Water and Waste Water Management

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Module No # 11
Lecture No # 51

Adsorption

Hello everyone, welcome back to the session relevant to adsorption. In the last session, we were just looking at adsorption versus absorption. One aspect is that adsorption refers to accumulation of the relevant compounds on a particular surface of the media. The media can be granular activated carbon. But absorption, which typically is sounding similar to adsorption is where you have dissolution of the particles into another phase.

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Adsorption

2 different phases completely and the relevant compound of interest penetrates the phase and entirely.

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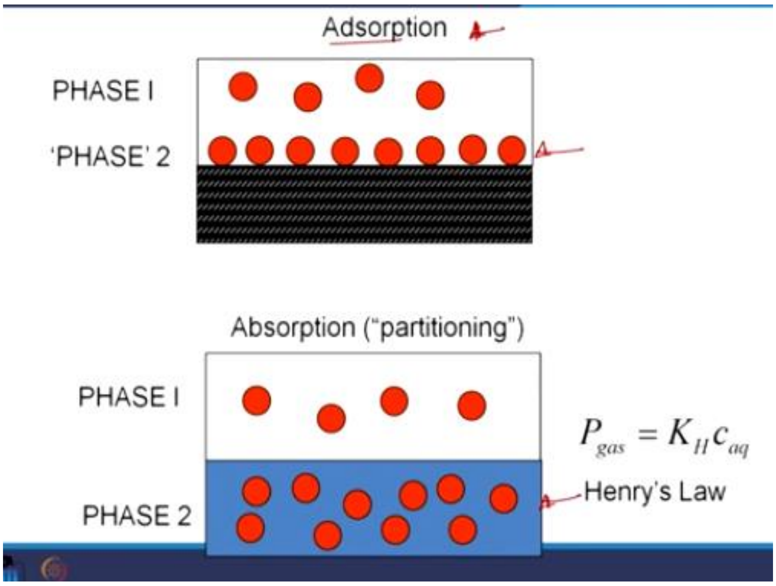

$$P_{gas} = K_H c_{aq}$$

That is what we see, one is adsorption; accumulation on the surface the other one is dissolution. Here we are going to talk about whenever we say adsorption, we are only going to talk about this accumulation of the relevant compound on the relevant surface of a particular media.

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GAC water treatment tank

→ SS → Pathogens

Org.

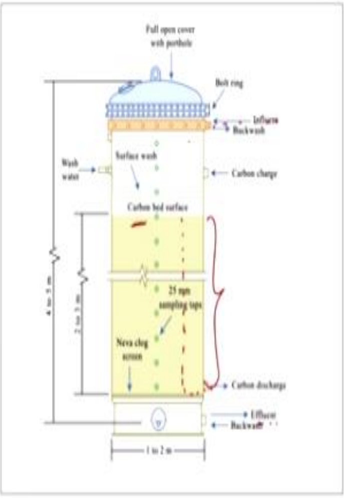

Figure by MIT OCW.
Source: Metcalf & Eddy Inc. *Wastewater Engineering: Treatment, Disposal, Reuse.* McGraw-Hill, New York, 1979.

What is it that I am talking about and in what context? Until now in my water treatment, I removed suspended solids various mechanisms. And then I removed pathogens by disinfection and depending upon the relevant calcium or magnesium, I would have removed them here and then gone on to looking at pathogens. But in some waters, you will have some organic compounds which are not removed during these different stages that we are looked at with respect to water treatment.

I need to remove these organic compounds but key aspect here is that we are talking about the end of the unit process. It will be just before pathogens or if it was for wastewater, it will be at the end of the relevant treatment process. This granular activated carbon based on adsorption-based technique can be or typically be deployed at the end of the treatment train.

And in general, we are trying to remove organic compounds in the relevant water those which are relatively more hydrophobic acid and they did not want to be in the water. What are we going to do? You are going to provide a friend which they want to be attracted towards and that is your media. And how does it look like? Here we see this particular figure.

And here where is the relevant inlet here? In front is coming in and you have the activated carbon bed surface. And then the effluent goes out here. While the water passes through this activated carbon which is relatively porous, the activated carbon is going to absorb the organic compounds. The water does not have this organic compound anywhere but it is changing phase.

I would not say phase in its entirety because it is accumulation on surface. But anyway, it is not in the water, it is being removed from the water, the organic compounds of interest are being removed from the water. This is what it looks like, we will come back to this later.

