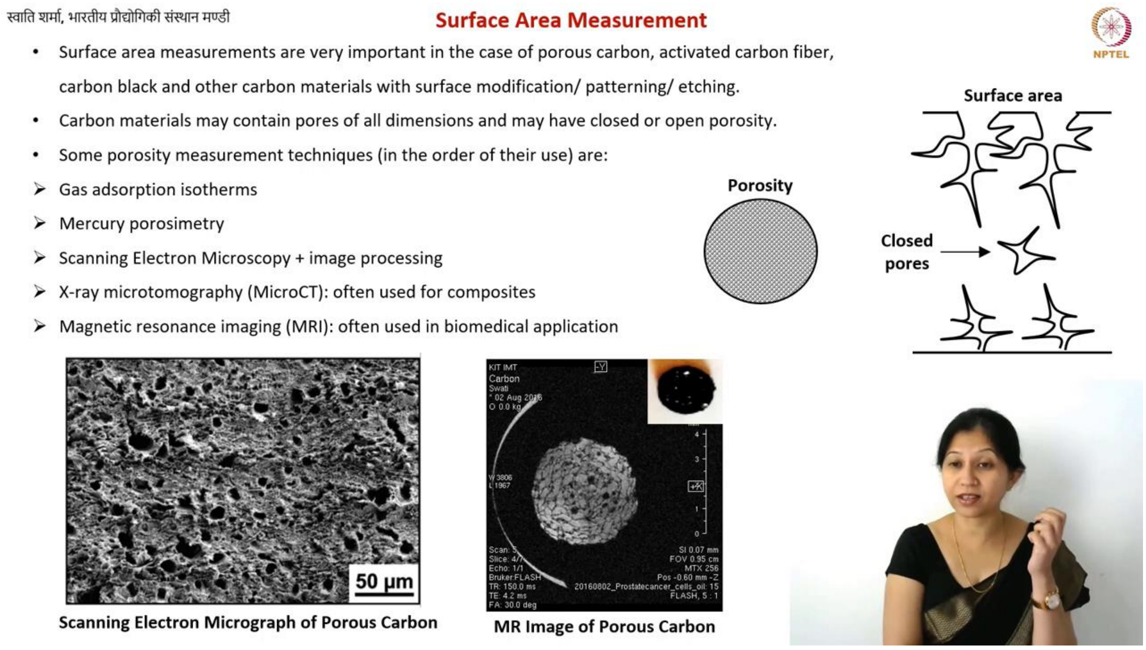
Carbon Materials and Manufacturing
Prof. Swati Sharma
Department of Metallurgy and Material Science
Indian Institute of Technology, Mandi

Lecture - 55
Surface Area Analysis of Carbon Materials

(Refer Slide Time: 00:13)



स्वाति शर्मा, भारतीय प्रौद्योगिकी संस्थान मण्डी

Surface Area Measurement

- Surface area measurements are very important in the case of porous carbon, activated carbon fiber, carbon black and other carbon materials with surface modification/ patterning/ etching.
- Carbon materials may contain pores of all dimensions and may have closed or open porosity.
- Some porosity measurement techniques (in the order of their use) are:
- ➢ Gas adsorption isotherms
- ➢ Mercury porosimetry
- ➢ Scanning Electron Microscopy + image processing
- ➢ X-ray microtomography (MicroCT): often used for composites
- ➢ Magnetic resonance imaging (MRI): often used in biomedical application

Scanning Electron Micrograph of Porous Carbon

MR Image of Porous Carbon

Hello everyone, in this lecture we are going to discuss one more characterization technique called Surface Area Measurement using Gas Adsorption Isotherm. We have discussed transmission electron microscopy, Raman’s spectroscopy and X-ray diffraction. These are some of the very important techniques for carbon materials. So, these are the techniques that are essential that you must know; that does not mean that there are no other characterization techniques. That will depend upon the exact application that you have and exact type of carbon material that you are using.

For example, if you want to use the magnetic property of certain carbon material; in that case, you will require a completely different set of additional characterization techniques, but these are the basic things you will always use because crystallinity is always important. Especially when we are talking about graphitic carbon materials, crystallinity is always important and for that, we use X-ray diffraction, Raman spectroscopy and also TEM at some point. We also use scanning electron microscopy, may be briefly I will discuss it here as well.

