Course: Adsorption Science and Technology: Fundamentals and Applications

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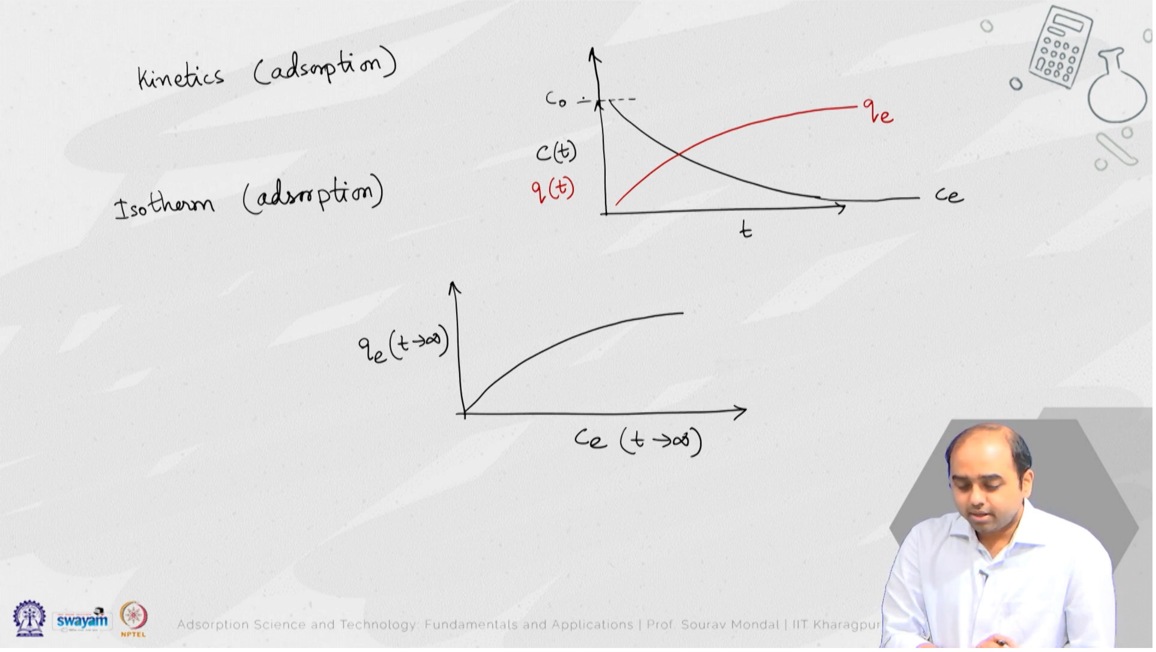
Week 02

Lecture 10 | Adsorption Kinetics

Hello everyone. Welcome to this last lecture of week 2 in this we will be talking about the kinetics of the adsorption. Now it is often you know conceived that although equilibrium sorry adsorption is an equilibrium process why does the kinetics is important to study. Now, this kinetics is often important for systems where this is the adsorption is limited is limited by many a times with mass transfer or the adsorption is very slow and there are other simultaneous you know transport phenomena either diffusion or chemical reaction which takes place. And in that case kinetics of this adsorption becomes very important as it becomes a rate governed process. Now coming to the kinetic models there are several models we will of course talk about them in this class itself. But before that I want to introduce that.