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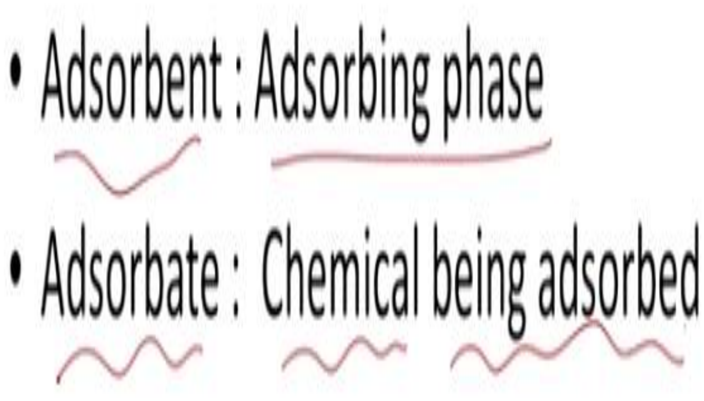

- Adsorbent : Adsorbing phase
- Adsorbate : Chemical being adsorbed

Adsorbent and adsorbate, so 2 aspects adsorbent is the absorbing phase here, what is the adsorbent? It is this activated carbon that we are talking about the relevant media, the phase which is absorbing the compounds of interest, what is adsorbate? The chemical or the compound which is being adsorbed onto the media, is in the relevant adsorbents and adsorbates. Here, this is the adsorbent. The media and here it is the adsorbate so that is should clarify, let us move on.

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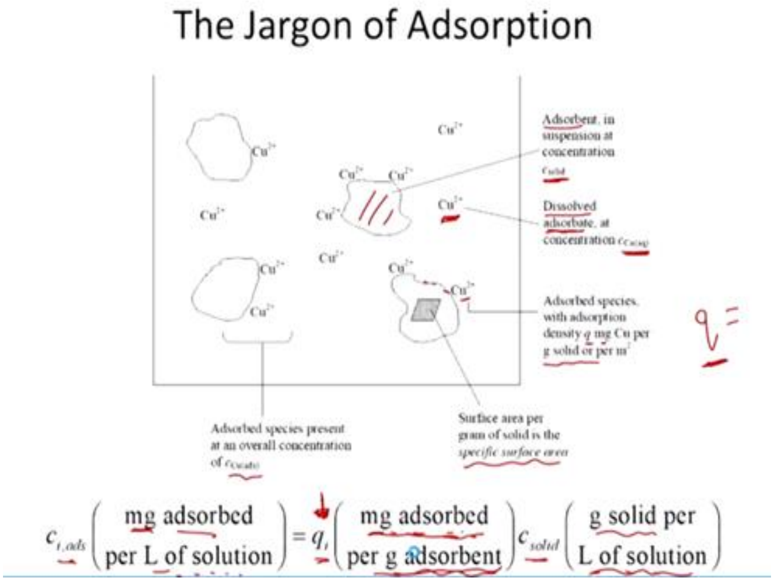

The Jargon of Adsorption

Adsorbent, in suspension at concentration c_{solid}

Dissolved adsorbate, at concentration $c_{Cu(aq)}$

Adsorbed species, with adsorption density q mg Cu per g solid or per m^2

Adsorbed species present at an overall concentration of $c_{Cu(ads)}$

Surface area per gram of solid is the *specific surface area*

$$c_{i,ads}\left(\frac{\text{mg adsorbed}}{\text{per L of solution}}\right)=q_i\left(\frac{\text{mg adsorbed}}{\text{per g adsorbent}}\right)c_{solid}\left(\frac{\text{g solid per}}{\text{L of solution}}\right)$$

How do we measure this or express this concentration and what are the relevant terms and units that I need to look at? Here we have a new phase. It is the solid phase or the adsorbent phase on which some of your compounds are being adsorbed. When you look at the removal, it is going to be equilibrium between the compound in the adsorbed phase and the compound in the aqueous phase.

It is relationship, equilibrium typically and then you are going to also have to express the concentration of the relevant compound on this media. We have to look at these variables, let us just look at them. What do we have here? This is the media, my adsorbent and it is suspended in my solution here, it is not a bed, it is suspended the concentration is C solid, let us we will look at these relevant aspects later.

C solid, it is grams of the solid per litre of solution and what is it trying to remove? It is trying to remove my particular a compound of interest. Here we are using the general aspect but the granular activated carbon is not used for removing metals, but we are looking at the general figure to be able to understand the different terms and the kinds of units.

