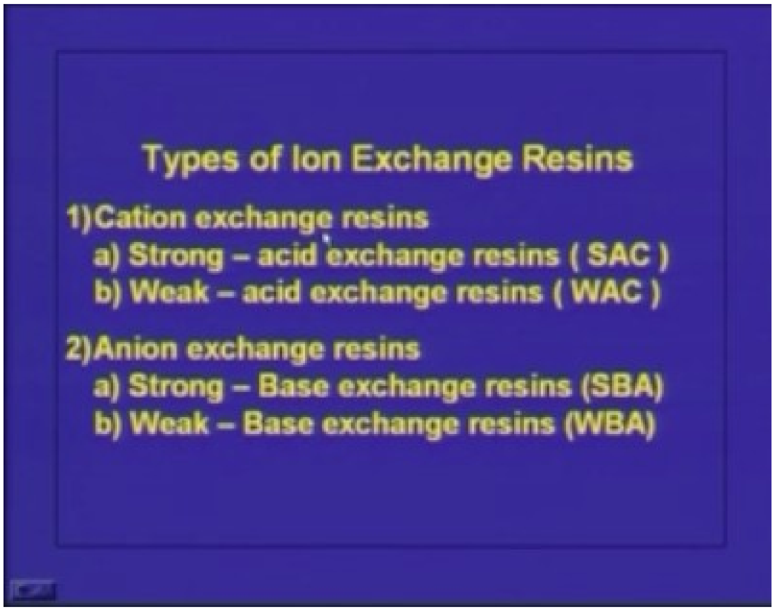

Types of Ion Exchange Resins

1)Cation exchange resins
  a) Strong – acid exchange resins (SAC)
  b) Weak – acid exchange resins (WAC)

2)Anion exchange resins
  a) Strong – Base exchange resins (SBA)
  b) Weak – Base exchange resins (WBA)

In anion exchange resins strong base exchange resins are there and weak base exchange resins are there. Now in detail we will see what is strong acid exchange resins and weak acid exchange resins, similarly what is the strong base exchange resins and weak base exchange resins.

A strong acid exchange resin is the one whose functional group is derived from a strong acid. This is very important. A strong acid exchange resin is a one whose functional group is derived from a strong acid. Their degree of ionization is analogous to that of a strong acid. That means it will be ionizing very fast which permits the hydrogen to be dissociated and ready for exchange over a wide pH range. Now we will see what a weak acid based resin is.

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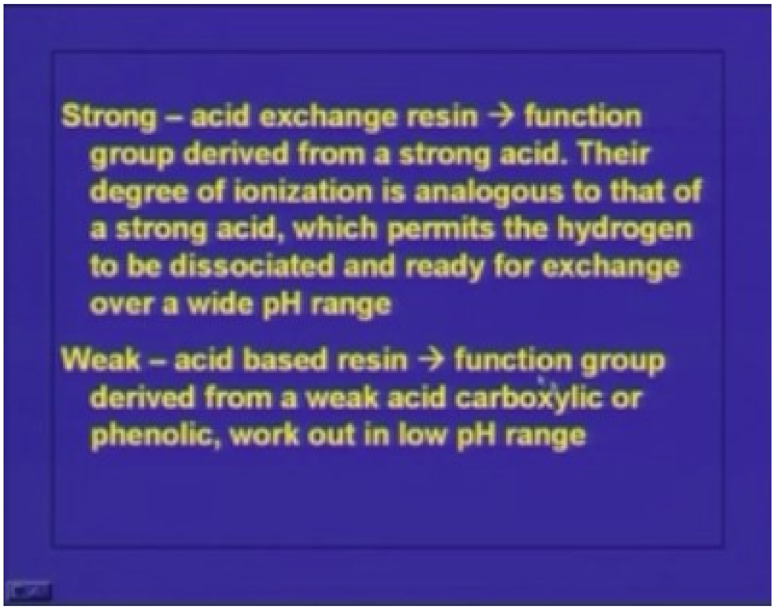

Strong – acid exchange resin → function group derived from a strong acid. Their degree of ionization is analogous to that of a strong acid, which permits the hydrogen to be dissociated and ready for exchange over a wide pH range

Weak – acid based resin → function group derived from a weak acid carboxylic or phenolic, work out in low pH range

Here the functional group is derived from a weak acid like carboxylic or phenolic acid and these resins are able to work only in pH range. So the difference is this is derived from a strong acid and it undergoes ionization very fast and it can function in a wide pH range whereas in a weak acid based resin the functional groups are generated or developed from weak acid like phenolic acid or carboxylic acid and the major disadvantage is such resins can be functional only in a small pH range below pH7. I will show you some examples of these strong acid exchange resins and weak acid exchange resins. This is a strong acid exchange resin R minus SO_3 minus H power plus this is the anionic group attached to the resin and this is the functional group which is derived from the acid. And if you add a salt NaCl then what will happen is this H plus will be replaced by Na so you will be getting a strong acid HCl and the other thing will be R - SO_3 minus NA to the power plus.

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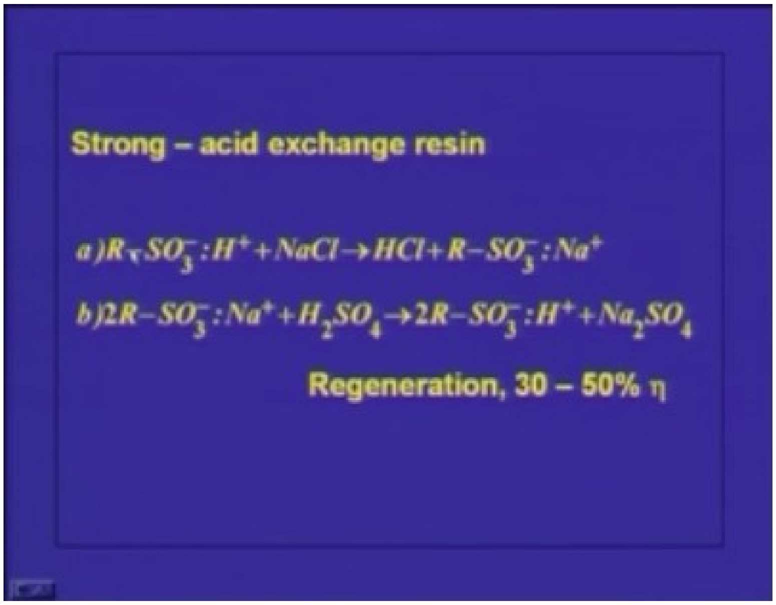

Strong – acid exchange resin

a) $R-SO_3^-:H^+ + NaCl \rightarrow HCl + R-SO_3^-:Na^+$

b) $2R-SO_3^-:Na^+ + H_2SO_4 \rightarrow 2R-SO_3^-:H^+ + Na_2SO_4$

Regeneration, 30 – 50% η

Similarly we can write this one. If you want to go for the regeneration then this (Refer Slide Time: 17:04) is already exchanged with NA to the power plus so you add the strong acid so it will be again coming back with H power plus ions and you will be getting the corresponding salt. The major disadvantage of this strong acid exchange resin is because it is having high affinity to this one compared to other cations so the regeneration efficiency will be very very less, the maximum regeneration you can get is 30 to 50 percentage but it can be used for a wide pH range. This is weak acid exchange resin so this is an organic acid so you are adding sodium bicarbonate and you are getting sodium salt of this one and H_2CO_3 is coming out and similarly for sodium salt if you can add an acid it will be replaced by H power plus ions and the salt will be coming.

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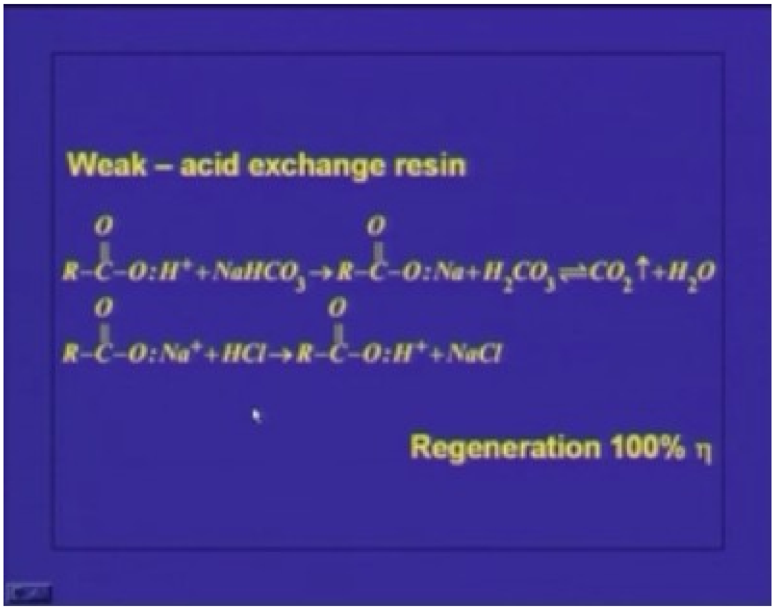

Weak – acid exchange resin

$$R-\overset{O}{\overset{\|}{C}}-O:H^+ + NaHCO_3 \rightarrow R-\overset{O}{\overset{\|}{C}}-O:Na + H_2CO_3 \rightleftharpoons CO_2\uparrow + H_2O$$

$$R-\overset{O}{\overset{\|}{C}}-O:Na^+ + HCl \rightarrow R-\overset{O}{\overset{\|}{C}}-O:H^+ + NaCl$$

Regeneration 100% η

So the advantage of this weak acid exchange resin is that the regeneration capacity is very very high, the reason is the affinity towards this one because it is functioning as a weak acid so this affinity will be not so high so we can easily replace this one that is why we are getting high regeneration efficiency.