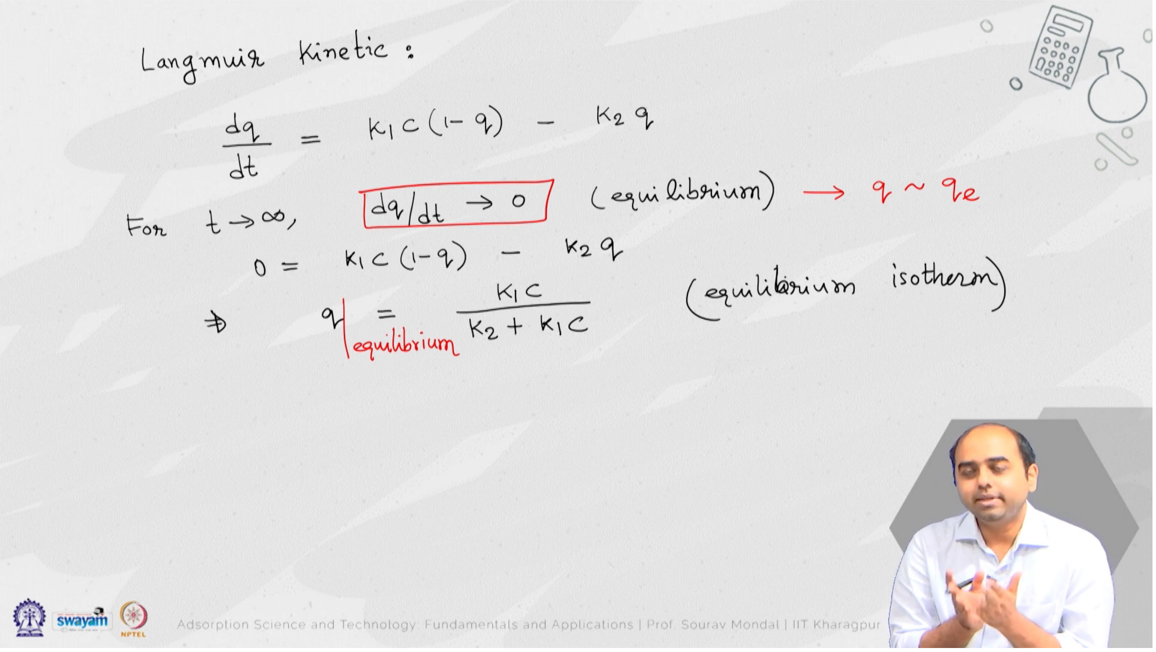
I want to emphasize that the kinetic study is done till the state when the concentration of the adsorbate reaches the equilibrium value. So, please note the for the case of the isotherms you prepare or you try to do an experiment to find out the equilibrium concentration of the adsorbate for different levels of the concentration Whereas, in the case that could be either by changing the amount of the adsorbent that you are adding or by increasing or changing the initial concentration of your solutions in that way you can actually tweak the relative uptake of the solution. But in the case of the kinetics it is a time dependent situation. So, for a particular sample you start with the initial concentration.

And then you track the change in the concentration in the solution phase with respect to time and from there you can work out what would be the concentration of the adsorbate in the absorbent with respect to time and then again how these two are related. So, here the during the kinetics it is generally you know the concentration in the solution phase is measured with respect to time starting from an initial concentration till it reaches an equilibrium. So, just to be clear I mean or I refer to the following situation that in the case of the kinetics this is often you know confused that in the case of the kinetics of the adsorption one measures the concentration of the adsorbate in in the solution phase with respect to time. So, this decreases and slowly it trades off to an equilibrium value whereas, the concentration profile in the adsorbate is increasing and then slowly it attains a steady state value right. So, this is what we do or what is measured in the kinetics.



In the case of the isotherm, it is the equilibrium scenario. So, in that one measures the different or one estimates the different you know equilibrium concentration and from there you try to work out or try to relate the equilibrium concentration in the adsorbent phase and that follows this strain. So, this is at equilibrium or when t tending to infinity. This is what we generally refer in the isotherm, but in the kinetics you measure the time dependent concentration profile. So, this this actually starts from an initial value of let us say C0. So, initially the Q value is 0. So, at time t is equal to 0 the Q value is 0 because there is no adsorption or no concentration of the adsorbate in the adsorbate phase. So, the Langmuir kinetics is actually derived from the equilibrium relation and until an equilibrium is reached the difference between the rate of adsorption and the desorption would be non-zero right and there these two rates would not be equal it is only at the equilibrium they are equal. So, at before equilibrium these two are not equal and essentially the difference between these two rates is represented by the accumulation term. So, this dq/dt is equal to the rate of the forward process minus the backward process.