Dissolved adsorbate, the compound which is dissolved, the adsorbate which I want to remove and it is presented at Ccu. This is something we are already familiar with and adsorbed species with adsorption density of q milligrams of copper per grams of solid or per meter square. Here, this copper is absorbed onto the media.

And I want to know how much copper is absorbed per mass of media, that is what it gives; q. Where is this milligram adsorbed per gram of adsorbent? This is typically used widely, this particular nomenclature and then what else do we have? Adsorbed species present at an overall concentration, If I want to know the overall concentration that is adsorbed

Then it is going to be milligrams adsorbed per litre. How will I get that? Here it has to be milligrams adsorbed that I will get from q in the numerator and then I want litre in the relevant denominator. I have to multiply q with the concentration of the solid in the solution, then I will get mass adsorbed per litre of solution. But this is not widely used, q is the factor or variable that is widely used.

And another aspect is surface area per gram of solid is the specific surface area but we will probably not go into that detail here. Aspect to notice is q; Mass absorbed of the adsorbate per mass of the adsorbent, milligram per gram.

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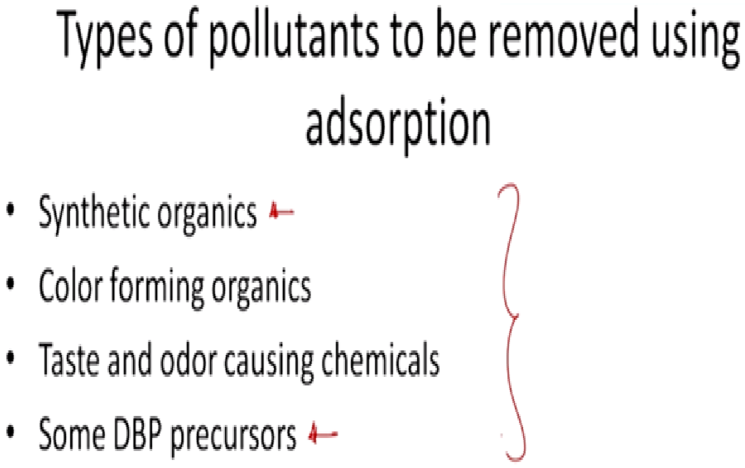

Types of pollutants to be removed using adsorption

- Synthetic organics
- Color forming organics
- Taste and odor causing chemicals
- Some DBP precursors

Typically, so types of pollutants to be removed; Synthetic organics, as and now they are due to different lifestyles. We are using different kinds of compounds, personal care products and these are synthetic organics which I do not want to be present in the water that I am supplying to my population, so some of them can be removed. Colour forming organics, even the dying wastewater industry, some people try to use activated carbon to remove some types of compounds which can cause colour.

Taste and odour causing chemicals and some disinfection by product precursor’s typically organic matter or natural organic matter let us write. Typically, organic compounds and those which are relatively hydrophobic which do not want to stay in the water, that is the key aspect here.

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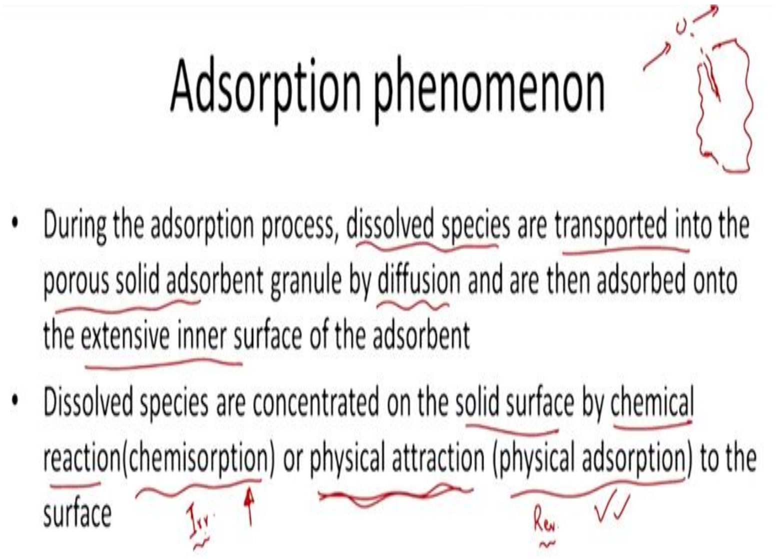

Adsorption phenomenon

- During the adsorption process, dissolved species are transported into the porous solid adsorbent granule by diffusion and are then adsorbed onto the extensive inner surface of the adsorbent
- Dissolved species are concentrated on the solid surface by chemical reaction(chemisorption) or physical attraction (physical adsorption) to the surface

Absorption phenomenon, so what is going to happen or how is it going to happen? During the process, the compounds which are dissolved in the aqueous phase meaning in water are transported into the porous solid. The GAC that we are going to look at is porous, we will have a pretty good figure. But let me draw a very rough figure here. This is the pore here.

