Physico-Chemical Processes for Wastewater Treatment
Professor V C Srivastava

Papartment of Chemical Engineering

Department of Chemical Engineering Indian Institute of Technology Roorkee

Lecture 33 Adsorption III

Good day everyone, welcome to these lectures on physico-chemical processes for wastewater treatment. And in the previous lectures we started studying regarding adsorption. So, previously in the previous two lectures we discussed regarding adsorption as a unit operation for water or wastewater treatment and the adsorption unit is generally used in the tertiary treatment of the water or it may be used beforehand also in some of the cases and in the previous lectures, we came to know that there are various types of adsorbents which are used for removal of pollutants from water or wastewater and activated carbon is one of the key adsorbents.

Along with that a lot of zeolite polymeric adsorbents etcetera are being used in the industry for water treatment as well as for wastewater treatment. Now, adsorbents are the key things which are actually being used for treatment of removal of these pollutants. Now, the adsorbent must have some key characteristics based upon that they may be used.

So, we found in the previous lecture that adsorbent properties, which are very, very important, they include the pore surface area that how much amount of the surface area within the pores is available for adsorption. And we found that adsorption surface area is measured in terms of meters square per gram and it is like for activated carbon it may be in the range of 1000 meters square per gram.

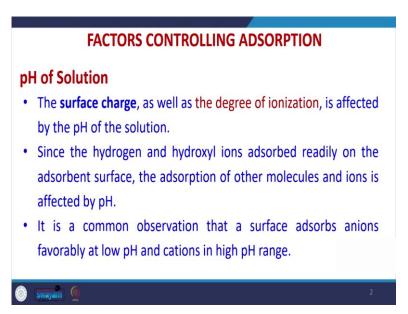
In addition to surface area, the pore size was also found to be the most important characteristics and pore size is like, so, pore sizes can be divided into three categories, micropores, meso-pores, and macro-pores. Microporous adsorbents are more commonly used for gas phase separation, because the size of molecular size of the various gaseous molecules are generally lower. So, they will fit very well in the category of microporous adsorption. For water and wastewater treatment the pollutants which may be present they have a bigger molecular size. So, because of that mesoporous adsorbents are more commonly used.

So, any adsorbent which is having more of the mesoporous force, they will be preferred for use in the water or wastewater treatment. Along with that surface area pore size, the

functionalities, which are present on the adsorbent, they are also very, very essential. So, for suppose we have to remove any acidic pollutant out of the water. So, it will be good if the, our adsorbent is basic in nature. So, some electrostatic attraction will happen and that is how the removal will increase.

So, in this way, the three important properties were found to be there. In addition to that, there are many other important properties with respect to adsorbate, which is being removed and adsorbent and the solution. So, these are all the key factors. In addition, we started studying regarding the factors which affect the adsorption process, and in particular, the adsorption capacity, etcetera. So, we will be continuing with the same topic and discuss those things today also.

(Refer Time Slide: 04:22)



So, in addition to the properties of adsorbent the pH of the solution, or solution properties are very, very important and they affect the adsorption process a large. Now, the surface charges, as well as the degree of ionization of the adsorbate in the solution is affected by the pH of the solution. So any dye molecule, any other organic molecule is there. So, whether it will be ionized that will depend upon the pH whether it is positive charge negative charge that will also depend upon the pH of the solution.

So, pH of wastewater is very, very important aspect, which affects the adsorption process. And if the surface charge varies, then we have to modify the adsorbent property in such a manner that it still we can remove that pollutant. For the case suppose the pH is high and under that condition that desired pollutant which has to be removed is in ionized form and it

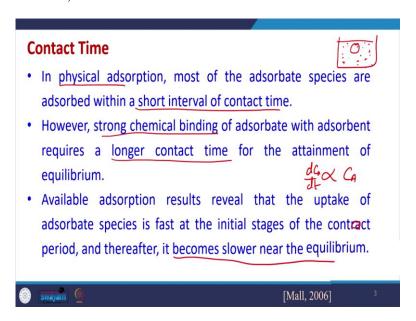
is in positive form. The under that condition we have to cross check that the adsorbent has a point of charge above that, so, that it is more negative charge and so, that we can attract, adsorbate can get attracted to the adsorbent and it can get removed.

