Physico-Chemical Processes for Wastewater Treatment
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Lecture 36
Adsorption - VI

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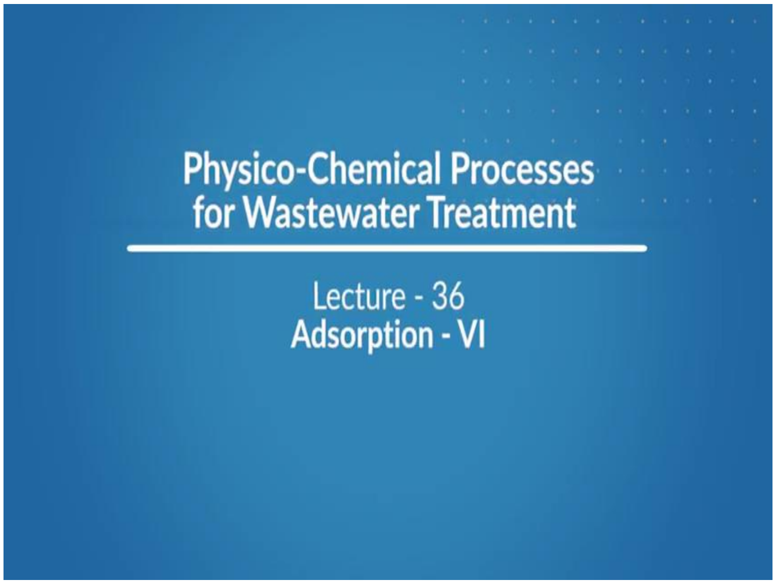

Good day everyone and welcome to these lectures on adsorption method, which is used as one of the Physico-Chemical Processes for Wastewater Treatment. And in the previous lectures we studied regarding various adsorbents, their properties which can be determined including pore size, pore surface area, etc. In addition, we tried to understand the basic concepts of adsorption kinetics and adsorption isotherm.

So, for determining adsorption kinetics and adsorption isotherm generally we use batch adsorption data. So, that means, we have some wastewater in which some adsorbent is added and we try to find out the treatment efficiency and the adsorbent capacity after some time. So, that is like a batch adsorption process. But in actual in the industry we will always be doing this water treatment in the adsorption unit which is operated in a continuous mode.

So, that means we will be having a continuous mode of operation where the water which contains some amount of pollutant will be fed from one side and we will be continuously be getting water, which is treated in the adsorption unit. So, for doing this generally we use packed-bed sorption column. So, these packed-bed sorption columns or packed-bed units are used other places also in various other unit operations.

So, but we will be considering the adsorption or sorption column where it is being used as an adsorbent. It is possible that some other types of reactions are also carried out in the packed-bed, so that is there. So, we will be having one column in which the water will be fed, we can see the wastewater to be treated is being fed. And from the outlet, we are getting the water which is already treated.

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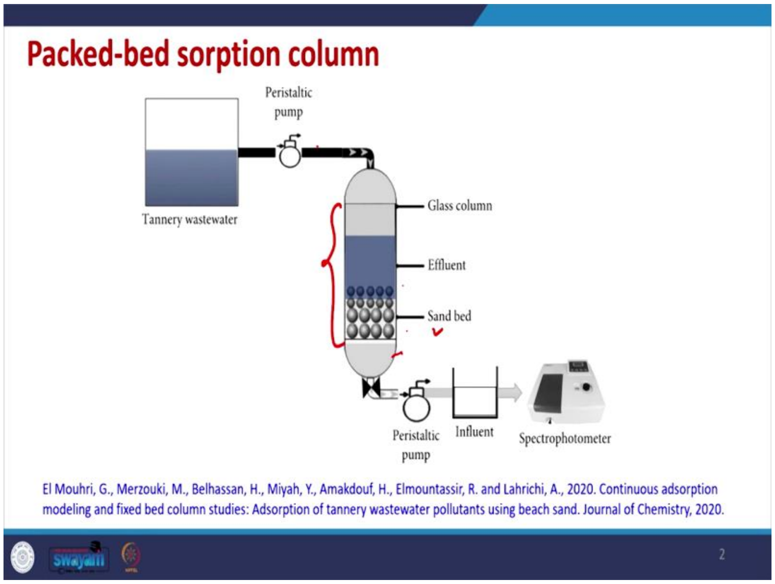

And we can analyze the water with respect to its treatment efficiencies and other things. So, these parameters we can find. And what we do is that we fill the bed with certain amount of adsorbents, it may be sand, it may be any other type of adsorbent.

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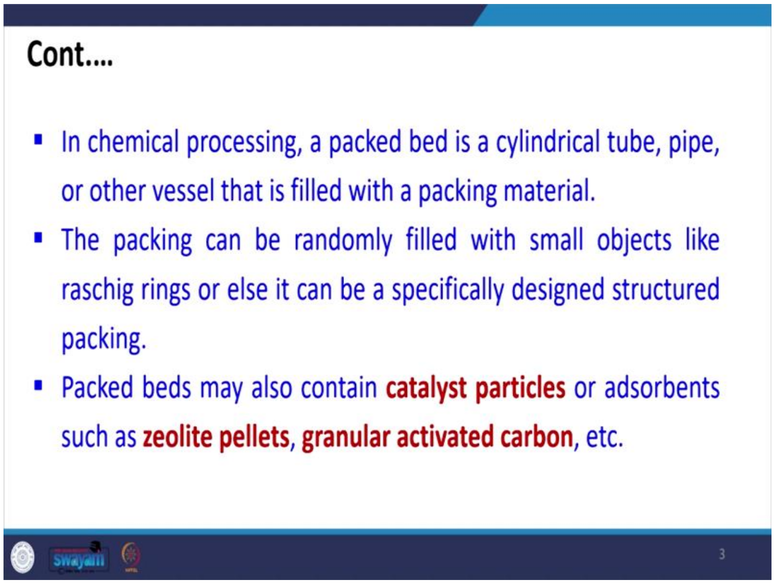

So, in general, in chemical processing, packed-beds are very common. And essentially the packed-beds they are cylindrical tubes or pipes or any other types of vessels, generally there will be tube or pipes. And that are filled with some packing material. The packing may be randomly filled with small objects like raschig rings, etc.

And packed-beds which are used for adsorption or for some other types of catalytic reactions, in place of packings we have catalyst particles or adsorbent. So, these adsorbent for adsorption case they may be zeolite, any granular activated carbon or any other type of adsorbent that we have to use for the water treatment.

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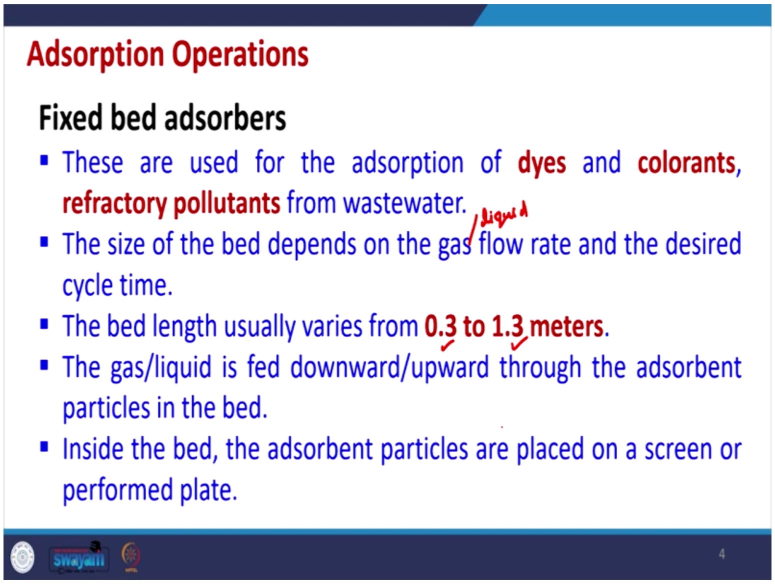

So, these other way around they may be called as fixed bed adsorbers also. So, in the fixed bed adsorbers, we can use them for removal of various types of dyes, colorants, reflective pollutants, many other types of toxic pollutants, etc., from water or wastewater. The size of the bed will depend upon the gas or the liquid flow rate or the, whatever is the treatment that has to be done. So, this will be dependent upon the size including the length and the diameter of the bed.

