

## Lec 36: Adsorption Kinetics

Hello everybody welcome to this massive open online course on solid fluid operations. So, as we are discussing about the adsorption, its principle, applications and also the isotherms in the previous lectures. Here in this lecture we will try to understand more about the adsorption principles and also its kinetics. What is that adsorption kinetics? So, this is basically regarded as one of the essential and also you can say that useful parameter to consider while designing the adsorption system. So, in this case this kinetics parameter will determine the rate at which that adsorption occurs and this kinetics are influenced by the surface complexity of the adsorbent solute and also concentration at its flow. Some of the kinetics that foretells the adsorbent adsorbate interactions also.

So, in adsorption kinetics we will have different types of kinetics based on which you can assess that the rate of the adsorption which is occurred on the surface of the adsorbent. And these kinetics can be considered based on the suitability of surface characteristics and also the adsorbent rate which is actually assessed by those kinetics with least error. So, that can be selected based on that fitting of that kinetic equation with the experimental data. Here in the slides we are showing here 4 types of adsorption kinetics.

One is called intra-particle kinetics, another is called pseudo-first order kinetics, pseudo-second order kinetics and some other kinetics it is called that Elovich kinetic out of which. So, in this case you will see that the suitability of any kinetic equation or model either it is pseudo-first order, pseudo-second order or Elovich kinetic or intra-particle kinetics that depends on the error level. That error can be assessed by that correlation coefficient or sum of square errors that can be done by different softwares or you can do it manually also just by calculating its least square value, least square error value. And out of these actually model you will see that a linear form of pseudo-second order model is preferred over that PFO model that is pseudo-first order model. And this kinetics can be presented based on that line or curve which can be drawn based on that experimental data and this kinetics will describe the rate of retention or release of that solute from an aqueous environment to solid-phase interface.

And in this case some variables to be considered those are a given adsorbent dose, temperature, flow rate and also at which pH this adsorption is being done. And during this adsorption two main processes are involved one is called physical adsorption another is called chemical adsorption as we have already discussed in our earlier lecture. Where physical adsorption will be a result of weak forces of attraction that is called Van der Waals force and also the chemical adsorption or it is called chemisorptions which will be involved formation of a strong bond between the solute and the adsorbent that involves the transfer of electrons. So, this mechanism we have already discussed in our earlier lecture please go through that lectures one again. And then pseudo-first order model that we will try to discuss about this what is that pseudo-first order model.

It is also known as Lagrange model this model basically describes the adsorption of solute

onto adsorbent following the first order mechanism and that first order mechanism can be represented by this equation number one here where it is written as  $\frac{dq_t}{dt} = k_1(Q_e - q_t)$  that will be equal to  $k_1(Q_e - q_t)$

Here the equation

$$\frac{dq_t}{dt} = k_1(Q_e - q_t)$$

where this  $q_t$  which is adsorbed onto adsorbent surface at time  $t$ . This is in milligram per gram generally being expressed and  $Q_e$  is the equilibrium adsorption capacity this is in terms of unit that is milligram per gram and  $k_1$  is called the rate constant per minute and then if you integrate this equation number one with boundary condition like if  $t$  is equal to 0 to  $t$  that means if within a time limit of 0 to  $t$  then this adsorbent which is adsorbed onto the adsorbent surface that can be expressed by 0 to  $q_t$  respectively and which yields this equation number two this is expressed as  $q_t = Q_e(1 - e^{-k_1 t})$

Here the Equation

$$q_t = Q_e(1 - e^{-k_1 t})$$

and the value of  $k_1$  here in this equation number two and also one this is called that rate constant and this rate constant can be determined by plotting this equation number two as per here in y-axis it will be  $\ln(Q_e - q_t)$  and in x-axis it will be  $t$ . So, if you draw the graph  $\ln(Q_e - q_t)$  versus  $t$  then you will be able to find out what will be the rate constant there and this rate constant is always inversely proportional to the initial concentration of the solute that you have to remember and also this constant will be varying under low pressure adsorption and under high adsorbent doses and this rate constant always will be inversely proportional to initial concentration because a longer time is required for a large initial solute concentration. So, that is why this rate constant will be inversely proportional to the initial concentration of the solute and then you have to calculate the  $Q_e$  value. So, how to calculate that  $Q_e$  value that is basically what is that  $Q_e$  value is equilibrium adsorption capacity.

