

## Lec 35: Analysis of Adsorption by Isotherms

Hello everybody. Welcome to this massive open online course on solid-fluid operations. As we are discussing about the adsorption on this solid-fluid operation as a module, so in this lecture we will try to discuss about that analysis of adsorption by different isotherms. In the previous lecture we have discussed about that what is the application, what is the basic principle of adsorption and how that adsorption can be classified based on that characteristics of the adsorption criteria and also we have discussed about that what are the different mechanism of that adsorption there. So here we will try to discuss about that adsorption characteristics by some isotherms or equilibrium condition. Now that there will be certain basis of adsorption that the adsorption separation basically is based on three distinct mechanism especially for you will see that when that gaseous molecule or liquid molecules to be adsorbed on the surface of reactive solid particles based on their characteristics.

So in this case there are three mechanisms that can be assessed here, one is called stearic mechanism, another is called equilibrium mechanism and third one is called kinetic mechanism. And in case of stearic mechanism you will see that the porous solid has force that will have some dimension such that it allows small molecules to enter while excluding large molecules from the entry. So this is called stearic mechanism. Whereas equilibrium mechanism that it is basically based on the solid that will have different abilities to accommodate their species that is a stronger adsorbing species is preferentially removed by the solid materials or not.

That based on that adsorbing capability this mechanism depends on. And kinetic mechanism is based on different rates of diffusion of different species into the pore and the faster diffusion species is preferentially removed by the solid by controlling the time of exposure. So all these mechanisms depend on the process parameter, what type of materials, whether is there any pores or not, whether that materials are enough strength to withstand the temperature or not or also that capability of the adsorbent to capture those organic or inorganic compounds based on their typical characteristics of that compounds. And also you will see that some materials that will be having the characteristics and they will have that capacity or enhance their capacity based on that you know modification of their surface and also the reducing their size of that materials by different techniques. So in that case that enhancement of that adsorption can be done by that solid materials just by modifying its surface.

So we are having that 3 mechanisms, one is called steering mechanism, equilibrium mechanism and kinetic mechanism. All those mechanisms that depend on that process parameter. In this case that process parameter will stand here like size of the particles, even amount of that particles, even the transport phenomena of that solid materials or gas or liquid molecules onto the surface and also the porosity of the materials. Some other intrinsic characteristics also actually effect on that this adsorption characteristics. Now to analyze those adsorption, it is one of the important condition or you can say that criteria to

assess that adsorption characteristics that is called adsorption equilibria or isotherms.

So adsorption equilibria of any pure components are the essential basis for the understanding of how much those components can be adsorbed by a solid adsorbent. So this is the basic key parameters you can say for understanding that how much compounds can be adsorbed on the solid surfaces and with this information that is adsorption equilibria or isotherms, with this information that adsorption kinetics of a component can be also analyzed. So here you will see that some materials whenever that adsorbent on the solid materials or an adsorbent you will see that after adsorbing their components and to get separated from that adsorbent it is required to desorb that material from that surfaces. So that adsorption and desorption of course what will be that equilibrium condition that also to be known there. So this is called equilibrium or isotherms.

Let us consider all those things here. So to analyze that equilibria there are several approaches. Some are called kinetic approaches and it is also called the fundamental equation how can be derived so that by that equation this equilibria can be analyzed and this theory that is kinetic approach this is one theory that allows to understand the monolayer surface which is formed at the surface of that adsorbent for the adsorption on an ideal surface and also you can say that the adsorption which will be due to the higher surface energy fluctuation that will be compared to the thermal energy of the molecule and this energy fluctuation on the surface will be periodic measure. So this type of approach it is called kinetic approach and then another approach it is called gives thermodynamic approach by which you can also analyze this equilibria. In this case, you have to assume that some forms of thermal equation of state which will be related to the number of mole of adsorbent and in this case you will see that the area and the spreading pressure also that the fundamental equations will be derived based on those you know area spreading pressure all those things and also that number of moles that will be adsorbed.