So, similarly, the hydrogen and hydroxyl ions, they also get adsorbed readily under adsorbent surface. So, adsorption of other molecules and ions is also affected by the pH. So, that is how, it is very important to understand what is the pH, what are the pKa value of targeted pollutants, whether they are positive charge or negative charge or they are neutral in the pH range in which the solution is going to come. So, this is there.

It is also a very common observation that is surface adsorbs anions favorably at low pH and cations in the high pH range. So, if this is happening, so, it is possible that our adsorbent may selectively remove one of the only pollutants it may not remove all the pollutant. The selectivity of the adsorbent to a different pollutant that also needs to be checked.

So, and it may be possible that we may have to carry out a multi stage removal, where some adsorbent is used in the first stage and another adsorbent is used in the second stage. So, that we can remove virtually all of the pollutants. So, this is there.

(Refer Time Slide: 07:06)



Now, in addition to pH the contact time is very, very important factor and it depends upon whether there is a physical adsorption, physisorption or chemisorption which is happening. Now, in the previous lecture we studied that in the physisorption, the van der Waal forces of

attraction play a role by which the adsorbate gets attached to the surface site at in the on the adsorbent surface.

Now, this van der Waal forces of attraction or physisorption, whenever it is happening the interval or the time of contact which is required is generally very short. For chemical bonding to occur in the chemisorption, it takes a lot of time. So, adsorbate when it has to bond with the adsorbent surface site, then it requires a larger contact time for attainment of equilibrium. And it is possible that it may have to search for appropriate site where the binding may occur.

So, that is how the key thing is that in the physical adsorption, the we have a shorter interval of contact time whereas in the chemisorption, we have a longer contact time. So, this is there. Now, based upon the generally the adsorption results which are available and they show that the uptake of adsorbate species it will always be very fast in the initial stages of contact. So, this is there. So, in the initial stages of contact, the uptake will be higher and this is because the driving force will always be higher.

Now, we know that any rate of removal of any pollutant dc by dt is always proportional to its concentration, now, concentration within the solution. Now, this concentration initially will be very high. So rate of adsorption and then there will be a driving force difference. So we have a solution. And where adsorbent is there and here the various pollutants are present.

Now since initially there is no adsorbate on the adsorbent particle. So it is virtually zero in this case. So on the solid surface, the concentration of the adsorbate is zero whereas in the solution it is very high. Now, after some time, what will happen that some of the adsorbate particles will move into the adsorbent.

So under that condition, the adsorbate is now for later stages some amount of adsorbate is already there on the adsorbent surface and the concentration also has reduced in the solution. So the driving force which is there with respect to concentration of adsorbate on the solution as well as on the adsorbent surface, that difference goes on decreasing. So, that is how the adsorption, rate of adsorption becomes slower when it reaches the equilibrium condition. So, because the driving force is not there, so, these are the important points.

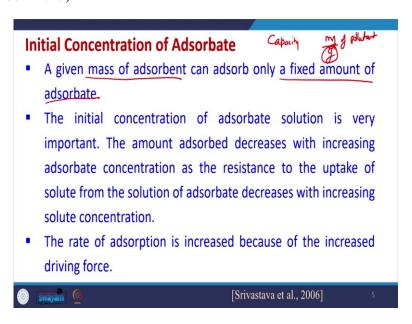
(Refer Time Slide: 10:21)

Cont.... In between these two stages of the uptake, the rate of adsorption is found to be nearly constant. This may be due to the fact that a large number of active surface sites are available for adsorption at initial stages and the rate of adsorption is a function of available vacant sites. Concentration of available vacant sites decreases and there is repulsion between solute molecules thereby reducing the adsorption rate.