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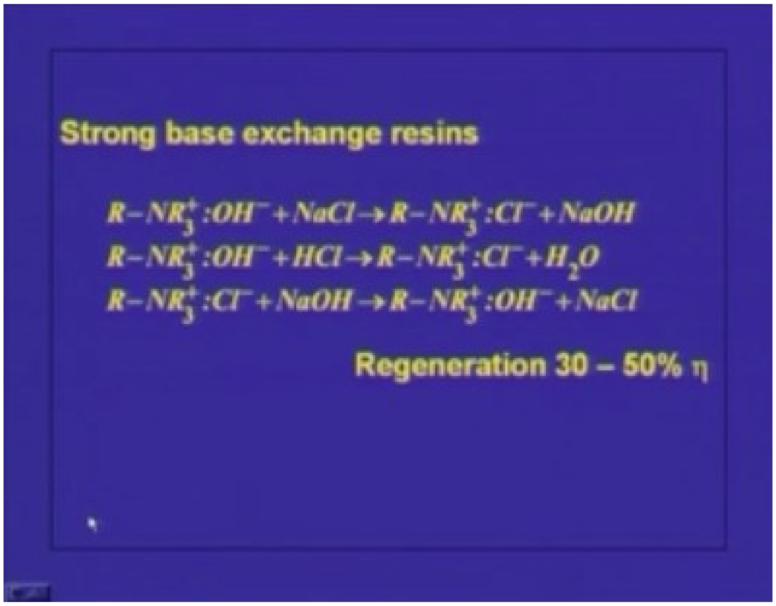

Strong base exchange resins

$$R-NR_3^+:OH^- + NaCl \rightarrow R-NR_3^+:Cl^- + NaOH$$

$$R-NR_3^+:OH^- + HCl \rightarrow R-NR_3^+:Cl^- + H_2O$$

$$R-NR_3^+:Cl^- + NaOH \rightarrow R-NR_3^+:OH^- + NaCl$$

Regeneration 30 – 50% η

Similarly the strong base exchange resins which is derived from a strong base. It is having a functional group OH. When we add some salt this Cl minus will be replacing this OH and you will be getting the corresponding base if you add HCl that is Cl and

H2O again the regeneration efficiency is very less here so you will be getting a regeneration efficiency of 30 to 50 percentage.

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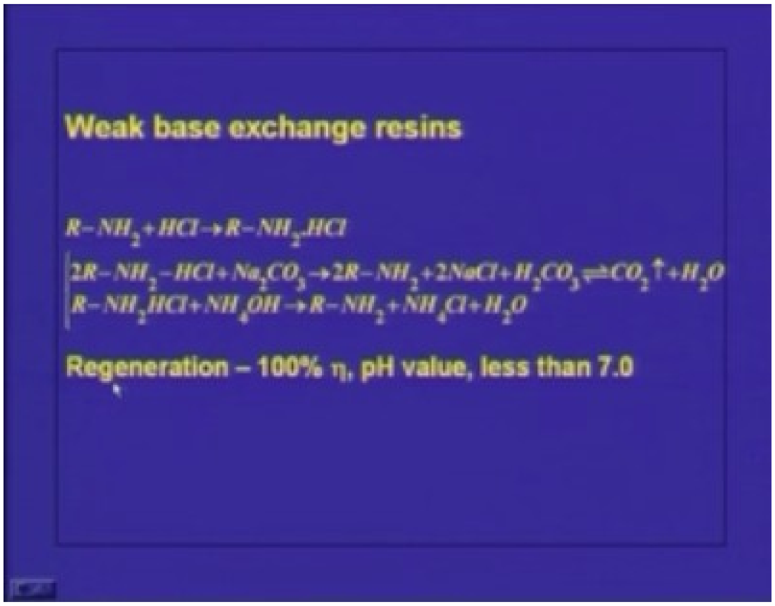

Weak base exchange resins

$R-NH_2+HCl \rightarrow R-NH_2.HCl$

$2R-NH_2-HCl+Na_2CO_3 \rightarrow 2R-NH_2+2NaCl+H_2CO_3 \rightleftharpoons CO_2\uparrow+H_2O$

$R-NH_2HCl+NH_4OH \rightarrow R-NH_2+NH_4Cl+H_2O$

Regeneration – 100% η, pH value, less than 7.0

The weak base exchange resin is just like weak acid exchange resins. The regeneration you get will be 100 percentage and pH value will be functional and the pH value will be less than 7.0. These are the different types of ion exchange resins.

Now we will see what all are the general characteristics of ion exchange resin. Whenever we want to go for an ion exchange process we should know what the general property is or what type of resin we have to select and what is the quantity we need to treat the effluent or treat to get the required treatment efficiency. So the most important parameter is ion exchange capacity. Now we will see what is this ion exchange capacity. It is nothing but the total capacity. The ion exchange capacity is a measure of the total quantity of the ions which theoretically can be exchanged. That means it is nothing but the number of ionizable group that is present in the ion exchange resin per unit mass or per unit volume of resin.

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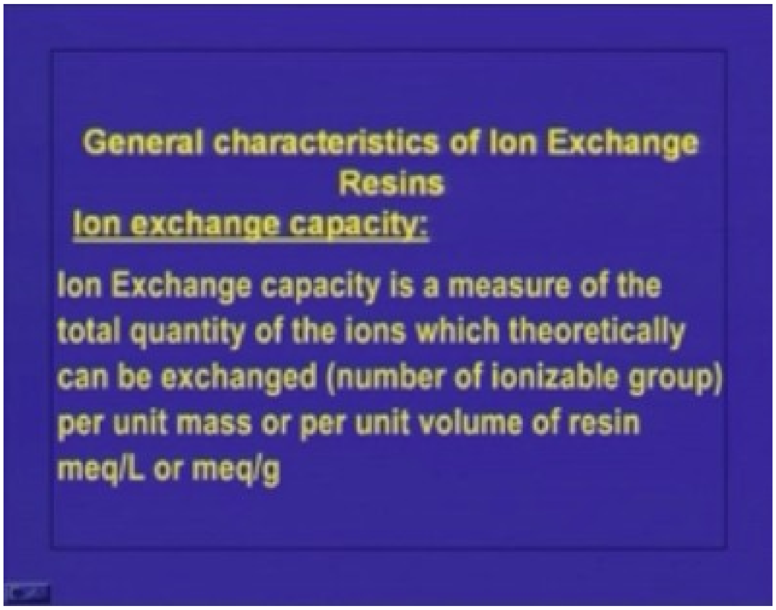

General characteristics of Ion Exchange Resins

Ion exchange capacity:

Ion Exchange capacity is a measure of the total quantity of the ions which theoretically can be exchanged (number of ionizable group) per unit mass or per unit volume of resin meq/L or meq/g

Usually it is expressed as milli equivalents per litre or milli equivalents per gram. That means what is the maximum number of ions? The ion exchange resins can exchange. That means it is nothing but the total ionizable group that present in the ion exchange resin. So, if the number of ionizable group is more then that much of ions can be exchanged for some other ions what is present in the wastewater so this ionizable groups or the amount of ionizable ions present in the ion exchange resin will give you the ion exchange capacity and the unit usually used is milli equivalents per litre if you want to express it in terms of volume or milli equivalents per gram if you want to express it in terms of weight. This is the total capacity.

Now, if you want to find the operating capacity, operating capacity is a measure of the actual useful capacity of the resin for exchanging ions from a solution flowing through a fixed bed of resin particles under specified conditions.

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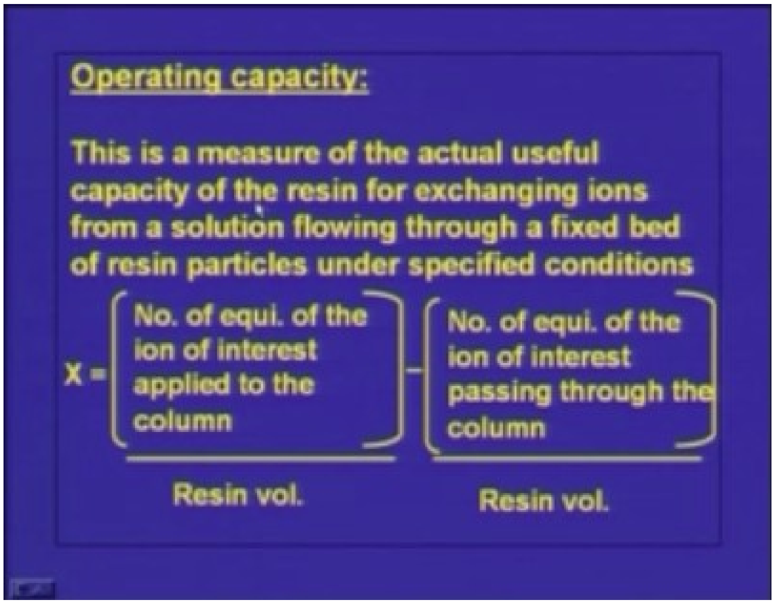

Operating capacity:

This is a measure of the actual useful capacity of the resin for exchanging ions from a solution flowing through a fixed bed of resin particles under specified conditions

$$X = \frac{\left(\text{No. of equi. of the ion of interest applied to the column}\right)}{\text{Resin vol.}} - \frac{\left(\text{No. of equi. of the ion of interest passing through the column}\right)}{\text{Resin vol.}}$$

So once again the operation or operating capacity is a measure of the actual useful capacity of the resin for exchanging ions from a solution flowing through a fixed bed of resin particles under specified conditions. This is very very important. We know what is the total exchangeable capacity or total ion exchange capacity of the resin because we know what is the exchangeable groups present in the ion exchange resin. But when we use this ion exchange resin in the treatment of wastewater then all the ionizable groups may not be exchanging and depending upon the wastewater conditions and the operating conditions the exchange capacity will be varying so the theoretical capacity and the actual capacity will be different so how can we find out the actual capacity. To find out the actual capacity we should know what is the total amount of ions we are passing through the column and we should know what is the ions whatever is coming out from the column. So if you take the difference between these two parameters we will be able to get the operating capacity.