And in this kind of approach you will see that such that linear isotherms that is called equilibria that some other form of equations will be like there it will be like linear isotherm some will be called Vollmer isotherm some will be called Healy-De-Boehr isotherm, Follmer-Guggenheim isotherm, even Harkins-Jesura isotherms. These are the names of that isotherms all those isotherms basically equation which is derived based on that state of that how many numbers of molecules to be adsorbed on the adsorbent and also at what condition of that surface area and the even under which pressure it is happened. So based on that these are the isotherms are developed. So these are the some names of that isotherms based on which you can analyze that how much amount of that adsorbent can be adsorbed on the surface of the adsorbent. Then another approach it is called practical approach.

In this case you will see that due to the complex pore and surface structure of that adsorbent sometimes you will not be able to analyze those fundamental transport of that molecules of gas or liquid which is transported to that adsorbent surface and also there are

so many other variables will be affecting on that adsorption process. So in that case you will see that due to the complex structure, due to the complex pore even surface structure that sometimes will not be giving that exact analysis of that adsorption process by that isotherm of that theoretical approach of like kinetic approach and thermodynamic approach. So in that case sometimes many successful semi-empirical approach can be you know proposed. some renowned scientists that they have proposed some isotherms based on that empirical approach. In that case they have correlated that adsorption capacity with that variables there.

They are making that some non-linear equations just empirical equations there will be no certain theory that will be followed from that mechanistic approach or kinetic approach or that thermodynamic approach. It is directly that some relations based on that transport phenomena. Since that transport phenomena depends on different parameters, different variables So in that case all those parameters, all those variables will be affecting in different way. So as an average they are making that one correlation along with that different variables to assess that final yield of that adsorption. So those isotherms that is developed empirically are called Frank-Lewis isotherms even sometimes it is called Schiff's isotherms that is called Langmuir-Frank-Lewis isotherms.

So some isotherms it is called Toth isotherms even Uniline isotherm even Dubinin-Radescobase isotherms. These are some empirical isotherms or empirical model based on which you can assess that adsorption capacity of that adsorbent. So we are getting three approaches of that analyze of equilibrium condition of that adsorption. One is called kinetic approach, another is called Gibbs thermodynamic approach and then practical approach it is called empirical approach. So discussion on that all those approach it will take different lecture for that but here we will only discuss two or three isotherms that is very widely used in different adsorption processes for analysis capacity of that adsorption.

So we will discuss here only those isotherms there. So let us consider first that Langmuir isotherms which is widely used isotherm for assessing that or analyzing that adsorption process. The most basic theory in adsorption it is called that the Langmuir theory. It is developed in 1918 and this theory allows to understand the monolayer surface adsorption on an ideal surface and adsorption onto a flat surface based on kinetic view of point. So this isotherm is basically based on that kinetic view point.

So in this case what is the theory that Langmuir theory? Here as per that Langmuir theory it is said that there is a continual process of bombardment of molecules onto the surface and a corresponding evaporation that is called desorption of molecules from the surface to maintain zero rate of accumulation at equilibrium. So here this Langmuir theory actually states what is that at an equilibrium condition, what are those molecules come into contact with that solid surface of adsorbent. Initially it will be adsorbed and then it will be desorbed and this adsorption and desorption will be in such rate that there will be that

zero rate of accumulation of that adsorbate onto the surface of the adsorbent. So this is the basic idea of this Langmuir theory. So at equilibrium we will have that always zero rate of accumulation of the adsorbent on the surface.

So for that there will be certain rate of adsorption and there will be certain rate of desorption. So both the rate adsorption and desorption will be in such way that there will be no adsorption and desorption occurs in that surfaces. So here in this case we can say that there will be an equilibrium, there will be equilibrium in such that there will be adsorption will be equal to desorption. Now to develop that Langmuir isotherms they have given some assumptions like that surface will be homogeneous in nature that is adsorption energy is constant over all sides of the adsorbent. Number 2, adsorption on surface is localized that is adsorbed atoms or molecules are adsorbed at the definite or localized sites.

And then each site can accommodate only one molecule or atom and gaseous molecule behave ideally only one monolayer will be formed, no adsorbate or adsorbate interactions will be there and adsorbate molecule will be immobile. So in this case these are the assumptions which are to be followed to develop that Langmuir isotherms. So these are the assumptions and then based on these assumptions the Langmuir theory as per that kinetic principle can be developed in such way that there the rate of adsorption will be equal to the rate of desorption from the surface. So this is the main motto of this development of isotherms. In this case the rate of striking or you can say that attaching or you can say that bombarding in mole per unit time and unit area that will be obtained from the kinetic theory of gas which is given in equation number 1.