The compound which is traveling out here along with the water, it is going to be transported to this porous solid and what is it? What is the phenomena? It is by diffusion. And then it is going to be adsorbed onto the inner surface of the adsorbent. That is the relevant aspect. Dissolved species are concentrated on the solid surface by two relevant mechanisms.

One is chemical reaction, which is chemisorption which is pretty rare in adsorption for water treatment and the other one is physical process based or physical attraction based or physical adsorption. This is the one that is widely relevant to us in the context of water treatment. This is irreversible typically and this is typically reversible. That is something to keep in mind.

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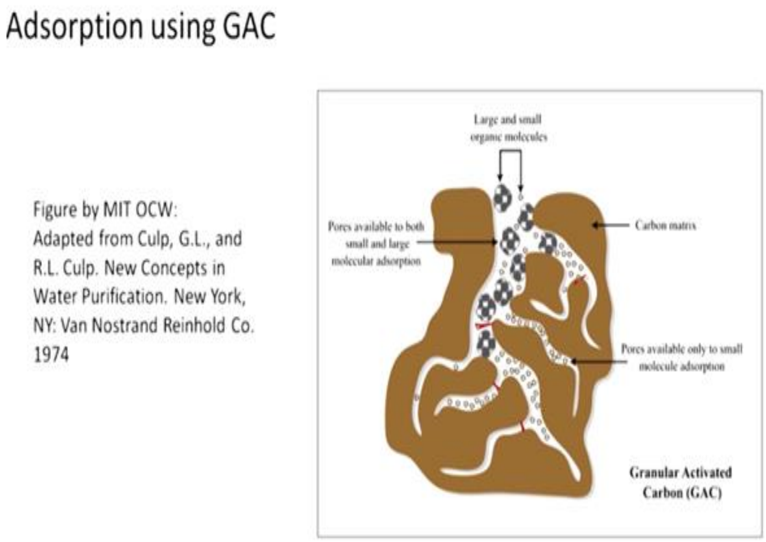

Adsorption using GAC

Figure by MIT OCW:
Adapted from Culp, G.L., and
R.L. Culp. New Concepts in
Water Purification. New York,
NY: Van Nostrand Reinhold Co.
1974

This is a great figure, this is the figure of the granular acquired carbon, the carbon matrix is presented here. We have the large pores and then we have small pores, that is something to keep in mind. This granular actuated carbon a typical media used for adsorption has different kinds of pores, it is not homogeneous. That is one thing to keep in mind, it is heterogeneous so that is one aspect.

You know large and small organic molecules, so pores available to both small and large molecule absorption. That is one thing and then due to size, some of the bigger molecules will not be able to go through to the other surfaces that are available but they will be available to the small molecules. That is something to keep in mind. Why is it that? This compound wants to be adsorbed onto this media, which is the granular actuated carbon.

The GAC is the example that we are using, there are different adsorbents but the one that is most widely used at least for tertiary treatment, or after tertiary treatment, or in tertiary treatment is GAC.

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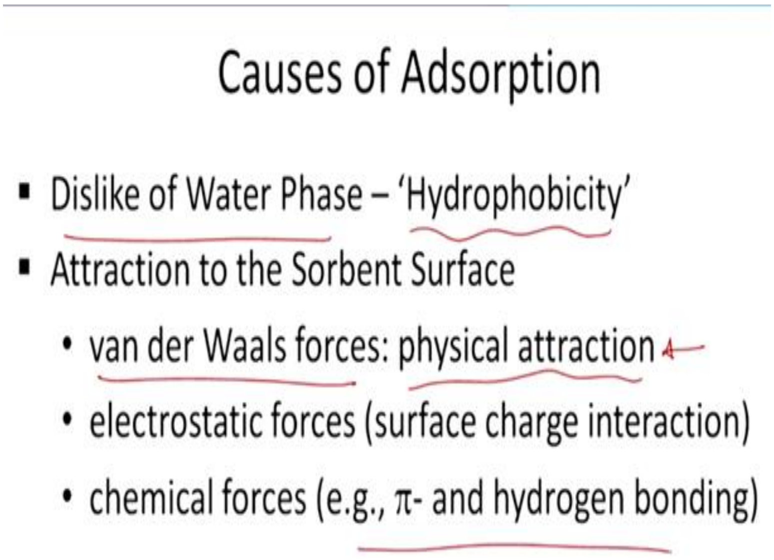

