Basic Environment Engineering and Pollution Abatement
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Lecture 37
Tertiary Treatment - 1

Hello, everyone. Now, we will discuss on the topic Tertiary Treatment Part 1. So, in our previous classes, we have seen that wastewater treatment contains different steps and last step is tertiary treatment, which starts after secondary treatment. And in this step, the main objective is to remove the residual BOD, COD and TDS and microorganisms. So, pathogens are also killed in this step.

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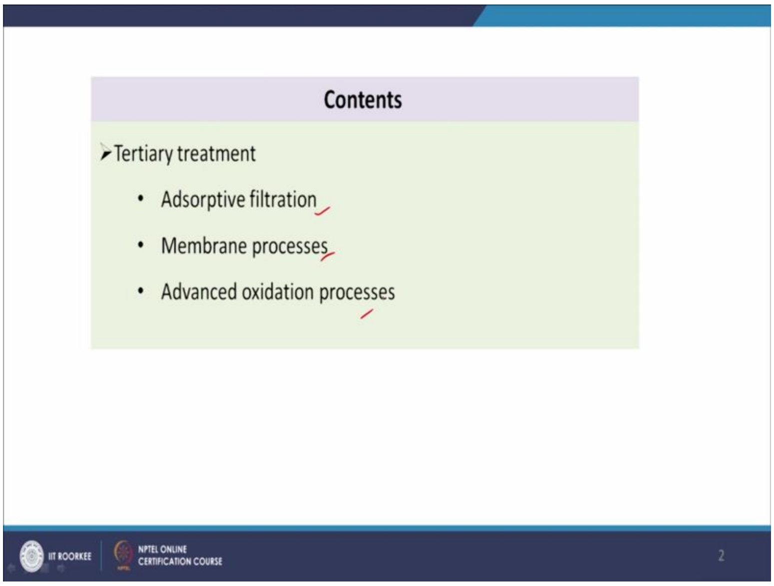

Contents

- Tertiary treatment
  - Adsorptive filtration
  - Membrane processes
  - Advanced oxidation processes

And we will discuss here on these topics that adsorptive filtration, then membrane processes and advanced oxidation processes.

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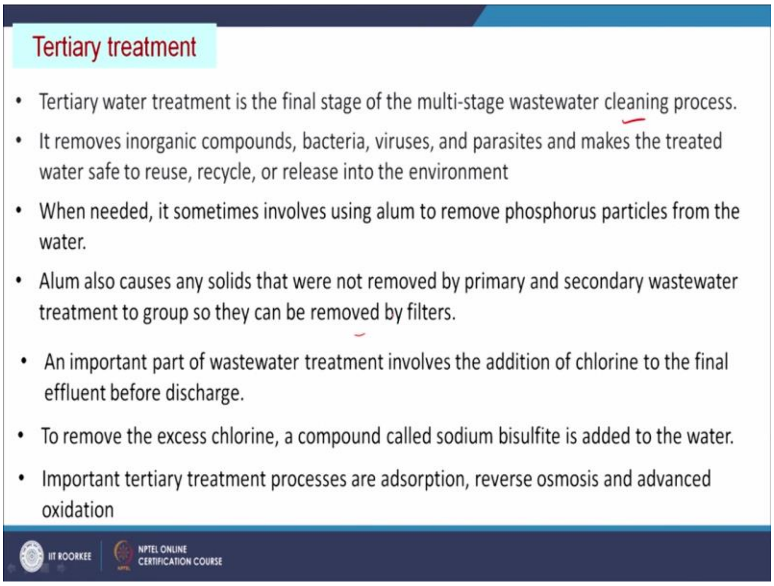

Tertiary treatment

- Tertiary water treatment is the final stage of the multi-stage wastewater cleaning process.
- It removes inorganic compounds, bacteria, viruses, and parasites and makes the treated water safe to reuse, recycle, or release into the environment
- When needed, it sometimes involves using alum to remove phosphorus particles from the water.
- Alum also causes any solids that were not removed by primary and secondary wastewater treatment to group so they can be removed by filters.
- An important part of wastewater treatment involves the addition of chlorine to the final effluent before discharge.
- To remove the excess chlorine, a compound called sodium bisulfite is added to the water.
- Important tertiary treatment processes are adsorption, reverse osmosis and advanced oxidation

So, as we have already mentioned that tertiary treatment is the final stage of multistage wastewater cleaning process. And it removes inorganic compound, bacteria viruses and parasites and makes the treated water safe to reuse, recycle or release into the environment. After this treatment step, we can consume the treated water for different applications.

We have already discussed that in normal practice the TDS and BOD are mostly removed in primary and secondary treatment steps, but some residual amount will be available. And in this case, the water is filtered through different beds or some membrane unit is used or some advanced oxidation processes can also be applied.

And it is possible that in the secondary treatment, some BODs still remaining and some coagulation is also required, apart from this adsorption and membrane process or any advance oxidation process. So, alum also causes any solids that were not removed by primary and secondary wastewater treatment to group. So, they can be removed by filters.

And as we have mentioned, that the disinfection or killing of the microorganisms, particularly the pathogens present in the treated water is very, very essential and disinfection state where chlorine is added is also included in the tertiary treatment step. But we also discussed that if the chlorine dose is not maintained, then the residual chlorine will be available. That is to remove that chlorine some chemicals like sodium bisulfite is added in the treated water.

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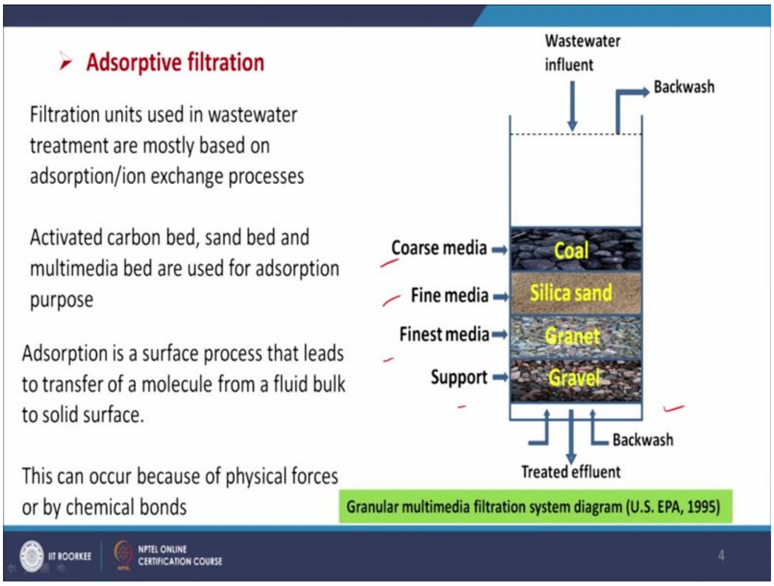

Adsorptive filtration

Filtration units used in wastewater treatment are mostly based on adsorption/ion exchange processes

Activated carbon bed, sand bed and multimedia bed are used for adsorption purpose

Adsorption is a surface process that leads to transfer of a molecule from a fluid bulk to solid surface.

This can occur because of physical forces or by chemical bonds

Granular multimedia filtration system diagram (U.S. EPA, 1995)

So, important tertiary treatment processes or adsorption, reverse osmosis and advanced oxidation. Now, we will discuss adsorptive filtration process, so as shown here in this filter, you need to see the wastewater is coming here that is after secondary treatment and then it is going to this bed where course media, then find media, then finest media and then support media then treated effluent is coming out. And during backwash we send water in reverse direction and we get the backwash.

So, in this case activated carbon is mostly used as shown here it is a coal, but activated carbon is mostly used and adsorption is the process which takes place here for the separation of the pollutants from this wastewater. And this adsorption is a surface phenomenon, where the pollutants are adsorbed on the surface of this adsorbents or different beds as mentioned here. So, this adsorption can take place by physical or chemical route.