So it will be regarded as  $R_s$  that will be equal to  $P$  by root over  $2\pi MR_g T$ .

Here the Equation

$$R_s = \frac{P}{\sqrt{2\pi MR_g T}}$$

So this is called rate of striking the surface in mole per unit time and unit area. So this is basically depending on pressure and molecular weight and also the temperature of that molecules which is to be transported to the adsorbent surfaces. So here you will see that the bombardant rate that is adsorption rate that will be equal to the evaporation rate as per this picture here and this rate of striking or bombardant depends on the pressure and temperature and that rate of striking or bombardant depend that can be expressed by this equation number 1 here. And then if you are considering that a fraction  $\alpha$  of gas molecules that is striking the surface will condense and is held by the surface force until these adsorbed molecules evaporate again.

So in that case  $\alpha$  will be the fraction of gas molecules that will be striking on the surface of the adsorbent and it will be condensed there. Now if you are suppose having that

alpha will be equal to 1 especially for ideal surface then alpha will be called as sticking coefficient. So here alpha less than 1 it will be for real surface and alpha is equal to 1 means here ideal surface that means all the molecules will be adsorbed on the surface and it will be condensed on that surface. And the rate of adsorption in mole adsorbed per unit bare surface area per unit time that can be expressed by this equation number 2 here. So it will be equal to what is that  $r_A$  that will be  $\alpha P$  by root over  $2 \pi m r g T$ .

Here the Equation

$$R_a = \frac{\alpha P}{\sqrt{2\pi MR_g T}}$$

So here basically this  $P$  by root over  $2 \pi m r g RT$  this is basically the rate of bombardant and whereas this alpha is the sticking coefficient which is a fraction of that bombardant. So that will be regarded as adsorption rate. So this is denoted by  $r_A$ . So  $r_A$  is equal to  $\alpha P$  by root over  $2 \pi m r g T$  and therefore the number of moles adsorbed per unit area covered and uncovered per unit time we can write by this equation. So here this  $r_A$  will be is equal to  $\alpha P$  into root over  $2 \pi m r g T$  into  $1 - \theta$ .

Here the Equation

$$R_a = \frac{\alpha P}{\sqrt{2\pi MR_g T}}(1 - \theta)$$

Here theta is what? The theta is equal to fractional coverage. Suppose after adsorption molecules will be sticking on the surface of the adsorbent and gradually it will be covered the surface of the adsorbent. So now what will be the fraction of that surface will be covered by its sticking molecules that is regarded by that theta which is called the fractional coverage and  $1 - \theta$  will be is equal to basically fraction of empty sites which is not actually covered by that molecules. So in that case we can write that rate of adsorption will be is equal to  $\alpha P$  into root over  $2 \pi m r g T$  into  $1 - \theta$ . So  $1 - \theta$  is basically that what will be the fraction of gas molecules that is sticking on the surface.

Whereas theta is the fractional coverage  $1 - \theta$  will be equal to not coverage and then rate of desorption from the covered surface now after adsorption that surface will be covered now what will be the rate of desorption that will be going to uncovered. So in that case RD can be represented by this RD for this rate of desorption.

Here the Equation

$$R_d = k_d \theta = k_{d\infty} \exp\left(-\frac{E_d}{R_g T}\right) \theta$$

So that will be equal to  $K_d$  into  $\theta$ . So here  $K_d$  is basically the desorption rate constant. Here  $K_d$  can be represented by this equation here  $K_d$  infinity exponent of minus  $E_d$  by  $R_g T$  and then  $\theta$  is basically the fractional coverage.