So, that  $Q_e$  value can be calculated by this equation number three. If that initial concentration of the solute and the concentration at a time  $t$  then what will be the difference of that concentration that means  $C_0 - C_t$

Here the Equation

$$q_t = \frac{(C_0 - C_t)V}{m}$$

this is the concentration difference into its volume of that solution then you will get what will be the amount of solute will be transported divided by mass of adsorbent that is  $M$ . So, by this equation you will be able to calculate at time  $t$  what will be the that adsorbate which is adsorbed onto the surface of the adsorbent. When in this case  $T_e$  is equal to the equilibrium contact time then in that case this  $C_t$  that means concentration of adsorbate at time  $t$  will be is equal to  $C_e$ ,  $C_e$  means what equilibrium concentration there and hence we can say that  $Q_t$  will be is equal to  $Q_e$  like this and then the amount of adsorbate which is adsorbed at equilibrium  $Q_e$  can be calculated using that equation. So, here in this graph in the slide it is shown that how  $Q_t$  is varying with respect to time this is the typical profile of  $Q_t$  versus time.

You will see that the adsorption amount will be increased with respect to time  $t$  and after a certain time this  $Q_t$  will be reached in an equilibrium condition. So, in the dotted line it is shown a typical equilibrium data they are in the graph for a typical value  $Q_t$  versus time plot. So, here this will be your equilibrium amount of adsorbate which is adsorbed onto the surface of adsorbent at equilibrium time  $T_e$ . Here this you will see that this adsorption amount will be increasing with respect to time as well as it will be increasing with respect to the increasing initial concentration. Let us have an example to calculate that  $Q_e$  value and also  $K_1$  value that means equilibrium adsorbate amount and also the rate of adsorption.

Here in this case the adsorption of cadmium ions onto bones has been studied using a base adsorbed. The experimental data was analyzed using adsorption kinetic models. The pseudo first order models can be considered for this experimental data and it is observed that this pseudo first order model will be fitting that in the least square with the least square error. So, in this case you have to find out the equilibrium amount of adsorbed and the rate constant. So, here in this table it is given for different initial concentration of that solute the  $Q_t$  versus time value are given in the table.

You will see the first two columns here there is a time versus  $Q_t$  with respect to initial concentration  $C_0$  at 2.14 millimole and similarly the third, fourth and fifth, sixth column the  $Q_t$  versus time values are given with respect to initial concentration of  $C_0$  respectively. So, under this or based on this experimental data you have to find out what will be the  $Q_e$  value and also rate constant. So, what to do here you have to plot the graph here as  $Q_t$  versus time as shown in the figure here it is drawn here with respect to this data at different initial concentration here. This data is this graph is for the initial concentration of 2.

14 millimole of solute. So, in this case  $Q_t$  versus time is keep on increasing and it will reach an equilibrium condition here which can be obtained from this point here. Similarly, for other initial concentration of 2.69 here the plot is like this red line here and here also after a certain time it will reach an equilibrium condition and corresponding equilibrium value you can get it from here and similarly for other initial concentration 3.17 millimole this here blue line it is shown here this equilibrium data.

So, from this equilibrium data you can easily calculate what will be the equilibrium amount of adsorbate which is adsorbed onto the adsorbent. And to calculate that  $k_1$  what you have to do you have to feed this equilibrium data with that model equation here given  $Q_t$  is equal to  $Q_e$  into  $1 - e^{-k_1 t}$ . So, in this case to calculate this  $k_1$  or  $Q_e$  value from this data you can do it like this  $Q_e - Q_t$  versus that time and then from that you will be able to calculate what will be the  $k_1$  value. So, after feeding or just you can do it just solving nonlinear equation by any numerical method you can also solve it and after solving you can get that corresponding value of  $Q_e$  and  $k_1$  value as given in this table here after calculation I have calculated. So, here  $Q_e$  will be equal to 0.

$k_1$  will be 0.619 for the initial concentration of 2.14. Similarly, for other initial concentration this corresponding value of  $Q_e$  and  $k_1$  are given here. So, I think you understood this problem from this experimental data of this time versus that  $Q_t$  value you will be able to calculate what will be the equilibrium amount of adsorbate and also what will be the rate constant just by fitting this CO2 first-order equation here.