We definitely use these techniques. Now when does surface area become very important? When we are dealing with activated carbons or other types of porous carbons or when we are dealing with carbon black. So, if you remember we have these fluffy carbon black particles, when something is fluffy; that means, there are some pores.

And then we need to somehow measure what is the surface area. By the way, surface area and porosity are very closely related; however, it is not that every time you induce porosity, you will have surface area increase because as the name itself suggest is just the area is the 2D thing.

So, if you are inducing some sort of volume porosity, it will enhance or increase the surface area if and only if your pores are reachable from the surface. If it is closed porosity, you already have an impression of the closed porosity maybe I will also describe a little bit more; so, if your pores are closed, in that case, it will not really reflect in your surface area measurements.

But in general, if the porosity is increased often it happens that the surface area also increases especially in the case of activated carbon because a lot of pores are connected percolated. If you remember that we talked about the fractal-like geometry which means you have larger pores smaller pores even smaller and smaller.

you have also the porosity very nicely distributed in porous carbon materials. Actually, this is also very interesting subject for surface area measurement because when you increase porosity, sometimes it is just one type of pore that charge; the number of these kinds of pores or fraction of these kinds of pores that increases.

And sometimes it is the fraction of all types of pores increases. That would depend upon your activation method and that also depends upon the type of carbon, whether it is formed by the charring process whether it is formed by the coking process or whether it is a very highly graphitic material; depending upon all of these things and also the physical structure of the material.

For example; are you activating carbon fibers or you are activating something in bulk or you have a well-patterned structure let us say micro nanoscale structure and then you are trying to activate it. So, it will always have just a different pattern of porosity all together.

And the idea is that should we able to measure the net surface area or is it also possible for us to know which types of pores do we have? Are the small pores that are increasing or the larger ones that are increasing? You know that both are important for us. We will see how we can do that. First of all, this is the image again from this activated carbon lecture.

So, you remember these pores; these are called the fractal-like geometries. Now let us say this was a piece of wood or it is a branch of a tree. On the top surface, it had some pores and now also on the bottom surface, there are some pores right. These may be smaller or they may be of the same size I have just drawn them.

You may also have some pores in the middle which are not reachable, which are not connected to top or bottom pores and these are the ones that we call closed pores. Basically irrespective of the geometry of the pore, whether it is spherical or not, does not matter as long as it is not reachable from the top or bottom or any open surface; in that case, we call it closed pore otherwise we call it an open pore.

We also have carbon black particles, here I have shown this porous kind of carbon particle. It does not have to be carbon black, it can be other forms of carbon as well. But, the idea is that you should have then very small crystallites, very small turbostratic crystallites and in that case, the porosity of these materials also becomes important.

See porosity has direct relations to adsorption. In fact, that is the principle that we are using for the measurement of porosity which also means that if you want to use certain carbon material for adsorption applications, in that case the porosity is very important to you. So, that is the reason we measure the porosity.

So, some common techniques I will first tell and a number of techniques that are used. And some of them are more common than others the one that we are going to discuss; gas adsorption isotherms is the most common technique. Now, of course, using that technique you can get information about closed pores. And you cannot even get very accurate information about the surface area which I am going to discuss; however, you get a very good idea of the surface area also if you want to make comparisons.

For example, if I have three types of carbon materials; one I have just taken as the sample itself. And then the second one I performed from some activation. On the third one, I performed even more activation. What do you mean? This means that you are inducing more and more porosity and also chemical functional groups, but in some cases, but you are inducing more porosity.in that case, I can definitely get a relative value of how my porosity is increasing and how effective is my treatment method.

So, this information may not be very accurate like if I say my whatever is the number of my activated carbon surface area maybe it is slightly more than that or maybe even it is slightly less than that, maybe some pores could not be reached, but at the same time, I get more or less accurate information because at least to understand my fabrication process. this is very important and this is very useful.

The first one we are going to discuss is gas adsorption isotherms. What is adsorption? It is just a surface phenomenon. So, adsorption means that something is going and sitting on your surface. Some molecules of gas because you see it is written in gas adsorption.