So, in between two stages of uptake, the rate of adsorption may be nearly constant. So, we will discuss these things more in detail when we are studying the kinetics today. So, now, why initially what will happen that there will be a large number of active surface sites, which are available for adsorption in the initial stage. Now, so, that is why the rate of adsorption will be high and it is will be a factor of two things the what is the concentration of adsorbate in the solution and how much amount of adsorbate are already present on the adsorbent.

Now, after some time, the rate of adsorption will again be will certainly be a function of vacant sites. So, vacant sites are going on decreasing and similarly, the concentration in the solution phase is also going on decreasing. So, both ways, we have decreased in the driving force which is there and because of which in the later stages the rate of removal of the pollutant via adsorption decreases. So, concentration of available vacant sites decreases and there is a repulsion also between the solid molecules or adsorbate molecules on the adsorbent surface itself. So, that also decreases the adsorption rate in the later stages.

(Refer Time Slide: 11:47)



In addition to contact time, the initial concentration of adsorbate and that also affects severely the how the removal, how the, how much amount of adsorbate can be removed by the adsorbent. Now, suppose we have a fixed mass of adsorbent, so, it will be having a certain capacity. So, in the previous lecture we studied there the capacity of adsorbent is given by this milligram per gram, milligram of pollutant which can be removed. So, it can be milligram it can be moles or anything. Now, if we have a fixed amount of adsorbent, so that means, it can take a fixed amount of adsorbate only.

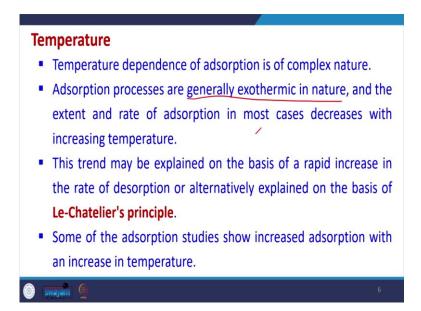
Now, if the concentration is very high, that means, the adsorbent will get exhausted very quickly. So, this is one thing. So, initial concentration of adsorbate solution, adsorbate in the solution is very important the amount adsorbed generally decrease with increase in adsorbate concentration as the resistance to the uptake of solute or the adsorbate from the solution of adsorbate decreases with increasing solute concentration.

So, generally the percentage removal which can it will always decrease with increase in the concentration of adsorbate and the rate of driving force may be higher if the concentration of adsorbate is higher in the initial stages, but since it has to reach equilibrium, it will certainly take some time to reach the equilibrium.

So, the key thing is that if the concentration of adsorbate in the solution is high, it will, it may reach up to its maximum adsorption capacity the adsorbent may adsorb that much amount, but the adsorbent will get exhausted in a within a very short span of time, but if the concentration is lower, so, the fixed bed or fixed mass of adsorbent will work very well for

longer duration. So, this is there, because they have a fixed capacity by themselves. So, this is the key thing. So, lower the concentration of adsorbate in the solution, a higher will be the amount of time for which the same bed of adsorbent may work. So, this is there.

(Refer Time Slide: 14:28)

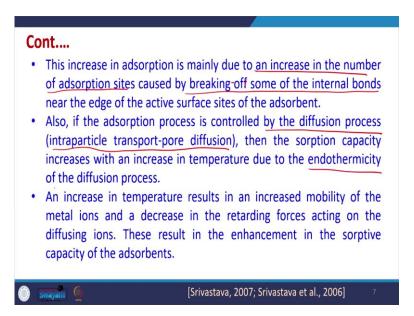


Now, temperature is also another parameter which affects the adsorption rate, as well as the equilibrium how much amount, has been adsorbed at the equilibrium. So, a temperature dependence is not a straightforward it is a complex nature. Generally, adsorption processes are exothermic in nature. So that will be there. So generally, they are exothermic in nature. And the extent and rate of adsorption in most cases decreases with increase in temperature.

