Carbon Materials and Manufacturing
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Lecture - 29
Activated Carbon: Introduction and Proprieties

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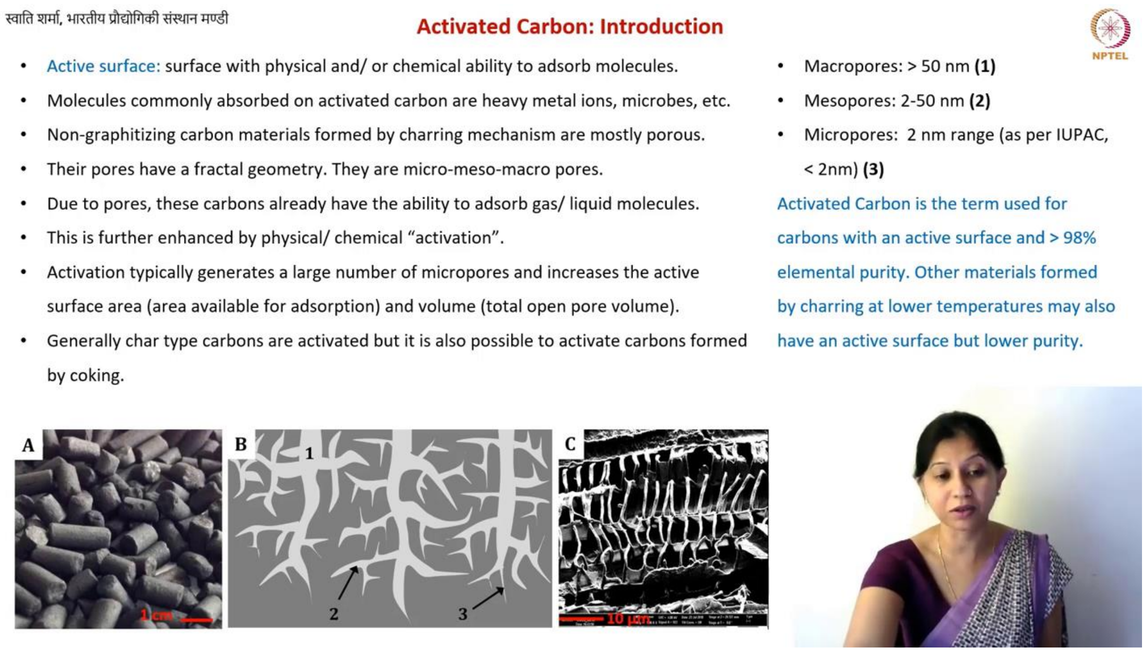

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Activated Carbon: Introduction

- Active surface: surface with physical and/ or chemical ability to adsorb molecules.
- Molecules commonly absorbed on activated carbon are heavy metal ions, microbes, etc.
- Non-graphitizing carbon materials formed by charring mechanism are mostly porous.
- Their pores have a fractal geometry. They are micro-meso-macro pores.
- Due to pores, these carbons already have the ability to adsorb gas/ liquid molecules.
- This is further enhanced by physical/ chemical "activation".
- Activation typically generates a large number of micropores and increases the active surface area (area available for adsorption) and volume (total open pore volume).
- Generally char type carbons are activated but it is also possible to activate carbons formed by coking.

- Macropores: > 50 nm **(1)**
- Mesopores: 2-50 nm **(2)**
- Micropores: 2 nm range (as per IUPAC, < 2nm) **(3)**

Activated Carbon is the term used for carbons with an active surface and > 98% elemental purity. Other materials formed by charring at lower temperatures may also have an active surface but lower purity.

Hello everyone, in this lecture we are going to move on to Activated Carbons. These are also form of non-graphitizing carbons and they are formed by the charring process that you know already. The fact is that the polymer precursor does not undergo a semi-solid phase after its degradation and that is why even though there will be some shrinkage. But there will be more pores rather than shrinkage in these carbons, because the skeleton of the polymer is preserved more or less. Natural polymers such as wood or the seeds of fruits or many cellulosic natural fibrous materials polymers would typically yield porous carbon.

Why do we say porous is activated and what does it mean to be active, first of all what is an active surface? The surface that is working out very active. Not really, the point is that an active surface is something that has certain chemical groups which make it, which render it active.