Here the Equation

$$k_d = k_{d\infty} \exp\left(-\frac{E_d}{R_g T}\right)$$

So in this case  $E_d$  here in this equation is equal to activation energy for desorption which is equal to the heat of adsorption for physically adsorbed species since there is no energy barrier for physical adsorption and  $K_d$  infinity it is the rate constant for desorption at infinite temperature. And this inverse of this parameter is denoted by  $\tau_{d\infty}$  which is called basically the average residence time of the adsorption

Here the Equation

$$\tau_{d\infty} = \frac{1}{k_{d\infty}}$$

and for physical adsorption this surface residence time is typically ranging between  $10^{-10}$  to  $10^{-13}$  second while for chemisorptions this residence time has a very wide range ranging from  $10^{-6}$  to  $10^{-9}$ . So I think you understood this that what is the rate of adsorption and what is the rate of desorption and this rate of desorption that actually depends on that average resistance time of the adsorption there. Now as for that Langmuir isotherms this rate of adsorption will be equal to rate of desorption. that rate of adsorption and desorption we can get this final form of equation 7 that will be equal to  $\theta$  is equal to  $\frac{bP}{1+bP}$

Here the Equation

$$\theta = \frac{bP}{1+bP}$$

where  $B$  is a term which is defined by this equation number 8 here that means  $\alpha$  exponent of  $Q$  by  $R_g T$  divided by  $K_d$  infinity root over  $2\pi M R_g T$  that will be equal to  $B$  infinity exponent of  $Q$  by  $R_g T$ .

Here the Equations

$$b = \frac{\alpha \exp\left(\frac{Q}{R_g T}\right)}{k_{d\infty} \sqrt{2\pi M R_g T}} = b_{\infty} \exp\left(\frac{Q}{R_g T}\right)$$

So this is basically that after simplification what is the coefficient B is coming based on the terms of that flow rate total heat of adsorption and also what is that you know temperature there and here in this case Q is basically the heat of adsorption and is equal to the activation energy for desorption ED and B infinity is basically defined as  $\alpha$  by  $K_d$  infinity root over  $2 \pi M R_g T$

Here the Equation

$$b_{\infty} = \frac{\alpha}{k_{d\infty} \sqrt{2\pi M R_g T}}$$

and B is equal to  $5.682 \times 10^{-5} (MT)^{-1/2}$  Torr<sup>-1</sup>

Here the Equation

$$b_{\infty} = 5.682 \times 10^{-5} (MT)^{-1/2} \text{ Torr}^{-1}$$

this is torr inverse. So this is actually applicable for the gas molecules of nitrogen which is to be adsorbed on the surface. Now based on this equation 7 so this is called Langmuir isotherms of this form theta is equal to  $\frac{bP}{1 + bP}$

Here the Equation

$$\theta = \frac{bP}{1 + bP}$$

$$b = b_{\infty} \exp\left(\frac{Q}{R_g T}\right)$$

and this equation basically depends on what is that this theta that means coverage of that fractional coverage of that adsorbate onto the adsorbent surface and it is a function of pressure. Now if we observe that fractional coverage of that adsorbent onto the surface based on that pressure you can get this type of profile here as shown in the slide here you will see that amount adsorbed will be increased as per pressure increase whereas that adsorbed of molecules onto the surface will be decreased if you increase the temperature whereas that amount adsorbed will be increased if your heat of adsorption will be increased there.

So in this way we can assess that what will be the amount of particles or molecules or that other ions to be adsorbed onto the surface of that adsorbent based on the pressure that you can assess by equation number 7 along with that equation number 8, 9 and 10. Now then the Langmuir equation, equation number 7 the written in terms of the amount adsorbed

useful for data correlation so theta will be is equal to BP by 1 plus BP this is the equation where B is given in equation number 8

Here the Equation

$$b = b_{\infty} \exp\left(\frac{Q}{R_g T}\right)$$

and this equation number 7 can be written by equation number 11 how the theta can be written as C<sub>μ</sub> by C<sub>μm</sub>

Here the Equation

$$C_{\mu} = C_{\mu m} \frac{bP}{1 + bP}$$

what is C<sub>μ</sub>? C<sub>μ</sub> here is defined as the amount of adsorbed in mole per unit mass or volume. So it is basically a concentration per unit mass or volume and C<sub>μm</sub> is basically the maximum adsorbed concentration that is corresponding to a complete monolayer coverage onto the surface of the adsorbent. So we are having here instead of theta that C<sub>μ</sub> by C<sub>μm</sub> so C<sub>μ</sub> will be is equal to C<sub>μm</sub> into BP by 1 plus BP that is given in equation number 11. Now in this case mu is one subscript here this is basically denoting the adsorbed phase and the volume of adsorbent particle is taken as the particle volume minus the void volume where molecules are present in free form.