So this is there. So, they are generally exothermic. But if suppose the pore size is small and the pore diffusion or diffusion, maybe film diffusion or pore diffusion is the controlling step. So, under that condition, since the diffusion itself is a endothermic process, that means, the rate of movement of the adsorbate increases with increase in temperature because diffusion is an endothermic process. So, and if the adsorption processes overall pore diffusion-controlled, so, it is possible that the adsorption process may itself become endothermic in nature.

So, it is highly complex, sometimes it will increase with increase in temperature, sometimes it may decrease and it depends upon various factors. So, this is there. So, generally, it will be exothermic in nature and there will be rapid increase in the rate of desorption or alternatively. So, that is why at higher temperature it will desorb out. So, that is why temperature are taken out and this is more true for gas phase adsorption. Some studies have shown that, that adsorption increased with increase in temperature.

(Refer Time Slide: 16:25)

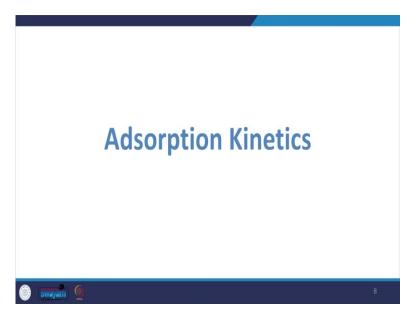


So, that means, it is endothermic for those cases and this is because, an increase in the number of adsorption sites caused by the breaking of some of the internal bond. So, sometimes some breaking may happen of the internal bonds or number of sites may increase. So, this may be one of the reason because of each increase in the adsorption may be there.

Also if the adsorption process is controlled by the diffusion process, that means intraparticle transport pore diffusion is controlling and under that condition the adsorption capacity may increase with an increase in temperature and this is because, the overall diffusion processes are endothermic in nature.

So, if adsorption is diffusion control, so, it is possible that the overall process may become endothermic in nature and this is because the diffusion increases with increase in temperature. So, that is why it may start increasing with increasing temperature and increase in temperature may this is because the increased mobility of the metal ions or any other molecule and because of which there will be a decrease in the retarding force acting on the diffusing ions. So, because of that the solution may, the adsorption process may increase. So, this is possible.

(Refer Time Slide: 17:52)



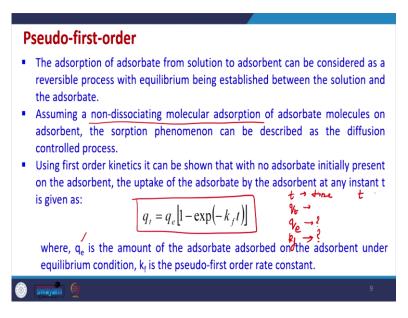
Now, going further, among all these parameters like kinetics equilibrium, now, whenever we are going for system design in a packed bed or otherwise, so, we always for system design we require two-three important things. One is that what is the rate of adsorption or can it be represented by some equation. So, and that will be used during the design of the system. So, adsorption kinetics is one of the important parameters that has to be studied. Similarly, for design for in particular, if you are from chemical engineering or other any other background for any unit design, we require equilibrium data also.

So, equilibrium data in adsorption is represented by adsorption isotherms. So adsorption kinetics, adsorption isotherm they are very, very important to understand and to determine before going for any further studies. So, we will start with the adsorption kinetics and adsorption kinetics is like trying to find out what is the rate of removal or how the pollutants are getting removed in a batch kinetic approach. So, the batch kinetic data can be used for design of a continuous react, continuous adsorption unit also using the same adsorbent and for the treatment of similar water. So, this is there.

So there are when we have this data, so, what we do is that we require data with respect to time that what is the rate for adsorption or not what is the residual concentration in the liquid solution. So, that data is taken and after that what we do is that, we fit that data with certain models and if they can fit those models, so, there are two things we can get from them. One thing is that all the models are derived on certain assumptions. So if that particular data is fitting some model, so that means, that model assumptions are being validated by that data.