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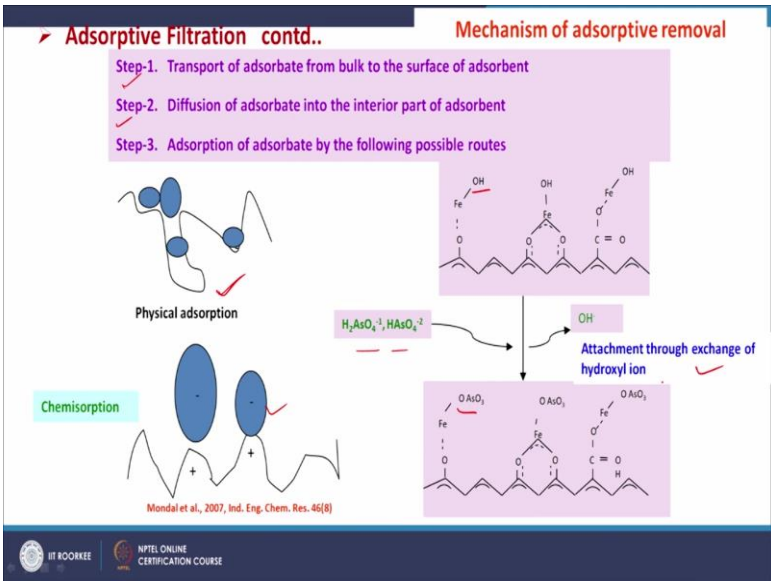

Adsorptive Filtration contd..

Mechanism of adsorptive removal

Step-1. Transport of adsorbate from bulk to the surface of adsorbent

Step-2. Diffusion of adsorbate into the interior part of adsorbent

Step-3. Adsorption of adsorbate by the following possible routes

Attachment through exchange of hydroxyl ion

Mondal et al., 2007, Ind. Eng. Chem. Res. 46(8)

And this slide gives us some information on the mechanism of the adsorption of the pollutants on the surface. So, the first step is transport of adsorbate from bulk to the surface of adsorbent. So, from the bulk of the solution the adsorbate comes on the surface of the adsorbent. And then second step is diffusion of adsorbate into the interior part of that adsorbent. So, pollutants are adsorbed gets entered into the interior part of it, and physically trapped. So, this is physical adsorption.

Then the third step is adsorptions of adsorbate by following possible routes, that is physical adsorption or maybe some chemical adsorption. That means, that adsorbents or pollutants are coming in the surface of this adsorbent as the surface is having some active sites as soon as a positively charged active sites and if our adsorbent is negatively charged, so, then they will be chemically attracted and will be attached like this. So this is chemical adsorption or chemisorption.

Similarly, negatively charged surface and positively charged ions can also be chemically adsorbed. Apart from that, ion exchange mechanism can also take place here like for example, see if we have ferrous oxide and ferrous hydroxide impregnated activated carbon surface. So, this is presented here, if in the solution, arsenic is present, that is, in this form that is negatively charged.

So, this OH^- ion can be replaced by this arsenate or arsenate ions, so, like this, the surface will be converted into this form. So, this OH is replaced by this one. So, that is called OH that is hydroxyl ion exchange. So, these are the different mechanisms through which the adsorption can take place.

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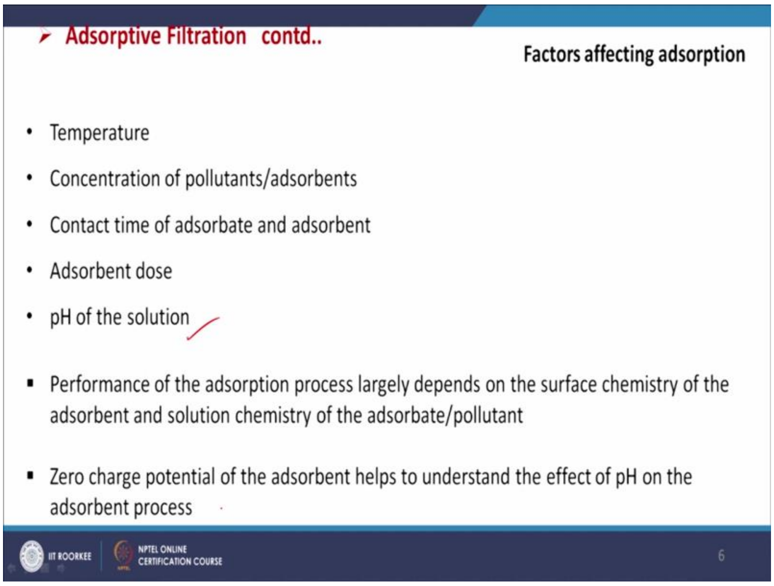

➢ Adsorptive Filtration contd..

Factors affecting adsorption

- Temperature
- Concentration of pollutants/adsorbents
- Contact time of adsorbate and adsorbent
- Adsorbent dose
- pH of the solution
- Performance of the adsorption process largely depends on the surface chemistry of the adsorbent and solution chemistry of the adsorbate/pollutant
- Zero charge potential of the adsorbent helps to understand the effect of pH on the adsorbent process

Now, there are many factors which influence the performance of the adsorption process, like say temperature, and concentration of pollutants or absorbance, then contact time adsorbate and adsorbent. That is why we need to provide sufficient residence time of the water in the adsorbent bed. And then adsorbent dose.

So, what is a dose? Particularly, we will see that this process may be a batch or continuous operation. In case of batch study, we will be talking about the adsorbent dose per unit volume of the solution or in case of continuous study, we will be talking about the amount of adsorbent used in the column.

And then pH of the solution. pH of the solution plays an important role because the adsorption phenomena is influenced by the solution phase chemistry of the adsorbent and the adsorbate as well as the surface charge of the adsorbent which changes with pH. So this is very important parameter out of all those parameters in terms of adsorption capacity or adsorption performance.

And zero charge potential of the adsorbent helps to understand the effect of pH on the adsorbent process. So, zero charge potentials, when there is some pH at which the surface charge becomes neutral or zero charge. So, above that pH, the surface of the adsorbent is negatively charged and below that pH the surface is positively charged.

So, if in the solution, negatively charged ion is present, so that will be preferably adsorbed when that pH is lower than the pH ZPC. And when in the solution positively charged ions are present, those will be preferably adsorbed on the adsorbent surface when pH ZPC value is more than the solution pH.

Now, we will some example how to improve the performance efficiency of adsorbent by surface modification. As we have discussed that positively charged sites will attract a negatively charged ions from the solution. So, if in the solution, we have negatively charged ion and adsorbent surface has some positive charge density, if we can increase the positive charge density, then it will attract more negatively charged ion or more effectively, it will attract negatively charged ion.

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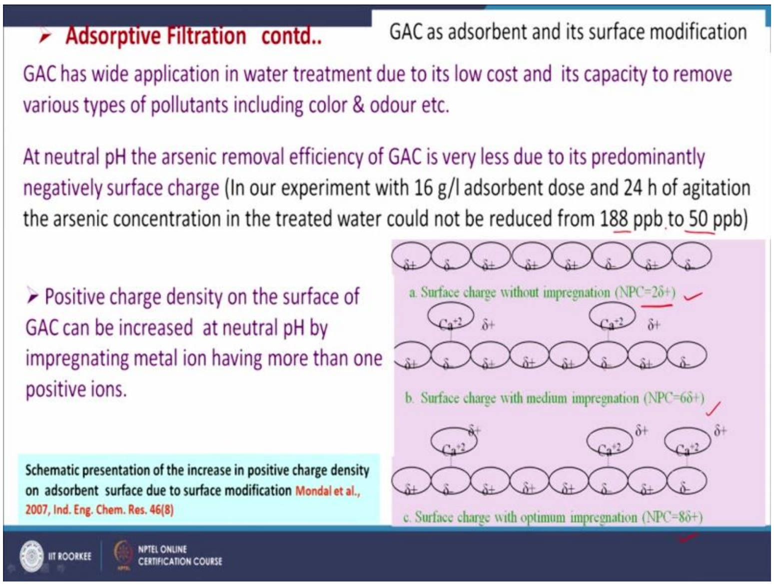

➤ Adsorptive Filtration contd..

GAC as adsorbent and its surface modification

GAC has wide application in water treatment due to its low cost and its capacity to remove various types of pollutants including color & odour etc.