So, the forward rate constants can be represented as something like this. So, this equation you this equation you realize that for t tending to infinity. dq/dt tends to 0 and that is where you attain equilibrium scenarios and in that case if you rearrange the equations you will be getting. So, this represents q is equal to. So, this is the equilibrium isotherm expression.



Langmuir Kinetic :

$$\frac{dq}{dt} = k_1 c(1-q) - k_2 q$$

For $t \to \infty$, $\boxed{dq/dt \to 0}$ (equilibrium) $\longrightarrow q \sim q_e$

$$0 = k_1 c(1-q) - k_2 q$$

$$\Rightarrow \quad q\Big|_{equilibrium} = \frac{k_1 c}{k_2 + k_1 c} \quad \text{(equilibrium isotherm)}$$

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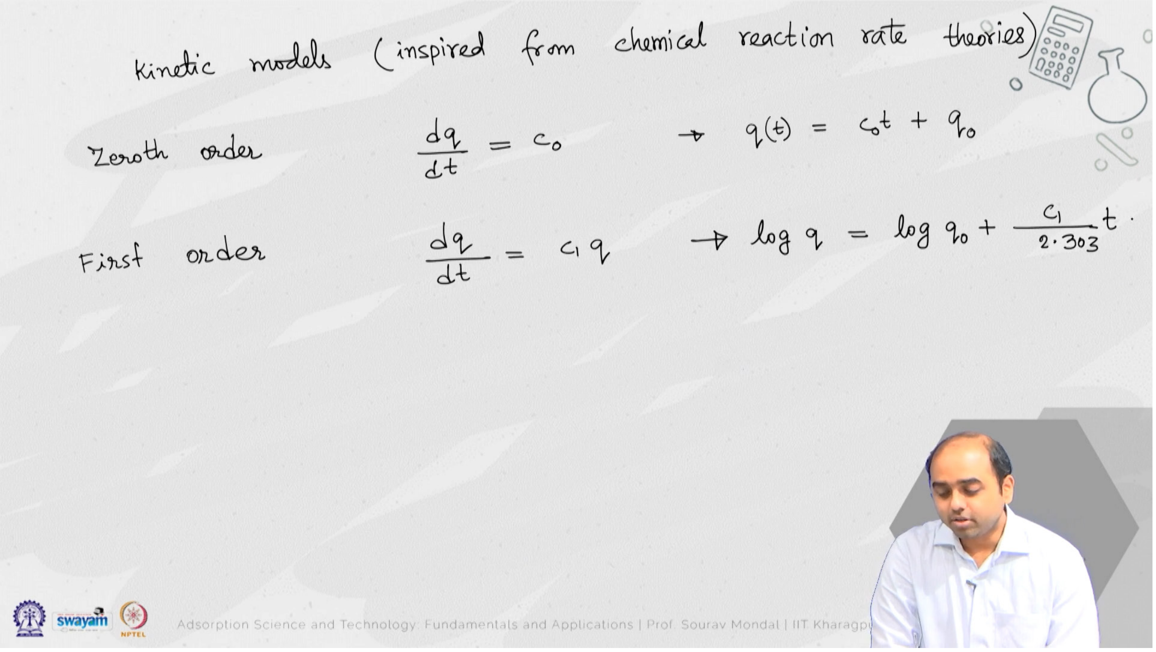
So, at equilibrium when dq/dt approaches to 0, q approaches to the equilibrium. So, this is the situation at equilibrium and you recover the equilibrium expression. So, if you know the Langmuir isotherm is applicable for your adsorption system, then it is advisable that for the kinetic process you try to use the Langmuir kinetic models. Of course, the Langmuir kinetic model can also be expressed by the other you know non-linear or the pseudo Lagergren models which we will introduce immediately. So, the other kinetic models that do exist which are all inspired from chemical reaction rate theories.