So that is very important. So that depends upon that how much water we have to treat. And if the liquid flow rate is very, very high, we can divide the flow rate into various parallel flow rates which can be treated further on by a number of parallel packed beds, which are being used there. Now, the bed length may vary from 0.3 meter to 1.3 meter or higher also, it is possible but these are the general length. We can go up to high length also 5 meters or beyond also that depending upon the type of adsorbent we are going to use, how much water we have to treat and what is the characteristic of water that has to be treated.

Now, the gas or liquid these packed-beds can be used for gas separation also. So, the gas or liquid flow rate may go downward or upward depending upon various properties and through the adsorbent particles which are there in the bed itself. Inside the bed, the adsorbent particles are placed on a screen or some perforated plate, so that we have proper channeling of the, proper distribution of the influent takes place before treatment.

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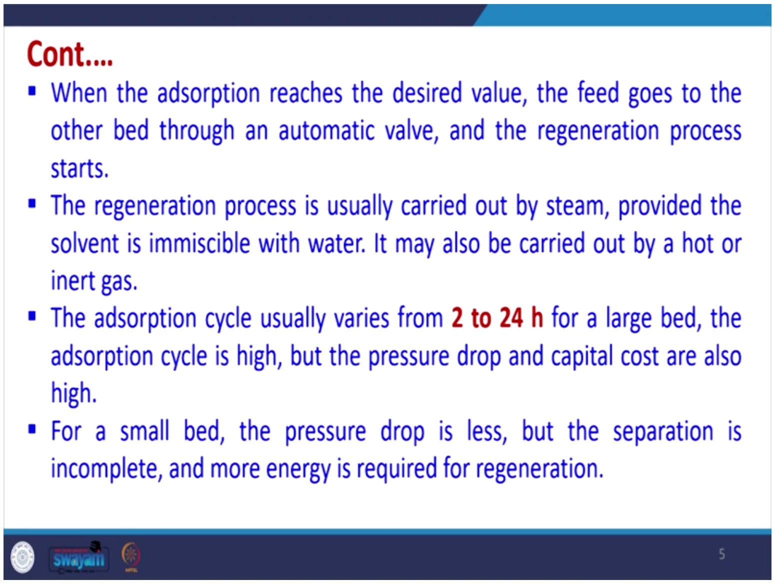

Now, when the adsorption reaches the desired value, so after a certain time. So whenever what we do is that, we have to see that the flow rate is decided in such a manner that the influent are the liquid that has to be treated that remains in the packed-bed for a certain duration of time which may be decided from the batch data itself. So, that desirability is already there with respect to residence time that we have to give.

So, the feed goes to the, when that much time is given and after the treatment the liquid comes out. So, if it is up to the desired level of treatment, it is okay otherwise, it may be fit to another bed, which may be there in the series or it is possible that this bed may further be operated in a regeneration mode, so that the spend adsorbent may be again be used again in the next cycle. So, this is possible.

The regeneration process in the, like for gas separation or for some of the pollutants can be carried out by steam or by using some solvents etc. So, this is possible. Now, the adsorption cycle may vary from different 2 to 24 hour or maybe higher for larger beds. So, depending upon this adsorption cycle may be decided. For a small bed, the pressure drop is one of the essential criteria.

So, the flow rates, pressure drop, all these are very important criteria which actually help in deciding whether we have to use how many beds or what should be the length of the bed or the diameter of the bed. So, these parameters can be decided depending upon a number of parameters.

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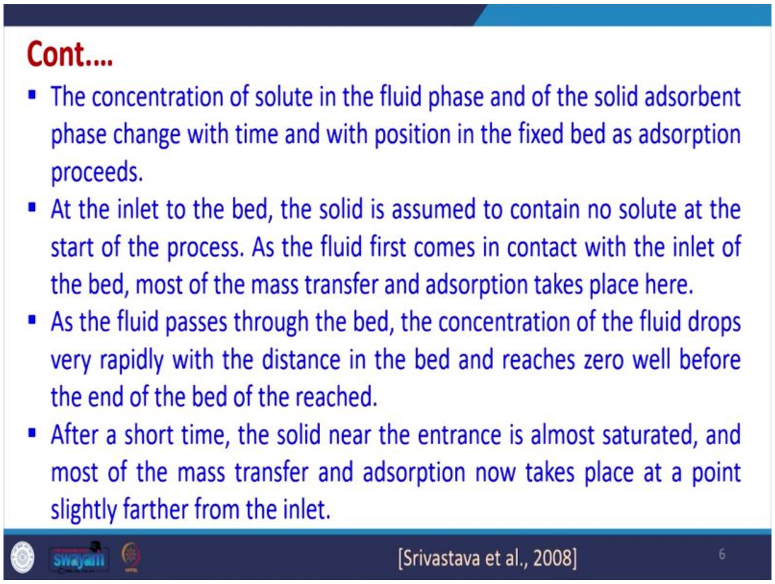

Now, the concentration of solute in the fluid phase and of the solid adsorbent phase, they change with time and with position in the fixed bed as the adsorption proceeds. So, when in the initial phases, the first layer of the bed will get exhausted, and similarly the second bed. So, it is possible that for long duration the solute which is coming, it is within the desired limit, but after some time the solute which will be coming out or the effluent which is coming out, it will not be up to the desired limit and it will break through conditions will be there, where the concentration limits have been breached and the desired treatment efficiency is not achieved. So, this is possible.

Similarly, the adsorption which occurs, so it also moves across the bed. So, this is written. So, we will try to understand this in further slides. At the inlet to the bed, the solid is assumed to contain no solute at the start of the process. But as the treatment goes on, these solid particles get exhausted and the adsorption mass transfer zone or adsorption in the adsorption zone moves through the bed. So, this is there.

And as the fluid or the liquid passes through the bed the concentration of the pollutant in the liquid drops very rapidly with the distance in the bed and reaches zero well before the end of the bed is reached. So, thus we achieve the targeted removal efficiency. So, but it is possible that after some time when saturation is reached and most of the mass transfer and adsorption will reach to the endpoint and after that the removal will not occur properly.

Now, in the packed bed there are a number of parameters that we should decide and one of the essential parameters are like empty bed contact time and sorbent usage rate or adsorbent usage rate also we can call it. Now, contact time or the duration in which the adsorbent or the liquid is inside the packed-bed that is very important parameter.