So, some gas molecules will go and get physically adsorbed on top of the surface of your carbon material. So, they go sit there and somehow we need to measure how many molecules are going and sitting there. If this is a flat surface then the number of these molecules will be less; if this is more, there is more surface area and more molecules will go inside these sites or pores.

If they can go far inside the material then there are even more molecules that are going inside the material. How do you measure that? Well, one easy way to measure is that you observe the change in the pressure of the gas the partial pressure. Because that is very much possible. The equipment that we have, I am going to show you schematic on the next slide. This equipment basically utilize the inert gases; in most cases nitrogen or argon also in the case of carbon and there you see argon.

You will have these inert gases which will go and sit on top of the surface on the porous carbon sites and then you will basically measure the difference in the pressure and initial pressure. So, this is the relative pressure that you are measuring. Why do we choose inert gases?

Because we want to make sure that the adsorption is just physical and not chemical. So, the gas itself should not react because if there is any attractive force when it comes to whatever your porous carbon or any other materials also not just carbons, will also have some surface properties.

And you do not want your gas itself to start reacting with the surface property. Now in some cases you will also use carbon dioxide. You will also make here and there also utilize the property of chemical adsorption. But then you need to be very specific about what are the surface groups on your surface and you are also confident that they are evenly distributed on top of your surface and then you also can actually use some chemical adsorption.

But in most cases, the physical adsorption is used. The molecules of whatever gas you are using should be small enough, so that they can go all the way inside because you may have very small pores; smaller than 2 nm pores. In fact, there are a lot of pores that are smaller than 2 nm. So, in that case, you should also have gas molecules that are small enough.

So, this is something we are going to discuss in further detail before that, let me tell you about the other techniques, other at least well-known techniques i.e. mercury porosimetry. I will not go to the details of this technique, but this is basically something that is used for large-scale pores.

When you have macro pores for example, or meso pores in that case, you typically would use mercury porosimetry; as the name itself suggest there is mercury involved in it. So, I will not go into the details this is yet another technique. SEM imaging, so we talked about TEM. SEM how can we use that?

So, SEM image of porous carbon, it can see even only tell you about the surface. Now, what you can do? Anyway, so, number 1 — you will only know about the surface, not about if your pores are cylindrical or how deep down to the go and also whether or not your pores in the middle of the material; let us say are connected to the top layer.

So, you only get the top view, if you take this kind of standard SEM image. And then you will see that there are some pores. Now based on the contrast in this image, you can actually perform some image processing and that will give you some idea of what is the volume or what is the surface that is covered by the pores, not volumes because right now we are talking about 2D.

You can extrapolate it to volume and I will also tell you tricks that will help you understand the volume porosity. But with this image you can plot your own histogram. So, you can also perform the image processing using some software that is available. Nowadays there are a lot of free software that are available.

You can basically use them and you can just upload your image and calculate the porosity, but that is something I do not recommend not just for SEM or image processing, but for anything. Even gas adsorption isotherm you have equipment; you upload your sample and you may actually get some data from it, some numbers from it.

But you need to know how exactly the isotherms were interpreted. So, interpretation of anything, you should know only then you can get accurate values and reproducible values. Also, same thing for image processing, you will see if you plot your own histogram, you will see that even by changing the parameters slightly, you may actually get different values of your porosity.

So, that is something you need to learn. If you want to just get a relative value or, if you keep on performing certain activation and you want to just get a relative value then you can use SEM images. So, I was saying that you could also see the volume porosity.

Can you think of something? If I want to see inside the material, let us say I have a film of some carbon material and this is a porous film and I want to see what is the porosity. Now I have just taken this image. Now, if I want to see the cross-section the film which is very thin.

So, I want to see the cross-section of this very thin film let us say it’s 50 micrometer. Now SEM machines typically allow me to tilt my sample a little bit but only to a certain degree. And also your sample depends; it might be very fragile and it depends also how nicely cut your edges.

What you can do? If you can take 2 structures and you can take some rigid material, for example, silicon wafer. You can take 2 silicon wafer and sandwich your thin film between them. And then accordingly you can now cut it with a diamond saw and then take the cross-sectional image.

You can use diamond saw, it will induce some defect, but it is not that bad because we are dealing with porosity and not microstructure right now. So, if you want to get at least the information about how deep your pores are and whether or not they are cylindrical; that kind of information you can get by this kind of cross-sectional imaging.

