Course: Adsorption Science and Technology: Fundamentals and Applications

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Week 01

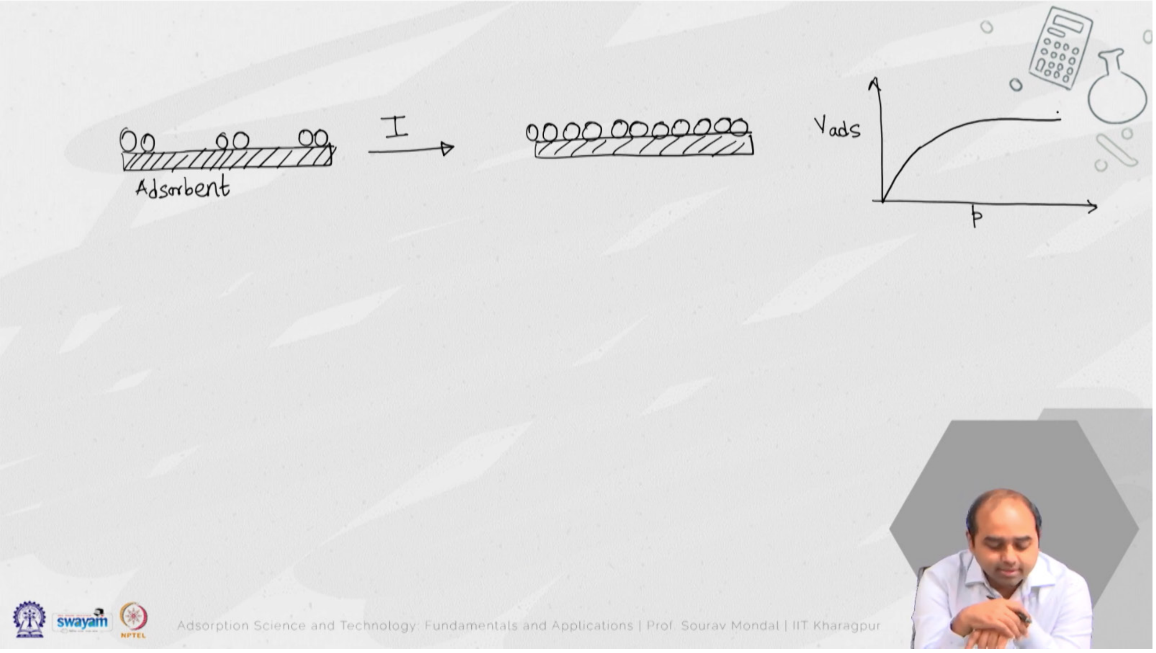
Lecture 4 | Adsorption Isotherm

Hello and welcome to everyone on this class of adsorption science and technology. And today we are going to talk about the different types of adsorption isotherms that is normally observed in this process. I hope all of you have gone through the previous lecture on the relevance of adsorption isotherm. So, adsorption isotherm is essentially the profile or the functional relation between the amount that can be absorbed with respect to the adsorbate concentration in the solution phase. Adsorption isotherm is very important and you will see that almost for characterizing any adsorbents, its capacities, its isotherm nature profile. It is in this range of the intermolecular forces all of these key information ah is actually available or actually can be obtained from the adsorption isotherm.

So, let us look into what essentially the adsorption isotherm, you know relates to and how we can relate and how we can connect this idea or this process mechanism to the different types of you know adsorption that is happens normally with any system. Now let us consider a layer of the solid on which the adsorbate species is getting bound So, let us say this is an adsorbent and over which there is some you know adsorbate species which is bounded. Now in this case you can clearly understand that this is a situation when the molecules are forming only a single monolayer of adsorption over the surface of the adsorbent. Of course, at this stage the number of molecules is not sufficient enough to provide a complete coverage or attachment to all the adsorbent sites and naturally it is partially covered.

Now, the next step from here is this, where we see more coverage of the surface of the adsorbent by the adsorbate species, right this is how normally it happens. So, first when the molecules diffuse and comes close to the adsorbent sites, it will start you know getting occupied at the different adsorbent locations or the sites. And slowly once all the locations are covered it will have more or less a mono layer or one molecular layer thick of this adsorbate molecules formed on the surface of the adsorbate. Let us call this as step 1. Now in this step 1, if we try to draw the isotherm diagram how does it look like.