Either because of these chemical surface functional groups or because of porosity which is a physical property or a combination of both, these surfaces have the ability to bind or at least form weak bonds with any chemical or biochemical entity, which means they can adsorb these things onto their surface.

This adsorbance is what makes them active, that is why we call them active carbons. Now, active carbons are very important industrial materials. So, about 30 percent of carbon-related research and of course, a lot of industrial applications are all related to activated carbons today even though we have a lot of carbon nanomaterials in electronic device applications and so on. We are working more on the nano-materials or advanced materials, but for a number of reasons adsorbance are always important. For example, water filtration columns, have always been there and they are very important. Nowadays we also have this zero-wastewater policy, so the water from the chemical industries should be completely clean.

These kinds of policies are now coming up all over the world. The point is that, how do you clean that industrial wastewater or the household wastewater or the drinking water? All kinds of water purifiers are made of activated carbons. They are predominantly made of activated carbons.

There are also some other materials such as zeolites which are used here and there, but they are relatively much more expensive. And we already understand the technology related to activated carbon very well. We know the adsorbance mechanism and so on. So, still predominantly these are the carbon materials which are used for filtration applications, not just water filtration also air filtration, we will see.

The point is that this remains a very important industrial carbon material as of date. This is an image where I have shown, there are three A, B, C, three images. I think I have shown this picture before that you get the cylinder, so you also get powders and so on.

They look like this is a greyish colour, with no shine and lush similar to glass-like carbon because of the porosity. So, this is the kind of carbon you will be able to buy. Now some types of coals and charcoal are also porous material, so they look very similar, but if something is porous that does not necessarily mean it is activated.

However, let us first talk about the porosity in these carbons. So, in this image b, what you see is how the pores go inside, this is the structure of the pores in these active or porous carbons. This is a wood-derived carbon. So, a lot of natural polymers have this what is known as fractal like geometry.

Then there are some larger pores and then the smaller ones. They branch out in a way and then the further have the smaller and smaller and smaller pores which kind of have a self-replicating structure or self-similarity.

Because of this kind of structure you can already see that if there is any molecule, it can get adsorbed on top of or it can go inside pore, the biggest one or the smaller one or the further smaller one and so on, and even very small molecules can get inside, they can get adsorbed.

Now, the difference between activated carbons and anything formed by coking, for example, glass-like carbon, is there you have nanoscale pores, but they are closed pores, there are these fullerene-like structures, so nothing can go inside them. At least a lot of pores are closed pores.

But here, in this case, you have open pores; pores that are percolated pores that are connected to each other. There is a sort of path then the adsorbate molecule can take and can go deep inside. The pores have these fractal structures and there also a lot of things that can get adsorbed on top of them.

For example, heavy metal ions which you often find in water becomes very important during water purification, various microbes, bacteria, and the number of small molecules and biomolecules can get trapped inside these pores so to say. As I said that a lot of materials that are formed by charring carbon materials are porous. But you also do certain activation processes that we will come to.

Now, as I mentioned the pores have fractal geometry. What does this mean? They have different pore dimensions. So they have micropores, mesopores and macropores. So, what do these pores mean? I think we earlier discussed that micropores are not micro-scale pores, they are nanoscale pores. Actually, when we talk about porosity, we are mostly talking about pores that are in the nanometers scale.

Macro pores, however, the largest ones. Something you can see on a carbon material or you can observe in a standard optical microscope, those things would be definitely larger than 50nm. So, anything that is larger than 5nm, you call them macropores, which is shown with number 1 in this image B.

The second type, the number 2, is the slightly smaller version. These are the pores between 2 to 50nm, in terms of their diameter, if we consider an equivalent sphere, so these are called mesopores. The smallest ones, which are of 2nm diameter range, are called micropores.

I mentioned that it is 2nm range, Typically in the literature you will find people up to 5nm pores are sometimes called micropores. But, as per the IUPAC definition, the pores that are smaller than 2nm in diameter, they should be called micropores.

In fact, these micropores are then further divided into super micropores and ultra micropores I think basically based on their diameters if they are between 0.7nm to 2nm. And then these are super micropores and then the ones that are smaller than even 0.7nmmolecules length scales, they are known as ultra micropores. Now, what are these fractal geometries, let me quickly tell you.