The other thing that we have here is X-ray micro tomography or MicroCT which is the commonly known term for this technique. You already understand X-ray imaging. X-ray imaging is the same principle that you know if I take the images my bone is pretty much the same principle; the only difference is that now we are taking images at a microscale, so the sample size is much smaller.

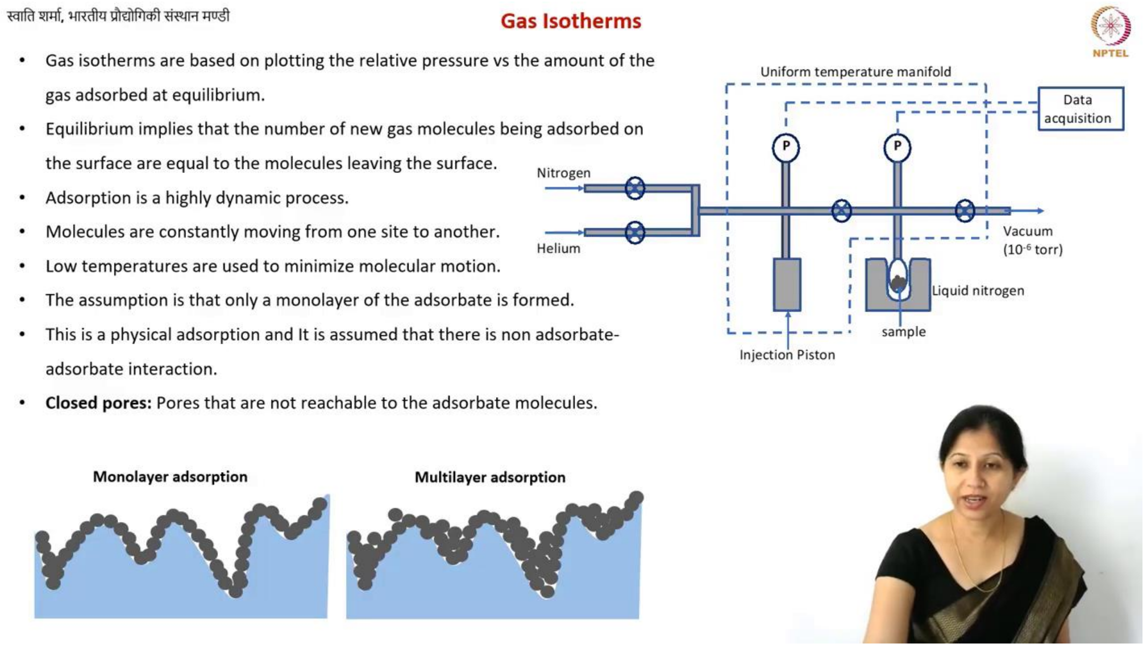
Now we are using a carbon material, often elemental carbon. It is challenging to perform MicroCT for carbon material, why? Because carbon materials have high transparency to X-rays. So, it is challenging to get a reasonable contrast in the image. But this is also one technique that has been tried out. What else? I have also written magnetic resonance imaging.

So, again MRI is a biomedical imaging technique, but you can also use carbon materials. Generally they do not often cause too much artifact or anything because you see the NMR active or MR active carbon isotopes C13 is only 1.1 percent. So, that does not really interfere with your imaging. So, you can actually perform imaging using MR techniques, but at the same time, there are certain challenges involved because you may get some air bubbles trapped inside your structure.

Air bubbles can cause a lot of artifacts; air bubbles often can be seen because, in the case of MRI you will often have heavy water-filled inside your structure and then you will try to image it and that is really challenging because of the presence of air bubbles. But this is also one technique that has been tried out. I have shown also 1 image of porous carbon.

If you remember this was this image I have shown you also before in some lecture now I do not remember, but this is basically a 5 mm. So, you see it is carbon, so the porous carbon structure which has a 5 mm diameter. So, these kinds of structures then you can image using MR also.