Therefore, the operating capacity can be represented by the term X. It is equal to number of equivalents of the ions of interest applied to the column per resin volume minus number of equivalents of the ions of interest passing through the column per resin volume. That means we know what is the total amount passed through the column and whatever is coming out of the column so rest of the ions will be taken up by the column that means that is the operating capacity.

Now how can we use these ion exchange resins for treating the wastewater? We can go for four different modes of operation. One is batch mode and another one is fixed bed mode, third one is fluidized bed and fourth one is continuous mode. We have already discussed all these things. We will see them once again.

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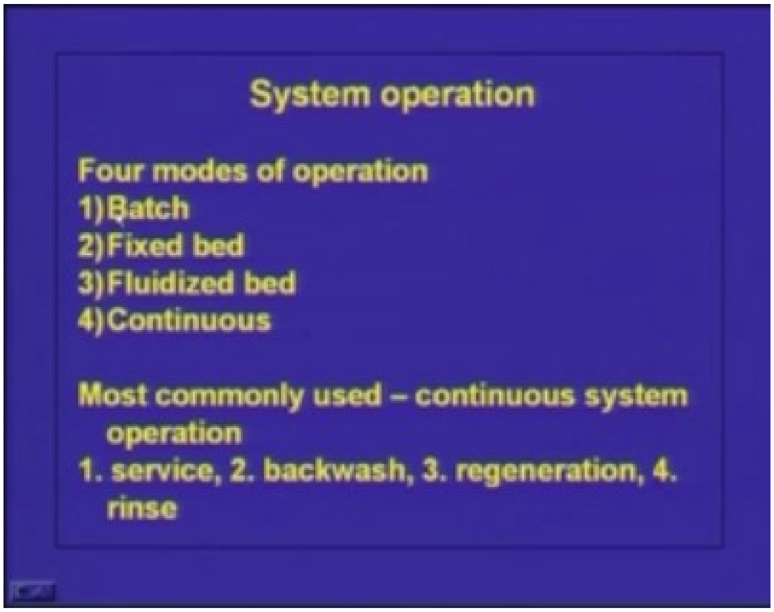

System operation

Four modes of operation
1)Batch
2)Fixed bed
3)Fluidized bed
4)Continuous

Most commonly used – continuous system operation
1. service, 2. backwash, 3. regeneration, 4. rinse

Batch mode means you will be taking the wastewater putting the ion exchange resin and give some time for reaction and afterwards remove the supernatant fixed bed means you will be having a fixed bed and through that one you are allowing the wastewater to flow and you will be getting the treated water.

In fluidized bed what is happening is the ion exchange resin will be present in a reactor and because of the wastewater flow velocity it will be in a fluidized form so the waste components will be having good contact with the ion exchange resin and ion exchange will be taking place. We have discussed about these fluidized bed in detail when we were talking about the anaerobic processes.

Continuous process: This is the most commonly used operational mode. In continuous process if you want to operate an ion exchange resin we can classify the operation into four categories. One is the service time, second one is the backwash time, then regeneration and fourth one is rinse. Service is the time when the pollutants are getting removed from the system and backwash means we are using this backwash to remove any turbid particles whatever is getting attached to the fixed bed column, in regeneration we are removing the exchanged ions with the initial ions. Usually some loose ions will be present in the column and if you want to remove those loose ions we will be using rinse.
I will explain this one.

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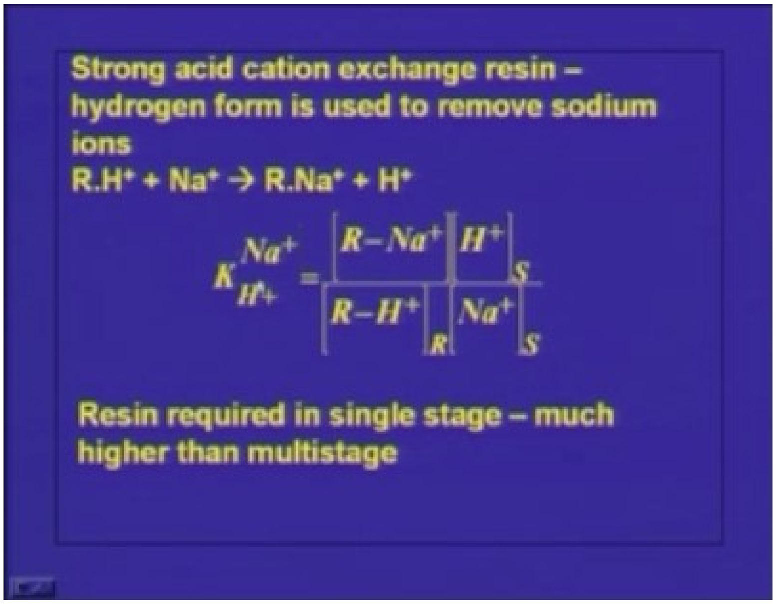

Strong acid cation exchange resin – hydrogen form is used to remove sodium ions

$R.H^{+} + Na^{+} \rightarrow R.Na^{+} + H^{+}$

$$K_{H^{+}}^{Na^{+}} = \frac{\left[R-Na^{+}\right]\left[H^{+}\right]_{S}}{\left[R-H^{+}\right]_{R}\left[Na^{+}\right]_{S}}$$

Resin required in single stage – much higher than multistage

If you want to use the ion exchange resin for the removal of sodium chloride for desalination purpose then we can go for a strong acid cation exchange resin where the hydrogen form is used. So this is RH plus strong cation exchange resin and if NaCl is there what will happen R Na will be forming and H power plus will be coming out. Now, if you want to find out the selectivity coefficient we can find out using this expression and whenever we go for a single stage resin you have to use more resins compared to a multistage process.

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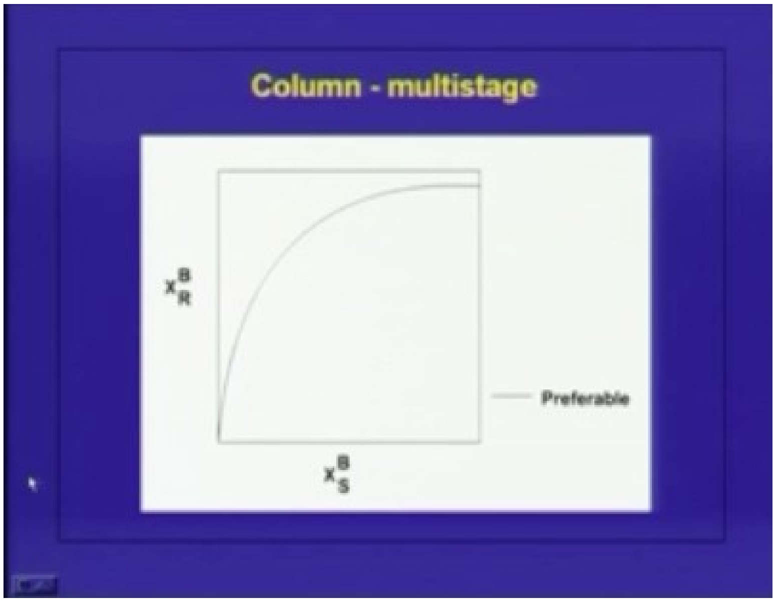

Column - multistage

If you want to plot XB over R that means the selectivity coefficient of B the ion to be exchanged from the pollutant water over the ion of the resin, here we are putting X of B in solution or what is the concentration of B in the resin and this is the concentration of B in the solution so if you get a graph like this or a trend like this, this is a preferable ion exchange. That means at any time the concentration of B ions which is of interest to us has to be removed from the solution. If this concentration is high on the resin compared to the concentration of B on the solution that means the ions are getting exchanged at a faster rate so this is a preferable ion exchange. And if you get in this way (Refer Slide Time: 26:45) that means if the concentration of B in solution is more when compared to the concentration of B on resin then it is an unpreferrable ion exchange. That means resin ion is having more attachment than the ion B which is present in the solution so in this process we cannot go for ion exchange.