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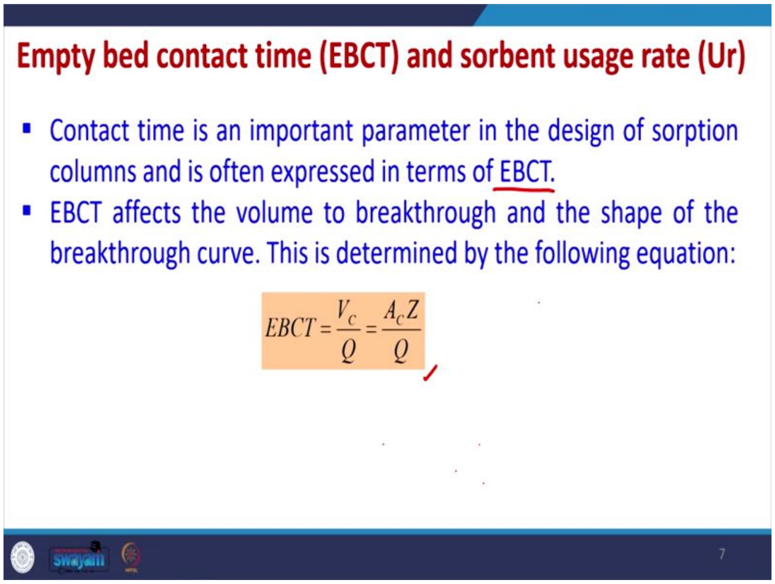

EBCT determined by the following equation:

$$EBCT = \frac{V_C}{Q} = \frac{A_C Z}{Q}$$

So, contact time is very important parameter in the design of adsorption columns and it is generally expressed as EBCT. EBCT means, empty bed contact time. So, it is one of the parameters that helps in deciding that what should be the EBCT or what should be the decedents time etc. So, EBCT affects the volume to break through and the shape of the break through curve. So, this is there.

And it is determined by using the following formula which is given here by Vc by Q and Vc is the actually the volume of the column, so total volume of the column and Q is the flow rate.

Now, Vc can further be written as Ac into Z. So, Ac is the cross sectional area of the column and where Z is the height of the column in which the packed-bed material is kept. So, this is there. So, it is very straightforward calculation.

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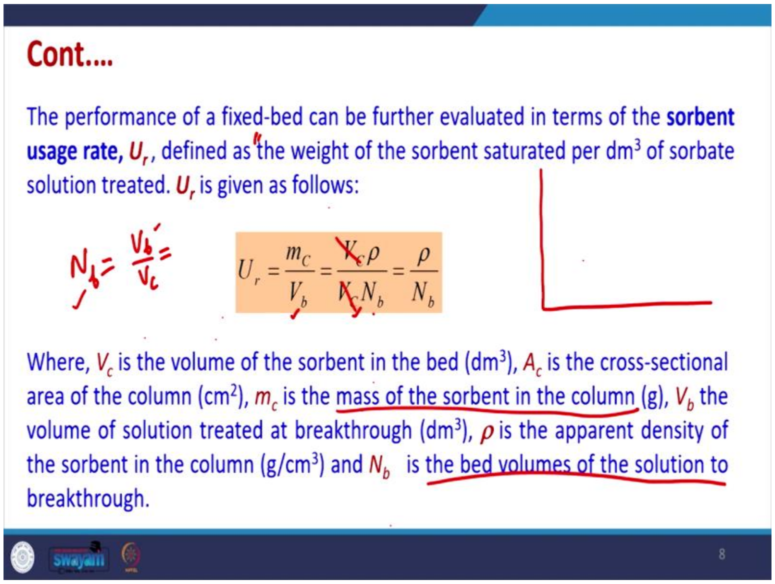
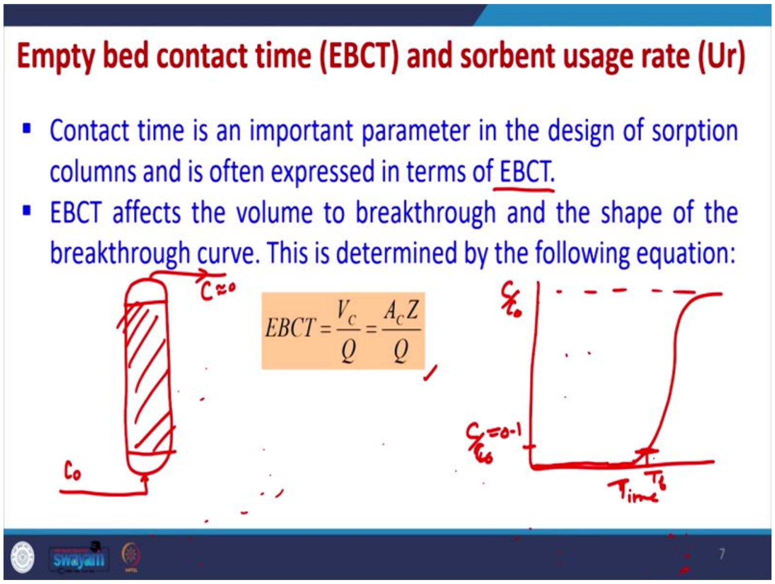


The performance of a fixed-bed can be further evaluated in terms of the sorbent usage rate, U_r , defined as the weight of the sorbent saturated per dm^3 of sorbate solution treated. U_r is given as follows:

$$U_r = \frac{m_C}{V_b} = \frac{V_C \rho}{V_C N_b} = \frac{\rho}{N_b}$$

Where, V_c is the volume of the sorbent in the bed (dm^3), A_c is the cross-sectional area of the column (cm^2), m_c is the mass of the sorbent in the column (g), V_b the volume of solution treated at breakthrough (dm^3), ρ is the apparent density of the sorbent in the column (g/cm^3) and N_b is the bed volumes of the solution to breakthrough.



Now, in addition to that, the performance of fixed bed can further be evaluated in terms of adsorbent usage rate. And which is defined as the weight of the sorbent or adsorbent saturated per decimeter cube or per liter of the adsorbate solution being treated. So, this is there. And it can be defined as like mc divided by Vb and further we can calculate is like Vc into density. So, this is mc is the mass of the sorbent in the column.

So, mass of the sorbent can be written as the volume of the sorbent into density. So, this is there. So, we can calculate and the break through Vb is called as the break through time. So, breakthrough time is like when we actually initially start the treatment process, what happens is that, so, we can understand it like here. So, we have a packed-bed. And in the packed bed some treatment is happening.

So, suppose the flow rate is upwards. And we have C0 is the concentration and after some time after treatment, the concentration here is C. So, this is there. So, when the adsorption will happen, so this is the time suppose. So, initially and we have on the y axis we decide like C by C0. So, this is there. So, initially what will happen that the concentration will be virtually nil here. So, whatever is the adsorbate that will get adsorbed inside this packed bed.

So, that is possible. So, inside this packed bed the treatment will occur. And here the concentration will be virtually be 0. So, the graph initially will be lying at the bottom, but after some time it will start increasing and it will go up like this. So, the time in which we have breakthrough is achieved. So, this is called TB, time for breakthrough. And where the concentration, suppose we want the C by C0 to be 0.1.

So, whenever the C by C0 reaches 0.1 condition so that will be called as breakthrough time. And the volume of water which has been treated up to this time is called breakthrough volume. So, this is what is given here. So, Vc is the volume of the sorbent total sorbent in the bed, volume Vb is the breakthrough volume. And breakthrough volume, we can always be, we can write in terms of this total, Nb is the number of bed volumes being treated up to breakthrough.

So, Nb is virtually define as Vb by Vc. So, up to break through how much amount of volume has been treated of water which is to be treated. Now, it is possible that breakthrough we reach during very large time. So, we always want this Nb value to be highest possible so that we can treat maximum amount of water. So, now, in this case we have replaced Vb by Vc into Nb.

So, this Vc Vc can go off and we can like row by Nb. So, these two parameters we always desired to be higher. So, sorbent usage rate, if it is how much sorbent is being used per liter of water being treated. So, we want the sorbent usage rate to be lowest possible because we do not want the sorbent to be used that much with respect to treatment of the per liter of the water or any other volume of water.