At neutral pH the arsenic removal efficiency of GAC is very less due to its predominantly negatively surface charge (In our experiment with 16 g/l adsorbent dose and 24 h of agitation the arsenic concentration in the treated water could not be reduced from 188 ppb to 50 ppb)

➤ Positive charge density on the surface of GAC can be increased at neutral pH by impregnating metal ion having more than one positive ions.

a. Surface charge without impregnation (NPC=2δ+)

b. Surface charge with medium impregnation (NPC=6δ+)

c. Surface charge with optimum impregnation (NPC=8δ+)

Schematic presentation of the increase in positive charge density on adsorbent surface due to surface modification Mondal et al., 2007, Ind. Eng. Chem. Res. 46(8)

So, for example, the GAC, granular activated carbon, if we see, in the GAC both positive and negative active sites are available as shown here. Positive, negative, positive, positive, positive, negative, positive, negative, like this surface charge is there. But due to the presence of these type of active sites, it is not very effective for the removal of the negatively charged ions like arsenic.

So, if we impregnate or if we modify the surface by some positively charged ions like Ca^{2+}. So this one Ca^{2+}, one ion will neutralize these negatively charged and it will create one positive charge. So, here is another Ca^{2+} coming in contact with this negatively sites and then it is giving another positively charged.

So, at the initial stage we have here 2δ+. So, you see 1, 2, 3, 4, 5 minus 3 negative So, then 2δ+ your net positive charge, but after surface modifications we are getting 6δ+ charge. Another calcium 2+ impregnation is resulting 8δ+ NPC, net positive charge.

So by the impregnation of metals we are able to increase the positive charge density in the surface of the adsorbent. As a result, its capacity to capture the negatively charged ions from the solution will increase. And as a result, the neutral pH, arsenic removal efficiency of GAC is very less due to its predominantly negatively charged surface.

In our experiment that is 16 g/L adsorbent dose and 24 hour agitation, the arsenic concentration in that treated water could not be reduced from 188 ppb to 50 ppb. So, this is our own study. So, but when it was impregnated with Ca^{2+} ion, so this arsenic removal was much more better than this.

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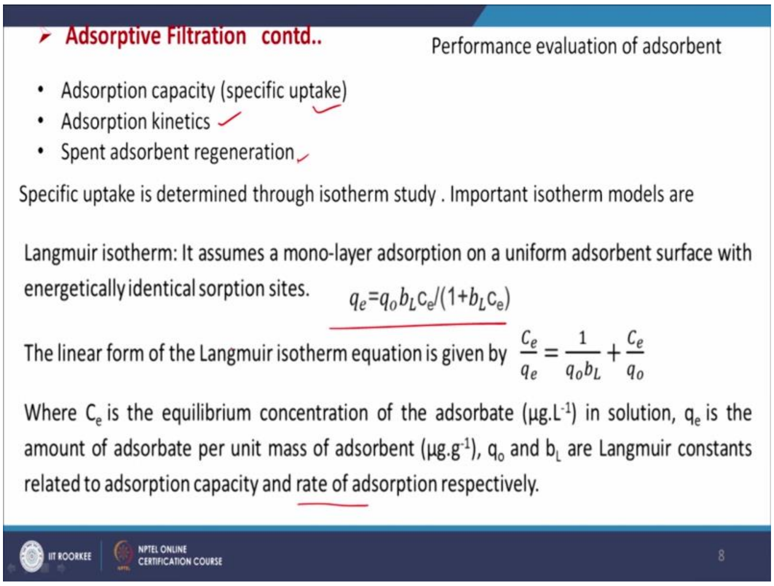

➢ **Adsorptive Filtration contd..**

Performance evaluation of adsorbent

- Adsorption capacity (specific uptake)
- Adsorption kinetics
- Spent adsorbent regeneration

Specific uptake is determined through isotherm study . Important isotherm models are

Langmuir isotherm: It assumes a mono-layer adsorption on a uniform adsorbent surface with energetically identical sorption sites. $q_e = q_o b_L C_e/(1+b_L C_e)$

The linear form of the Langmuir isotherm equation is given by $\frac{C_e}{q_e} = \frac{1}{q_o b_L} + \frac{C_e}{q_o}$

Where C_e is the equilibrium concentration of the adsorbate (μg.L^{-1}) in solution, q_e is the amount of adsorbate per unit mass of adsorbent (μg.g^{-1}), q_o and b_L are Langmuir constants related to adsorption capacity and rate of adsorption respectively.

And then how can we evaluate the performance? Performance means say if we are asked to design a adsorption column or any filter unit for the treatment of wastewater, so, we have to decide its size, we have to decides the amount of adsorbent required. So, one is adsorption capacity, that is specific uptake.

So, that is mg/g unit, that is mass of adsorbate captured on unit mass of the adsorbent. So, that way, we can evaluate the performance of the absorbents. And adsorption kinetics, what is the rate of that absorptions? So, what will be the retention time, we have to provide during its attachment or during the removal of the pollutants from the wastewater?

So, that absorption kinetics is also important. And after that, the spent adsorbent management or regeneration, what we will do with the spent adsorbent that is also an issue. So, all those information we should have and we should have good knowledge on that so that we can understand the phenomena and we can design a system for the effective treatment of wastewater.

So, specific uptake is determined through its isotherm study and important isotherm models are Langmuir isotherm. So, Langmuir isotherm, it assumes a monolayer adsorption on a uniform adsorbent surface with energetically identical substance sites. And this is the formula.

$q_e = q_o b_L c_e/(1+b_L c_e)$

Where C_e is the equilibrium concentration of the pollutant and q_e is the specific uptake at equilibrium, q is the maximum adsorption capacity or maximum specific uptake and b_L is the Langmuir constant which gives some idea about the rate of adsorption.

So, this is Langmuir isotherm, and mostly, it is used to calculate the maximum adsorption capacity of the adsorbent for that particular pollutants within certain range of initial concentration of the pollutant or adsorbate. Similarly, another mostly used isotherm is your Freundlich isotherm. Before that, we will discuss on the suitability of use of Langmuir isotherm.

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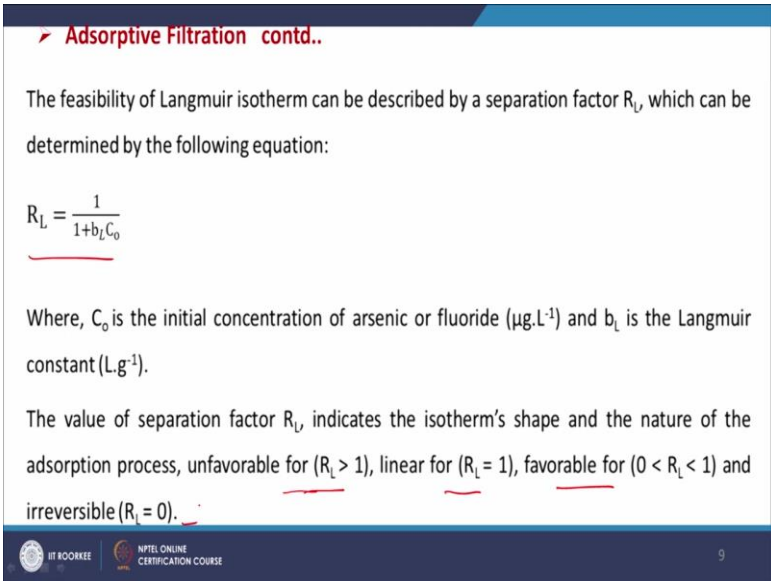

Adsorptive Filtration contd..

The feasibility of Langmuir isotherm can be described by a separation factor R_L, which can be determined by the following equation:

$$R_L = \frac{1}{1+b_L C_o}$$

Where, C_o is the initial concentration of arsenic or fluoride ($\mu g.L^{-1}$) and b_L is the Langmuir constant ($L.g^{-1}$).

The value of separation factor R_L, indicates the isotherm's shape and the nature of the adsorption process, unfavorable for ($R_L > 1$), linear for ($R_L = 1$), favorable for ($0 < R_L < 1$) and irreversible ($R_L = 0$).