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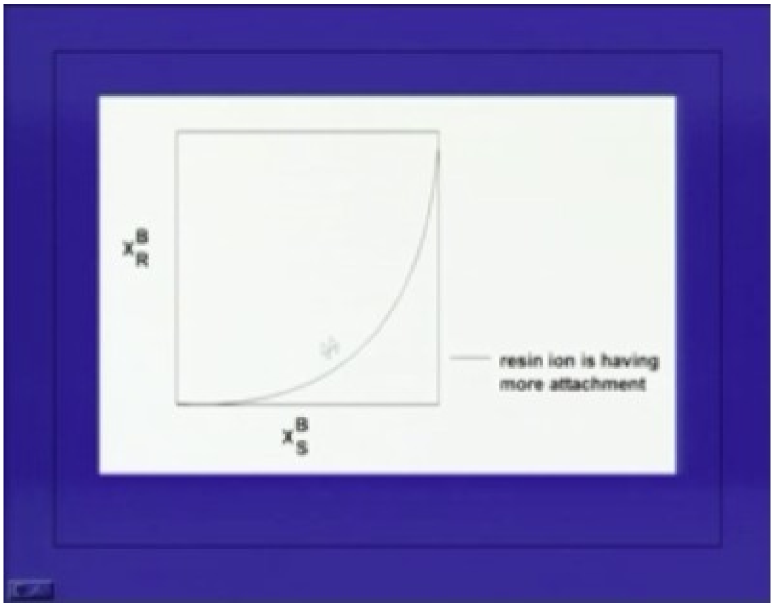

Now we will see how the back washing because the

In operation period we know that depending upon the ion we have to select the resin and we also have to decide on which cycle it has to run then we can find out whether ion exchange is feasible or non feasible then we can select the process. Once the capacity of the resin is over first we have to go for back washing. So back washing is employed after the operating capacity of the ion exchange is reached or the capacity is exhausted. How to do the back washing?

So first we have to break up the resin clumps, remove the finely divided suspended material in the resin by filtration and eliminate the gas pockets, restart the resin bed and ensure a uniform distribution of flow during down flow operation. These are the things happening in a back washing.

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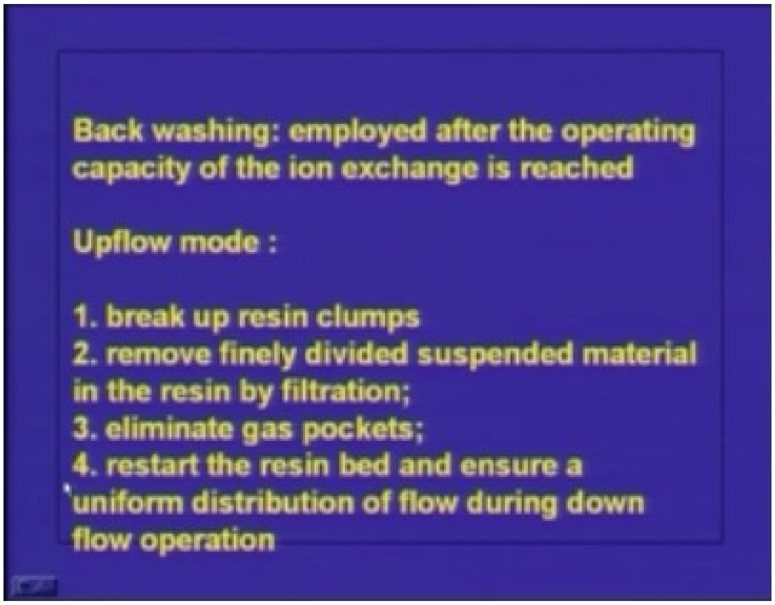

Back washing: employed after the operating capacity of the ion exchange is reached

Upflow mode :

1. break up resin clumps
2. remove finely divided suspended material in the resin by filtration;
3. eliminate gas pockets;
4. restart the resin bed and ensure a uniform distribution of flow during down flow operation

Now we will see what is happening in regeneration? It replaces ions exchanged during the service and returns the resin to its critical exchange capacity or to any derived level depending upon the amount of regenerant used.

In other words what they are doing is replacing the exchanged ions and bringing back the ion exchange resin to its original capacity. Or sometimes what will happen is, for example, for the strong cation exchange resins and strong acid cation resins we will not be getting 100 percentage regeneration efficiency but we will be getting only 30 to 50 percentage hence regeneration will be increasing or replacing the ions whatever is exchanged to the resin up to 50 percentage which is the maximum possible limit. But if it is a weak exchange resin then we can go for it or we will be achieving 100 percentage efficiency. This is what is happening in regeneration.

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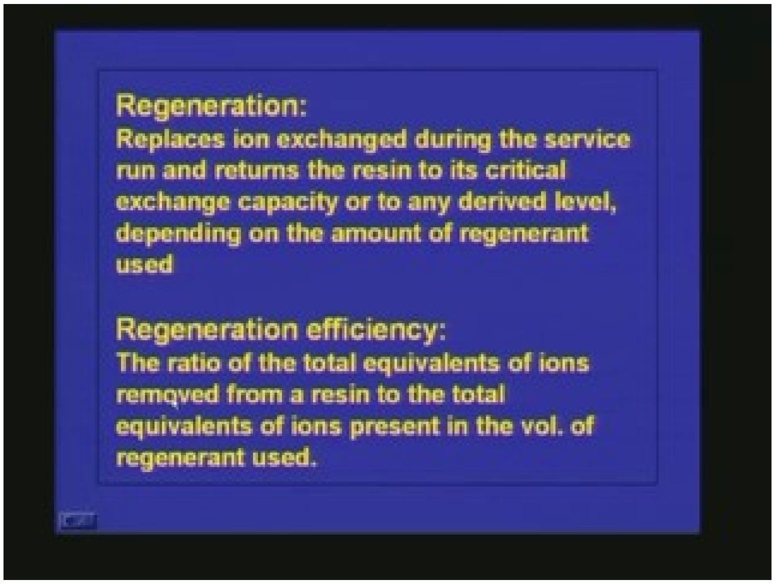

Regeneration:

Replaces ion exchanged during the service run and returns the resin to its critical exchange capacity or to any derived level, depending on the amount of regenerant used

Regeneration efficiency:

The ratio of the total equivalents of ions removed from a resin to the total equivalents of ions present in the vol. of regenerant used.

If you want to calculate the regeneration efficiency it is nothing but the ratio of the total equivalents of ions removed from a resin to the total equivalents of ions present in the volume of regenerant used. This is regeneration efficiency. If you know what are the equivalents of ions present in the resin and we know what is the equivalents of ions present in the regenerant solution we will be taking the ratio of these two and that will give you the efficiency. If it is having 100 percentage efficiency it should replace the entire equivalents of ions present in the resin by the equivalents of ions present in the regenerant solution. If the efficiency is not 100 percent only a fraction will be getting replaced.

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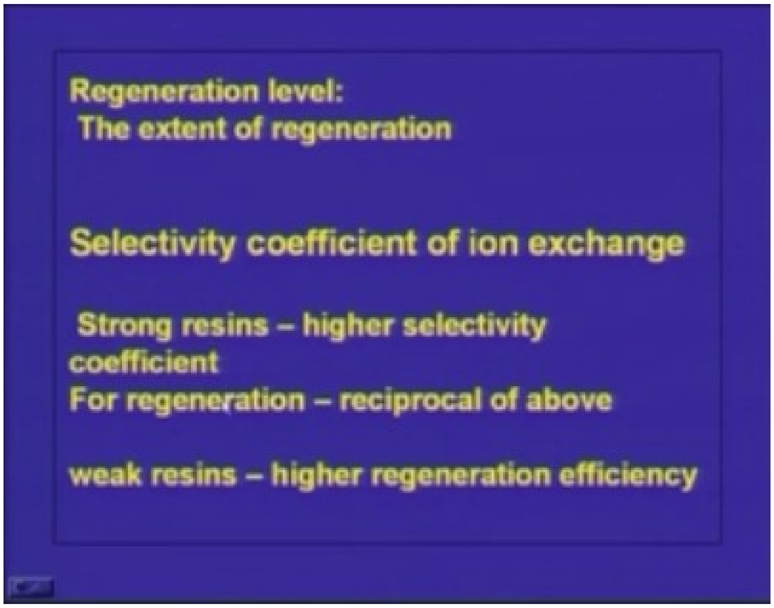

Regeneration level:
The extent of regeneration

Selectivity coefficient of ion exchange

Strong resins – higher selectivity coefficient
For regeneration – reciprocal of above

weak resins – higher regeneration efficiency

Regeneration level is extent of regeneration and selectivity coefficient of ion exchange resin. This plays an important role in regeneration. Strong resins is having a higher selectivity coefficient so what will happen is for removal it will be very very good but for regeneration the exchanged ion will be having more preference over the ions whatever is present already in the resins so in regeneration the exchange will not be proper or regeneration efficiency will not be high. But in case of weak resins it will be having high affinity to the initial ions whatever is present in the resin it will be having high regeneration efficiency. So, if selectivity coefficient is high removal is easy but regeneration is difficult and if selectivity coefficient is less removal is difficult but regeneration is easy.

The last step is rinsing. It is to displace regenerant and the waste from the resin. After regeneration some of the loose ions will be sitting on the resin column so if you want to remove then the next cycle or the service run ions will be coming out along with the treated water so it is not preferable. The rinse is meant to remove the loosely attached ions present in the ion exchange column. And in operating mode we can either go for counter current mode or co-current mode.