So, if I try to draw it as a function of the volume of the adsorbate species with respect to the you know partial pressure of the particular species molecule or the concentration whatever. As the concentration or the partial pressure is increasing the volume of adsorption is also increasing continuously until a point till this coverage is complete. So, beyond this coverage is complete there will be no further adsorption unless we talk about further detail there is other possibilities. So, in this step 1 we can expect that this volume of adsorption or the species the volume occupied by the adsorbed species is increasing proportionately with the partial pressure and there will be a saturation because beyond that point all the adsorbent sites would be covered and no further adsorption would be possible. So, this is what would look like in this step 1.



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Now, let us see what happens you know beyond this. So, what I mean that from here if you further increase the concentration of the species and if there is a possibility or of more and more adsorption, then will be one molecular layer thick of first of the adsorbate species and over which there will be formation of more attachments. Of course, this may not be possible with all adsorbent, but if this is possible then this kind of adsorption will start to happen. Similarly, here also if this multiple layer adsorption is allowed or it if it happens then there is a possibility that something like this is also happening here even at the this discrete locations like this. So, even before complete coverage of one molecular layer thick process there could be formation of the multi layers right.

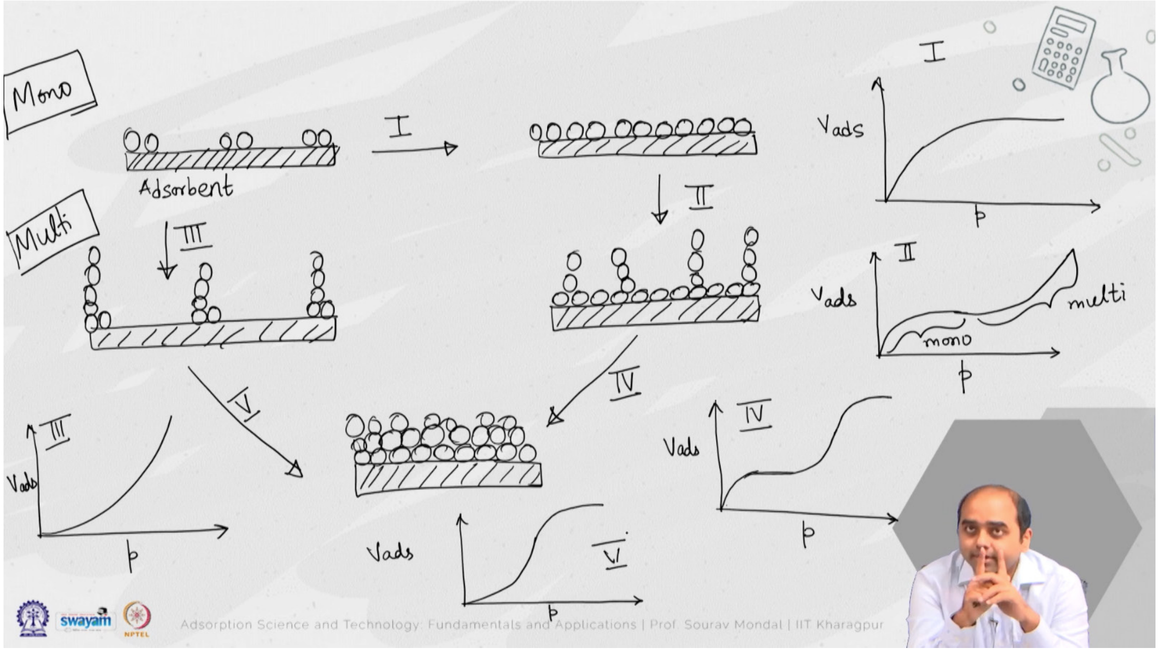
So, let us designate this step as number 3 maybe this as number 2 something like this. Now from here, from step 3 or step 4, what essentially one can get is something like this, formation of complete coverage of multi layers. Now this can happen from here as more and more molecules get deposited attached with multilayer formation. So after monolayer multilayer starts to form and then there is multilayer coverage. Maybe we designate this as step 4.