Then coming to that CO2 second-order model here also this model can be used to assess that to find out what will be the equilibrium value of adsorbate and also what will be the rate constant. In this case this model generally assumes that the rate of adsorption of solute is proportional to the available sites on the adsorbent and the reaction rate is dependent on the amount of solute on the surface of the adsorbent and the driving force for this is  $Q_e - Q_t$  it will be proportional to the number of active sites that is available on the adsorbent surface and the general form of this CO2 second-order model is given by equation number 4 here that is  $dQ_t/dt$  is equal to  $k_2(Q_e - Q_t)^2$ .

Here the Equation

$$\frac{dQ_t}{dt} = k_2 (Q_e - Q_t)^2$$

The parameter here  $k_2$  is called that CO2 second-order rate constant and after integration of this equation number 4 with this boundary condition here given the  $t$  is equal to 0 to  $t$  at this time interval the  $Q_t$  will be equal to 0 to  $Q_t$  within this range respectively and with this boundary condition after integration it will yield like  $t$  by  $Q_t$  that will be equal to  $1/k_2(Q_e - Q_t)^2 + 1/Q_e$ .

Here the Equation

$$\frac{t}{Q_t} = \left( \frac{1}{k_2 Q_e^2} \right) + \frac{t}{Q_e}$$

Now this pseudo second-order constants can be determined from a graph of  $t/Q_t$  versus  $t$  and when this solute concentration is low this equation will explain that adsorption mechanism more than any other kinetic model. Whereas at high initial concentration this

pseudo first-order model is favored accordingly at this low concentration of solute.

Let us do an example for this also in this case the adsorption of cadmium ions onto bones has been studied using a base adsorbent. The experimental data was analyzed using adsorption kinetic models that is second-order pseudo second-order model. In this case also you have to find out what would be the equilibrium amount of adsorbed and the rate constant. So, here also same data are given here for different initial concentration of the solute at different time what will be the amount of adsorbate adsorbed at time  $t$  that is given in the respective column. So, here also you have to find out that equilibrium constant and also that equilibrium amount of adsorbed amount.

So, here in this way also we have drawn this graph based on this experimental data. Here we have actually you that simplified this equation like this  $t$  by  $q_t$  equal to  $t$  by  $q_e$  plus  $1$  by  $k_2 q_e$  square that is equal to  $y$  is equal to  $mx$  plus  $c$  where  $y$  is equal to  $q$  by  $kt$  and  $m$  will be equal to what here. Here it will be I think this time what is the time here no this is a slope will be is equal to  $1$  by  $q_e$  and intercept will be is equal to what  $1$  by  $k_2 q_e$  square. So, if you plot this that is  $t$  by  $q_t$  versus time then you will be able to find out what will be the that  $1$  by  $q_e$  value and also  $1$  by  $k_2 q_e$  square value. So, from this slope and intercept you will be able to find out this value of  $q_e$  and  $k_2$  value.

So, here in this graph it is shown that for different solute concentration initial solute concentration these plots are given. At initial concentration of 2.14 the plot is given here this one I think this one is your this one is your for 2.14 and this bundle is 2.

69 and this one is for 3.17. So, from this data and you will be find out what will be the slope and what will be the intercept. So, from this slope and intercept you can easily calculate what will be the  $q_e$  and  $k_2$  value and here after calculation this  $q_e$  and  $k_2$  value are given for the respective initial concentration of  $C_0$  at 2.14 and 2.

69 and 2.17 millimole. And you will see that if you increase the initial concentration this you will see that equilibrium value is decreasing whereas this rate constant it will be that increasing in order. Then another model by which you can also analyze this rate equation for this adsorption. In this case it is called intra particle diffusion model IP model and the model is widely applied to examine the rate limiting step during a adsorption. The adsorption of solute in a solution that involves mass transfer of adsorbate surface diffusion and pore diffusion and film diffusion here is an that independent step whereas surface and pore diffusion may occur simultaneously. So, here we are having that mass transfer of adsorbate that will be accessed based on that film diffusion, surface diffusion and pore diffusion whereas this film diffusion is an independent step whereas surface diffusion and pore diffusion may vary or occur simultaneously.

It is also called Weber and Morris model that you have to remember. The model is expressed by this equation here  $q_t$  is equal to  $k_p$  root over  $T$  plus  $C$ . Here  $k_p$  is called rate

constant which will be expressed by this unit here mg by gram minute to the power 0.5 and C is the boundary layer thickness which determines the boundary layer effect. Higher values will give you the greater effect here.