So in this way you can have this final form of this Langmuir equation here as equation number 11. Now this equation number 11 from this you can find it out what will be the parameter B what will be the parameter C<sub>μm</sub> that means what will be the maximum adsorbed concentration corresponding to a complete monolayer coverage that you can find it out and also what will be the parameter B as defined in equation number 11. Now how to do that, that you have to find it out that B or C<sub>μm</sub> from the experimental data. In that case the parameter B and C<sub>μm</sub> can be obtained by fitting that linearized form of this equation just with that experimental data. So from that equation number 11 you first rearrange this equation number 11 as per equation number 12 where it will be as 1 by C<sub>μ</sub> that will be equal to 1 by C<sub>μm</sub> minus 1 by C<sub>μm</sub> B into 1 by P.

Here the Equation

$$\frac{1}{C_{\mu}} = \frac{1}{C_{\mu m}} + \frac{1}{C_{\mu m} b P}$$

So in this case you will see that here you will see that this will be equation of straight line here this will be actually plus this is plus 1 by this. So this will be equation of straight line. So here you can make a plot 1 by C<sub>μ</sub> versus 1 by P here as shown in the slide here a graph

of that in x axis it will be  $1/P$  and y axis it will be  $1/C_m$ . So parameters B and you will see that this  $C_m$  to be obtained from that slope and the intercept from this plotted data. So that intercept will give you that what will be the  $C_m$  that means  $1/\text{intercept}$  and slope means  $1/C_m B$  is equal to slope and from that slope and intercept you can easily calculate what will be the B value there.

So from that experimental data you will be able to calculate what will be the maximum adsorbed concentration and also that parameter as in equation number 11 or 12 as per that Langmuir isotherm. So from that Langmuir isotherms from the experimental data you can easily find it out what will be the maximum adsorbed concentration of that solute onto the surface of the adsorbent and for that you have to do the experiment in such a way that with respect to change of pressure you have to collect that concentration of that solute onto the surface with respect to pressure. Now let us do an example for this theory. In this case one example it is given that the propane gas is adsorbed in activated carbon experimentally in a laboratory at different temperatures. The adsorption data of propane on activated carbon at 283 degree Celsius, 303 degree Celsius not it is in Kelvin 283, 303 and 333 Kelvin.

Here  $C_m$  is given in millimole per gram of that propane gas and find the parameter of Langmuir isotherm. So in this case in table it is given that at different temperature at different pressure what will be the concentration of that propane gas that is adsorbed onto the surface of the adsorbent and here in the table it is shown and after that what we have to do you have to plot this experimental data in this graph here. You have to plot where in x-axis it will be  $1/P$  and in y-axis it will be  $1/C_m$ . So you have to calculate what will be the  $1/P$ , what will be the  $1/C_m$  also from this table and then you plot it. So at different temperature you will get this different profile and if you feed this profile by least square method you will have this slope and intercept.

So suppose if you consider this the profile at this 283 K so this will be your profile and this profile will give you the slope as 0.2511 and intercept will be 0.2283. So we are getting this slope and intercept and once you get this slope and intercept then what will be the value of  $C_m$ . So  $C_m$  is equal to  $1/\text{intercept}$  then you can calculate and B will be equal to  $\text{intercept} \times \text{slope}$  then you can easily calculate what will be the  $C_m$  and B for respective temperature similarly.

So for 283 K we are getting  $C_m$  will be equal to 4.51 and B is equal to 0.883 whereas at 303 K this  $C_m$  will be equal to what 3.88 and B is equal to 0.

671 and at 333 K  $C_m$  will be equal to 3.68 and B will be equal to 0.197. So in this way you will be able to calculate at a different temperature what will be the maximum adsorbed concentration of that solute onto the surface of the adsorbent. So if you increase the temperature this  $C_m$  is coming to decrease whereas B value is also it is seen that will be decreased. So  $C_m$  and B this is actually the parameter these are the parameters from that Langmuir isotherm.