It can be also possible that individually there is partial coverage at discrete locations and then there is formation of multiple layers at those discrete locations and then you have monolayer coverage. Let us call this as step 5. Now, let us try to see how does the adsorption profile looks like. So, this is for the first step. For second step that is this scenario this second step of first monolayer and then there is formation of the multilayers.

So, we will have the monolayer profile like this and then once the multilayer starts it will continue to increase. So, this is like step 2 where this part is monolayer and this part is multilayer. So, this is first monolayer and this is multilayer. So, both step 2, 3, 4, 5 all are multilayer step 1 is monolayer formation. So, this is how it looks here on the you know mono then multilayer.

So, this is step 2. In the case of a step 3, there is no monolayer formation right. It is only at partially covered locations and then start to formation of the monolayer. So, in step 3 or in the kind of if if the adsorption process is dominantly of step 3 type where there is multilayer formation without the formation of any monolayer. Then one would get something like this.

So, this is step 3 type or type 3 mode where there is continuous you know multilayer formation there is no question of any monolayer any step. Now, coming to step 4 and step 5. So, in step 4 first, you have monolayer, then you have multilayer and then you again have complete coverage of the multiple layers. So, step 4 would look something like this, first monolayer then multilayer and then there is saturation because multilayers are again getting converted like as sets of monolayer. So, first you have monolayer, then you have multilayer and then multiple layers forming like you like different you know multiple monolayers. So, this is what one would designate a type IV adsorption.

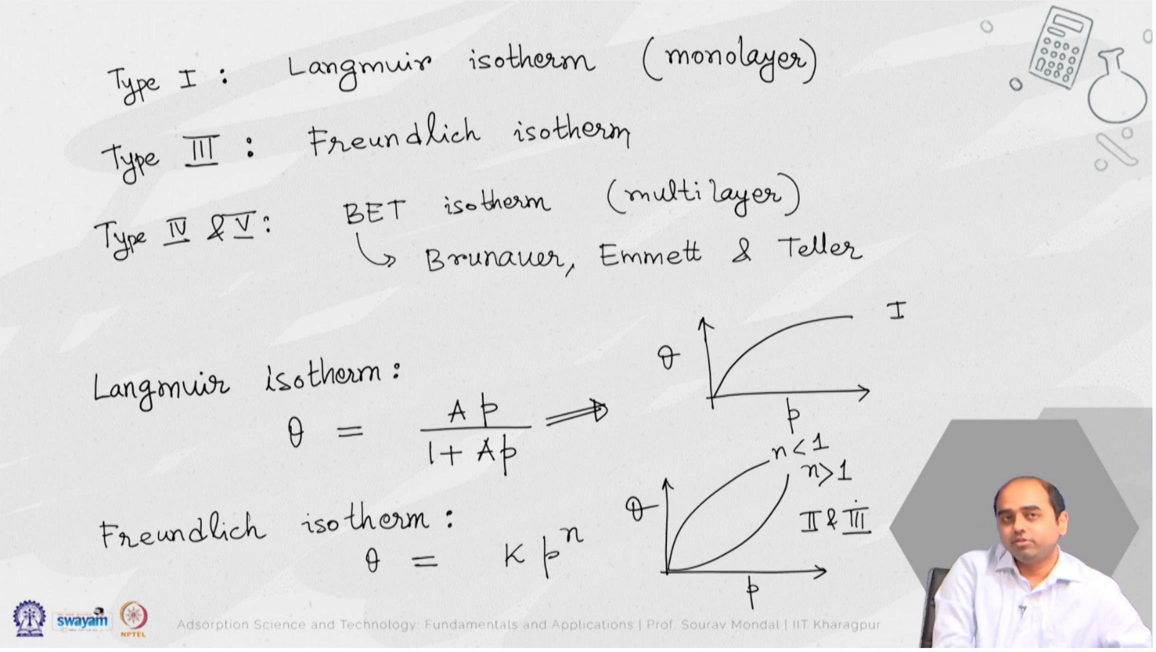


and type V would look like first completely multilayers and then multilayers getting saturated as monolayer. So, this is type V nature of the isotherm. So, all of these different types, these are the only possible five types of adsorption that happens. And I have tried to explain you the different nature of the adsorption isotherms that can be explained from the basis of their type of adsorption. Type 1 that we have discussed formation of the monolayer is designated as the Langmuir isotherm model.