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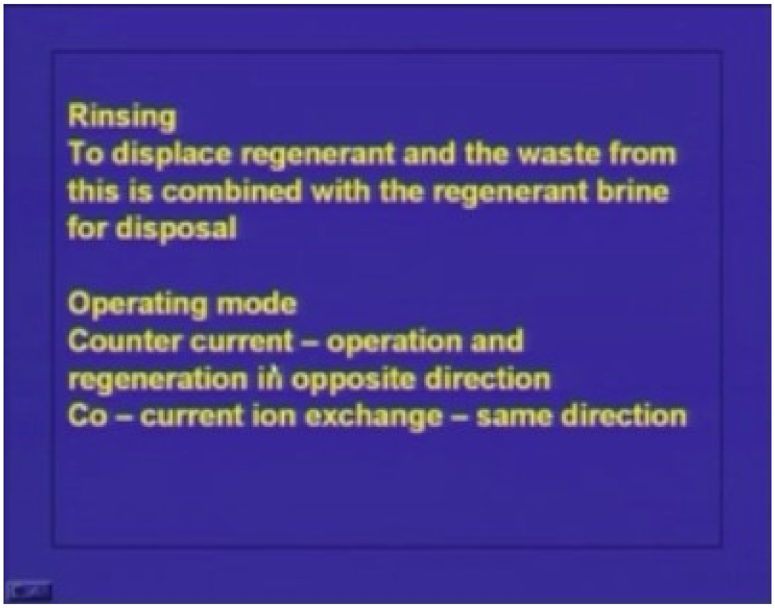

Rinsing

To displace regenerant and the waste from this is combined with the regenerant brine for disposal

Operating mode

Counter current – operation and regeneration in opposite direction

Co – current ion exchange – same direction

In counter current mode what is happening is operation takes place in one direction and regeneration in the opposite direction. In co-current ion exchange both operation and regeneration are performed in the same direction. That is the difference between a counter current mode and a co-current mode. Now we will see what all are the applications of ion exchange process. It is used for the removal of colors because color is a very common problem in most of the industries. It is very difficult to remove the color effectively. And unlike other pollutants the color is having other problems. Even though the concentration is very very less what will happen is a slight amount of the color will be visible so the public will be having a feeling that the industry is not going for proper treatment. So color removal is very very important and this ion exchange resin can be used for that purpose.

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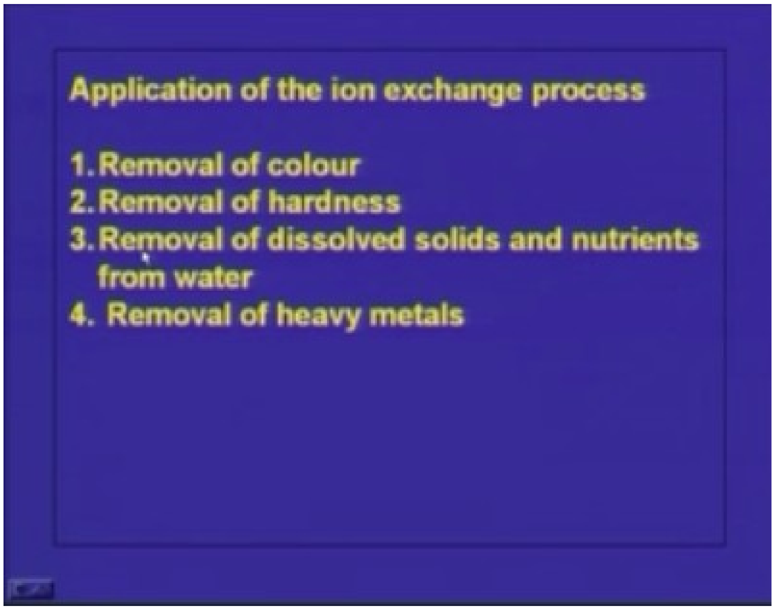

Application of the ion exchange process

1. Removal of colour
2. Removal of hardness
3. Removal of dissolved solids and nutrients from water
4. Removal of heavy metals

The other one is hardness removal. We have seen this in detail when we were discussing about softening. Another one is removal of dissolved solids and nutrients from water like nitrate and phosphate for that one also anion exchange resins can be used effectively. Then for removal of heavy metals also we can use the ion exchange resins effectively.

Now we will see the other advanced wastewater treatment process that is nothing but advanced oxidation process. Here what we are doing is we are using some strong non conventional oxidizing agents which is having such a high oxidizing capacity. Especially the non degradable organic toxic compounds or whichever pollutant that is present in your system can be treated with this advanced oxidation process. What will happen is these oxidizing agents will be reacting with the organic pollutants which are non bio degradable and convert it into some other form which is non toxic or sometimes they will be converting it into carbon dioxide, water and other inorganic substance which is environmental friendly. That is what is happening in advanced oxidation process. It is to oxidize complex organic constituents to simpler end products. Because we know that all the organic compounds are non bio degradable and some of the persistent toxic compounds are complex organic compounds. In such cases we can go for this advanced oxidation.

Here different terms are there. We will see what are all the important terms coming under this advanced oxidation process. First one is primary degradation.

Primary degradation is a structural change in the parent compound. When it undergoes some oxidation it need not be complete oxidation so only some structural changes are taking place in the complex organic compound that is known as primary degradation. The other term is acceptable degradation.

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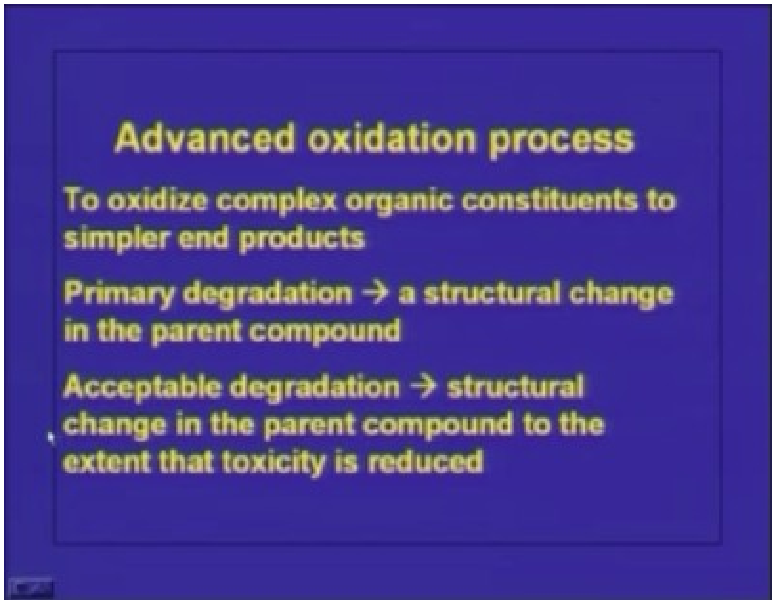

Advanced oxidation process

To oxidize complex organic constituents to simpler end products

Primary degradation → a structural change in the parent compound

Acceptable degradation → structural change in the parent compound to the extent that toxicity is reduced

In acceptable degradation structural change in the parent compound is taking place and because of the structural change the toxicity of the compound is reduced that is known as acceptable degradation.

Another term is ultimate degradation. Ultimate degradation means complete oxidation is taking place so the complex organic matter is converted into carbon dioxide and water.

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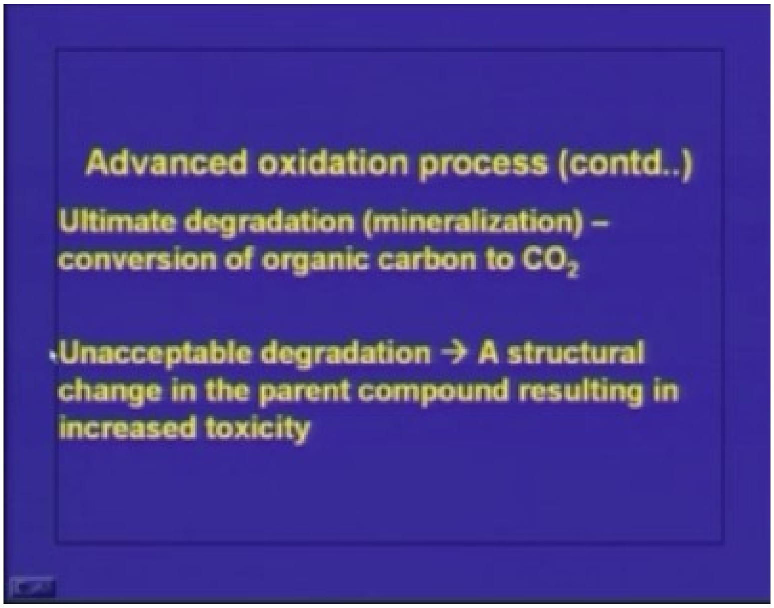

Advanced oxidation process (contd..)

Ultimate degradation (mineralization) – conversion of organic carbon to CO_2

Unacceptable degradation → A structural change in the parent compound resulting in increased toxicity

Unacceptable degradation: A structural change in the parent compound can take place which results in increased toxicity. We have seen what is primary degradation, acceptable degradation, ultimate degradation and unacceptable degradation. We are only interested in acceptable degradation or ultimate degradation. For example, endosulfan is a pesticide. It is very commonly used in India. So, if you go for this advanced oxidation either it can get converted into carbon dioxide, water and nitrogen and sometimes what will happen is some other compounds like endosulfan sulphate or endosulfan diol can be formed. This endosulfan sulphate is much more toxic than the endosulfan itself and is known as unacceptable degradation. I am just giving this as an example.

Now we will see what are the oxidizing agents commonly used for this advanced oxidation. This table shows you the compound and its electrochemical oxidation potential. The higher the electrochemical oxidation potential the more active the compound is.