So for the case of you know a simple zeroth order kinetics which suggest that this dq/dt is essentially constant. So let us represent the constant by C0. So this integrated form of this expression q as a function of t takes like this this two constants. So, I mean this is evaluated at t is equal to 0, q is equal to q0. So, obviously, this tells you I mean this this order model cannot predict the equilibrium behavior because this is closely related to the situation for initial times because when t reaches infinity that q does not achieve equilibrium concentration instead q also becomes unbounded on infinity. So, this model as you can understand is only to explain the initial trend. For example, here when the profile of q with respect to time is linear. So, in the linearized zone or in the zone initial time this you know zeroth order model is generally very good to explain this behavior. Coming to the other versions that is the first order model. So, the first order model is very similar to first order rate equation. So, the integrated form of this equation takes this form. So, this factor of 2.3 comes from the fact that you convert ln to log . Here this also even though this can explain the non-linear trend of the. So, this is like the non-linear trend non-linear trend of q as a function of time can be you know tracked from this model.



Kinetic models (inspired from chemical reaction rate theories)

Zeroth order $\frac{dq}{dt} = c_0 \rightarrow q(t) = c_0 t + q_0$

First order $\frac{dq}{dt} = c_1 q \rightarrow \log q = \log q_0 + \frac{c_1}{2.303} t$.

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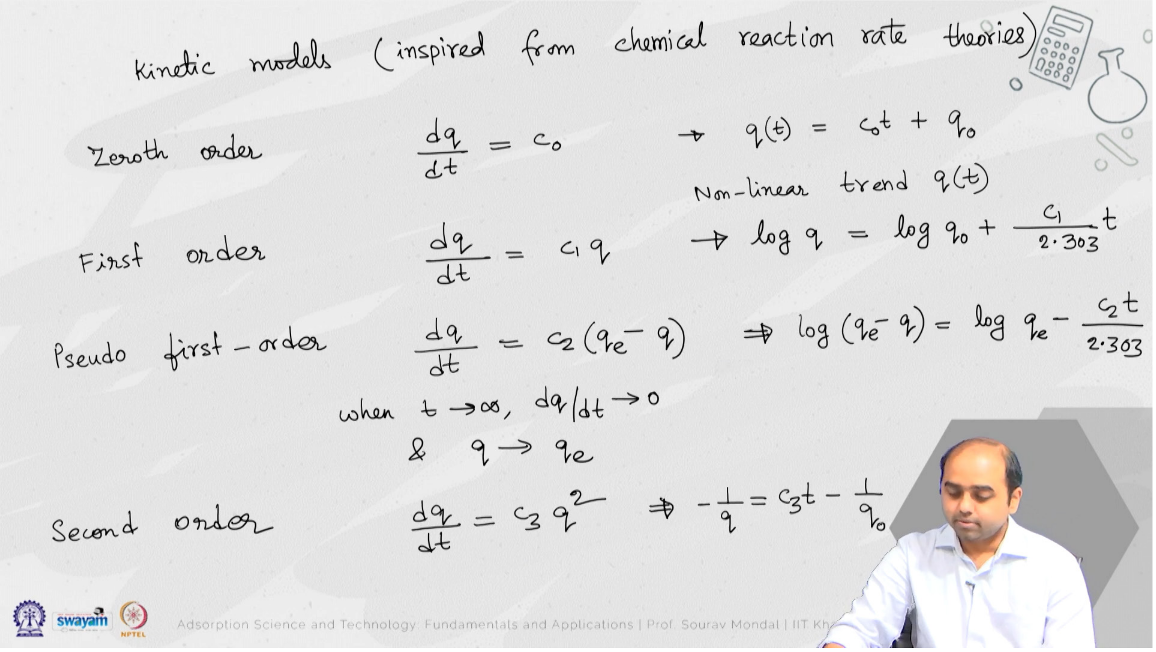
So, this can explain the situation beyond the initial time phase or the initial time period, but this also does not capture the the part or this phenomenon that for when T tends to infinity that Q should approach the equilibrium value or the equilibrium concentration in the adsorbent phase. So, to consider I mean to bring into this idea, pseudo first order models has been proposed and these are generally you know quite effective in capturing the non-linear trend as well as the equilibrium value at large times or close to the equilibrium scenario. So, in this case the dq/dt model is represented as, like this. So, you can clearly realize that when t tends to infinity q approaches to qe even if I do not write the integration integrated form still it tells us that when this model when t tends to infinity dq/dt tends to 0 and naturally q approaches to qe this is of course not true for the previous 0 that are on the first order model. So, the integrated version of this looks something like this, and from here also you can realize that when t approaches to infinity q also approaches to qe.