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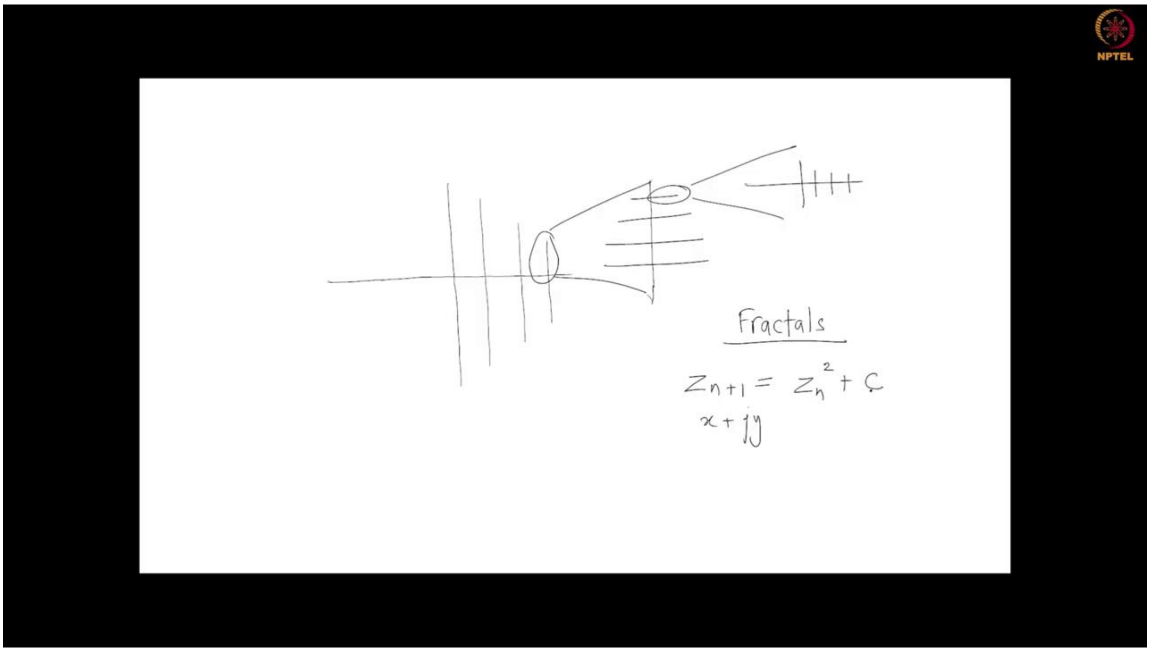

So, what are fractal structures again? The structure that I have shown you for the porosity of carbon structures. We will only talk in the context of porous carbons. You see these kinds of branches in these structures.

Now, if I take one of these branches and I zoom in, then I am going to get something that is very similar, the geometry that is very similar. So, these are basically known as self-symmetric structures.

Again, if I take another branch, then zoom in further then I will get the same kind of structure. So these kinds of structures are basically known as fractal geometries. Now, fractal geometries are used not just by scientists, but to understand a lot of natural materials, and also by artists.

So, a lot of computer-generated art is nowadays based on fractal structure. So, if you further interested of course, you can read more about it very briefly. If you want to mathematically represent these kinds of structures then this is the representation.

$$Z_{n+1} = Z_n^2 + C;$$

Where C is a constant and n is the number of sequences and Z is any complex number. So, in this formula, you can put in any complex number of form x + j y and then you can get the n plus 1st term.

So, this is how you can keep on calculating. Basically, your next term is going to have the self symmetry to the current term. Now, most of the natural structures are not perfect fractals. So, these repeating units that I have shown here may not be exactly the same as the previous structure, but they are approximate and they have approximate symmetries in the case of most of the natural structures. But of course, in the case of computer generated art you have this perfectly symmetrical structures.

Now, if you are interested as I mentioned, you can read more about what is known as a Julia set and what is known as Mandelbrot set. These are basically in one case you have a C as constant and the in the other case C is allowed to change. So, this is a field of research in itself, so you can read more about it.