(Refer Slide Time: 15:58)



स्वाति शर्मा, भारतीय प्रौद्योगिकी संस्थान मण्डी

Gas Isotherms

- Gas isotherms are based on plotting the relative pressure vs the amount of the gas adsorbed at equilibrium.
- Equilibrium implies that the number of new gas molecules being adsorbed on the surface are equal to the molecules leaving the surface.
- Adsorption is a highly dynamic process.
- Molecules are constantly moving from one site to another.
- Low temperatures are used to minimize molecular motion.
- The assumption is that only a monolayer of the adsorbate is formed.
- This is a physical adsorption and It is assumed that there is non adsorbate-adsorbate interaction.
- **Closed pores:** Pores that are not reachable to the adsorbate molecules.

Now coming to the gas adsorption isotherms. So, again you know what is adsorption. And we also now know that we have an inert gas that is getting adsorbed and we are measuring the partial pressures. This is what I have written here. These basically are the plots of the relative pressure versus the amount of gas adsorbed at equilibrium.

The important term is at equilibrium because this is highly dynamic process: the adsorption of gas molecules on top of certain surface because these gases are very dynamic. The molecules are moving all times and the frequency of the movements is actually very high.

So, at any given point, you do have a lot of gas molecules being adsorbed on the surface of the structure and also leaving the surface. So, equilibrium basically means when we have the number of adsorbed molecules and the number of molecules leaving the surface equal, that is what we call equilibrium.

At equilibrium the value of the partial pressures that you will get; if you plot it against the concentration of the gas or you know among being adsorbed, in that case, these plots are known as gas isotherms. Here I have shown in the schematic of the equipment, that is typically used.one important thing here is that there are a lot of valves and there is some detector and there is sample holder and so on.

Important thing is that you have liquid nitrogen-filled around your sample. Why are you using it here? Of course, you are using some gas for adsorption. So, it can be nitrogen, it can also be argon, helium, but you also have the liquid nitrogen to maintain temperatures when you are performing this experiment.

And why? Because see this is a very dynamic process, I already told you. it is used to minimize the motion of the molecules; we have to use a very low temperature. So, liquid nitrogen are used for this purpose. These are the things that I already told you that adsorption is highly dynamic process and in fact, also we want essentially physical adsorption.

But it is also possible that here and there, you will have some chemical adsorption, let us take the example activated carbons. They have very a variety of surface functional groups that would depend upon your activation method. Although they will not form chemical bonds with the inert gas at that given temperature, but there can be some sites that are more active than the others.

So, there may be some, not chemical adsorption, but there may be some sites which are more open to adsorbing something than the other sites. So, the values that you will get is not necessarily accurate.

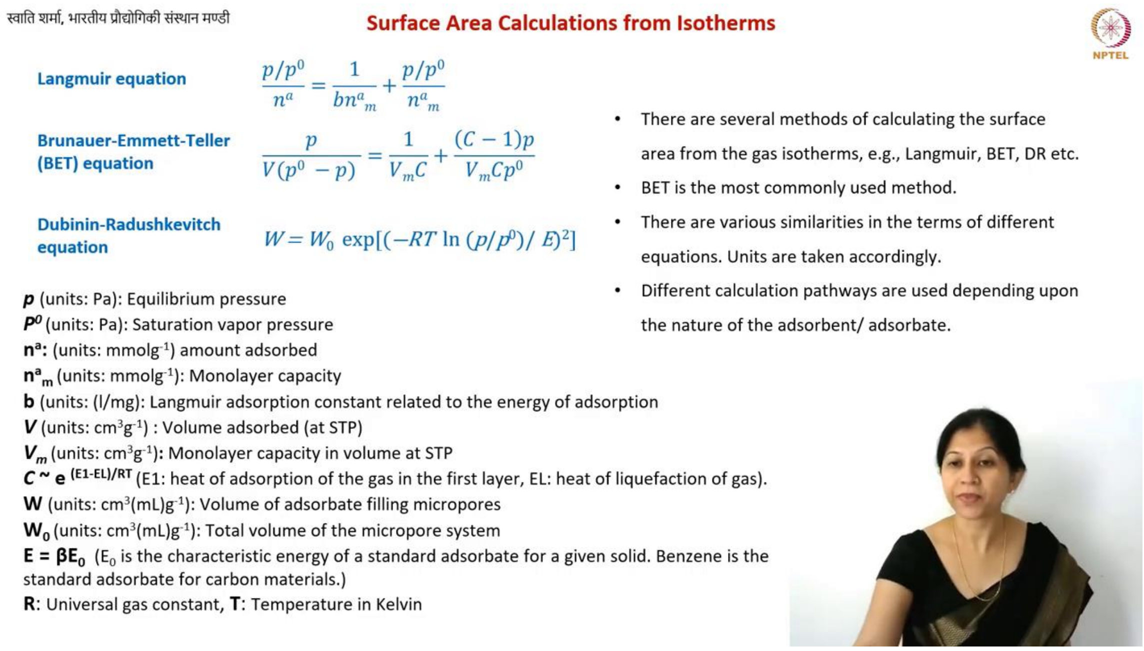
So, we use low temperatures.one more important thing is that if you remember we talked about mono layer and multi-layer adsorption, I think again it was about it was the activated carbon lecture. What is the mono layer adsorption? Now from this picture, you can see, it can be come out clear that you have only a single layer of gas molecules adsorbed on top of your surface.