Also, that means that we get to know some mechanism, some understanding of mechanism by which the adsorption was occurring. So, there are few models which are commonly used pseudo-first-order, pseudo-second-order model etcetera. So, these are common. Similarly, second interpretation that we get when the fitting is done is that, we can use the same data, the fitting parameters, and design the system later on. So, we need not use the basic data we directly go for using the fitted model in the design of the system. So, this is there.

(Refer Time Slide: 21:09)



Now, we will start with the some of the basic models which have been used to describe the kinetic expressions for adsorption. So, first model is pseudo-first-order kinetic model. So, in this case the adsorption of adsorbate from the solution to the adsorbent is considered to be a reversible process with equilibrium being established between the solution and adsorbate after some time, so, this is there.

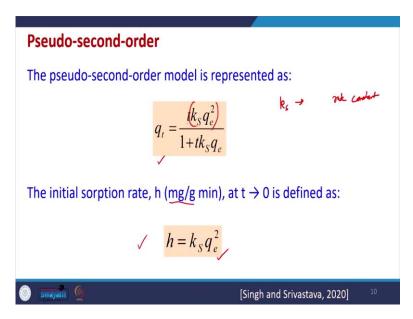
Another assumption is that it assumes that there is a non-dissociating molecular adsorption. So, that means, there is no breaking of any of the molecules which is, so, it is like a non-dissociating molecular adsorption of adsorbate molecules and adsorption and this can be described as a diffuse and control process like. So, using first-order kinetics. So, in the first-order kinetics, what we assume is that, that how much far away it is from the equilibrium.

So, using that approach dq by dt directly proportional to qe minus qt which is the driving force or that difference with respect to equilibrium, and if you solve under certain conditions, we can get this particular equation which is called pseudo first order model. And in this case,

qe is the amount of adsorbate, adsorbed on the adsorbent under equilibrium condition. Kf is the pseudo-first-order rate constant.

So, we have three terms here, four terms in the way t is the time, which is already given here at any time instant and qt and qe and then, in addition, we always try to find out this Kf. So, this is the unknown which we want to find this also we can get experimentally also, and we can determine theoretically also and qt is the data that we try to observe from the experiment. So, generally what we will be having is that t versus qt data will be available to us and we have to find out the value of Kf qe. So, this is there.

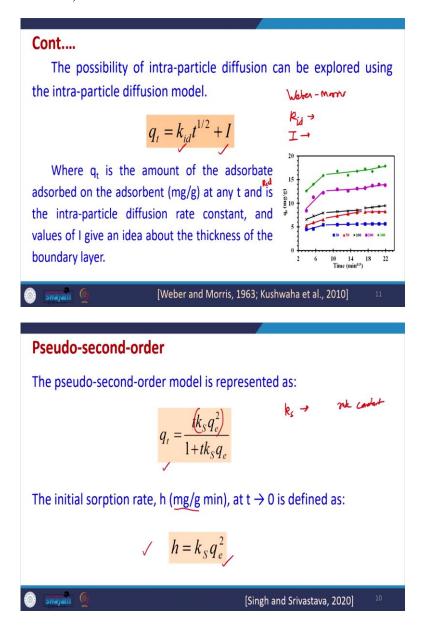
(Refer Time Slide: 23:14)



Now, going further similarly, we have a pseudo-second-order model is also there. So, the pseudo-second-order model it can be represented by this particular expression after we solve the model or initial assumption that the rate of adsorption is directly proportional to up to second order with respect to difference in the driving force. So, that is there. In this expression, the ks is the pseudo-second-order rate constant.

So, this is a ks is the pseudo-second-order rate constant and t is time as earlier and q is also time. Now, this t ks qe square they are together also called as initial sorption rate. So, how much milligram per unit gram of adsorbent per unit minute adsorption is occurring. So, that is like initial sorption rate and it can be determined by using this expression. So, this we can find out initial sorption rate.