Next we have the second order models. So, the second order models is again inspired from the second order chemical reaction rate Q squared and this integrated form of this expression looks like this. So, q0 is the initial value and here also you see that interestingly this q is inversely proportional to this time. So, which suggest that q is as time is increasing q is decreasing. So, this is a very important phenomena that you can observe here that in the case of the second order model, which is not very usual to see that with the increase in time it is found out that q is actually decreasing or these are inversely proportional of course, that can be moderated with the value of q0 in this case.



Kinetic models (inspired from chemical reaction rate theories)

Zeroth order $\frac{dq}{dt} = c_0 \rightarrow q(t) = c_0 t + q_0$

Non-linear trend $q(t)$

First order $\frac{dq}{dt} = c_1 q \rightarrow \log q = \log q_0 + \frac{c_1}{2.303} t$

Pseudo first-order $\frac{dq}{dt} = c_2 (q_e - q) \Rightarrow \log (q_e - q) = \log q_e - \frac{c_2 t}{2.303}$

when $t \rightarrow \infty$, $dq/dt \rightarrow 0$

& $q \rightarrow q_e$

Second order $\frac{dq}{dt} = c_3 q^2 \Rightarrow -\frac{1}{q} = c_3 t - \frac{1}{q_0}$

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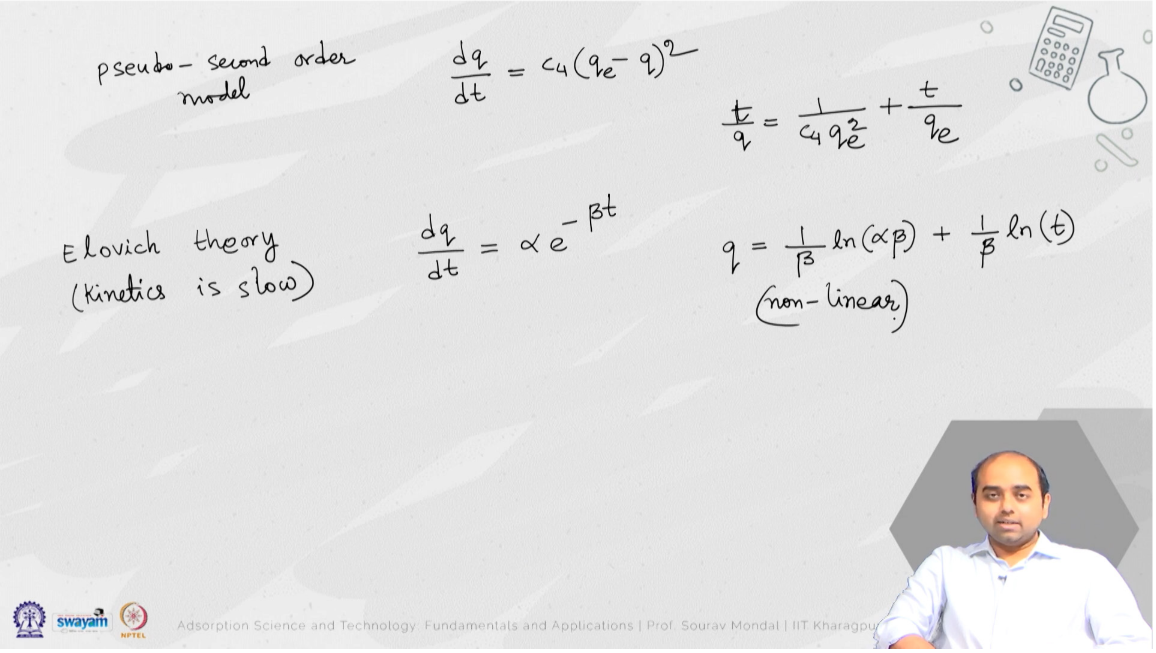
But naturally the trend of the profile suggest that q is decreasing and this is a space very specific observation in this case. So, normally second order models are not very you know popular and very widely used and it is only in very few circumstances the second order model is actually applicable particularly when there is additional you know mass transfer effects which actually affects the adsorption besides being a purely adsorption based phenomenon. There is also the existence of the pseudo second order model which is represented as this. So, in this case also as t tends to infinity q approaches to qe. So, this also captures the equilibrium behavior in the long term or close to the equilibrium and in this case the integrated version is like this.