Causes of Adsorption

- Dislike of Water Phase – 'Hydrophobicity'
- Attraction to the Sorbent Surface
  - van der Waals forces: physical attraction
  - electrostatic forces (surface charge interaction)
  - chemical forces (e.g., π- and hydrogen bonding)

The driving force is hydrophobicity, dislike of the water phase. And then attraction to the sorbent phase, it wants to leave the water and then why does it want to be absorbed onto the surface? Vander Waals forces, physical attraction and this is the most relevant one especially for removal of or the applications in water. And this Vander Waals forces, why is that coming into play? It is based on the structure of the GAC and that is where it comes into play.

Electrostatic forces, surface charge interaction, chemical forces but here in general, we are not concerned with chemical forces at least in the chemisorption. In the context of what we are discussing here. Primarily, it is the physical forces or physical attraction or physical adsorption.

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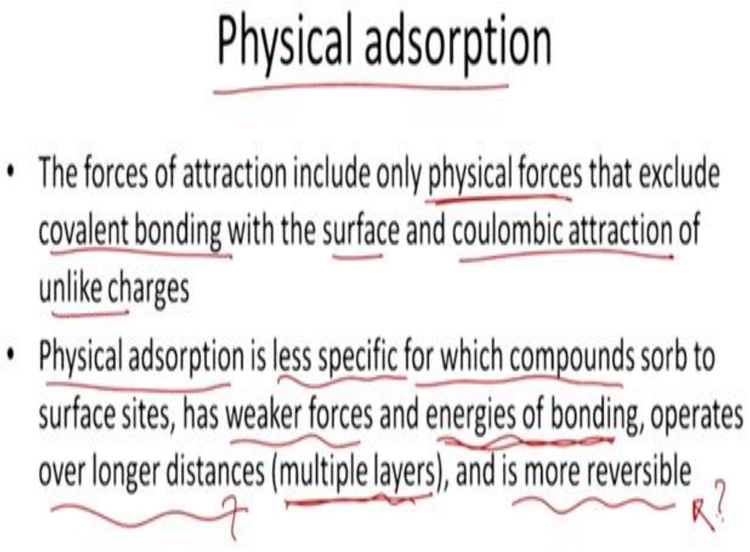

Physical adsorption

- The forces of attraction include only physical forces that exclude covalent bonding with the surface and coulombic attraction of unlike charges
- Physical adsorption is less specific for which compounds sorb to surface sites, has weaker forces and energies of bonding, operates over longer distances (multiple layers), and is more reversible

Physical adsorption, the forces of attraction include only physical forces and exclude covalent bonding with the surface and also the coulombic attraction of unlike charges, we are looking at only the physical forces excluding covalent bonding with the surface. And physical absorption is less specific with respect to which compounds adsorbed onto the surface sides, it is not picky. That is one thing.

And it is relatively weaker and energies of bonding as weaker forces and energies of bonding, operates over long distances, why is that relevant? As can be seen here there are multiple layers, with respect to GAC, you can have one layer of adsorption then a second layer, third layer. It will allow for multiple layers and is relatively more reversible, why is this important?

For example, I am using GAC in to treat or remove some of the organics from my water here, the media has a certain capacity, think of me as being the media. And a poor analogy is that I am trying to take up some of the organic content on my skin, after a certain time, most of the skin or my surface will be filled up with the organic content.

My skin or my surface is not available or does not have any more adsorption sites. Then I have to do what now? I can dump the activated carbon in a hazardous waste treatment storage and disposal facility at high costs. And also, that space is limited or you can regenerate it, you can reverse this physical adsorption. But please note that along with physical absorption, some of the adsorption is going to be chemisorption or chemical adsorption, that is irreversible.