(Refer Time Slide: 24:19)

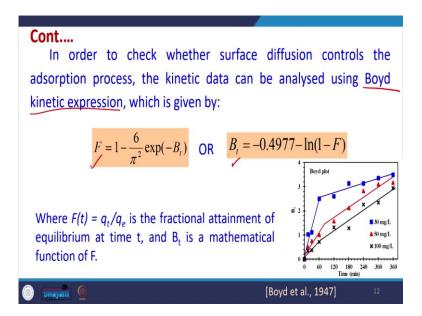


Now, in addition to this pseudo-first-order, pseudo-second-order we can have a number of other equations also. We can generally we can fit a polymeric any polynomial equation also for representing the data if the fit is not correct. So, for these two models can be used. In addition, the possibility of intra-particle diffusion can be explored using the intraparticle diffusion model which is given by this and it is also called Weber Morris model, remember Weber Morris model and this has been its original paper is given in the reference section.

So, this is the, in this the k id which is given, actually this is the intraparticle diffusion model. So, it is a constant with respect to this. So this constant we always try to determine k id and i is the intercept which is there and k id is the intraparticle diffusion rate constant and values of

i give an idea about the thickness of the boundary layer which may be there on the adsorbent particle. So, we can determine these parameters from this.

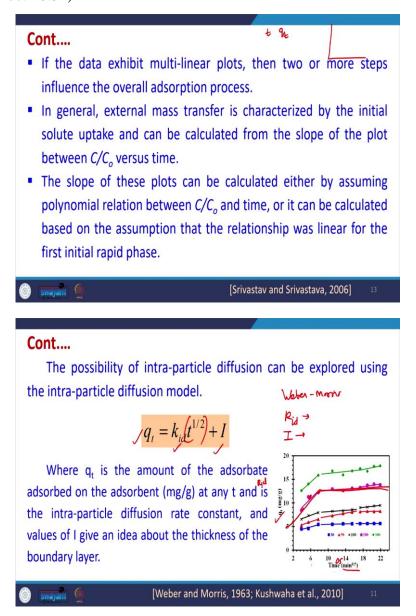
(Refer Time Slide: 25:38)



In addition, there is another Boyd model. So, this is called like Boyd model. So, Boyd kinetic expression can also be used to find out that diffusivity parameters. So, this is possible to determine this Boyd model also. Generally, it is not well used in the simple adsorption case, but it can be used for determining the diffusivity values using the kinetic expression data.

So, this can be used, where here f is the fractional attainment of equilibrium at time t and Bt is a mathematical function which is given by this and so, we can always convert this and we can use the kinetic data to determine this expression and through this we can find out diffusivity values also.

(Refer Time Slide: 26:32)

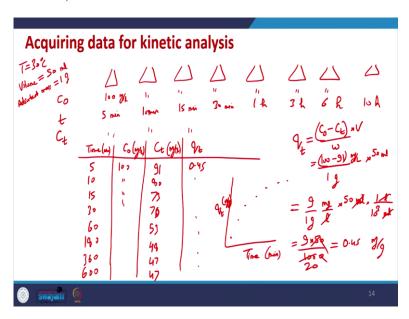


So, now, if any of the systems like in the kinetic data what we do is that, we try to find out the qt versus t data. So, already I have told, so, this data is plotted in a way in the Weber Morris model like this. So, what we do is that we plot qt versus t half. So, you can see here this is t half actually, time raise to 0.5 and this is qt. So, if the model is the data can be represented by multi slots. So, we can see here one example is here. So, it has a multilinear plots.

So, we can interpret lots of information from these data if the data exhibits multilinear plots then that two or more steps are influencing the overall adsorption process. And whichever process is the slower so, in this case, this process is slower because despite the time increasing the amount of adsorption or that adsorption capacity is not increasing that much. So, this second step is the rate-controlling step under that condition.