So, here also the same trend is there, but interestingly the qe values are nicely captured in this case and the system tend towards the equilibrium values at long times, but here also you one can observe that with a increasing time the qe values are q values are not you know proportional. And this is something that is very interesting for this system . Now if there is one more kinetic model which is known as this Elovich theory and this is in exponential format. So, in this case the integration form makes this shape. So, this is also a highly non-linear process and this is particularly useful to predict the adsorption behavior when the kinetics is very slow.

So, Elovich is very good when kinetics is slow or the adsorption kinetics is the rate determining step in the transport phenomena of the system. Now this and of course, this is non-linear in nature 2. So, except the zeroth order, all the other models first order, second order, then you have this pseudo first order and the pseudo second order all of these models are non-linear in nature. These kinetic theories particularly the pseudo versions the pseudo first order and the pseudo second order were actually proposed or originally proposed by this Lagergren theory. So, Lagergren actually proposed this pseudo order models to take into account that this kinetic behavior should approach the equilibrium values at long times or at large times which is not existence in the classical you know rate expressions or the rate theories.



pseudo-second order model

$$\frac{dq}{dt} = c_4 (q_e - q)^2$$

$$\frac{t}{q} = \frac{1}{c_4 q_e^2} + \frac{t}{q_e}$$

Elovich theory
(Kinetics is slow)

$$\frac{dq}{dt} = \alpha e^{-\beta t}$$

$$q = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$$

(non-linear)

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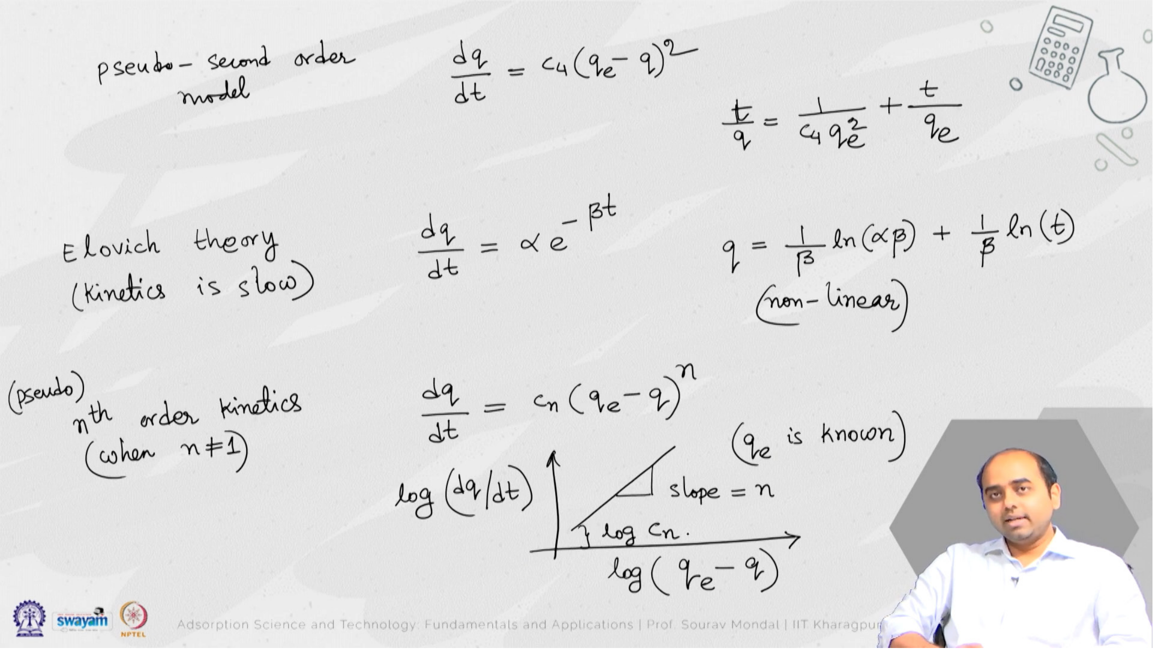
So, now it is understood that the kinetics of the adsorption also plays a you know important role particularly in situations when the equilibrium value is takes considerably you know finite time which is comparable and the time scale of the adsorption if it is comparable with other phenomena for example, diffusion or chemical reaction then this is an important aspect of the problem or the coupled physics of the system and kinetics needs to be evaluated. So, the kinetic theory helps us to relate how does the concentration in the adsorbate in the adsorbent phase actually changes with respect to the time. There are several different theories the zeroth order model explains the linear regime which is generally true for small time. The first order models captures the non-linear behavior I mean the both the first orders and pseudo first order captures the non-linear behavior, but particularly the pseudo first order model takes into account of the fact that this equilibrium concentration is attained at large times. The second order models is slightly different than the first order as in this case you can see from the expression, that with increasing the time the concentration profile may sorry the concentration or the adsorption in the adsorbent may decrease depending on the capacity of the adsorbent.