Even after regeneration, your particular media would not have all the adsorption capacity, similar to the Virgin granular actuated carbon. It is going to lose some of its adsorption capacity. Different aspects one is that chemisorption, that is the aspect relevant to more reversibility.

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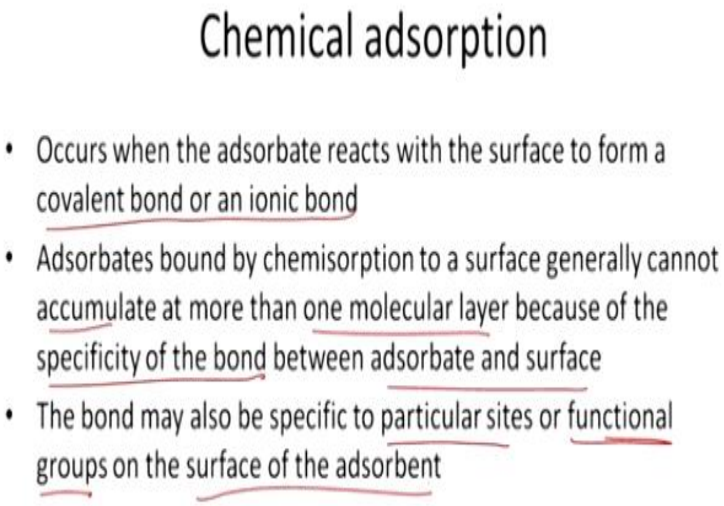

Chemical adsorption

- Occurs when the adsorbate reacts with the surface to form a covalent bond or an ionic bond
- Adsorbates bound by chemisorption to a surface generally cannot accumulate at more than one molecular layer because of the specificity of the bond between adsorbate and surface
- The bond may also be specific to particular sites or functional groups on the surface of the adsorbent

Chemical adsorption occurs when the adsorbate reacts with the surface to form a covalent or an ionic bond. And they generally cannot accumulate it more than one molecular layer because of the specific bond between adsorbate and surface. This chemical adsorption is specific. It cannot form multiple layers. It is specific to that particular site at that particular location due to the characteristics of both that adsorbent and the adsorbate.

It is specific so it cannot form beyond one particular layer that is something to keep in mind. The bond may also be specific to particular sights as I mentioned functional groups on the surface of the adsorbent, this is what we just discussed.

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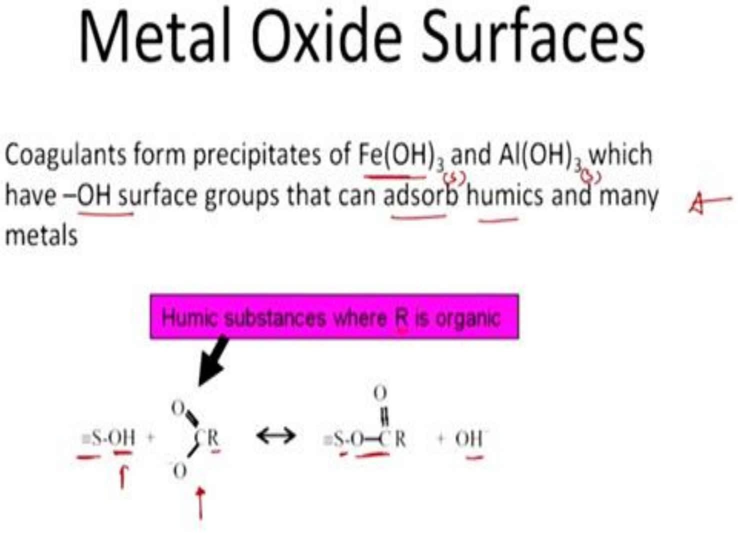

Metal Oxide Surfaces

Coagulants form precipitates of $Fe(OH)_3$ and $Al(OH)_3$ which have –OH surface groups that can adsorb humics and many metals

Humic substances where R is organic

$$\equiv S\text{-}OH + {}^{-}O(O)C\text{-}R \leftrightarrow \equiv S\text{-}O\text{-}C(=O)\text{-}R + OH^{-}$$

And another aspect which we discussed in another context; coagulants we know that can form precipitate $Fe(OH)_3$ the solid ferric or aluminium hydroxides. These can have OH surface groups and this is the precipitate out here, this is the OH surface groups. And these can adsorb humics and metals. And this is what we discussed when we talked about removal of NOM in the context of coagulation, flocculation and then precipitation.