So, as you can understand this is strictly a monolayer formation basis. Type III right as well as to some extent you know type II is represented by the Freundlich isotherm, right. Type 4 and 5 which are strictly you know multilayer formations, they are described by the BET isotherm. So, the name BET stands for name of after three scientist who actually have pioneered this description of the multilayered adsorption process. Brunauer, Emmett and Teller, they are represented strictly the multilayer formation isotherm mechanisms.

We will discuss in detail about the Langmuir isotherms in the upcoming classes. So, here I want to talk about nature of the different isotherm models. So, the Langmuir isotherm is represented, by this mathematical formula, theta as a p or I can write it in a slightly different form as this. So, this is a one constant model where theta represents the fraction of the surface coverage or the fraction of the amount that is absorbed. The Freundlich isotherm is a two constant model.

It can be represented in the form as, this amount that is absorbed something like theta is equal to some constant let us say k partial pressure to the power n. So, mathematically this Langmuir isotherm the nature of this curve if you try to plot this mathematically as theta versus you know p this will take the shape of like this. Whereas the Freundlich isotherm, so this is strictly type 1. If you see in just now we have discussed type 1 here. Whereas for the Freundlich isotherm this will take the form of this shape for n greater than 1 which is of type 3, a multilayer formation.



Type I : Langmuir isotherm (monolayer)

Type III : Freundlich isotherm

Type IV & V : BET isotherm (multilayer)

↳ Brunauer, Emmett & Teller

Langmuir isotherm:

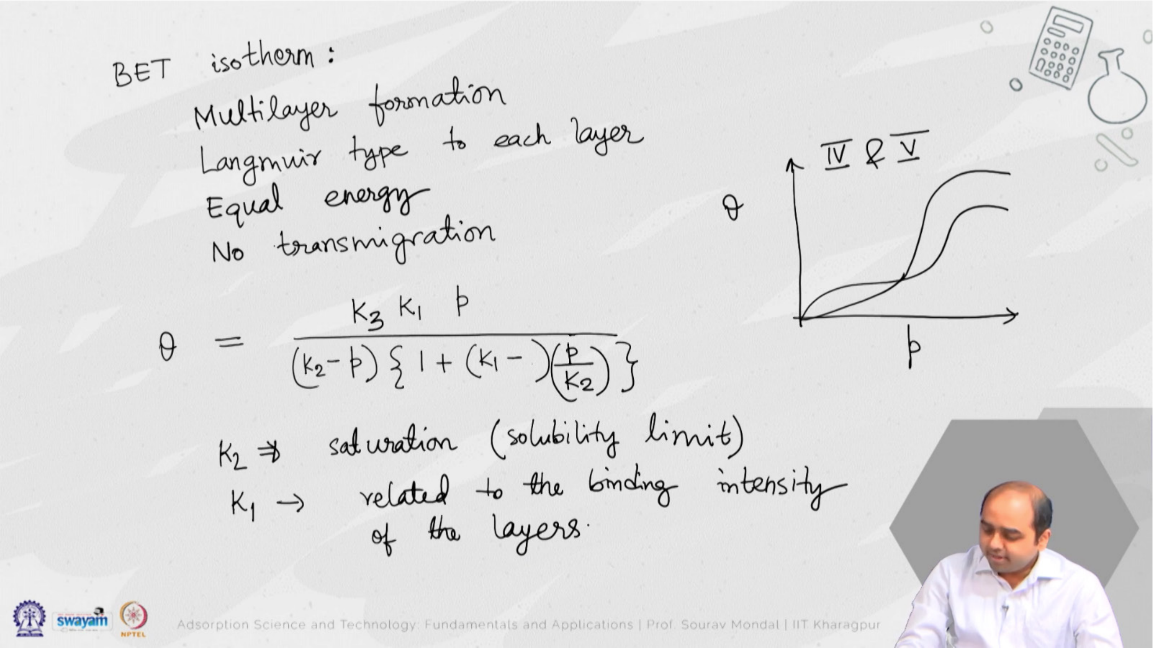
$$\theta = \frac{Ap}{1+Ap} \Rightarrow$$