So, we can determine lot of we can have a lot of inferences from these type of curves. And in general the external mass transfer is characterized by the initial solute uptake and can be calculated from the slope of the plot of like C by C0 versus time, also from there we can put a linear or polynomial relationship we can have lots of relationship or we can use the any of the models also. So, we will try to understand this more by doing some modeling or numerical solving and how to get the or acquire the kinetic data. So, this we are going to learn and then we will solve some problem later on.

(Refer Time Slide: 28:46)



So, what we how we conduct the test. So, what we do is that for kinetic analysis we require data, so, acquiring the data is essential. So, what we do is that will take a certain number of beakers suppose this all these beakers are taken and they will be having and then they will be having a initial concentration.

So, we are taking a wastewater which is already having some initial concentration of pollutant which may be there. So, this will be fixed. So, C0 is constant for the time being I am assuming this to be 100 milligram per liter for simplicity in each of them. So, this is one parameter is fixed. Now, the other parameters could be temperature. So, we are assuming that temperature is to be like 30 degrees centigrade, we are keeping that constant.

Now, what we do is that we add certain amount of adsorbent in each of them. So, what we do is that we take volume of solution to be suppose 50 ml in each of them. So, each of the beaker contains 50 ml of the solution which is having a concentration of 100 milligram per liter. So, this is fixed. Now, in each of the beakers, we add some adsorbent, and that adsorbent mass is also fixed. Like suppose for the time being, we take value of 1 gram though this is higher just for simplicity, I am taking 1 gram. So, this is added in each of them.

Now, what we do is that as soon as we add it, we add all the beakers in certain like incubator shakers, which will be there, and where we will keep each of the beaker for different time. So, like the first beaker may be kept for only 5 minutes, it may be for 10 minutes, it may be 15 minutes, then after that 30 minute and 1 hour, 3 hour, 6 hour like similarly, there is another one which is kept for 10 hours.

So, we have we keep shaking these beakers for this much duration and after that, we take out the beaker and we separate the adsorbent or via centrifugation or otherwise from the and supernatant we analyze for residual concentration. So, we tried to find out the concentrations Ct after this much time and these values are noted down. So, if we plot it in a simple manner, so, this will be the time we can like write like this, so this is time this will be if we write in minutes. So, example can be taken 5 10 15 30 60 180 360 and then maybe 600 minutes. So, this is there.

Now initially each was having a concentration of 100 milligram per liter. So, in each of the solution, we had only 100 milligram per liter in each of them. So there is nothing to write and after time t we determine the concentration Ct and that we, I am arbitrarily assuming some values. So, suppose it is 91 after 5 minutes and then it is 80 73 75, oh sorry 70 minutes 70 or and then maybe 53, 48, then 47 suppose after 600 also 47. So this is the concentration which is remaining residual concentration after this time.

So, once this is known, what we can do is that we can determine that qt value and how to determine the qt value in the previous lecture we studied this, qt is determined at C0 minus Ct divided by w upon into v. So for the first case like for time 5 minutes, it will be 100 minus 91 divided by, how much amount we have taken? We have taken 1 gram, so, here it will be 1 gram and this will be everything will be in milligram per liter and volume we have taken as 50 ml. So, this we are taking 50 ml and so, we can further solve it. So, it will be 9 milligram per liter, here it is 1 gram.

And now, here it is 50 ml and 50 ml and 1 liter is equal to 10 raise to 3 ml. So, ml ml goes off liter liter goes off we have milligram per gram and we can solve this to get the answer in milligram per gram. So, this is how we try to solve it and we can get the answer. So, it will be 9 into 50 divided by 1000. So, 1 1 goes off 520 So, it will be 0.45, this will be milligram per gram this will be the value of qt at this place.

So, similarly, we can get all this and we can draw a graph of time in minute and the qt value in milligram per gram. So, and we can have some data like this. So, this is how we get the data. And in the second step we can fit all these models which were given earlier, pseudo-first-order, pseudo-second-order etcetera and we can try to solve it. So we will try to solve one questions are more in the next lecture. So, right now we end this lecture. Thank you very much.