So how to calculate that Langmuir isotherm parameters from the experimental data you can understand now. Now let us discuss another isotherm that is empirical it is widely used also it is called Freundley's empirical isotherm and in this case this isotherm is expressed by this equation number 13 and it is developed in 1909 by scientist it is called Herbert Freundley's this is German chemist and he has suggested that this adsorption concentration which is varying with that pressure will be related by this equation 13 that will be equal to  $C_{\mu}$  that will be equal to  $k p$  to the power  $1/n$

Here the Equation

$$C_{\mu} = KP^{1/n}$$

where  $n$  is a some coefficient or constant you can say and this  $n$  value will give you that the characteristics or behavior of that molecules adsorption onto the surface of the adsorbent. In that case if  $n$  is greater than 1 or is larger the value of  $n$  the adsorption isotherm becomes more nonlinear as its behavior deviates further away from the linear isotherms and for  $n$  is greater than 10 the adsorption isotherms is approaching it is called that rectangular isotherms or irreversible isotherms it is called the pressure or concentration needs to go down to an extremely low value before adsorbent molecules would desorb from the surface. So, this is the criteria where if you are getting that  $n$  is greater than 10 in that case you have to control that surface of that adsorbent molecule to get your better yield. So, another coefficient is called  $k$ ,  $k$  is also a parameter that actually decreases or depends on that temperature and also other characteristics of that flow condition even flow pattern like this.

So, we are having this  $C_{\mu}$  is equal to  $k p$  to the power  $1/n$  here

Here the Equation

$$C_{\mu} = KP^{1/n}$$

also you have to find out that parameters  $k$  and  $n$  from the experimental data. So, to do that you have to take a logarithm on both sides and then plotting that data after calculating from that experimental observation. So, in this case you will have some limitation of this Prandtl's empirical isotherm this is actually though popularly used in adsorption of organics from aqueous streams on to the activated carbon but it does not have a finite limit when pressure is sufficiently high and also to find that parameters that you have to follow this equation 15 and 16.

$$\ln(C_{\mu}) = \ln(K) + \frac{1}{n} \ln(P)$$

$$K = (\delta A_0) P_0^{-R_g T / A_0}$$

$$\frac{1}{n} = \frac{R_g T}{A_0}$$

So, what you have to do you have to take a logarithm on both sides of that equation number 13 here that is Prandtl's isotherms empirical isotherms and then k where this k can be calculated based on this equation number 16 and here  $1/n$  will be equal to here  $R_g T$  by  $A_0$ . So, this  $n$  basically depends on that characteristics adsorption potential that is denoted by  $A_0$  and also this temperature of that adsorption condition and this constant  $k$  depends on that pressure as well as temperature there and also some characteristic adsorption potential.

So, you have to find it out that  $C_{mu}$  and  $k$  and then  $n$  value from that experimental data. Now let us do an example of the same propane gas adsorption on to the activated carbon which is done experimentally and the experimental data as are given here in the table and then in this case again we can calculate that what is the  $\log P$  or  $\ln P$  you can say and what is the  $\ln C_{mu}$  and after that you just plot it in a graph and then that you will get that different profile at different temperature and from that temperature you will get that different coefficient and slope and that coefficient and slope will give you that value of  $k$  and  $n$  value. So at 283 k will be equal to 2.58 and  $n$  will be 7.

01 whereas at 303 Kelvin that  $k$  value will be equal to 2.13 and  $n$  will be equal to 6.38 and at 333 Kelvin this  $k$  value will be coming down to 1.75 and  $n$  will be equal to 5.98. So in this way you can easily calculate what will be the value of  $k$  and  $n$  from the experimental data.

So I think you understood that what are the different adsorption isotherms or adsorption equilibria based on which you can assess that what extent of molecules or concentration can be adsorbed onto the surface of the molecule based on pressure and temperature change. And I think you understood if you have any other doubt you can consult with me by this email and the next lecture will try to understand more about this adsorption and there we will discuss about that some kinetics theory based on which how that adsorption also can be assessed whether it will be the first order or pseudo first order reaction or not or some other conditions for that adsorption or not. So I think you will understand these things and you please go through the slides once more if you have any other doubt for this mathematical expression for isotherms and also to solve. So thank you for your attention. Have a nice day. Thank you.