For us what is important is that we have these fractal-like geometries in the pores of many natural polymers and that is why in the porous carbon after carbonization, we get these kinds of geometries. Since we already have porosity in these carbon materials, even without the activation, even when they just come out of the furnace they can adsorb some things.

They do have the geometry to trap the molecules which can be molecules of a gas, of a liquid or they can also be some other biological entities. So, the point is that their geometric structure already enables them to trap these molecules. However, now we can further enhance this adsorbance by what is known as the activation process. That is why these carbons are known as activated carbons.

They are not known as active carbons, although you will occasionally hear this term, but the point is that when we are performing the activation process then we call these carbons, activated carbons. Now, how do you do the activation? So, there are certain physical methods and there are also certain chemical methods that we are going to talk about.

But, what you need to understand is what does it do? The activation process generates more micropores. Micropores again are smaller than 2nm, then the activation process generates many more of them. So, initially when your carbon comes out of the furnace ,when it has this fractal geometry pores, let us say wood-derived carbon, it will have all sorts of pores in pretty much similar fraction. But after the activation process, now the micro pores will dominate. So, the fraction of micropores becomes much higher. So, that is what happens by the activation process and then you calculate the porosity.

Now, what is important for us is the surface area that is available. Because you see, now we are doing absorption. So, whatever the more the better, the surface area that is available to us, so that becomes an important parameter and the total open pore volume. So, if you have closed pores, they are not useful for you.

So, these are the two important factors, now we need to increase these two things. We need to increase the surface area and we need to increase the open pore volume. Now, as I mentioned that we are doing this artificial activation in many cases.

You can do the activation of glassy carbon; you can do activation of other types of carbons also and then you can also call them activated carbon. There is no point in doing it because if we want to use this material as an adsorbent then there is we need to have these open and percolated pores.

Because, if you activate the glassy carbon surface which people are doing with it, for example, if you want to attach certain other chemicals on top of it because glassy carbon is generally very inert so it is very difficult to attach anything on top of it. So you can do some physical and chemical activation and then that is often known as not activation but surface modification because it is happening only at the surface and not inside the material. But for the adsorbent fabrication, it makes much more sense to activate the porous carbons. Now one more thing, as I am using exchangeably the terms porous carbons and activation carbon, but they are not the same.

So, porous carbon is the carbon structure that you get after the charring process. But, when you further do the chemical or physical activation and increase the number of micropores that is known as that is the activation process. However, industrially the term activated carbon is used when the purity of the carbon is also high enough.

So, in many low-temperature carbonization processes, you will get certain types of chars. So these are also very porous, but their purity is pretty low. In the case of industrial applications, you will call it activated carbon when it is at least 98 percent in terms purity, which means also that the temperature should be reasonably high.

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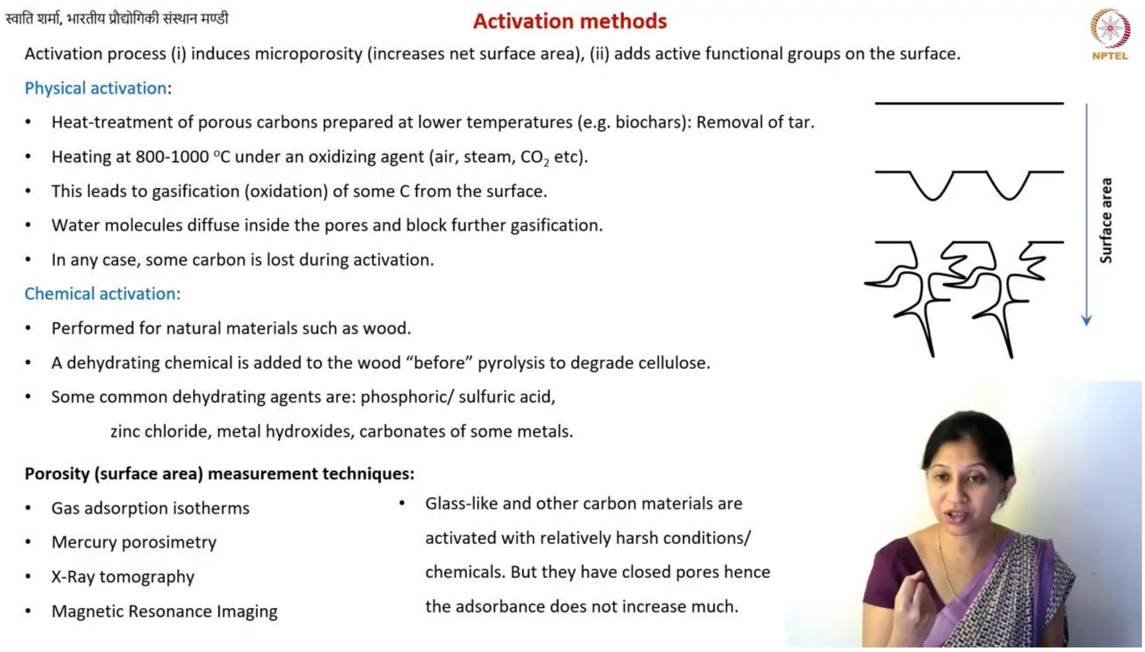