So, here we see that the feasibility of Langmuir isotherm can be described by separation factor R_L which can be determined by following equation,

$$R_L = \frac{1}{1+b_L C_o}$$

So, now, if R_L value is greater than 1 that means adsorption process unfavorable, if R_L equal to 1, then it is linear and it is 0 or less than 1, then this is favorable, and irreversible when R_L is equal to 0. So, this R_L value, if we determined from the experiment, then we can get some idea whether the absorptions will be favorable or not.

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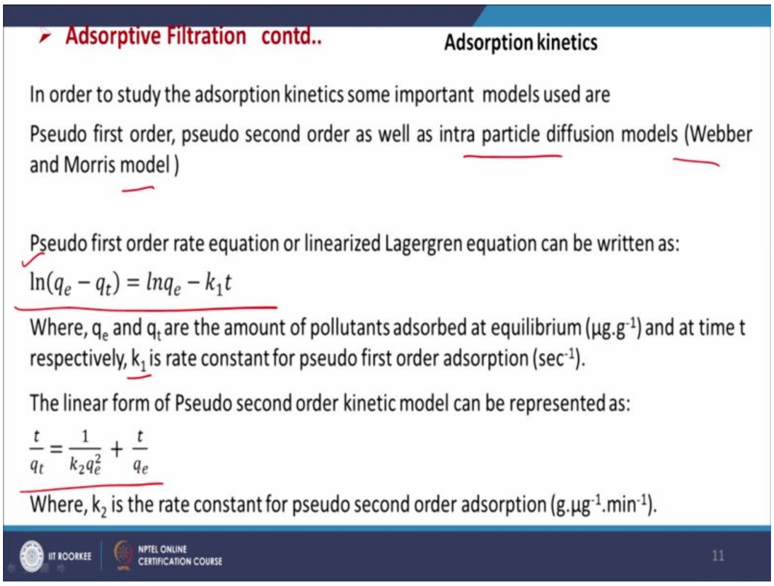

Adsorptive Filtration contd..

Adsorption kinetics

In order to study the adsorption kinetics some important models used are

Pseudo first order, pseudo second order as well as intra particle diffusion models (Webber and Morris model)

Pseudo first order rate equation or linearized Lagergren equation can be written as:

$$\ln(q_e - q_t) = ln q_e - k_1 t$$

Where, q_e and q_t are the amount of pollutants adsorbed at equilibrium ($\mu g.g^{-1}$) and at time t respectively, k_1 is rate constant for pseudo first order adsorption (sec^{-1}).

The linear form of Pseudo second order kinetic model can be represented as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Where, k_2 is the rate constant for pseudo second order adsorption ($g.\mu g^{-1}.min^{-1}$).

And then another absorption, isotherm which is mostly used that is Freundlich isotherm and Freundlich adsorption isotherm describes equilibrium on heterogeneous surfaces and hence does not assume mono layer capacity. The logarithmic form of the Freundlich isotherm expressions is given in this expression,

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

So, by doing experiment, we can find out the value of K_F and n. So, this K_F and n are Freundlich constant. And this can be determined from the experiment. And this can be used to get some idea whether the adsorption process is following these routes or these phenomena or not.

So, this is for single component adsorption, but if there are multiple pollutants and multiple adsorbate, then for that multi-component systems modified, competitive Langmiur model, extended Langmiur model and extended Freundlich model are used.

Adsorption kinetics, different models are used, that is pseudo first order model, pseudo second order model and Webber and Morris model, that is intra particle diffusion models are used. So, the pseudo first order model expressions is

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

Where k_1 is the rate constant, and then q_e, equilibrium specific uptake, and q_t specific uptake at any time.

And for the second order, pseudo second order kinetic model, the expression is like this.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

So, in both expressions, we have one rate constant and other is q_e value we can calculate. So, from this we can calculate that q_e value. And theoretically how much q_e equilibrium specific uptake we are calculating, experimentally, and which you are getting from this, that will give us some error, and the error value will help us to determine which method is more accurately representing the phenomena.

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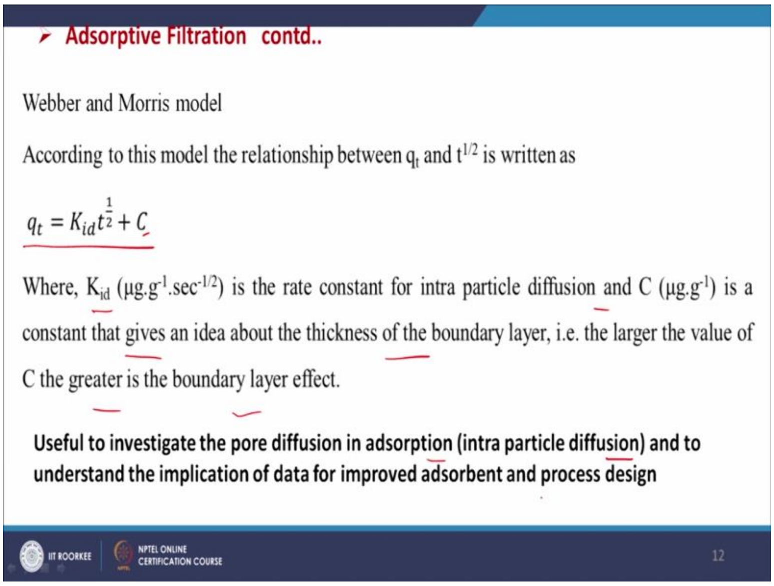

Adsorptive Filtration contd..

Webber and Morris model

According to this model the relationship between q_t and $t^{1/2}$ is written as

$$q_t = K_{id} t^{\frac{1}{2}} + C$$

Where, K_{id} ($\mu g.g^{-1}.sec^{-1/2}$) is the rate constant for intra particle diffusion and C ($\mu g.g^{-1}$) is a constant that gives an idea about the thickness of the boundary layer, i.e. the larger the value of C the greater is the boundary layer effect.

Useful to investigate the pore diffusion in adsorption (intra particle diffusion) and to understand the implication of data for improved adsorbent and process design

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And Webber and Morris model,

$$q_t = K_{id} t^{\frac{1}{2}} + C$$

This is used to give more interpretation on intra particle diffusion. And here K_{id} and C, these two are the constants and the rate constant $K_{i\,d}$ for intra particle diffusion and C is a constant that gives an idea about the thickness of the boundary layer. The larger the value of the C the greater is the boundary layer effect. So, this model is very useful to investigate the pore diffusion in adsorption, that is intra particle diffusion and to understand the implication of data for improved adsorbent and process design.

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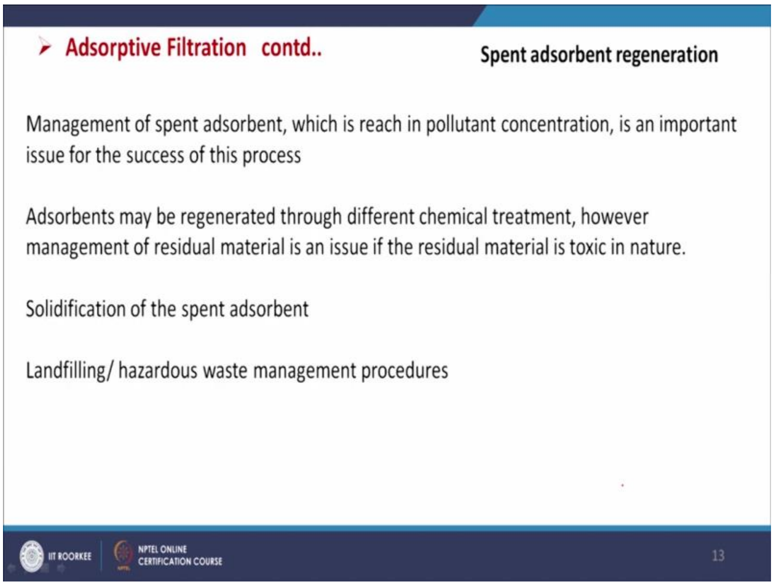

Adsorptive Filtration contd..

Spent adsorbent regeneration

Management of spent adsorbent, which is reach in pollutant concentration, is an important issue for the success of this process

Adsorbents may be regenerated through different chemical treatment, however management of residual material is an issue if the residual material is toxic in nature.