Freundlich isotherm:

$$\theta = K p^n$$

It can also be used to draw curves of n less than 1 which can describe types 2. So, combining n less than 1 and greater than 1 can be used to describe type 2. So, both type 2 and type 3 can be described by Freundlich isotherm. BET isotherm is slightly more mathematically complex. So, this is based on the assumption that there is multiple ah you know multi-layer formation and essentially you also assume that it is Langmuir type in each of these layers.

There is monolayer formation in each of these layers is also established in this multilayer formation. Each of these layers also have equal energy that is maintained. There is no transmigration or there is no inter particle or intermolecular interaction, after it is adsorbed. This is typically represented using a three constant model, we can write them as like this. and this can be used I mean the nature of this curve if I try to draw with respect to the partial pressure this can describe both this type of nature as well as, all these curves which essentially as you know are type 4 and type 5 processes.



BET isotherm :

Multilayer formation
Langmuir type to each layer
Equal energy
No transmigration

$$\theta = \frac{K_3 K_1 p}{(K_2 - p)\left\{1 + (K_1 -)\left(\frac{p}{K_2}\right)\right\}}$$

K_2 ⇒ saturation (solubility limit)
K_1 → related to the binding intensity of the layers.

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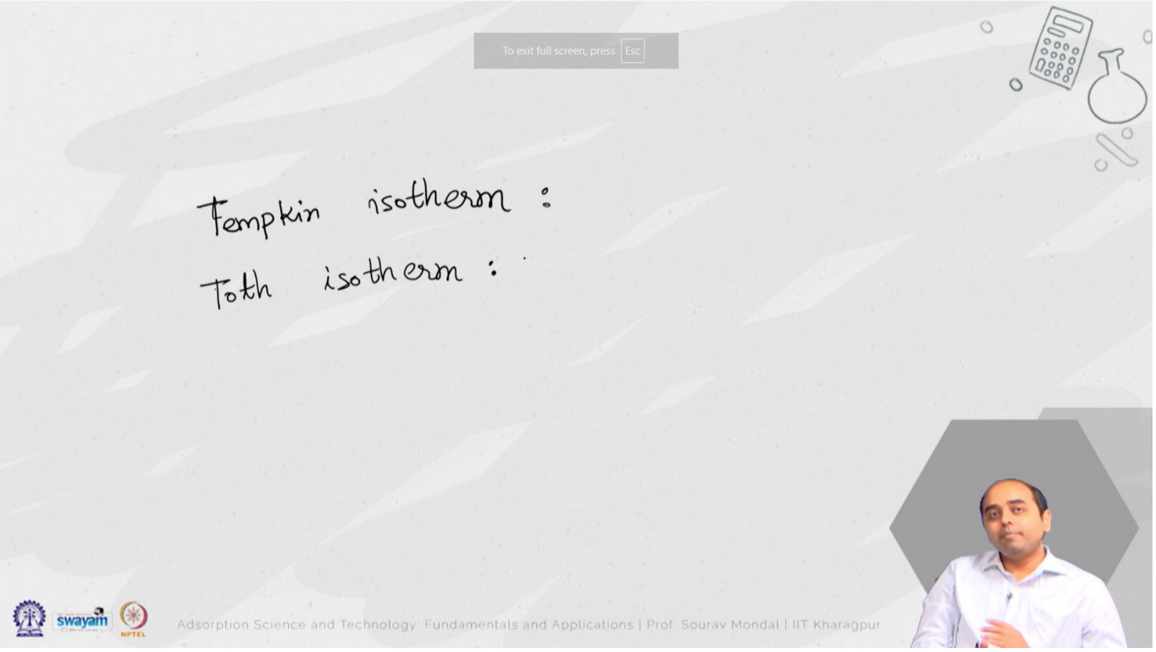
Here typically this parameter k2 represents the saturation or the solubility limit and this K1 represents or related to the binding intensity of the layers. So, these are the different types of isotherms which are generally used or generally relevant. There are also some other types of isotherm for example, Temkin isotherm is there then you have TOTH isotherm ah which are also something ah quite ah you know popular ah I can write the names ah we have Temkin isotherm then we have this dot isotherm. So, each of these different isotherms are actually evolved, you know based on the understanding of the process trying to explain the behavioural dependence of the molecular interaction or the adsorption mechanism with respect to its molecular level picture. And also it helps to relate ah the equilibrium behavior of the adsorbate species with respect to the adsorbent.