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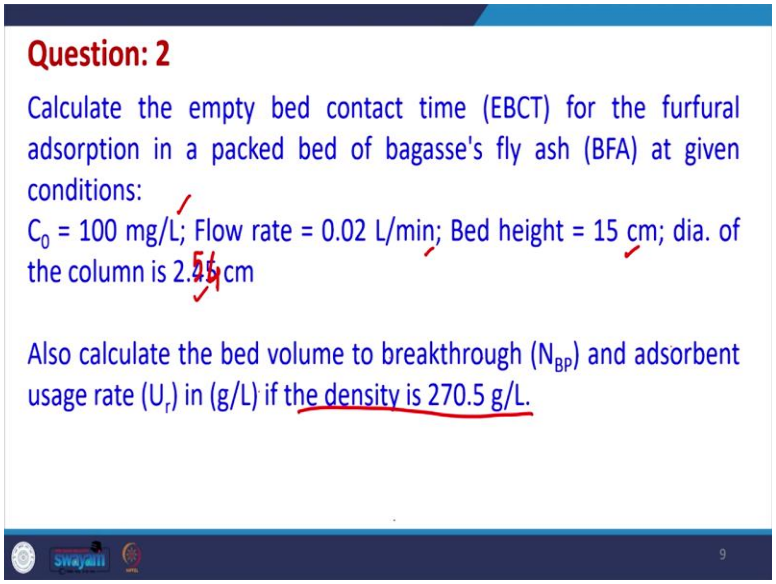

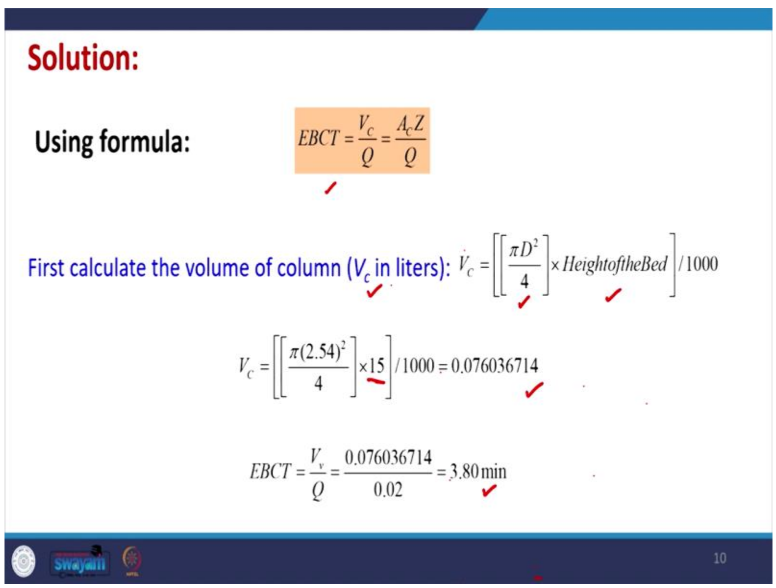

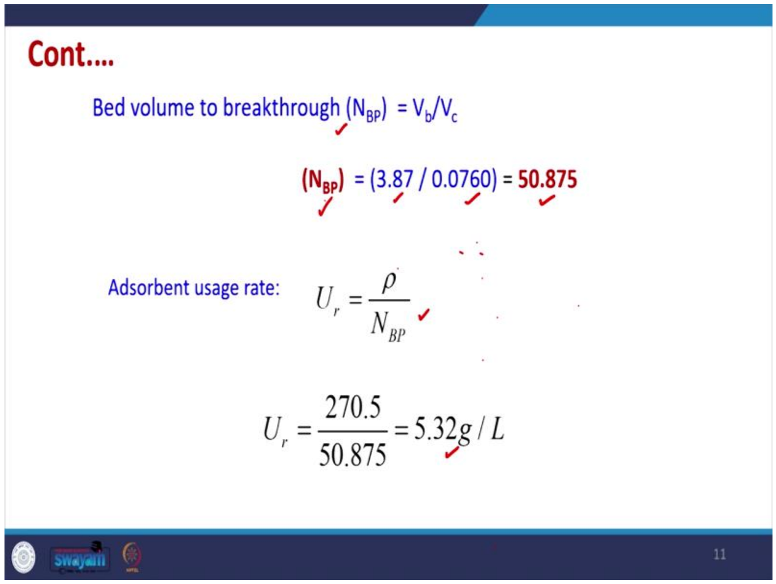

So, we can calculate some of the calculations, we can perform here like calculate the empty bed contact time for the furfural adsorption in a packed bed of bagasse's fly ash at given conditions. So, the concentration, suppose the initial concentration is 100 milligram per liter, flow rate is 0.02 liter per minute, bed height suppose is, we are carrying out this work only in lab scale.

So, suppose the bed height is only 15 centimeter and diameter of column is 2.45 centimeter. So, under that condition calculate the bed volume to break through and adsorbent usage rate, actually this is 2.54 that is 1 inch column, so this is 2.54. And so, what we do is then we try to find out the empty bed contact time and the density is given that the density is 270.5 gram per liter for the adsorbent.

Now, this is given. So, EBCT will be Vc by Q and Vc is equal to Ac into Z by Q. Now, so first we have to calculate the Vc that how much volume of water has been treated. So, this is the cross sectional area into height of the bed. So, height of the bed is already given 15 centimeter. So, from here and 2.54 is the diameter of the column. So, and depending upon that we can find out the Vc. Now, the flow rate is also given 0.02 liter per minute. So, from here we divide by 0.02 to get the empty bed contact time of 3.80 minute which is for this column.

Similarly, we can find out the adsorbent usage rate because bed volume which has been, number of bed volumes which have been heated up to breakthrough can be found out by using this equation. So, number of bed volumes to breakthrough can be obtained by using this particular equation, which is Vb by Vc. Now, the volume in the column is already calculated and 3.87 is the volume which has been treated up to the breakthrough.

So, if this is the condition which is already known to us, we can divide, so 50.875 will be the breakthrough, up to the breakthrough this much is the bed volume which have been treated, number of bed volumes which can be treated. So, now adsorbent usage rate will be the density divided by NBP which is the number of bed volumes which have been treated up to break through. So, we can calculate this is 5.32 grams per liter.

So, we can, through this we can find out the absorbent usage rate. And similarly we can calculate different other parameters by carrying out experiment in the lab scale. Now, in addition to EBCT and adsorbent usage rate there are other parameters that need to be calculated.

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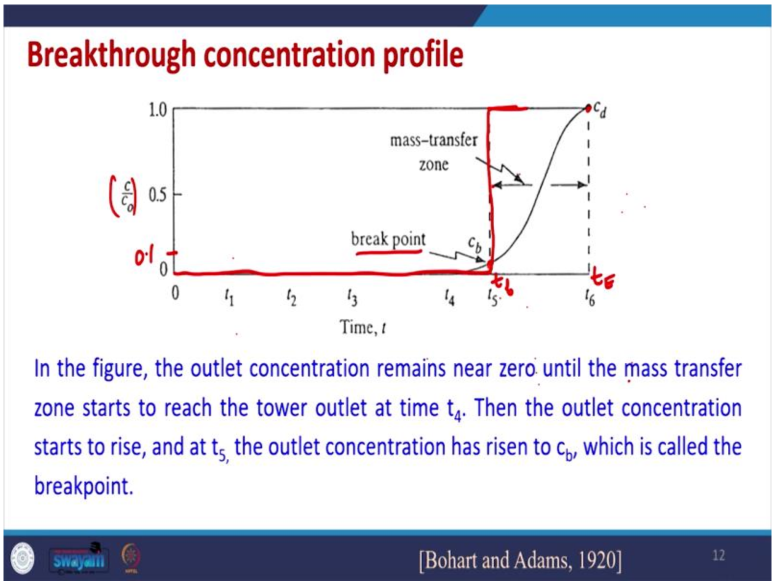

So, this is the breakthrough point that we have pointed out earlier, the breakthrough point, when the adsorbent reaches the characteristic limit, suppose this is 0.01. So, if it is reaches this condition that means after that the bed is not good enough and the water which is coming out, it contains the adsorbent up to a concentration which is not desirable. And after some time, there will be a point where the C by C0 value will reach 1.