But that is the ideal case, that is the assumption that we have made, but this may not always be the case because you will often have multi-layer adsorption because your gas molecules are also interacting with other gas molecules, your gas molecules are also interacting with the carbon molecules and also the surface functional groups.

So, there are multiple molecular interactions going on and that is why you will often have mutli layer formation. But we assume that this is a monolayer adsorption for the relative values, it is fine. Because if i take 2 or 3 or 5 carbon samples just with varied porosity, in that case, if the monolayer is forming on one sample then it is also forming on another, or the multilayer.

So, in that case, the relative values you will get, are more or less accurate. Another assumption is that we assume that there is no adsorbate-adsorbate interaction. So, this is the assumption we have to make in order to calculate the surface area. Closed pores I already described on the previous slide.

(Refer Slide Time: 20:30)



स्वाति शर्मा, भारतीय प्रौद्योगिकी संस्थान मण्डी

Surface Area Calculations from Isotherms

Langmuir equation

$$\frac{p/p^0}{n^a} = \frac{1}{bn^a{}_m} + \frac{p/p^0}{n^a{}_m}$$

Brunauer-Emmett-Teller (BET) equation

$$\frac{p}{V(p^0 - p)} = \frac{1}{V_m C} + \frac{(C-1)p}{V_m C p^0}$$

Dubinin-Radushkevitch equation

$$W = W_0 \exp[(-RT \ln (p/p^0)/ E)^2]$$

p (units: Pa): Equilibrium pressure
P^0 (units: Pa): Saturation vapor pressure
n^a: (units: mmolg^{-1}) amount adsorbed
$n^a{}_m$ (units: mmolg^{-1}): Monolayer capacity
b (units: (l/mg): Langmuir adsorption constant related to the energy of adsorption
V (units: cm^{3}g^{-1}) : Volume adsorbed (at STP)
V_m (units: cm^{3}g^{-1})**:** Monolayer capacity in volume at STP
$C \sim e^{(E1-EL)/RT}$ (E1: heat of adsorption of the gas in the first layer, EL: heat of liquefaction of gas).
W (units: cm^3(mL)g^{-1}): Volume of adsorbate filling micropores
W_0 (units: cm^3(mL)g^{-1}): Total volume of the micropore system
$E = \beta E_0$ (E_0 is the characteristic energy of a standard adsorbate for a given solid. Benzene is the standard adsorbate for carbon materials.)
R: Universal gas constant, **T**: Temperature in Kelvin

- There are several methods of calculating the surface area from the gas isotherms, e.g., Langmuir, BET, DR etc.
- BET is the most commonly used method.
- There are various similarities in the terms of different equations. Units are taken accordingly.
- Different calculation pathways are used depending upon the nature of the adsorbent/ adsorbate.

So, how do we now calculate the surface area from these isotherms? I have the pictures here or on the next slide maybe. So, isotherms are some sort of plots and now you need to get the values of your surface area. What you are doing is, you are plotting pressures, you are going to have some pressure terms when you want to calculate the isotherms or when you want to calculate the area from the isotherms.

There are several calculation methods and I have written 3 equations here. So, the first one is known as the Langmuir equation the second one is BET equation. This is the equation that is most commonly used in fact, often you will also hear BET surface area analysis for carbon materials.