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Activation methods

Activation process (i) induces microporosity (increases net surface area), (ii) adds active functional groups on the surface.

Physical activation:

- Heat-treatment of porous carbons prepared at lower temperatures (e.g. biochars): Removal of tar.
- Heating at 800-1000 ^oC under an oxidizing agent (air, steam, CO_2 etc).
- This leads to gasification (oxidation) of some C from the surface.
- Water molecules diffuse inside the pores and block further gasification.
- In any case, some carbon is lost during activation.

Chemical activation:

- Performed for natural materials such as wood.
- A dehydrating chemical is added to the wood "before" pyrolysis to degrade cellulose.
- Some common dehydrating agents are: phosphoric/ sulfuric acid, zinc chloride, metal hydroxides, carbonates of some metals.

Porosity (surface area) measurement techniques:

- Gas adsorption isotherms
- Mercury porosimetry
- X-Ray tomography
- Magnetic Resonance Imaging

- Glass-like and other carbon materials are activated with relatively harsh conditions/ chemicals. But they have closed pores hence the adsorbance does not increase much.

So, let us now talk about the activation methods. I told you that you can do physical activation and chemical activation. So, what does the activation do? Number 1, it increases the microporosity. Microporosity increment means that the net available surface area is being increased. It will also induce the activation process especially in the case of the chemical activation process. You may end up getting certain active surface functional groups. So, these are chemical groups that have the ability to attract molecules. So typically they are radicals. They are oxygenated functional groups. They can be various functional groups and because in most cases you will use these activated carbons for adsorbing things that are hydrophilic or that are present in water or even anything that is biological they are typically hydrophilic molecules.

So you will often induce hydrophilic surface functional groups on top of these by the activation process. These are the two things that actually take place. Now, as I said that the microporosity or any kind of porosities directly related to the surface area. This is something very easy to understand.

This is, let us say a very flat surface, this line. The second one is a little bit rough surface, so you can have these holes or pits or you can also have hill-like structures, basically you have certain roughness on top of your surface. In that case, you have a higher surface area.

If you had to walk on this, you will have to now walk more. Now, if I have the structure which is what we have in the case of natural pores carbons, then you see that the area surface area is several times more. So that is how surface area increases with porosity.

Now, let us talk about the activation methods. The physical activation; basically first of all when you get these porous carbons, let us say I prepared my porous carbon or some sort of chary material. Even if I made it from the waste material and agricultural waste, and I prepared it at not very high temperatures, which is often the case with porous carbons, they are not prepared at least initially at a very high temperature. There is a reason for that. If we increase the pyrolysis temperature then the graphitic content increases and more graphitization would mean that the surface becomes more inactive and then you also get harder carbons and you actually lose porosity at a certain point.

So you do not go for very high pyrolysis temperatures, but let us say between 800 and 1000, in that case, you get reasonably good porosity, but the problem is that you may still have some of tarry by-products which may coat the surface of your pores. In that case, the first thing that you will do in the name of physical activation is to again perform the heat treatment in inert atmosphere. You are trying to get rid of this tar that was on the surface. So, basically now you get more surface area. The pores that were blocked by the tars, they open. So, that is one method of physical activation, which is often almost often done it is in most of cases.