So, that is here the exhaustion of the bed has happened. So, this is the breakthrough or the concentration profile that is always there. So, this point is called breakthrough point, this point is called exhaustion point, sometimes we will be writing here tb, sometimes we will writing be here te which is called as exhaustion point. And this ideally, the condition should be that and this is the zone from where the breakthrough point to exhaust point it is called mass transfer zone.

So, what does mass transfer zone measures, we will try to understand that. And in the mass transfer zone, we always desire this mass transfer zone to be lowest possible. And in the actual case in the ideal case, the profile should be like this, it should be 0 and it should be, it should reach the desired like it will, when the bed should exhaust. So, in the, it should, the breakthrough point and exhaustion point should be same.

So, this is the ideal scenario, but this is never the case. And we have tried to find out predict the breakthrough point and exhaustion point also. So, prediction of breakthrough point is one of the important considerations, which can be observed from carrying out experiments in the lab scale and then up scaling it to the actual condition in the plant scale. So, this is there.

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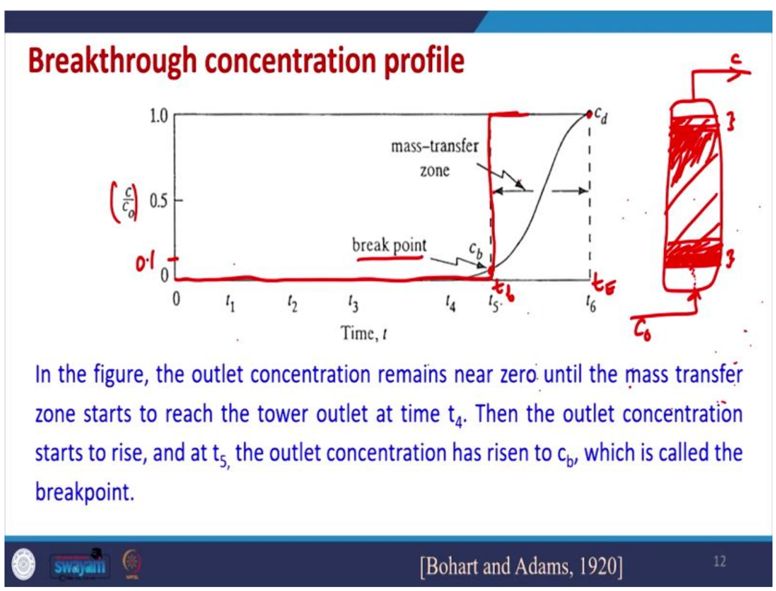

Now, going further these examples are given. So, we can see here that as the height is increasing, we can see the breakthrough point is suppose we are taking the breakthrough point of 0.1. So, this data is given here for phenol sorption and bagasse's fly ash bed at different bed lens and at different flow rates.

So, we can see here clearly, so breakthrough points is increasing with the increase in height of the bed. Similarly, with increase in flow rate, we can see here the flow rates are increasing and with respect to flow rate as the flow rate is increasing, the breakthrough time is decreasing. So, we can have a number of parameters which we have to analyze with respect to flow rate, with respect to height, with respect to diameter of the bed, etc.

And we can optimize all those parameters in such a manner that the breakthrough time in highest possible. And prediction of breakthrough time with respect to various flow rates, height, etc., is one of the important thing that we have to determine. Within this breakthrough concentration profile, the mass transfer zone, determination of mass transfer zone and minimization of mass transfer zone is also one of the important consideration.

Now, before we can go further, we should understand what is mass transfer zone. So, if we again draw the same packed-bed. And here suppose the bed is the adsorbents are filled all throughout this packed bed. And here again the C0 is a concentration which is going inside and the concentration which is coming out here is C. So, initially, what will happen as the liquid enters this, so the adsorption will happen in certain zone.

So, suppose this is the zone in which the adsorption takes place. So, initially this will be the area which will get exhausted, after some time the adsorption will start occurring in the next zone. So, that next zone, this in the next case this area will get exhausted. So, as these areas get exhausted they will reach a point where suppose, this up till this area has been exhausted.

Now, the whole bed below this is already exhausted. And when, now the adsorption will occur in this zone. So, some of the water will suddenly come out, that will be the point which is called a breakthrough point. And when whole of the bed will get exhausted, so that will be the point which is called as the exhaustion point.

So, in practical this is called the mass, this is called the zone in which adsorption is occurring and this is called the mass transfer zone. So, we always want this mass transfer zone to be minimum possible. We also want to determine different parameters with respect to mass transfer zone.

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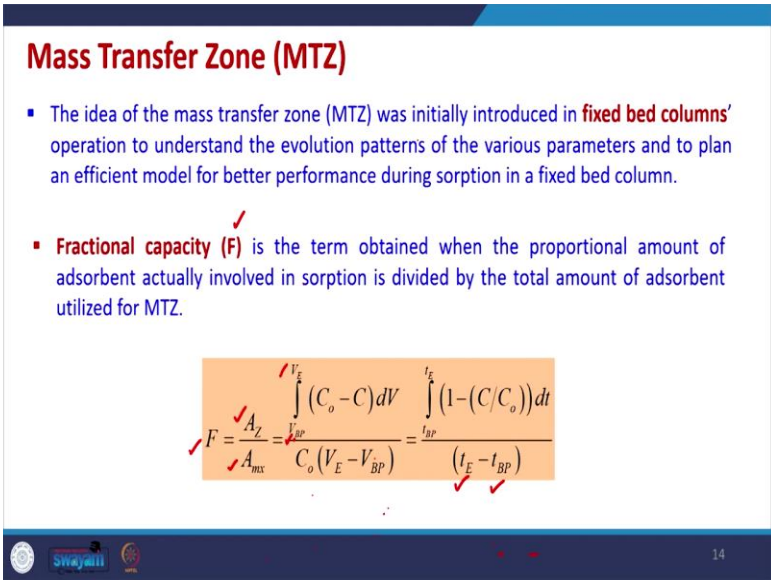

Fractional capacity (F)

$$F = \frac{A_Z}{A_{mx}} = \frac{\int_{V_{BP}}^{V_E} (C_o - C)\, dV}{C_o (V_E - V_{BP})} = \frac{\int_{t_{BP}}^{t_E} \left(1 - (C/C_o)\right) dt}{(t_E - t_{BP})}$$

So, this was, this is there. So, important thing is that mass transfer zone was introduced in the fixed bed columns operation to understand the evolution patterns or the breakthrough patterns which are there and to plan an efficient model for performance using adsorption in a fixed bed column.

So, some of the important parameters which are determined for mass transfer zone are like fractional capacity F and this is obtained when the proportional amount of adsorbent actually involved in the sorption is divided by the total amount of adsorbent utilized for the mass transfer zone. So, what is the total amount of adsorbent and what is the actually being used. So, mass transfer zone with respect to previous curve, which is given here we can easily calculate by using this formula.

So, from breakthrough point to the exhaustion point. So, volume at the breakthrough, volume at the exhaustion point, and we tried to find out the area under the curve of 1 minus C by C0 and tE is the exhaustion point and tBP is the breakthrough point. So, through that we tried to find out the fractional capacity within the mass transfer zone.