Solidification of the spent adsorbent

Landfilling/ hazardous waste management procedures

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Then spent adsorbent generation, so, after the adsorption process, the all pollutants or adsorbates are adsorbed on the surface of the adsorbent. So, depending upon the toxicity of the adsorbate or the pollutants, the adsorbents will also be toxic. So, we need to handle it very carefully. So, we can regenerate it, so we can dissolve the adsorbed pollutants or adsorbate.

But in that case, again we are creating some toxic substances. Management of that is also very essential. Or we can use this spent adsorbent for solidification purpose so, that that will be solidified with concrete. So, that will not come into the environment, or we can use it for land filling or we can manage it as per the Hazardous Waste Management procedure. Now, we will see the adsorption types and reactors used.

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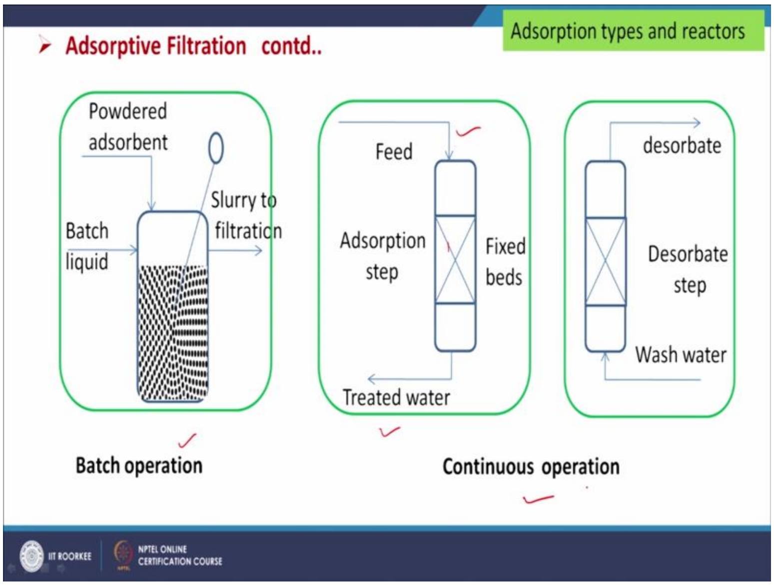

Adsorption types and reactors

➤ Adsorptive Filtration contd..

Batch operation

Continuous operation

So, as shown here, there are one batch type of operation and continuous type of operation, we are seeing here. So, this is a slurry reactor that you can say in a batch liquid is coming and then powdered adsorbent is put and then we are providing some agitation, and mixing, and a slurry is formed and pollutants present in the water, bulk of the solution comes on the surface of it and gets absorbed.

So, after certain time interval, we get the removal of the pollutants from the water. So, with increasing of agitation time the concentration of the pollutants in the solution gradually decreases and after certain time, it becomes free from the pollutants. And here we see the continuous operation, we are sending the feed from the top and from the bottom we are getting the treated water, and this is our adsorption bed, this is a fixed bed.

And after certain time of operation, this fixed bed will be adjusted that means, the adsorbent will be converted to spent adsorbent and at that time the concentration of the pollutants present in the feed and the treated water will be same. So, that will not be working. So, we need desorption. So, at that time we have to give wash water or some other methods, we can apply for the desorption of the adsorbed pollutants from it. And then these bed will be free and can be used further.

So, that in a cycle, one bed is in operation and other bed is in regeneration can be possible. Here we have seen that from the top the feed is coming on vice versa, the feed may come from the bottom and it can be treated water can go from the top also. Different configurations can be used as already we have discussed in previous classes.

So, this is the continuous operation and this is our batch operation. And for the application point of view, we go for continuous operation, and for basic understanding of the process, whether the particular pollutant will be removed by a particular type of adsorbent or not, what will be the residence time requirement and what will be the specific capacity, so, all those things we can determine in the batch scale.

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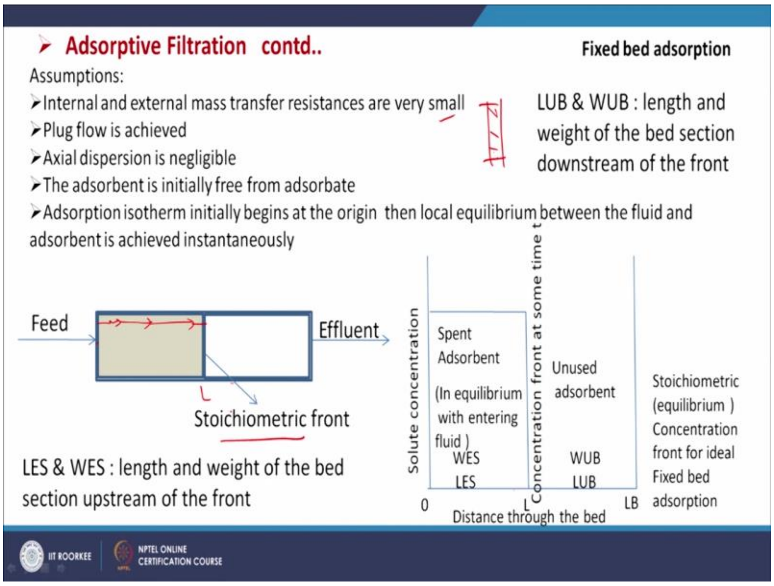

➤ Adsorptive Filtration contd..

Fixed bed adsorption

Assumptions:

- Internal and external mass transfer resistances are very small
- Plug flow is achieved
- Axial dispersion is negligible
- The adsorbent is initially free from adsorbate
- Adsorption isotherm initially begins at the origin then local equilibrium between the fluid and adsorbent is achieved instantaneously

LUB & WUB : length and weight of the bed section downstream of the front

LES & WES : length and weight of the bed section upstream of the front

Stoichiometric (equilibrium) Concentration front for ideal Fixed bed adsorption

Now, we will discuss how we will understand the phenomena which is going on in a fixed bed adsorption column or how can we model this, how can we determine different parameters during the adsorptions in the fixed bed, that, we will be discussing. Now, you see, we have to make some assumptions to simplify the phenomena for the initial understanding.

So, those assumptions are internal and external mass transfer resistances are very small. When the water is flowing in this bed. So, then we are assuming that there is no internal and external mass transfer resistances. That is very simple assumption, but this will never happen in reality, and plug flow is achieved.

We are assuming that the flow is following a plug flow through this bed. That means axial dispersion is negligible. The concentration across this diameter is always constant. And then the adsorbents is initially free from the adsorbate, initially this adsorbent is not having any adsorbate. The adsorbate is only available in the feed. Adsorbate means pollutant here.

So, pollutant is present in feed, but there is no pollutant in the adsorbent or the initial stage and adsorption isotherm initially begins at the origin. So, at the very starting point the pollutants are being captured by the absorbent, so with more runtime, next layers are getting, are capturing the pollutants, that means with time, the exhausted bed size is increasing.

So, this is one typical example. Say for this is length, up to this length this bed is exhausted first, then this bed will be exhausted. That means here the pollutants are captured by the adsorbent and here the pollutants are not captured by the adsorbent because pollutants are not available, all pollutants have been captured in this adsorbent.

So these are our assumptions basically. Adsorption isotherm initially begins at the origin then local equilibrium between that fluid and adsorbent is achieved instantaneously. And then in that case, which we see in the whole bed some part will be exhausted, some part of the adsorbent will not be exhausted at all it will be free for the adsorption.

So, this is our stoichiometric front. So, this line is our stoichiometric front. What does it mean by stoichiometry or by mass balance? We can calculate what is the length of the this part where the pollutants have been captured. That means total pollutants present in this feed, that will be available in a zone.

That means that amount of pollutants is being captured by the material present in this zone. So, we can repeat it like this. So, solute concentration at the very zero stage with respect to this position. So here, the solute concentration is a feed concentration maximum, then this is L, after that solid concentration is zero.

So, there is in the water there is no solute. So, this is, so this part is our LUB and the material present in it that is WUB. So, LUB and WUB length and weight of the bed section downstream of the stoichiometric front, and LES and WES, the length and bed of the bed section upstream of the front, so, this is provided here. So, this is our stoichiometric front.