Now, one more physical activation method is that you take an oxidizing agent, oxidizing agent is something that can change oxygen. So, for example, air or steam or carbon dioxide often a mixture of these things; so steam plus carbon dioxide. You will have this inside your furnace when you heat treat it and this heat treatment again is not performed at very high temperatures, but between 800 and 1000 °C.

So, this kind of activation what does it do? It leads to gasification or oxidation of some of the carbons or some of the carbon from your carbon material because it has oxygen. So, when you have oxygen then there is a possibility of oxidation carbon, the formation of carbon dioxide, but at the same time, you also have this steam over there.

Now, water molecules are smaller than carbon dioxide molecules, so they actually diffuse inside these extremely small pores that you have. That sort of blocks further gasification. So when you perform the pyrolysis in steam, then you end up getting these highly porous carbons, but you must remember that because there is some gasification or oxide formation happening. You do lose some carbon.

So, the time of carbonization must be optimized. So if you perform activation for a very long time then you may end up losing a lot of carbon mass. Now, coming to chemical activation methods, as the name suggests, you are adding certain chemical, but at what stage?

This kind of activation is often performed for wood or other natural materials. So, biological-based and natural polymers. Now, you actually add a certain chemical before the pyrolysis. So, when you have a piece of wood you will first add certain chemical to it and there is a long list of such chemicals. So, there are strong acids and then you have metal hydroxides, chlorides, carbonates and so on. These dehydrating agents partially degrade the cellulose even before it is taken for carbonization. And now you perform the paralysis and that is when you get an enhanced surface area.

There are many other methods also. There are various advanced porosity or activation methods, where you may also utilize the combination of both. Here and there you will also do plasma activation. So plasma etching of the surface, which is also done for device applications, for glass like carbons and so on. There are various activation methods for increasing its adsorbance.

Now, how do you measure the porosity? We will also learn about this when we learn about the characterization technique. There are some standard processes. The most common process in the case of carbon porosity measurement is known as gas adsorption isotherms, and this is also known as BET method. We will talk about this. There is something known as mercury porosimetry.

Then you can also perform X-Ray tomography, other imaging techniques even Magnetic Resonance Imaging MRI can give you porosity values. Now, I have already told you that other types of carbon can also be activated, but for industrial adsorbent applications why would you do that? You rather will use relatively cheaper char like carbon which already has a lot of porosity and then you will perform the activation for that.

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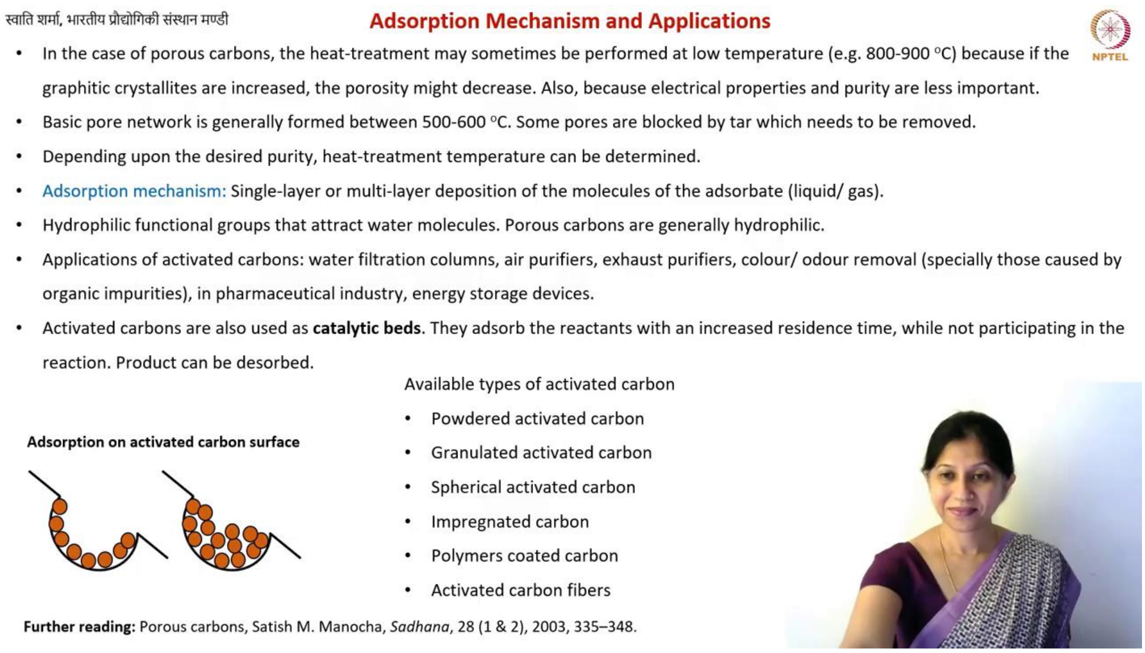