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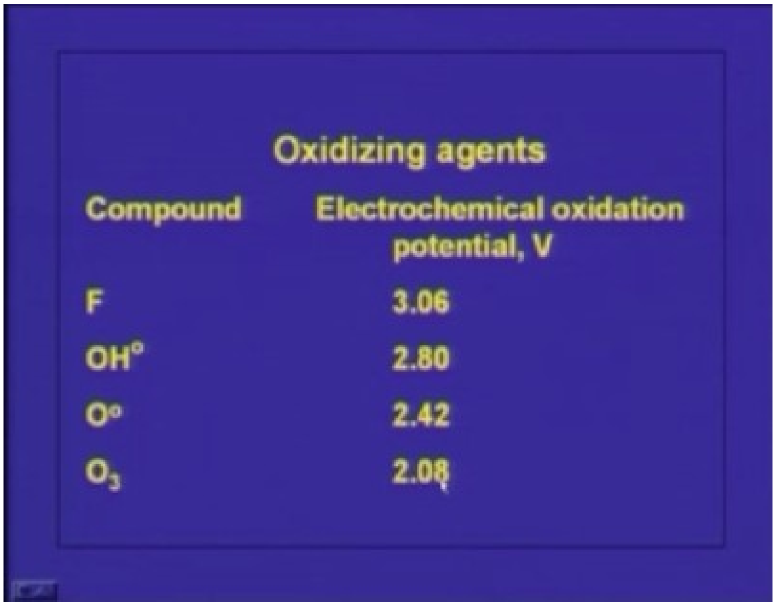

Oxidizing agents

Compound	Electrochemical oxidation potential, V
F	3.06
OH°	2.80
O°	2.42
O_3	2.08

Fluorine is having the electrochemical oxidation potential of 3.06, hydroxil radical OH radical is having 2.8 and this is the nascent oxygen (Refer Slide Time: 36:50) it is having 2.42 and this is ozone it is having 2.08 and hydrogen peroxide is having 1.78, HOCl is having 1.47, ClO_2 is having 1.27 and oxygen is having 1.23.

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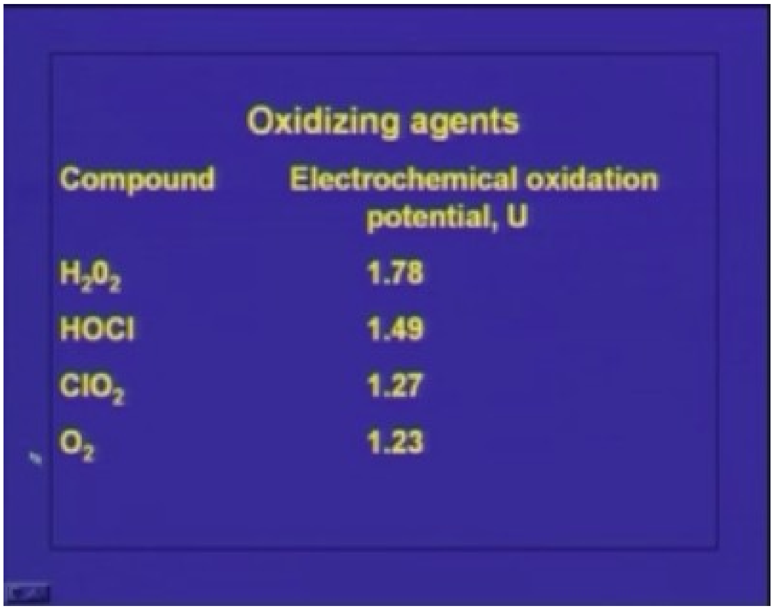

Oxidizing agents

Compound	Electrochemical oxidation potential, U
H_2O_2	1.78
HOCl	1.49
ClO_2	1.27
O_2	1.23

But in usual chemical oxidation we are using oxygen or any other oxidizing agent but in advanced oxidation process the oxidizing agents used are having very high electrochemical oxidation potential compared to oxygen so there oxidation potential will be so high and the oxidation reaction will be very fast.

The last one coming under the advanced wastewater treatment is distillation. We all know what distillation is. What we do is we boil the water and take the vapour and condense it and get the cloud water, this is known as distillation. We will see how a distillation unit is functioning.

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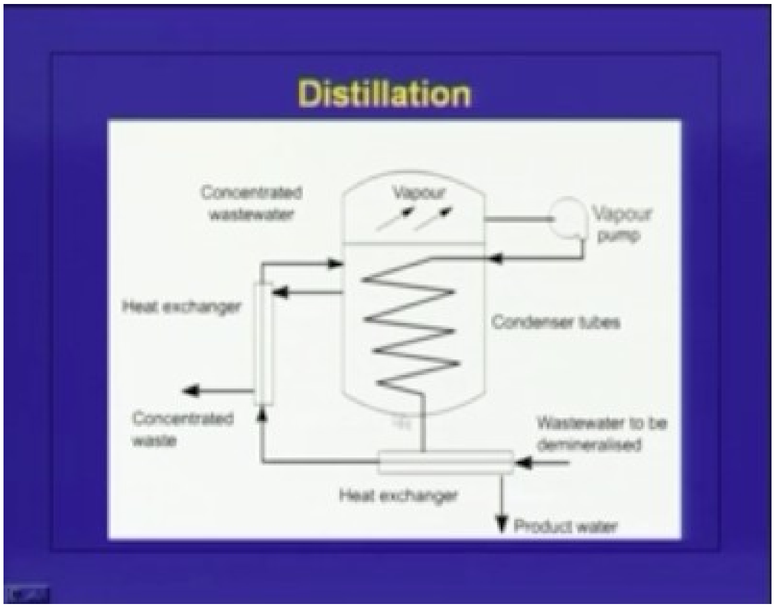
Distillation

This is the wastewater to be demineralized (Refer Slide Time: 37:50), it is entering here and this is the heat exchanger so when it passes through this one it will be evaporating and the vapour will be going through this one, this is the condenser tube and the concentrated waste is coming here and this is the heat exchanger that means the heat exchanger and the temperature will be recovered or the temperature of the wastewater stream will be recovered or the temperature will be reduced and the heat energy will be recovered and the concentrated waste is going out here and whatever the cooled waste is will be used here to condense the vapour coming here and this is the vapour and this is the vapour pump it is going through these condenser tubes and it gets condensed and we will be getting product water.

So what we are doing? We are taking the wastewater, boiling it and we will be getting the steam and here the concentrated waste is going out. The water that is cooled will be used for cooling down the vapour and we will be collecting the condensed vapour as the product water. This is known as distillation unit. Distillation is a unit operation in which the components of a liquid solution are separated by vaporization and condensation.

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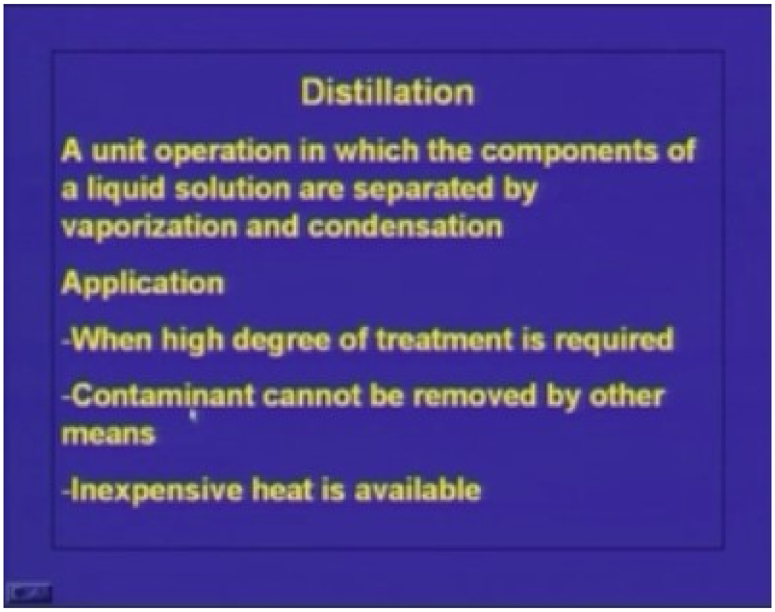

Distillation

A unit operation in which the components of a liquid solution are separated by vaporization and condensation

Application

-When high degree of treatment is required

-Contaminant cannot be removed by other means

-Inexpensive heat is available

Application is;

- When high degree of treatment is required
- contaminant cannot be removed by other means
- inexpensive heat is available

This method is used if you have brackish water or salt water. If you want to get good water for drinking purpose you can go for this distillation so we can make a household unit for this distillation purpose or for cleaning the brackish water and get the cleaned water for drinking. there we are using the heat energy from the sun so what you have to do is take a bottle, boil the water and collect the vapors and allow it to condense and whatever energy that is coming from the sunlight can be used for the distillation purpose. This is practiced in some houses where they don’t have any pure water for drinking.