So, this is commonly used for carbon materials. Actually there are multiple methods of calculating surface area from the isotherms and the other one is Dubinin Radushkevitch; this is a method that is used for calculating not just carbon material, but also in the case of liquid adsorption isotherms, this method is commonly used.

Why do we use different methods? That depends upon your material and also the gas that you have used and also the type of porosity that you are expecting. Sometimes you can use the same isotherm and calculate the porosity using all 3 equations.

And you getting the same values. Here I have written all the terms. There are p, p^0 or your different pressure terms: equilibrium pressure or the saturation pressure. And also in these equations you see it has some term called n^a and $n^a{}_m$ in this equation.

Second equation if you see again, you have the pressure term that is common, but instead of n you have a v term now; so this is the volume term. And in the third equation also you still have the p, but you have e which is some energy term now. The idea here is that if we are pretty much calculating the same thing, but only the units differ.

Now, we do not calculate the adsorbed gas in terms of volume, but rather the overall quantities. So, the very important thing is the units? So, in all cases, I have mentioned the units. Because even if you do not understand the exact name whether it is volume-based or what do you mean by quantity and amount and all of that, the units will make it clear to you?

So, in the case for example, of Langmuir equation you have millimole per gram that is your unit of calculating the monolayer capacity; it means how many molecules are adsorbed on the monolayer. So, similarly in the case of your BET equation you have the calculations in terms of volume.

So, this is the only thing that differs in all of these calculation methods, but you can typically use anything and there may be certain methods where you will get more accurate information using one of these 3 things; because in all of these equations also you will have some constants. The third one, actually the DR equation, there you see this energy term. This is also calculated based on the characteristics of your material.

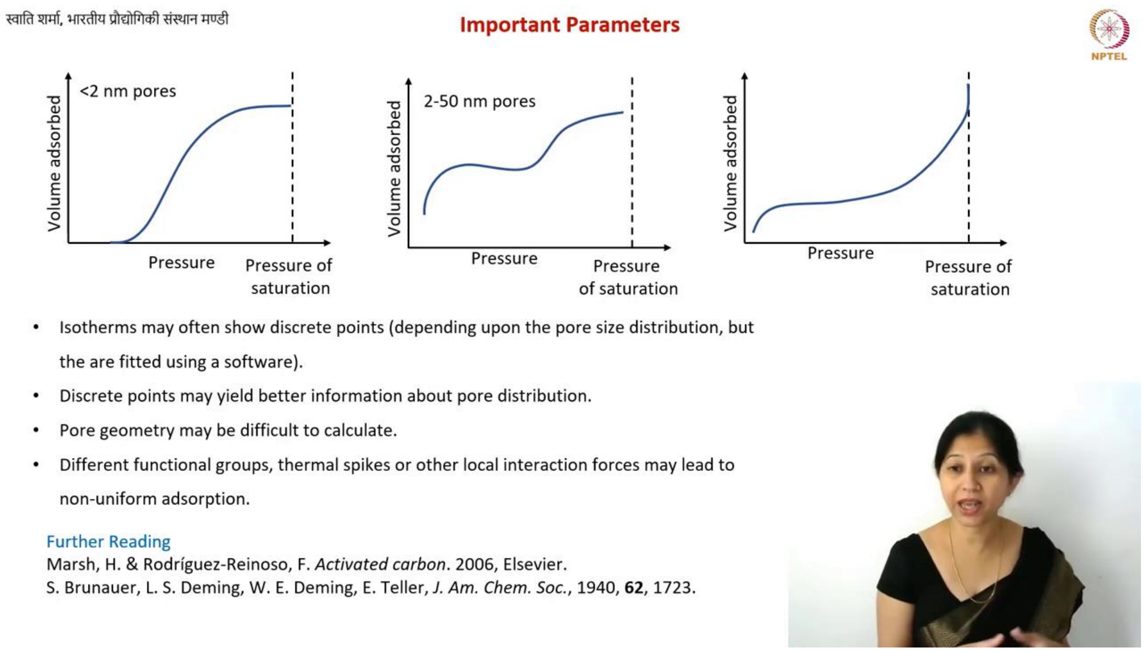
So, what you will actually see? You will actually assume that there is some standard adsorbate for every type of material and the characteristic and energy of adsorption of that particular standard adsorbate is what you will take as the value of E0; and beta is constant then you will calculate the value of E.