If C is equal to 0 in that case you can say that this intra particle diffusion model that will control the adsorption process. And if C is not equal to 0 then the plot gives the multiple linear sections and these sections correspond to the different mechanism that control the adsorption process. So, here this is also another important model that is the intra particle diffusion model. Here basically considering that whenever solute will be adsorbing onto the surface how that mass transfer happens? That mass transfer happens that means solute transfer happens by diffusion. Now there are three types of diffusion one is called film diffusion another is called surface diffusion and also pore diffusion and those diffusion whose diffusion will be controlled or you can say that whether this all those diffusion will be controlled or not that can be assessed by this equation model equation which is called the intra particle diffusion model equation.

And this model equation says that it will be actually proportional to that square root of time and where proportionality constant will be regarded as what is that rate constant whereas that extra term that is C here added this term basically will give you that whether this adsorption will be that diffusion controlled or not. In this case if C is equal to 0 then you can say that intra particle diffusion controls the adsorption process. If there is a suppose boundary layer of that film that is that thickness will give you to you and in that boundary layer thickness will determine the adsorption process whether it will be that film diffusion or not. So in that case boundary layer effect will be there and this higher values of C it will be that effect will be more in that case and if suppose C is not 0 and the plot gives multiple linear sections there. So in that case those sections will correspond to the different mechanism of that adsorption process by dominated by that surface diffusion or pore diffusion there.

So here in this case that C value will give you that corresponding value. Let us do an example here also to find out that rate constant and C value here. The adsorption again the same problem that adsorption of cadmium ions onto bones has been studied using a base adsorption process and the experimental data also is given as per earlier whatever given in the tables here also the same data are given and here also you have to analyze this data based on this intra particle diffusion and in this case also you have to find out that model parameters like your  $q_t$  and C.

Here the equation

$$q_t = K_p \sqrt{t} + C$$

So in this case simply you have to plot that  $qt$  versus  $\sqrt{t}$ , you have to find it out what will be the  $\sqrt{t}$  value and then  $qt$  corresponding value. So if you plot it you will get this value and if you fit that straight line equation here again with this then you will have this corresponding value of slope and intercept and from those slope and intercept you will be having that  $K_p$  value and  $C$  value respectively.

So for different initial concentration of that solute you will be having this  $K_p$  value and  $C$  value for different initial solute concentration like this here. Here also we can see that as solute concentration increased there that rate constant will also increased and this diffusion control or not as a surface control or diffusion control that will give you based on this  $C$  value. If since  $C$  is not equal to 0 so we can say that it will be either surface control or diffusion control adsorption process. If suppose  $C$  is equal to 0 it is not coming exactly 0 so you cannot say that there will be that diffusion control that adsorption process. So I think you understood this problem of that different model like one is called pseudo first-order model pseudo second-order model and also intra-particle model.

These 3 models are very important you have to know these 3 only as per your logic curriculum I think it is more than enough to know and in also other courses I think in mass transfer operations that you will learn more about this adsorption and there are also different techniques for that you will be I think knowing there. So here we are limiting up to these 3 models here there are so many other different kinetic models are there so we will not be discussing here you can learn it by consulting other books if you have some other interest there. And then also we have discussed that different mechanism of that controlling adsorption here. First mechanism like this mass transfer that bulk movement of that solid particle is happened as soon as the adsorbent surface is dropped onto the solution also after desorption and this process is too fast thus it is not considered during the design of kinetic system. And in the second mechanism is that it is called the film diffusion it involves the slow movement of the solutes from the boundary layer to the adsorbent surface and third mechanism is that when the solute reach the surface of the adsorbent they move to the force of the adsorbent.

And fourth mechanism is that the final mechanism it is involves the rapid adsorptive attachment of the solute on the active sites of the force and in this case it will be a rapid process and it is not considered during the engineering design of kinetics. So, if the system is characterized by poor mixing small solute size and low concentration film diffusion becomes the rate controlling step otherwise intra-particle diffusion controls the process. So, this point is very important you have to remember it. So, we have discussed that in the adsorption module what is the basic principle and what is application what are the different isotherms and also in this lecture we have discussed that what is the kinetic equations based on which you can analyze the adsorption process to find it out what will be the rate constant of that adsorption by first order reaction, second order reaction and also that intra-particle diffusion model and from those models you will be able to find out what will be the rate constant and also equilibrium amount of adsorbent which is adsorbed by the

adsorbent. So, I think you understood this process and here we will give you the last lecture and by this last lecture I want to say that please go through that lectures again and if you have any doubt in the lectures that you can contact with me directly by through this mail or through that portal as per NPTEL and in this regard I wish you all the best for the course. Thank you. .