Distillation process can be done in various ways;

- Boiling with submerged tube heating surfaces
- Boiling with long tube vertical evaporators
- Flash evaporation
- Forced circulation with vapour compression or
- Solar evaporation

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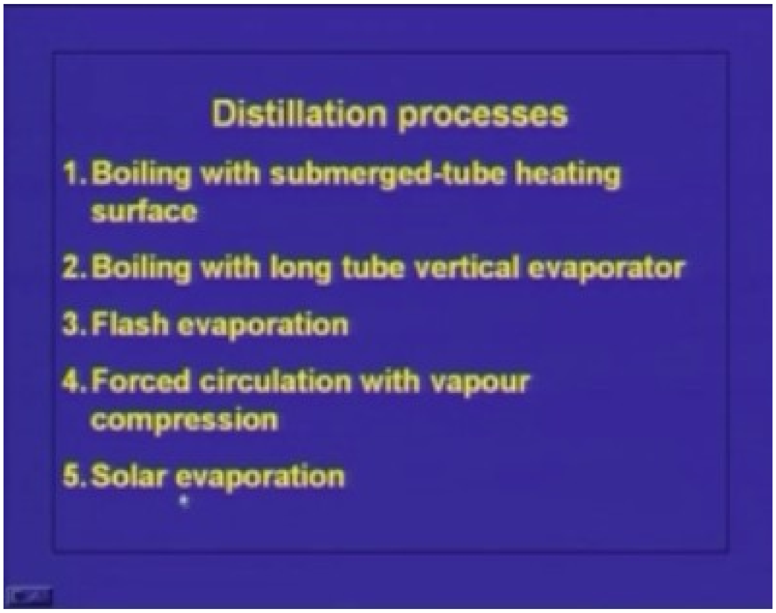

Distillation processes

1. Boiling with submerged-tube heating surface
2. Boiling with long tube vertical evaporator
3. Flash evaporation
4. Forced circulation with vapour compression
5. Solar evaporation

This is a low cost technology so we can also go for;

- Rotating surface evaporation
- Wiped surface evaporation
- Vapor reheating process
- Direct heat transfer using immiscible liquid or
- Condensing vapour heat transfer

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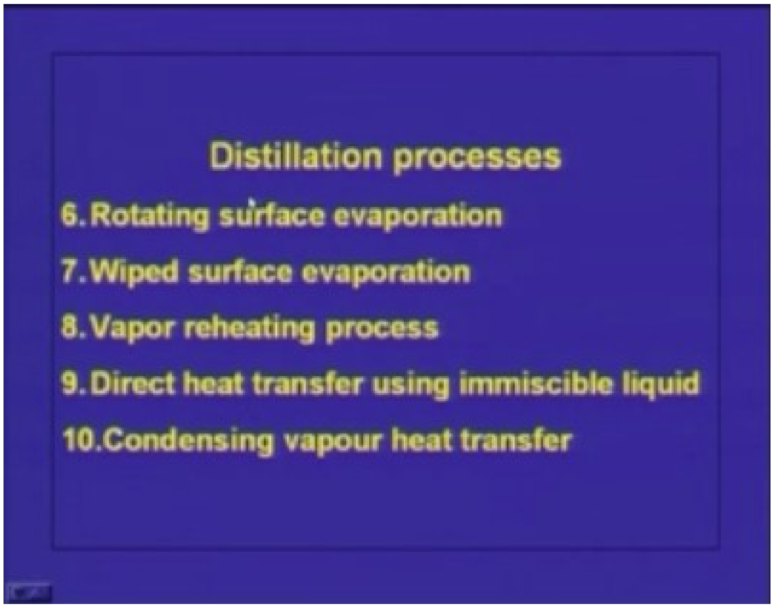

Distillation processes

6. Rotating surface evaporation
7. Wiped surface evaporation
8. Vapor reheating process
9. Direct heat transfer using immiscible liquid
10. Condensing vapour heat transfer

There are many many ways we can use this distillation process to clarify the water but the only problem is this process is very very costly. If you don't have any other treatment option then only we can go for this distillation process and other one is if you can get inexpensive heat energy then you can go for this distillation. Most of you must have seen the distillation units. In laboratory purpose we use distilled water for making the chemical solutions so we are having a distillation unit and it is working in the same principle.

Till now we were discussing about advanced wastewater treatment processes including membrane processes, adsorption, ion exchange, advanced oxidation reduction then distillation. Why we wanted to use this one is because, we know that the conventional wastewater treatment basically were derived for treating the domestic wastewater which is having lot of bio degradable organic matter. But nowadays so many non conventional pollutants and emerging pollutants are coming along with the wastewater. Where are these non conventional and emerging pollutants coming from? Mostly it is because of the industrial activities. All these advanced wastewater treatment processes we have discussed so far can be used for industrial wastewater treatment depending upon the nature of the pollutant.

So, if you want to go for selection of a process what we have to do?
We will be having the industrial wastewater, first we have to characterize the wastewater or we have to find out what are the characteristics of that wastewater. and then if you see that it is having lot of chemical oxygen demand that means it is having a lot of organic matter, it doesn't mean that all the organic matter present in the system is biodegradable so how can we choose whether we have to go for a biological system or we have to go for some physiochemical advanced treatment processes? So, for that we have to do some treatment study or treatability studies. Treatability study will tell you which treatment is suitable for the wastewater treatment.

For example, if you have a high COD wastewater and we want to find out whether it is biodegradable or non biodegradable then we can go and find out what is the bio chemical oxygen demand of that wastewater. So, if you get a high biochemical oxygen demand and you have a high COD then you take the BOD by COD ratio. That means if biochemical oxygen demand divided by the chemical oxygen demand ratio is more than 0.5 then more than 50 percentage of the waste is biodegradable then it is advisable to go for a biological treatment first followed by some physiochemical treatment or advanced wastewater treatment. But the BOD itself will not be telling you whether it is completely biodegradable because when we do the BOD test for any industrial wastewater we take the industrial wastewater and we will be diluting it with the dilution water along with the nutrients.

The industrial wastewater will be having lot of other toxic chemicals and toxic metals along with the organic matter but when we dilute it the toxic effects of those compounds will be coming down so you may be getting a high biochemical oxygen demand. But in actual practice the dilution is not taking place so you may not be able to achieve that much of biodegradation in the treatment plants. That is why after measuring the BOD by

COD ratio we have to go for a treatability study. So what you do is take the actual waste and conduct the biodegradation studies and if the biodegradation is happening or if you can achieve the COD reduction above 50 percentage by the biological means then in the field also we can practice the same thing. But in the lab itself it is failing then definitely in the field you will be getting much less efficiency. These points have to be kept in mind whenever we decide any process or especially industry.

In municipal wastewater treatment we won't be having any problem because we know that the most important pollutant whatever is present in the domestic wastewater is nothing but organic matter and most of them are easily biodegradable. Along with the organic wastewater some of the non conventional and emerging pollutants will be coming so their concentration will be less compared to whatever is coming in industrial wastewater. So, before going for any treatment process it is advisable to have a treatability study in the laboratory and see how the system is performing then you scale up and put it in the field.

Now we will see what all are the other important points we have to consider when we go for this industrial wastewater treatment. What is the effect of industrial wastewater on streams? Whenever we talk about e industry especially the public will be telling that if some industry is going to come up it is going to pollute the streams, it is going to pollute the environment, it is going to pollute the atmosphere and so on. Why the public is having that type of a feeling is what we are going to see in detail.

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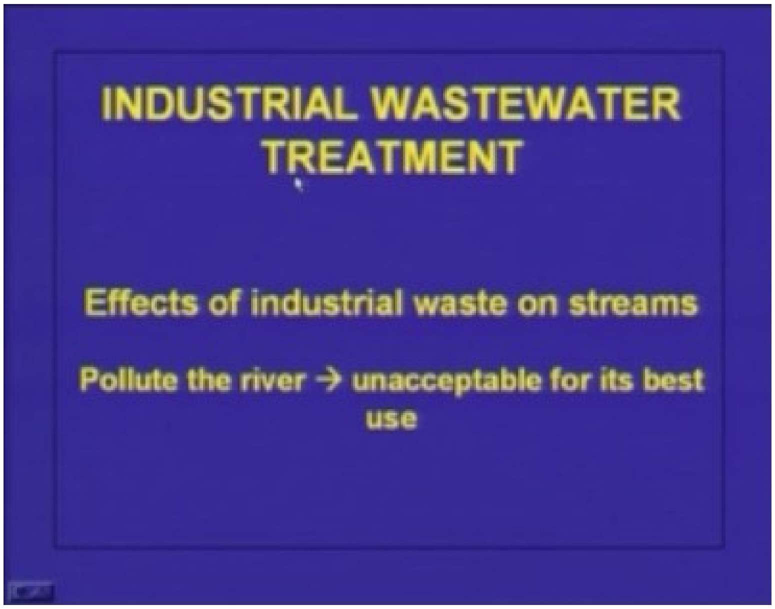
INDUSTRIAL WASTEWATER TREATMENT

Effects of industrial waste on streams

Pollute the river → unacceptable for its best use

We will also see what all are the important points the industry has to take into account in terms of pollution control. If the industry is discharging wastewater it will be polluting the river and it will become unacceptable for its best use. That will be happening if you discharge any waste to any water sources that's why we were telling that it is always advisable to go for water reuse than the effluent discharge. We discussed this in detail in the earlier classes.

When we talk about the industry what all are the different sources which can generate pollution in the industry. The sources of industrial pollution are;
Extraction and transporting virgin renewable and non renewable raw materials: this is the first source of industrial pollution because for example if you take any metallurgy industry what will happen is they have to extract the ores from the from earth core and during the extraction process itself some ore will be left over there and leaching will be there and the lechate will be contaminating the water courses on the downstream side and the lechate will be percolating through the soil and it will be contaminating the soil and during transport also so much of this raw material will be spilling over and that will be polluting the bay. Therefore, all those things are coming under this category of extraction and transporting virgin renewable and non renewable raw materials.
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Sources of industrial pollution

1. Extraction and transporting virgin renewable and non-renewable raw materials
2. Process pollution originating from the production
3. Product pollution – everyday use of products
4. Residual pollution – disposal of products

Second one is process pollution originating from the production. There is no need of explaining this point. The reason is all of us know the industrial process. It will be involving various reactions, various raw materials and various products. so as a result what will happen is these things will be coming along with the effluent whatever is coming out of the industry so definitely the process and the raw materials whatever is used in the industry will be polluting the bay.