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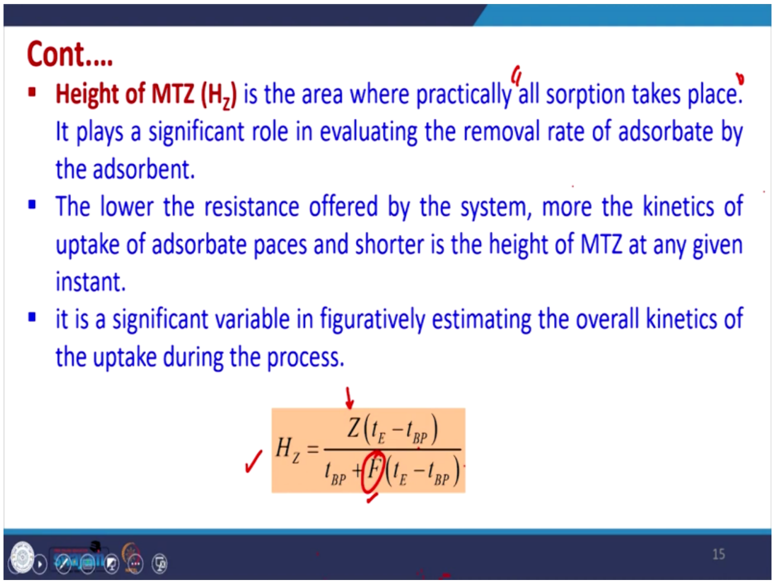

The overall kinetics of the uptake during the process:

$$H_Z = \frac{Z\left(t_E - t_{BP}\right)}{t_{BP} + F\left(t_E - t_{BP}\right)}$$

Similarly, height ofr ass transfer zone can be determined and it is actually the area where practically all the sorption takes place during the adsorption which is there. So, height, what is the height of the mass transfer zone, it is, it has a very important role in evaluating that removal rate of the adsorbent, adsorbate by the adsorbent. Lower is the resistance offered by the system, more the kinetics of uptake for adsorbate which is there and shorter is the height at any given instant. So, it can be calculated by using this formula which is given here.

So, remember F is already known, and since F is already known fractional capacity, we can find out the height of mass transfer zone using this formula. And in this the z is actually the total height of the bed. So, we are assuming that from exhaustion point to the breakthrough point. So, these are the value and what are the actual fractional capacity within the adsorption zone at the end. So, this parameter we already know. So, from this we can find out the height of mass transfer zone.

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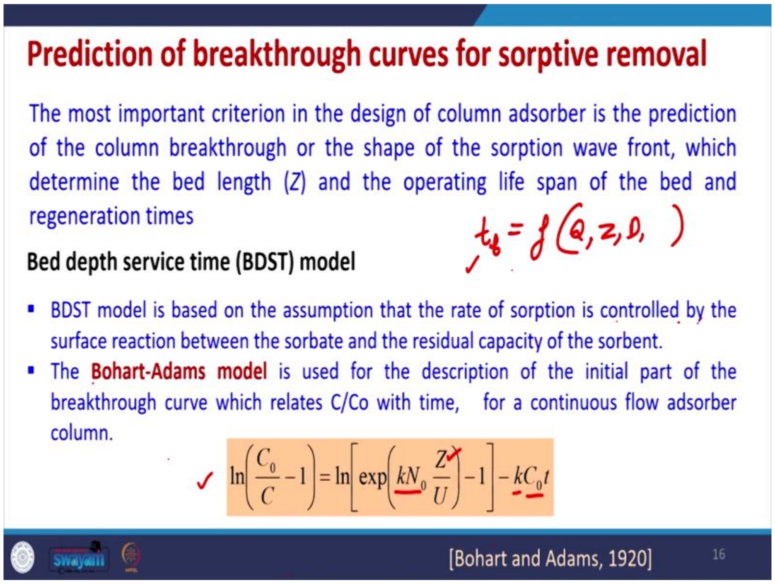

The Bohart-Adams model is used for the description of the initial part of the breakthrough curve which relates C/Co with time, for a continuous flow adsorber column:

$$\ln\left(\frac{C_0}{C}-1\right)=\ln\left[\exp\left(kN_0\frac{Z}{U}\right)-1\right]-kC_0t$$

Similarly, we always, as already told, we always want that we should be able to predict the breakthrough point tB and which can be a function of various parameters, these parameters could be flow rate, height, diameter of the column, etc. And the particle size of the suppose adsorbent. So, all these parameters are there. So, we, it is always desirable to predict the break through time, higher the bed, it is always desirable to have the highest possible breakthrough time.

Now, there are within certain limitation that we want to keep the pressure drop within certain limits, etc. So, those parameters are also there. So, this is always a desirability that we want to predict the breakthrough curve for sorptive removal. So, because of that a number of models were developed by different scientists and they are used in predicting the breakthrough time.

So, one of the earliest model is called bed depth service time model and it is, it was developed by Bohart-Adams, so it is given by this expression. So, in this slides we have actually just summarize different types of models. If anybody wishes to go further they can always look into the literature and the references which are given at the end. So, they can find out the number of more details of these models.

And the equation that we have represented here in these slides are linear form of these models. So, and they can be used for prediction of various types of breakthrough curve. So, and in these models, a number of parameters are there, like, we can see Z is already known to us, so, kN0, so, and this k is already known from the kinetics. So, the kC0, C0 is already known, because we, at what condition what concentration we are carrying out experiments. So, like kN0 are the parameters with respect to Bohart-Adams models or bed depth service time model.

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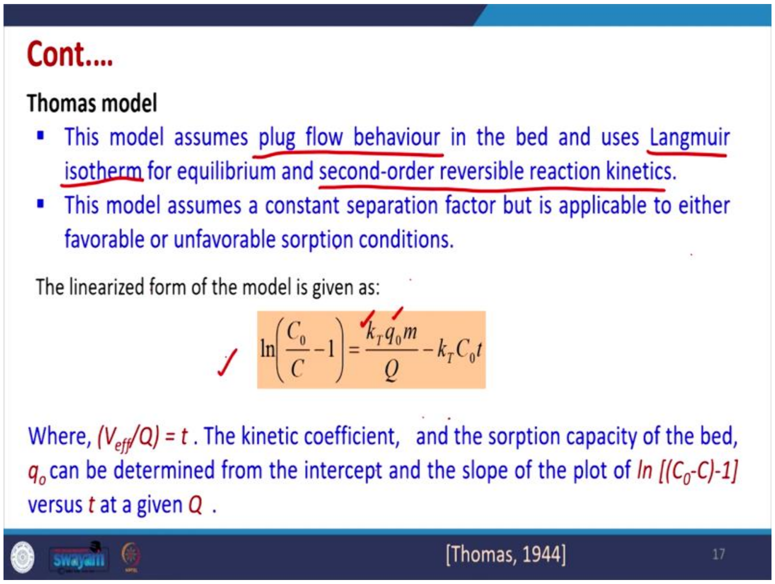

The linearized form of the Thomas model is given as:

$$\ln\left(\frac{C_0}{C}-1\right)=\frac{k_T q_0 m}{Q}-k_T C_0 t$$

Where, $(V_{eff}/Q) = t$. The kinetic coefficient, and the sorption capacity of the bed, q_o can be determined from the intercept and the slope of the plot of $ln\ [(C_0\text{-}C)\text{-}1]$ versus t at a given Q .

Similarly, there is a model which is given as Thomas model and it assumes a plug flow behavior. So, this is one of the common assumptions of Thomas model and it also uses the data of Langmuir isotherm. So, if in any condition we have Langmuir isotherm which is being followed and in the kinetics we have second order reversible reaction kinetics, so Thomas model will fit very well.

Or opposite way we can fit the data and cross check that whether this model is getting the fitted or not and then we can use this model for prediction of breakthrough curves at various conditions. And it has certain parameters kT q0, etc., that we have to find out from the data that is there with respect to C by C0 versus time, so that I will try to define little later. So, this is linearized form of the model.