Tempkin isotherm :

Toth isotherm :

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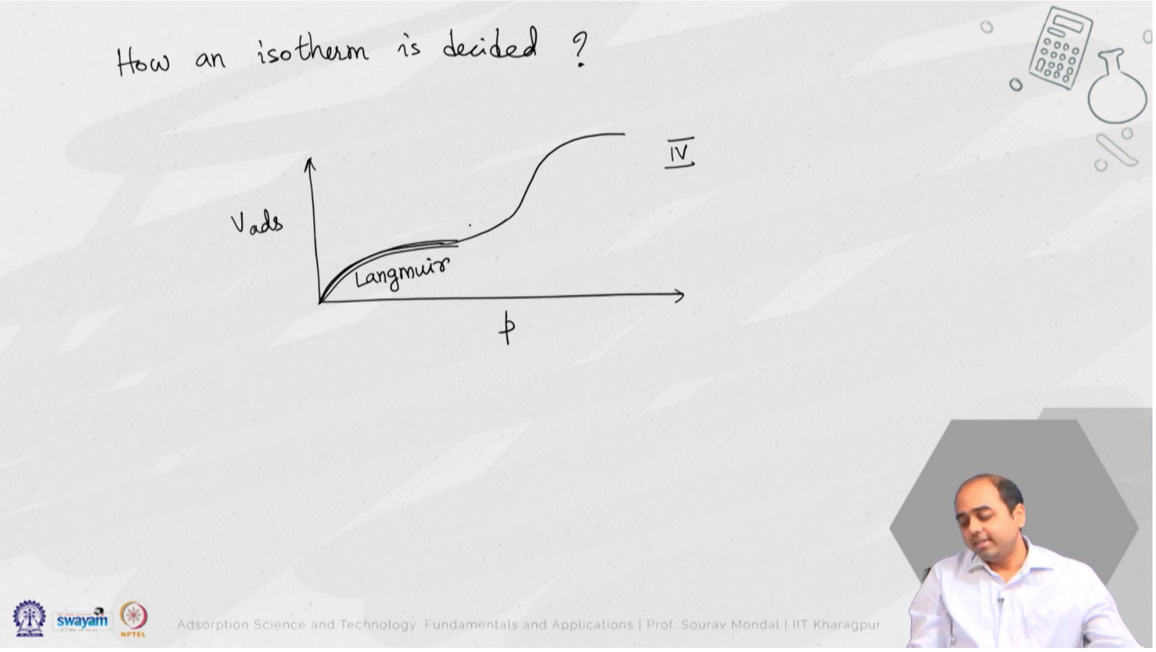
Each of these you know, isotherms has its own application in terms of describing the molecular picture as well as the process mechanism. How an isotherm is decided? So, typically what is done is that based on your experimental data of the amount that is adsorbed with respect to the concentration or the partial pressure of the species, one should attempt to fit that, you know that experimental data with the different mathematical models corresponding to the different types of the adsorption isotherm equations that are available or that one things is applicable in this case. Then you find out what is the regression coefficient or what is the level of fitting the statistical quantity that regression ah adjacent regression. um coefficient uh how how close is it to unity is something helps you to decide that which one is a good fit so for example if you have an experimental data you would like to fit i mean you do not know whether it is a monolayer or a multilayer which of these five types it ah you know it follows. Then you fit this experimental data with your you know Langmuir model, Freundlich model or BET model and see what is the regression fit or how good is your regression or how good is your mathematical fit ah the model fitting to the ah you know to your experimental data.