You will also need to know some of these constants and parameters and also the value of C. I have shown how to calculate C, it is the constant in BET equation. So, the point is that you need to also then understand if you are using the DR equation you need to know what is the standard adsorbent that you would like to use.

Typically, the one that is taken for carbon materials is benzene. So, these are the different calculation methods so I will not go into the derivation. Actually these are very simple derivations.

So, just change in pressure, and based on the number of molecules that are being adsorbed; the number of molecules can be number or volume or the mole fraction that is the only difference. So, you need to also see the chemical structure and physical structure all of that and then accordingly you can select your calculation pathway.

(Refer Slide Time: 25:04)



स्वाति शर्मा, भारतीय प्रौद्योगिकी संस्थान मण्डी

Important Parameters

- Isotherms may often show discrete points (depending upon the pore size distribution, but the are fitted using a software).
- Discrete points may yield better information about pore distribution.
- Pore geometry may be difficult to calculate.
- Different functional groups, thermal spikes or other local interaction forces may lead to non-uniform adsorption.

Further Reading

Marsh, H. & Rodríguez-Reinoso, F. *Activated carbon*. 2006, Elsevier.

S. Brunauer, L. S. Deming, W. E. Deming, E. Teller, *J. Am. Chem. Soc.*, 1940, **62**, 1723.

Here I have shown some different shapes of the isotherm. There are many different shapes that you can observe, but these are the common ones that you will observe especially for carbon materials.

One important parameter that I want to tell you here is the discrete values we get from our gas adsorption isotherms and then we often plot these lines and we are actually fitting the curves. So, there is some information lost during the fitting because the number of pores is not continuous. It is not that you have 2 nm pores and then 3 nm and then 5 nm and then you know all the way up to several micrometers.

It is not like that, usually you will have certain types of pores let us say 2 to 5 nm or below 2 nm, you will have a bunch of these pores and then nothing for some time and then a bunch of slightly larger let us say 30 to 50 nm pores and then a bunch of macropores.

You can understand it from fractal geometry. So, you do not have a constant linear increase in the pore size. So, you rather have 3 or 4 different regions which you will get in the adsorption data, but often when you already plot the isotherms. Especially if you doing it using computer software then you may lose that information. So it will be good also to have a look at the raw data, that will give you better information; what is the region where you have more of more pores.

This is what I have written here. Pore geometry is very difficult to calculate from the isotherms because you cannot guess whether these are cylindrical pores or what exactly is the geometry of your pores. In fact, sometimes what can also happen is that the number that you get for the surface area from very different materials or structures, can also be the same number.

Because then it depends; it does not tell you anything about the pore shapes and size. If I have these circular or hemispherical types of pores or I have cylindrical pores or I have fractal-like pores what I am calculating is just the number of molecules that are adsorbed.

So, it is very difficult to calculate the pore geometry. The closed porosity, you cannot guess from here. By the way from X- ray tomography and MRI although these are techniques that are challenging, but the advantage of these techniques is that you can also get information on the closed porosity.

If you know you have slices of images. Basically, when you take the MRI of your brain or X-ray of your hand; you do not have to cut open the brain right; this is the non-destructive imaging. So, that is why these techniques are very useful. These are non-destructive techniques that can also give you the information about closed porosity.

So, if your material has a lot of closed porosity, you might want to try one of these techniques. What else? You have different functional groups. You also have what is known as different thermal spikes.

So, at different positions of your samples, you may even have certain temperature gradients and that is why although we are trying our best to ensure that we do not have these gradients and we are trying to minimize the temperature or the molecular motion by using the liquid nitrogen and so on.

But there are possibilities of having even minor thermal spikes, it can change the adsorption behavior locally. So, there are various parameters actually that can change the local adsorption behavior. If you may have you have the fractal-like structure maybe sometimes the gas molecules cannot go all the way inside all the pores and there are some parts of the molecules that are blocking some other pores.

So, there is a possibility of errors and that you need to understand for your particular material. Here I have mentioned some resources for further reading. The first one is the book and from there, you can get also a lot of information specific to carbon materials and the surface area measurements of carbon materials.

the second one is the paper from where you can get the information about the origins of the BET theory. So, there can be several more resources that you could utilize.