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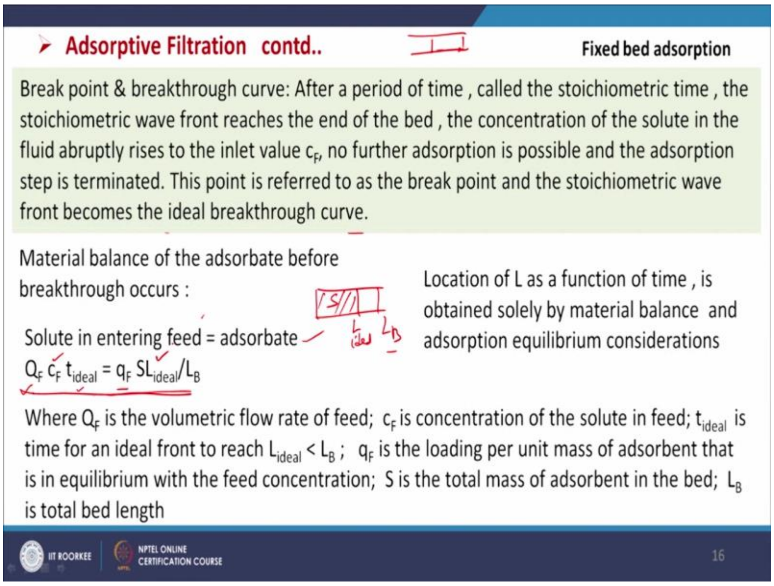

Adsorptive Filtration contd..

Fixed bed adsorption

Break point & breakthrough curve: After a period of time , called the stoichiometric time , the stoichiometric wave front reaches the end of the bed , the concentration of the solute in the fluid abruptly rises to the inlet value c_F, no further adsorption is possible and the adsorption step is terminated. This point is referred to as the break point and the stoichiometric wave front becomes the ideal breakthrough curve.

Material balance of the adsorbate before breakthrough occurs :

Solute in entering feed = adsorbate

$Q_F\ c_F\ t_{ideal} = q_F\ SL_{ideal}/L_B$

Location of L as a function of time , is obtained solely by material balance and adsorption equilibrium considerations

Where Q_F is the volumetric flow rate of feed; c_F is concentration of the solute in feed; t_{ideal} is time for an ideal front to reach $L_{ideal} < L_B$; q_F is the loading per unit mass of adsorbent that is in equilibrium with the feed concentration; S is the total mass of adsorbent in the bed; L_B is total bed length

Now, this is as per our assumption, then the main assumption is that there is no mass transfer resistance and plug flow situation prevails in the bed. So, in this case, what we will see, after a certain time called the stoichiometric time, the stoichiometric wavefront reaches the end of the bed. So, if this is the bed which we had, this was front, certain time this front will reach here.

The concentration of the solute in the fluid abruptly rises to the inlet value C_F, no further adsorption is possible and the adsorption step is terminated. This point is referred to as the break point and the stoichiometric wavefront becomes the ideal breakthrough curve. So, this is the ideal breakthrough curve.

And if any length that we are talking about which is less than that L_B, so, this is our L_B and this is our L any length less than the L_B we can calculate the value of L by mass balance that is equal to LES. So, how we can do it? That is by mass balance solute in, entering feed and that is equal to adsorbate captured by the material in a L_{ideal}.

$Q_F\ C_F\ t_{ideal} = q_F\ SL_{ideal}/L_B$

So, these are the same. So, by equating these two, we can calculate the value of L_{ideal}. We can get the value of L_{ideal}.

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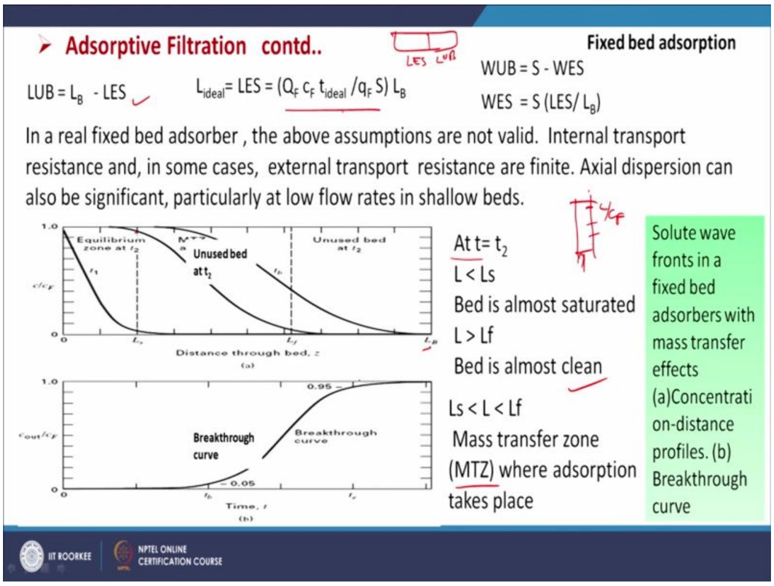

Adsorptive Filtration contd..

Fixed bed adsorption

$LUB = L_B - LES$

$L_{ideal} = LES = (Q_F\, c_F\, t_{ideal} / q_F\, S)\, L_B$

$WUB = S - WES$

$WES = S\,(LES / L_B)$

In a real fixed bed adsorber , the above assumptions are not valid. Internal transport resistance and, in some cases, external transport resistance are finite. Axial dispersion can also be significant, particularly at low flow rates in shallow beds.

At $t = t_2$

$L < Ls$

Bed is almost saturated

$L > Lf$

Bed is almost clean

$Ls < L < Lf$

Mass transfer zone (MTZ) where adsorption takes place

Solute wave fronts in a fixed bed adsorbers with mass transfer effects (a)Concentration-distance profiles. (b) Breakthrough curve

And L_{ideal} is nothing but LES. So LES, we can calculate now

$L_{ideal} = LES = (Q_F\, C_F\, t_{ideal} / q_F\, S)\, L_B$

So, then how we can get the LUB? $LUB = L_B - LES$

So, $L_B = LUB + LES$ or $LUB = L_B - LES$.

So, that we can, once the L_B is known LES is calculated by this, we can calculate the value of LUB. So, this is possible for ideal condition. But in nature this will not happen. In a real fixed bed adsorber, the above assumptions are not valid. Internal transport resistance and in some cases external transport resistance are finite and axial dispersion can also be significant, particularly at low flow rates in shallow beds.

So, here, say if we have a bed here and with respect to time we are measuring the concentration here, it is a different length. So, we are taking sample here. So, at t = 0 in all the cases, the concentration of the pollutants will be 0, but when will be increasing the time, so after say half an hour, 20 minutes or 10 minutes, after 10 minutes, 15 minutes, 20 minutes, if we carry out the experiment, then we will see that the concentration here will be increasing gradually.

Still, here the concentration will be zero. Further, we can go ahead and the same trend we will get. So, with respect to length if we see the C/C_F value, that is a C is the concentration of pollutants in the outlet, and C_F is the concentration of pollutants in the inlet. So, that value with respect to, that will be changing like this, with length for a constant time.

Let us say for t_1, we are taking this one, but for t_2, this will be like this and for t_b this will be like this. So, if we take one case for a time t_2, this curve if we consider, so, here this is L s and Lf, so, this Lf is showing that most of the material when L is then Ls, so, this Ls and Lf, now, if L is less than Ls for t equal to t_2 that means this part then we can say that the bed is almost saturated because C/C_F it almost nearer to 1 upto this.

Then it is gradually decreasing, and here at Lf and L is greater than Lf, that means, this side this part is not used at all, unused bed so, almost clean bed, but in between Ls and Lf, then there is a mass transfer. So, this is mass transfer zone, this part. And if we represent this C/C_F with respect to time for the whole, this, L_B, then that will be changing like this with respect to time, the S shaped curve we will get, that is called Breakthrough curve.