Similarly, for the case of the pseudo second order even though it approaches the equilibrium value the trend of the adsorption profile may be you know different than the first order or the zeroth order model. The Elovich theory captures the kinetics for slow behavior or the when the kinetics is very slow and in this case the this q or this adsorbate concentration in the solid phase varies with respect to the time in the logarithmic scale. So, these are the different adsorption models that are present and that are widely used to study this behavior of the kinetics. In general if many a times it is observed that the kinetics do not follow either a zeroth order or a first order model. So, in that case for nth order kinetics when n is not equal to 1 the generalized kinetic expression can be written down as I am writing the pseudo version something like this.

The nth order kinetic expression can be expressed in this form is a three constant model expression. So, from the plot of your q versus t you can work out what would be these kinetic constants and generally the equilibrium value is known before. So, this the only two constants in this model whether it is zeroth order, first order, second order, pseudo first order or whatever is actually plotted from this expression of the values of log of dq by dt, with respect to q. So, in this case the qe values qe is known are known and are known from the fact that if you allow this equilibration to happen you can know what is the equilibrium concentration. So, that is generally the equilibrium concentration are known for any kinetic experiments and from this plot of this you know log of dq by dt versus q generally the profile in this case is, I mean is better to write log of qe minus q and in this case the slope represents slope represents the value of the n and intercept represents the value of log of c n.



pseudo- second order model

$$\frac{dq}{dt} = c_4 (q_e - q)^2$$

$$\frac{t}{q} = \frac{1}{c_4 q_e^2} + \frac{t}{q_e}$$

Elovich theory (Kinetics is slow)

$$\frac{dq}{dt} = \alpha e^{-\beta t}$$

$$q = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$$

(non-linear)

(pseudo) nth order kinetics (when $n \neq 1$)

$$\frac{dq}{dt} = c_n (q_e - q)^n$$

(q_e is known)

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So, from this expression or from this correlation you can work out what would be the constant or particularly the exponent whether it is close to first order or second order can be worked out by analyzing the kinetic data from your experiments, provided the values of qe are known already and which is easily available since qe is the equilibrium concentration and that is obtained at large times for any you know kinetic experiment. So, I hope all of you have got a fair understanding of the kinetics particularly when the kinetic theory is important for your case and it is also relevant to realize that the kinetics does play an important role particularly when there is another transport phenomena happening along with adsorption. So, the different kinetic theories that has been explained here pertains to different types of scenario involving different you know physics or different adsorbate adsorbent interactions in different scenarios whether it is gas or whether it is liquid, solutes, organic molecules you know gas yes molecules inert molecules the kinetic theory does hold for different types of system. I hope all of you have found this information and this lecture contents useful. See you all next week.