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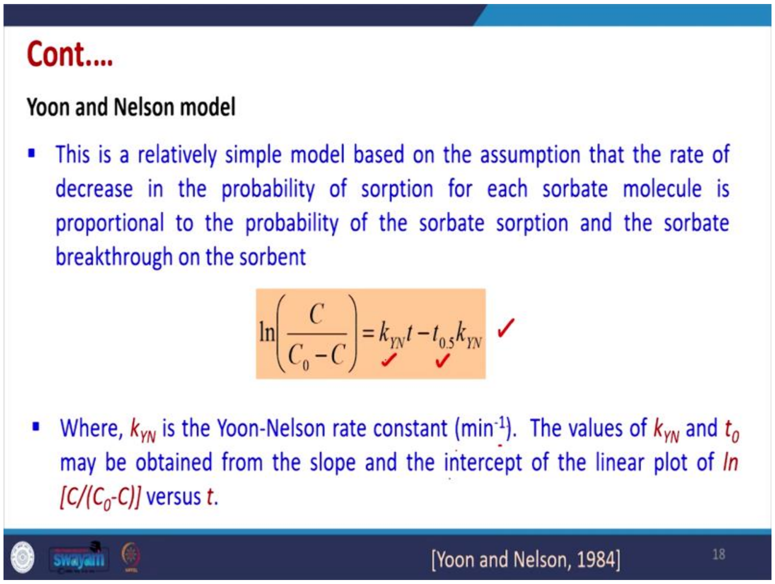

Yoon and Nelson model is given as:

$$\ln\left(\frac{C}{C_0 - C}\right) = k_{YN}t - t_{0.5}k_{YN}$$

Where, k_{YN} is the Yoon-Nelson rate constant (min^{-1}). The values of k_{YN} and t_0 may be obtained from the slope and the intercept of the linear plot of *ln [C/(*C_0*-C)]* versus *t*.

Similarly, there is a Yoon-Nelson model and it is based upon that the assumption that the rate of decrease in the probability of sorption for each sorbate molecule is proportional to the probability of the sorbate sorption and the sorbate breakthrough on the sorbent. So, this is the very simple model and we can, in this we try to find out that what is the breakthrough time with respect to 50 percent break through time, so that is there. And this equation can be used for finding out the Yoon-Nelson model.

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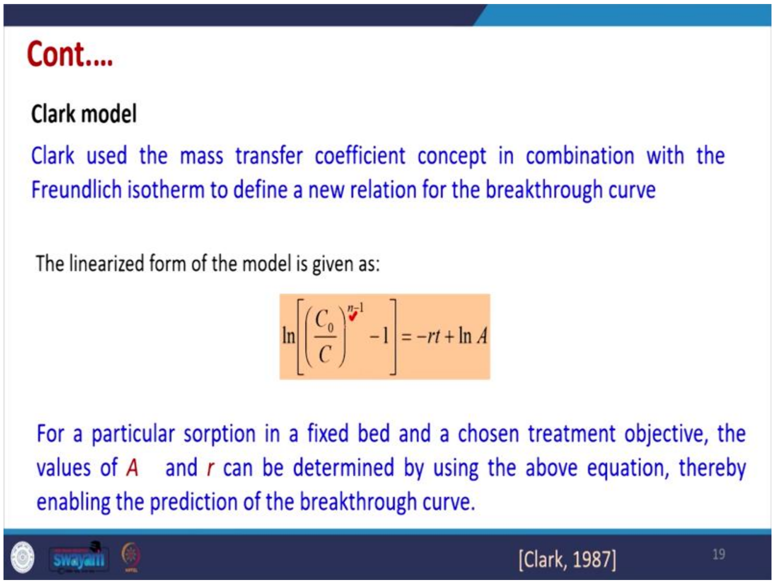

The linearized form of the Clark model is given as:

$$\ln\left[\left(\frac{C_0}{C}\right)^{n-1}-1\right]=-rt+\ln A$$

Similarly, Clark model is there. So, Clark model can be used for finding out various parameters. Here, n represents the Freundlich parameter. So, if Freundlich model is fitting very well, so Clark model can be used. If Langmuir model is fitting well, then we can use the Thomas model.

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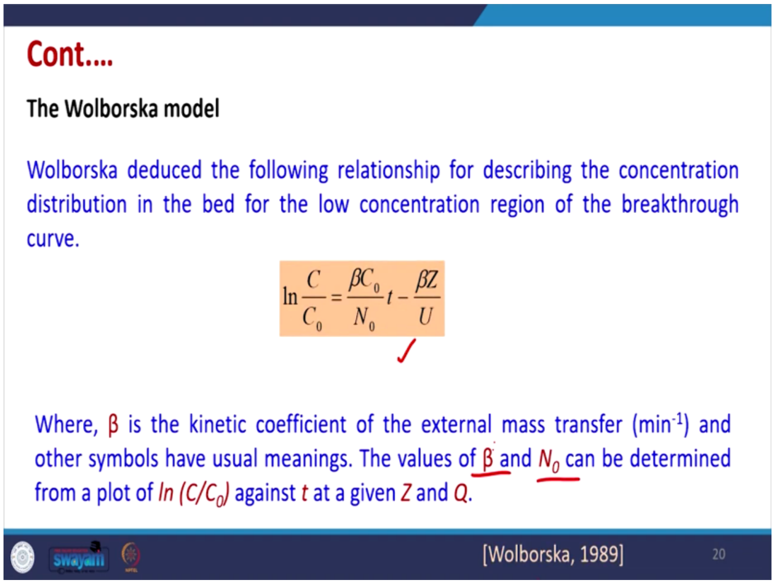

The Wolborska model is given as:

$$\ln\frac{C}{C_0}=\frac{\beta C_0}{N_0}t-\frac{\beta Z}{U}$$

Where, β is the kinetic coefficient of the external mass transfer (min^{-1}) and other symbols have usual meanings. The values of β and N_0 can be determined from a plot of $ln\,(C/C_0)$ against t at a given Z and Q.

Similarly, Wolborska model gives fitting up to 50 percent breakthrough curve very well and this was the, this relationship can be used for determining the fitting of the Wolborska model. So, this is there. So, we can find out different number of parameters which are listed here. So, in summary, these are the different types of models, which are there.

Now, how to use the breakthrough data at the lab scale for finding out these parameters and these parameters, how can they can further be used.

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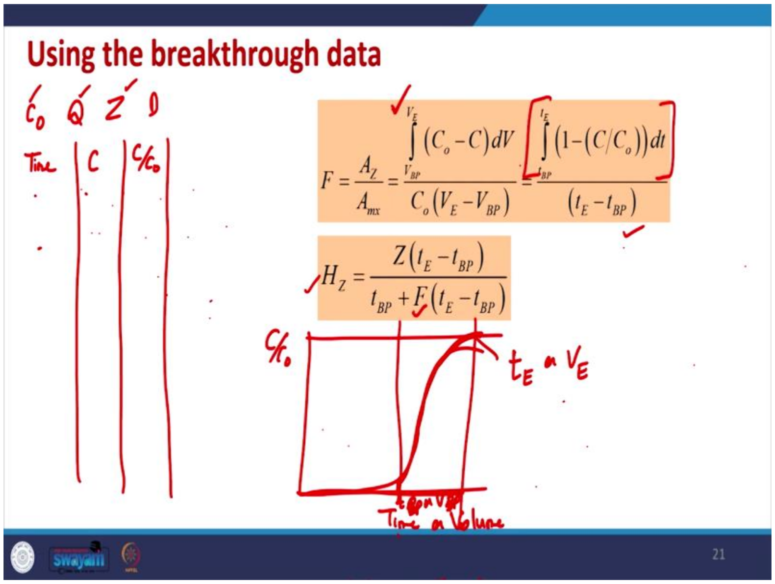

So, let us try to see. So, what we do is that in the lab scale, we perform some experiments, like where we have two, three different types of small beds, which may be there. And in the bed they may be of different diameter, we can keep different height also and we can certainly change the flow rates also. So, at any flow rate suppose, C0, where the flow, at one flow rate we have initial concentration is known and Z is also fixed and diameter is also fixed.