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Adsorption Mechanism and Applications

- In the case of porous carbons, the heat-treatment may sometimes be performed at low temperature (e.g. 800-900 °C) because if the graphitic crystallites are increased, the porosity might decrease. Also, because electrical properties and purity are less important.
- Basic pore network is generally formed between 500-600 °C. Some pores are blocked by tar which needs to be removed.
- Depending upon the desired purity, heat-treatment temperature can be determined.
- Adsorption mechanism: Single-layer or multi-layer deposition of the molecules of the adsorbate (liquid/ gas).
- Hydrophilic functional groups that attract water molecules. Porous carbons are generally hydrophilic.
- Applications of activated carbons: water filtration columns, air purifiers, exhaust purifiers, colour/ odour removal (specially those caused by organic impurities), in pharmaceutical industry, energy storage devices.
- Activated carbons are also used as **catalytic beds**. They adsorb the reactants with an increased residence time, while not participating in the reaction. Product can be desorbed.

Adsorption on activated carbon surface

Available types of activated carbon

- Powdered activated carbon
- Granulated activated carbon
- Spherical activated carbon
- Impregnated carbon
- Polymers coated carbon
- Activated carbon fibers

Further reading: Porous carbons, Satish M. Manocha, *Sadhana*, 28 (1 & 2), 2003, 335–348.

So, what is the adsorption mechanism? And we also will talk about some of the applications here. Before that, I have already mentioned to you that the heat treatment is sometimes performed at lower temperatures say 800, 900, 1000 °C just to avoid making the carbon very hard. By the way, a lot of non-graphitizing carbons are also known as hard carbons because they are hard and brittle. As compared to graphite which is softs because of the layered structures. So, the carbon becomes harder if you increase the heat treatment temperature. So, you would often get them at lower temperatures that also reduces the cost of these kinds of carbons.

However, because of this little bit of tar that is leftover. In order to get rid of that, you will further heat treat it. If you understand the mechanism of pyrolysis with these kinds of carbons, the framework of these pores is already formed between 500-600 °C. There you already have a good porous network. Before that the material may still be arranging itself or it may still not have the good carbon backbone, well-defined carbon backbone, but at 500, 600; even though you do have a lot of impurities you understand that even pyrolysis goes on till 700 typically.

So, you have still a lot of impurities, but you do get the pores network. So, you can basically stop your heat treatment at some point after this. Often it is done to 800 °C initially and then do heat treatment after cooling down.

Now the important thing is that also I told you that activated carbons need to have 98 percent purity. If you have low pyrolysis temperatures then you will not get the desired purity. Now, what you need to figure out the trade-off. You need to find out what is important for you. If the purity is very important then you will keep on heating the material.

Also, if in a certain case for example, if you are using this for energy storage application, and you also need a good electrical conductivity, in that case you need to go to higher pyrolysis temperatures. But, if you making a filtration column, where reasonable purity, let us say 96 percent is alright for you, in that case, what is more important? You do not care about whether you have short-range order or not, and what is the La Lc value? What is electrical conductivity? You do not really care about that you rather care about the good porous network. So, depending upon that you will determine your heat treatment temperature.

So now, we talk about the adsorption mechanism. This is simple, if you have an active surface, certain functional groups that can attract the molecules of whatever is being adsorbed, then those molecules will just come and they will deposit on top of the surface.

This can happen due to both physical and chemical reasons. Physical reasons is the pores that you have, which are of the size of the molecule itself. In order to control environmental pollution or the pollution of drinking water with nanoparticles, which is, by the way, a big problem.