The third one is product pollution. It is nothing but the pollution generated by everyday use of the products. For example, pesticide is an industrial product so if you use the pesticide daily what will happen is when you apply the pesticide it is killing the pest or it is destroying the pest. this is the positive side of the pesticide. But what will happen is some amount will be going to the atmosphere by volatilization and something will be sticking on the plants? When we take the plant parts either fruits or the leaves or the stem for our food purpose or eating purpose then that will be coming into our body and during the spraying of this pesticide some portion will be going to the soil and if precipitation or rainfall comes then whatever is mixed in soil will be coming along with the run off water and sometimes during the rain some water will be percolating through the ground and it will be reaching the groundwater. Therefore in all the ways it will be polluting ground water, surface water, soil and the atmosphere. This is what is meant by product pollution.

The last one is residual pollution. This residual pollution is nothing but the disposal of products. So, if you have something left over, we can take the same case of the pesticide. You will be using the pesticide for agriculture purpose or controlling the pest in the houses so some portion of the pesticide will be left over in the bottles and after sometime the expiry date will be over and it will become useless. So what we usually do is just throw it away to the water stream or you put it in the dust bin so definitely it will be going through different hands and finally reaching either the soil or the water which will end up creating lot of pollutants. Therefore, these are the major sources of industrial pollution. One is the extraction and transportation of raw materials, second one is production itself, third one is the use of the products, fourth one is the residual pollution that means the discarding process.

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Materials responsible for pollution

Inorganic salts
Acids and alkalis
Organic matter
Suspended solids
Floating solids and liquids
heated water
color
toxic chemicals
microorganisms
foam producing matter

Now we will see what materials are responsible for this industrial pollution. We can classify them into these groups.

- Inorganic salts
- Acids and alkalis
- Organic matter

- Suspended solids
- Floating solids and liquids
- Heated water
- Color
- Toxic chemicals
- Microorganisms and
- Foam producing matter

We all know from where these pollutants are originating.

Inorganic salts: We know that lot of industrial pollutants use lot of chemicals for their product formation or whatever the thing be especially the chemical industries. So whatever are the left over salts used in the process that will be coming along with the wastewater so definitely the wastewater from the industries will be containing lot of inorganic salts. And acids and alkalis are also being used in industrial process. For example if you take the electrochemical industry, for removing the rust or for the pickling process we will be using lot of acid so what will happen is that acid will be coming along with the wastewater from the industry, similarly, organic matter depending upon the industry. For example if you take the case of tannery, a lot of organic matter will be coming and similarly in textile industry also lot of organic matter will be coming, in distillery industry again a lot of organic matter will be coming.

The other one is suspended solids. Depending upon the raw material the industrial effluent will be having lot of suspended solids.

Floating solids and liquids: The liquids definitely will be coming from the industrial process.

Heated water: The heated water is coming out of the coolers because in most of the cases the industry needs lot of cooling water because so much of heat is generated in the industrial process and in order to cool them we need to use the cooling water. Thus, after cooling what will happen is the water temperature will be increasing and the heated water will be coming out.

The next one is color. If you take the case of textile industry we know how many different types of colors organic and inorganic or synthetic and natural colors are used for the textile industry. Not only the textile industry but other industries are also using many dyes and pigments for their processes. So color is an important component of industrial wastewater.

The other one is toxic chemicals like heavy metals etc or cyanide. These are very commonly found toxic compounds in industrial wastewater.

Another one is micro organisms. Whenever we talk about food and pharmaceutical industries these micro organisms are present in large quantities so we have to take care of that one also. And the other one is foam producing matter. These are the materials responsible for pollution in the industry. So whenever we design any treatment process the process should be able to take care of each of these pollutants. Most of the time one process alone may not be possible to take care of all these components so we may have to go for a battery of processes so that we will be getting the treated water which is meeting the effluent discharge standards.

Now we will see what is the major difference between the industrial and municipal wastes. Difference between the industry and municipality is that the industry's major objective is to produce the best possible product at the lowest possible cost because they have to survive in the market. So, if their product cost increases definitely the cost of their product will be more and definitely the customers will be looking for a product of the same quality which can be available at a low cost. So the major objective of the industry is to produce the best possible product at the lowest possible cost. If the industry wants to reduce the cost of production the most obvious area of cost reduction is nothing but the wastewater treatment because if they go for the wastewater treatment it is not going to add anything to their product so definitely they will be having a feeling that if they want to treat the wastewater properly they can reduce the cost of the product. Because if you go for wastewater treatment also that cost will also come into effect with the product.

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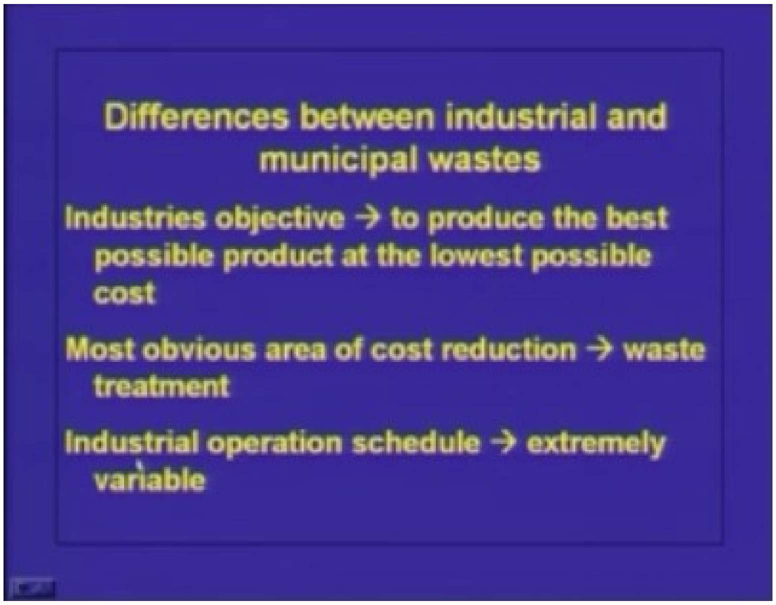

Differences between industrial and municipal wastes

Industries objective → to produce the best possible product at the lowest possible cost

Most obvious area of cost reduction → waste treatment

Industrial operation schedule → extremely variable

Another important thing is the industrial operation schedule is extremely variable compared to the municipalities. The industry views that the wastewater treatment is an imposed necessity on them. We have already seen their pollutants. Many many different contaminants are present at different concentrations whereas in municipality or municipal wastewater it will be the organic waste.

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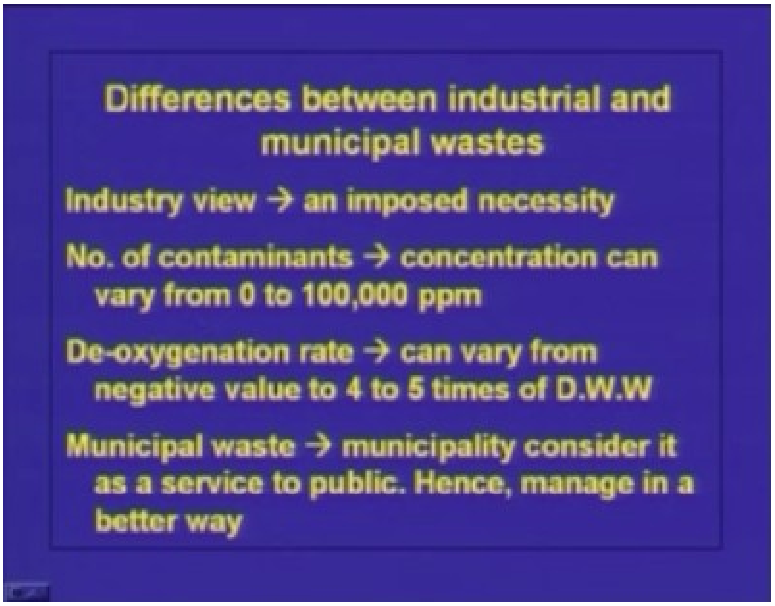

Differences between industrial and municipal wastes

Industry view → an imposed necessity

No. of contaminants → concentration can vary from 0 to 100,000 ppm

De-oxygenation rate → can vary from negative value to 4 to 5 times of D.W.W

Municipal waste → municipality consider it as a service to public. Hence, manage in a better way

So whenever we talk about the industrial wastewater management we should keep all these points in mind. We will discuss these aspects in detail in the next class as what all are the theory or what all are the things we can follow so that the industrial pollution can be minimized because there is not point in going on polluting and treating. If we can control the pollution in the source itself then it is the best strategy than initially polluting and controlling the pollution. Because we know that pollution is nothing but the resource out of its place as far as the industry is concerned because if more pollution is there more resource or more raw materials are getting wasted. We will be discussing this approach in detail in the next class.

Let us take a look at what are all the things we have seen till now. We have discussed in detail about the ion exchange process and we have seen the different types of ion exchange resins we can use. We have also seen the different ways in which we can put up the reactor for this ion exchange process. Those are batch mode, fixed bed mode, fluidized bed reactors and we can even go for continuous mode systems and the four operating stages. One is the service time, second one is the backwashing, third one is the regeneration and fourth one is the rinse period. These four operations are associated with ion exchange.

Afterwards we discussed about the advanced oxidation process. Here we are using very strong oxidizing agents for the oxidation of complex organic compounds and we are looking for either complete oxidation or acceptable oxidation. We also discussed about distillation and we have seen that this process is a costly process and if no other process is available only then we can go for distillation.