So, what we do is that we try to find out with respect to time. So, the initial data that we get is with respect to time, we try to find out the final concentration which is coming out. So, this type of data will be there with us. Now, once this is there, what we will do is that we will try to find out C by C0. So, if C by C0 is there, so we will be getting the graph that we already discussed few times so we will be having this type of graph.

And from this type of graph, which will be there. We can easily find out the breakthrough point. So, this is the, within the timeline. We can experimentally find out the time for breakthrough tB. So, this is possible. And since we have this data which is there, so we can integrate this curve numerically to find out this value. So, since flow rate is known, we can either draw the graph with respect to time, with respect to volume also we can draw the graph. So, this will be tB or it will be VB.

And similarly, this point will be tE exhaustion point, this can we exhaustion point or volume at exhaustion point. So, both will be known to us. So, if we can numerically integrate this part of the curve, we can get this value which is there at the top or this value. And once this is known, and tE by tBP is already known to us, so we can find out the breakthrough point also and through this we can find out the fractional capacity, if fractional capacity is known, we can find out the height of transfer zone. So, mass transfer zone, so Hz can be found out.

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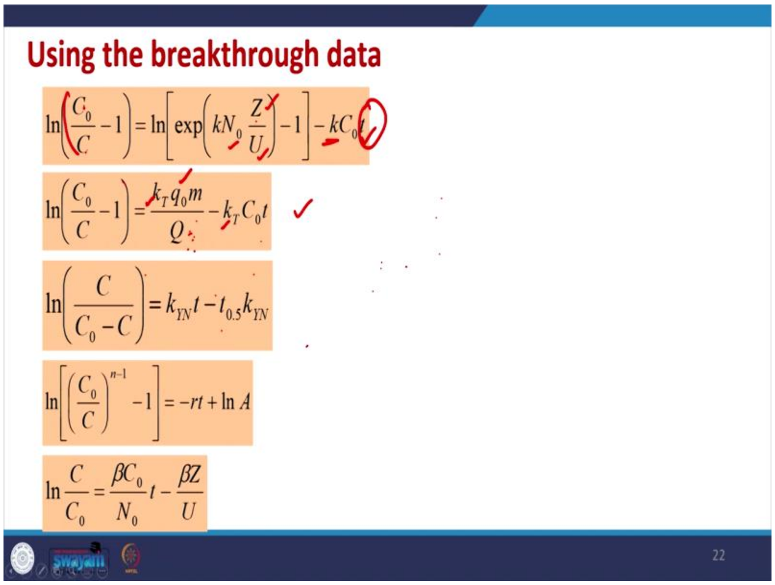

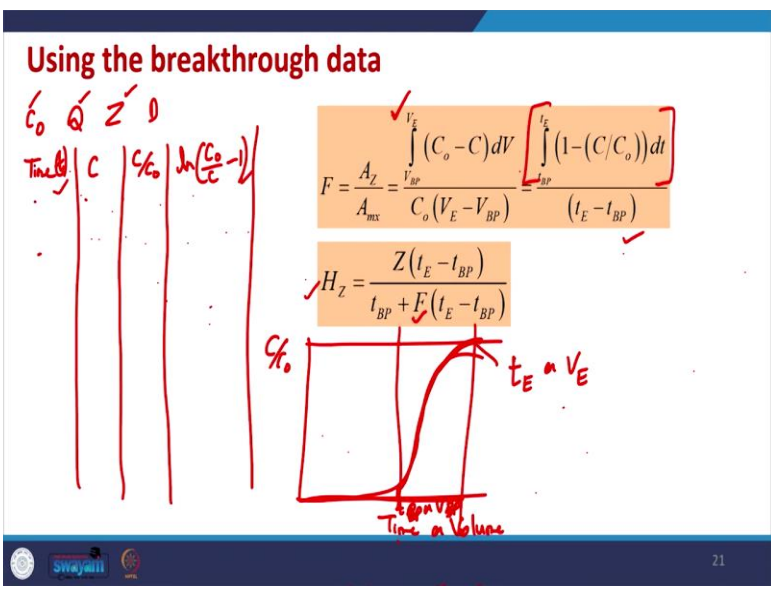

Similarly, we can use the same data. So, we have C by C0 versus time data. So, we can use convert that data into this form and take log of that and draw the curve with respect to time. So, if we can draw the curve and C0 since already it is known. So, slope of the curve will give k and once k is known other parameters like Z can be known, U is already known to we can find out N0.

So, if all these parameters are known, we can find out the t value at any other condition. So, like if we take C by C0 or C0 by C equal to 10. So, we can predict at what Z and C0 values etc,, what will be the breakthrough time.

Similarly, we can use the same data for finding these parameters. So, this is again known to us, we can easily, in this graph we can easily calculate this value. So, this is known. We can draw the linear line with respect to this versus time and in this because it is fitted to with respect to Langmuir model, we can find out q0 from Langmuir model itself, we can find out the kT value and m is, m values and from that again we can predict that.

So, any of these models can be fitted and the best fitted model can be used, they have certain assumptions that we have to cross check that whether in the batch adsorption those assumptions are being met. So, we can be selective in using any of these models, which have been listed here. And once we can, we are already selected okay this is Thomas model we are going to use.

So, we can fit the Thomas model we can find out the parameters of the Thomas model and then the fitted model can be used for predicting the breakthrough at any other conditions also. So, this is how we do this. And this way, we can decide the Z flow rate and other parameters so that our breakthrough time is highest possible. So, through this we will end the adsorption section.

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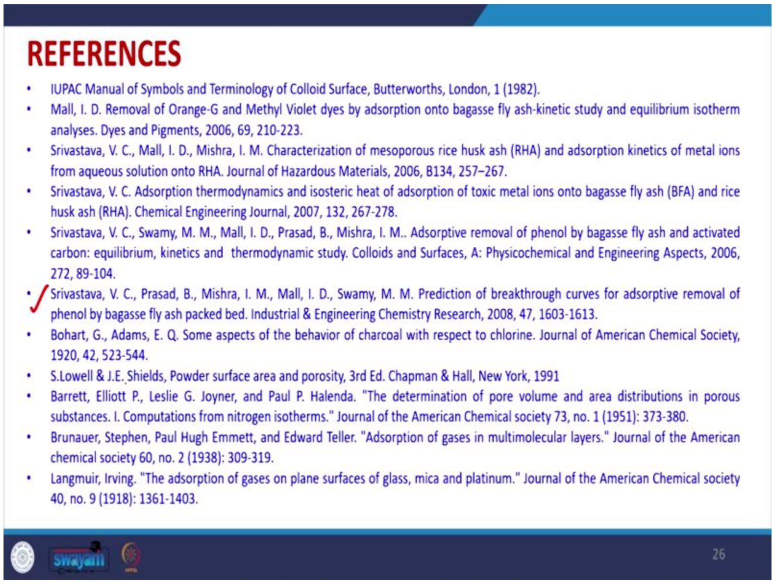

These are the various papers which have been used in find, in adsorption section. So, you can refer to any of these. Some of the papers are very good with respect to breakthrough times and others. So, you can always refer those papers. So, all these papers have been used in all other sections, so you can use any of them. So, thank you very much. This paper is very good with respect to prediction of breakthrough curves. So, you can refer these papers and find out the legitimacy of how to use these models, etc. So, thank you very much.