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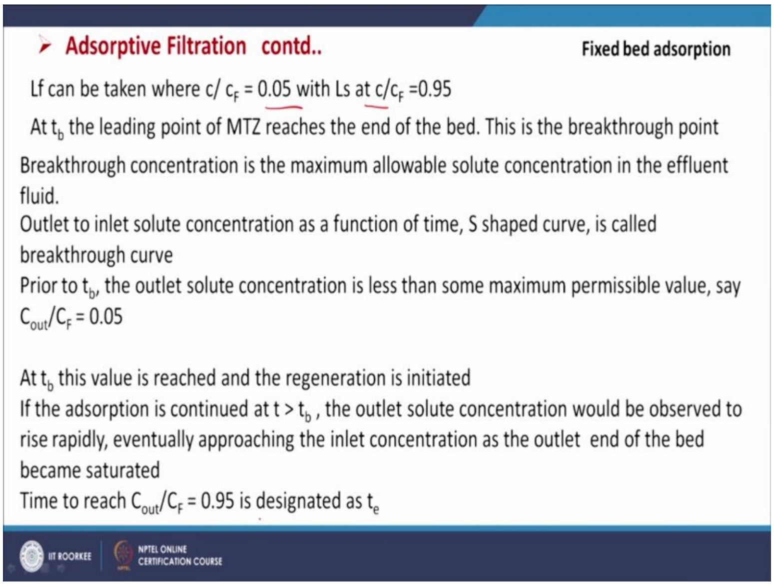

Adsorptive Filtration contd..

Fixed bed adsorption

Lf can be taken where $c/c_F = 0.05$ with Ls at $c/c_F = 0.95$

At t_b the leading point of MTZ reaches the end of the bed. This is the breakthrough point

Breakthrough concentration is the maximum allowable solute concentration in the effluent fluid.

Outlet to inlet solute concentration as a function of time, S shaped curve, is called breakthrough curve

Prior to t_b, the outlet solute concentration is less than some maximum permissible value, say $C_{out}/C_F = 0.05$

At t_b this value is reached and the regeneration is initiated

If the adsorption is continued at $t > t_b$, the outlet solute concentration would be observed to rise rapidly, eventually approaching the inlet concentration as the outlet end of the bed became saturated

Time to reach $C_{out}/C_F = 0.95$ is designated as t_e

And Lf can be taken where $C/C_F = 0.5$ and Ls = $C/C_F = 0.95$. So, this Ls and Lf consideration one condition is that when $C/C_F = 0.95$ then Ls and Lf when C/C_F =0.05,. So, this is the condition. Similarly, here tb, and this tb which is valued here, that is equal to $C/C_F = 0.05$. And here, tb equal to when and $C/C_F = 0.95$. So, these are some convention, it is considered.

And at tb, the leading point MTZ reaches the end of the bed, and tb we are considering, the empty MTZ, end point reaches the L_B, so, this is breakthrough point. So, breakthrough concentration is the maximum allowable solute concentration in the effluent fluid. Outlet to inlet solid concentration as a function of time, S shaped curve is called a breakthrough curve, already we have discussed.

And prior to t_b, the outlet solid concentration is less than some maximum permissible value say C_{out} /C_F equal to 0.05. So, when we are getting C/C_F is equal to 0.05, it, there is one condition that up to this we should attain the maximum permissible limit allowable. Like for example, if we use a fluoride solution here say 6 ppm, but here my allowable limit is 1.5 ppm. So, 1.5/6, that value should be here when this graph, we are considering.

So, now, at tb this value is reached and the regeneration is initiated. So, in case of fluoride say the water present here is equal to say more than 1.5, then it is not acceptable. So, we have to regenerate the bed. If the adsorption is continued at t greater than tb, the outlet solute concentration should be observed to be rise rapidly, eventually approaching the inlet concentration such the outlet end of the bed becomes saturated. Time to reach Cout/C_F is designated as te.

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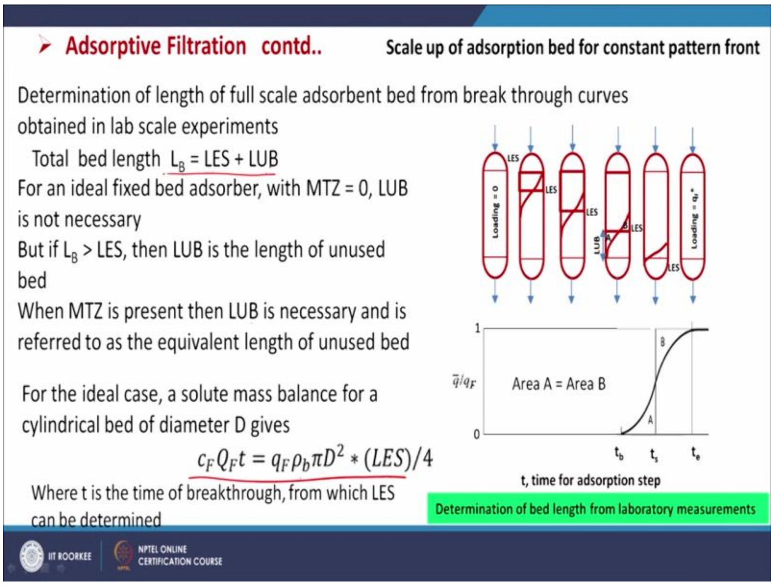

➢ Adsorptive Filtration contd..

Scale up of adsorption bed for constant pattern front

Determination of length of full scale adsorbent bed from break through curves obtained in lab scale experiments

Total bed length L_B = LES + LUB

For an ideal fixed bed adsorber, with MTZ = 0, LUB is not necessary

But if L_B > LES, then LUB is the length of unused bed

When MTZ is present then LUB is necessary and is referred to as the equivalent length of unused bed

For the ideal case, a solute mass balance for a cylindrical bed of diameter D gives

$$c_F Q_F t = q_F \rho_b \pi D^2 * (LES)/4$$

Where t is the time of breakthrough, from which LES can be determined

Determination of bed length from laboratory measurements

Now, scale up of adsorption bed for constant pattern front. So, here, say if we want to calculate the length or if we want to know the LES and LUB, then we can assume that initially, the water is going through this bed and the LES is gradually increasing, and this front is not like this. It is actually is an S-shaped curve.

So, this is like this, but in ideal case it would be like this, all the bed is exhausted and these bed is non exhausted, unused, but here this portion is also unused, like this. And this portion is used. So this graph is like this. So, with a time, we will see the one condition is here that is called ts and last condition is te, and here we are getting tb.

So, this front head, two part is not there, only one part. So, this total length we are getting here. So, that is equal to the length of the bed. So, if we divide the total length by this ts, that will be the front head speed. So that that will be there. So, that concept, we will be using to find out the value of LUB.

So, as L_B = LES + LUB and if it is an ideal condition LUB is equal to 0, but if it is not ideal conditions, so if there is any, these mass transfer zone is there, in that case, LUB we have to calculate, but in all the cases LES can be calculated by these mass balance we have already discussed.

$$c_F Q_F t = q_F \rho_b \pi D^2 * (LES)/4$$

So that way, we can get the value of LES.

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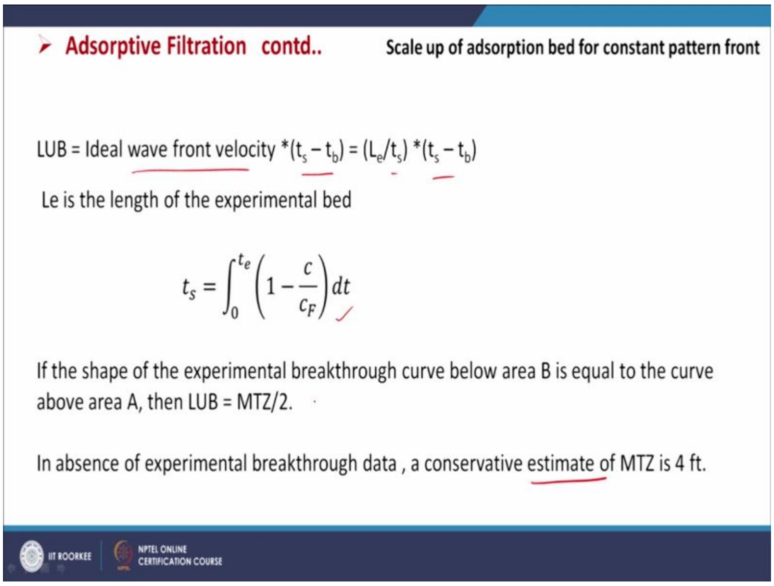

Adsorptive Filtration contd..