Nowadays you have a lot of nanoparticles in the cosmetics, when you wash your face then these particles get mixed into the water and then finally, into the groundwater. So, if you want to remove these nanoparticles, maybe the size of the nanoparticles is of the same range as the micropores. So, in that case this can also be physical trapping.

In most cases, it is a combination of both physical trapping and chemical attractive forces which can be due to the fact that you have radicals on the surface, or they may also be weak Van der Waals forces. The point is that you may have either a single layer of these molecules that are adsorbed or you can also have multiple layers. And this is important because that determines how your adsorption isotherms look like.

You can have these two types of mechanisms of absorption on top of the surface. And that will actually depend upon the molecule that is being adsorbed. What are the properties of that molecule? As I said that hydrophilic functional groups will attract the water molecules, and generally most of the applications require water-related molecules or hydrophilic molecules then typically you will have a hydrophilic surface.

Now, coming to the applications. Water filtration I already told you. There are also air purifiers, nowadays you can buy a lot of purifiers for removing odour, removing colour from things that are mixed in water. For example, in a restaurant you get a lot smell of food because there is food being cooked all the time.

So in the kitchens of various places, you may find some bag hanging there, which is there to remove the odour, these bags would contain basically activated carbons. You can also buy something for your car exhaust that adsorbs fumes or at least a few organic materials and unburned tar-like materials that are coming out of your car. You are using activated carbons various adsorbent applications.

This is also used in the pharmaceutical industry and energy storage devices. Energy storage devices are batteries and supercapacitors. In this case surface area is very important. In that case, also you use electrodes made of activated carbons, you often have reasonable electrical conductivity in this case.

Now, one more very important application is catalytic beds. So, what are catalytic beds? In a chemical reaction if you add catalyst then the reaction rate increases because the activation energy goes down. Let us say you have in a certain solvent; you have two chemicals mixed and you can also add your catalyst in the same solution or you can also provide a solid support for this reaction.

So, you take an activated carbon bed, on top of that you add both your reactants, and you also add the catalyst. This increases the residence time; residence time means the time when all three entities can interact in the solution. They are always moving, but here they have solid support. And if you have pores of this kind then inside these pores you can trap, the molecules of whatever reactants you have and also the catalyst, or sometimes you can already load your catalyst. Loading means you already have the catalyst on top of your activated carbon surface because of the porosity, it will also go all deep inside the pores and everywhere.

The more surface area of the catalyst is also available to catalyse the reaction. So, this is also an industrial application of activated carbons by the way. One important thing is that the catalytic bed should not participate in the reaction. In in general carbon is unreactive but its surface is active, but it will not degrade, it will not corrode, it will not participate in the reaction by itself that is why it makes a very good catalytic bed. Now, just based on the available types of activated carbon, so, we can also classify them.

For example, depending upon what is available in the market, you have powdered activated carbons, you have cylinder-like structures, you have also what is known as granulated activated carbon. So, grains are larger than powders. You will find yeah you can have spherical particles.

You can have cylindrical particles, you have basically grains, granulated particles although sometimes they are randomly shaped grains of activated carbon and spherical as I already mentioned. You also can have impregnated activated carbon. Impregnated means, you already load something. Let us say a metal ion on top of these activated carbons. These are typically used for catalytic beds and other chemical reactions. And then you also have some other advanced versions like polymer-coated activated carbons and so on. That depends; that is very specific to the application area.

So, why would you do polymer coating when you are kind of reducing the active surface? Well, you often use these things for biological applications. You will have a biocompatible polymer coated on top of the surface so that, these are for biological applications. Porosity, the porous network you are still using.

So, these carbons are sort of porous carbons, but they are coated with polymer. So this is a different activation method. Activation can be done in any desired way if you want from the surface or not. What is also very important is something you are going to learn in the carbon fiber section. We can activate the carbon fibers as well.

Carbon fibers, of course, some of them are made of natural polymers like cellulose and they are also made of some synthetic polymers, we will talk about them. So, activated carbon fibers are also a very interesting field, because carbon fibers already offer a lot of surface area compared to a bulk solid. And if you further activate them, then you have a very large surface area available and then you can make really very high efficiency adsorbent structures.

If you are further interested this is a wonderful paper by Dr. Satish Manocha and there are also several lectures available on NPTEL as well as other open sources.