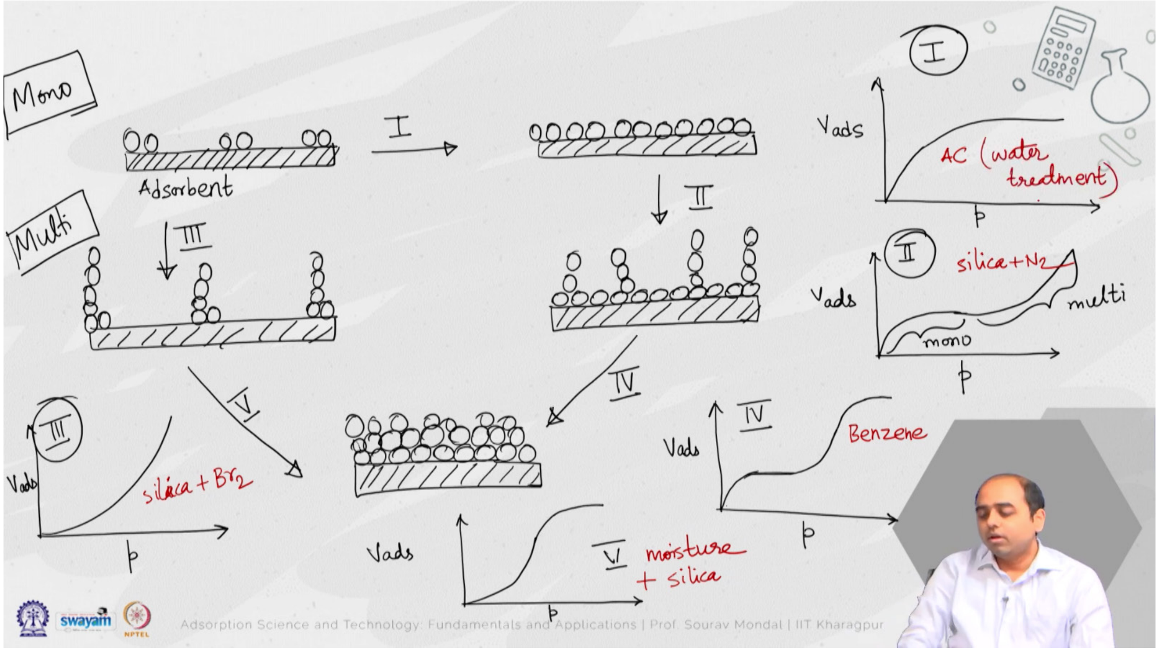


How an isotherm is decided ?

The depending on the goodness of your fit you can decide which is more dominant or which phenomena is more dominant in this case. It may be noted that you know the range over which you would like to do your actual you know process application, the isotherm should identically be you know established at that level of the concentration. So, why this is important or why I am emphasizing on this point is that the at increasing levels as you can see for type 3 and 4 at increasing levels of your concentration or partial pressure the nature of the isotherm can actually change. So, this is for example, is a type 4. So, you can see that at low concentration or at low pressure this behavior is of Langmuir type right.

So, if your operation is at low concentration, then you may not be actually encountering a situation of multi layer formation and the process is good enough or can be explained with respect to the Langmuir type behavior, but even though there is a possibility of multi layer formation you may not be in that kind of range. So, the isotherm should be established only within the range of your experimental domain and you should make sure that the correct mathematical model is decided for that particular range. One thing I must say or add here is the different types of isotherms that we have discussed here. Let me give you some small examples or one example for each case as a relevance. So type 1 is the normal Langmuir type.

So you can think of any activated carbon. you know operation with any water treatment or organic molecules or you know removal of carbon dioxide or you know this ammonia is mostly of this type ah type two is generally you know silica ah for removal of moisture type ah three the friend which type is like ah silica sorry silica removal of bromine. Type 4 is benzene with removal using ferric chloride or ferrous chloride. Type 5 again could be removal of you know moisture with respect to silica or activated carbon.



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So, with this I would like to close this lecture, I hope all of you have found this useful.

In the next class I will talk about ah Langmuir isotherm its derivation and its ah physical ah significance. Thank you for all your attention, hope you find this useful.