Scale up of adsorption bed for constant pattern front

LUB = Ideal wave front velocity *($t_s – t_b$) = (L_e/t_s) *($t_s – t_b$)

Le is the length of the experimental bed

$$t_s = \int_0^{t_e} \left(1 - \frac{c}{c_F}\right) dt$$

If the shape of the experimental breakthrough curve below area B is equal to the curve above area A, then LUB = MTZ/2.

In absence of experimental breakthrough data , a conservative estimate of MTZ is 4 ft.

And we can calculate the LUB by this formula,

LUB = Ideal wave front velocity *($t_s – t_b$) = (L_e/t_s) *($t_s – t_b$)

So, ideal wave front velocity that means, as we are talking about say up to ts is the time and then bed, whole bed has been covered by the adsorption process, and whole bed is exhausted now.

$$t_s = \int_0^{t_e} \left(1 - \frac{c}{c_F}\right) dt$$

So, LUB, we can calculate it that way, LES can be calculated as discussed in the previous slide. So, total L_B, you can calculate. And if the shape of the experimental breakthrough curve below area V is equal to the curve above area A, like this A and B if these areas are same in that case, we can consider that LUB is equal to half of the MTZ, mass transfer zone, and in absence of the experimental breakthrough data, a conservative estimate of MTZ is 4 feet. So, LUB = 4/2 = 2 feet, so, 2 feet LUB may be considered as default value.

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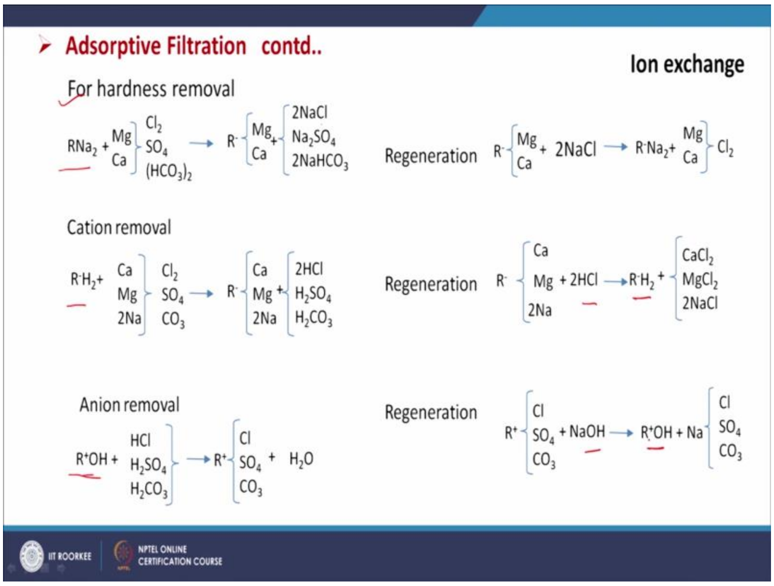

Adsorptive Filtration contd..

Ion exchange

For hardness removal

$$RNa_2 + \left.\begin{matrix}Mg\\Ca\end{matrix}\right\} \begin{matrix}Cl_2\\SO_4\\(HCO_3)_2\end{matrix} \rightarrow R^- \left\{\begin{matrix}Mg\\Ca\end{matrix}\right. + \left\{\begin{matrix}2NaCl\\Na_2SO_4\\2NaHCO_3\end{matrix}\right.$$

Regeneration $R^- \left\{\begin{matrix}Mg\\Ca\end{matrix}\right. + 2NaCl \rightarrow R^-Na_2 + \left.\begin{matrix}Mg\\Ca\end{matrix}\right\} Cl_2$

Cation removal

$$R^-H_2 + \left.\begin{matrix}Ca\\Mg\\2Na\end{matrix}\right\} \begin{matrix}Cl_2\\SO_4\\CO_3\end{matrix} \rightarrow R^- \left\{\begin{matrix}Ca\\Mg\\2Na\end{matrix}\right. + \left\{\begin{matrix}2HCl\\H_2SO_4\\H_2CO_3\end{matrix}\right.$$

Regeneration $R^- \left\{\begin{matrix}Ca\\Mg\\2Na\end{matrix}\right. + 2HCl \rightarrow R^-H_2 + \left\{\begin{matrix}CaCl_2\\MgCl_2\\2NaCl\end{matrix}\right.$

Anion removal

$$R^+OH + \left.\begin{matrix}HCl\\H_2SO_4\\H_2CO_3\end{matrix}\right\} \rightarrow R^+ \left\{\begin{matrix}Cl\\SO_4\\CO_3\end{matrix}\right. + H_2O$$

Regeneration $R^+ \left\{\begin{matrix}Cl\\SO_4\\CO_3\end{matrix}\right. + NaOH \rightarrow R^+OH + Na^- \left\{\begin{matrix}Cl\\SO_4\\CO_3\end{matrix}\right.$

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So, then we see that ion exchange phenomena can also be responsible for adsorption process. And apart from that, to get more purified water, we use the ion exchange method. So, as discussed in our previous class on drinking water treatment, then we have seen that for hardness removal there is ion exchange can be used.

So, here are the reagents which are used that are present in RNa_2 form and then calcium magnesium and other anions present in the solution. And then this cations are attached by these R part and Na is released, and these are the Na salt of these anions are formed. And when we go for the regeneration, again NaCl is added because we have to make RNa_2.

But in case of say cation removal. So, this resin is converted to RH_2 form and then these all cations are taken up, not only calcium, magnesium, any other cations, and then it is converted into this and then the hydrogen, hydride form of these anions. And then during regeneration, again, we use the HCl so that RH_2 form can be regenerated.

And when we want anion removal, then, when you want to remove anions, at that time, this is formed in R^+OH, and then different anions are removed and these are R^+ these ones. And then during regeneration, we add it with NaOH because again we need to convert R^+OH. So this is the regeneration process, and which are followed for the treatment of the wastewater or to make more pure treated water with negligible amount of cations and anions for specific application.

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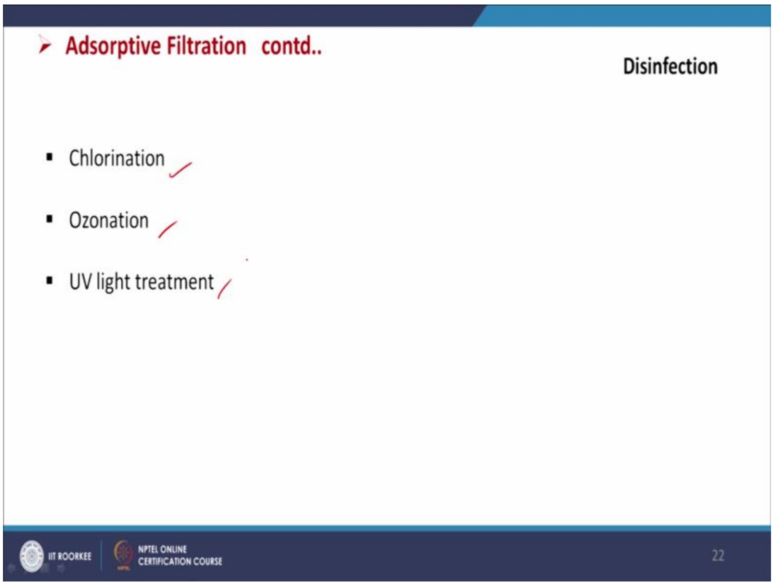

Adsorptive Filtration contd..

Disinfection

- Chlorination ✓
- Ozonation ✓
- UV light treatment ✓

And then disinfection, in this step which simultaneously takes at the last stage of the treatment, as tertiary treatment, it is a coupled, we can say, so this disinfection is coupled with any tertiary treatment step. So, here our main objective is to remove the pathogens, and then chlorination, ozonations and UV light treatments are normally used and we have made discussion during drinking water treatment, and same process are also followed in the industrial treatment as well.

Up to this, in this class. Thank you very much for your patience.