We saw that some of the NOM can be removed, how is that? The relevant principle adsorption was occurring there. This is my particular organic compound, humic substance where is representative of the organic compound, COO-, this depends on the pH too. What happens when OH- is released, and this COOH, which COO- that is going to be bound to this particular precipitate or the metal oxide surface and it is going to be removed that is something to keep in mind.

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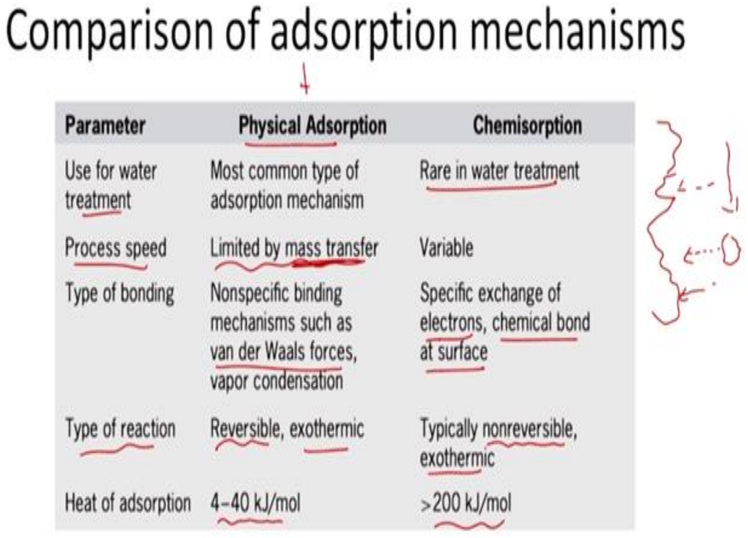

Comparison of adsorption mechanisms

Parameter	Physical Adsorption	Chemisorption
Use for water treatment	Most common type of adsorption mechanism	Rare in water treatment
Process speed	Limited by mass transfer	Variable
Type of bonding	Nonspecific binding mechanisms such as van der Waals forces, vapor condensation	Specific exchange of electrons, chemical bond at surface
Type of reaction	Reversible, exothermic	Typically nonreversible, exothermic
Heat of adsorption	4–40 kJ/mol	>200 kJ/mol

Comparison of adsorption mechanisms, physical adsorption is the predominant one that is used for or that comes into play with respect to water treatment, relatively rare in water treatment though. Process speed, what is the limiting factor? It is limited by mass transfer the water or the compound is flowing here. And this is my media and so this has to be transported to the media surface.

It is limited by mass transfer type of bonding, it is nonspecific, but in general, we are dealing with Vander Waal forces of attraction. Here it is specific exchange of electrons or chemical bond at the surface. And thus, this particular physical adsorption is reversible, while the chemisorption is typically non reversible and both are exothermic.

But if you look at the heat of adsorption, it is 4 to 40, relatively less for physical and much higher for chemisorption, that is one of the reasons with respect to the weaker and stronger bonds. That is something to keep in mind. But for our context, here, we are primarily concerned with physical adsorbent.

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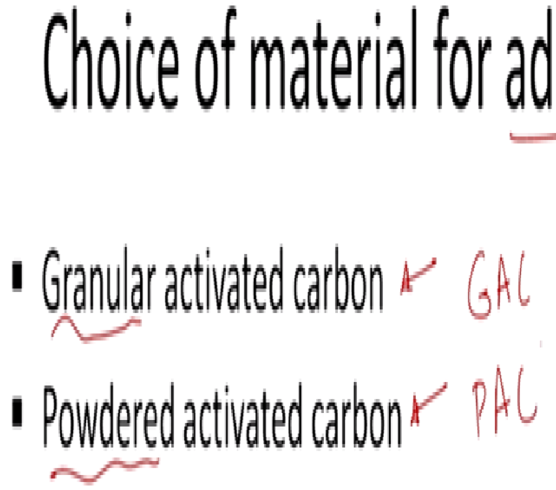

Choice of material for adsorbent ?

- Granular activated carbon GAC
- Powdered activated carbon PAC

How do I choose or what do I need to look at when considering choosing adsorbents? As I mentioned, typically, we use granular activated carbon and sometimes powdered activated carbon but this is really not as much used in practice. Key aspect or difference is that granular and powdered; the size of the relevant particle is the relevant issue or concern or the distinguishing factor between GAC granular activated carbon and powdered activated carbon.

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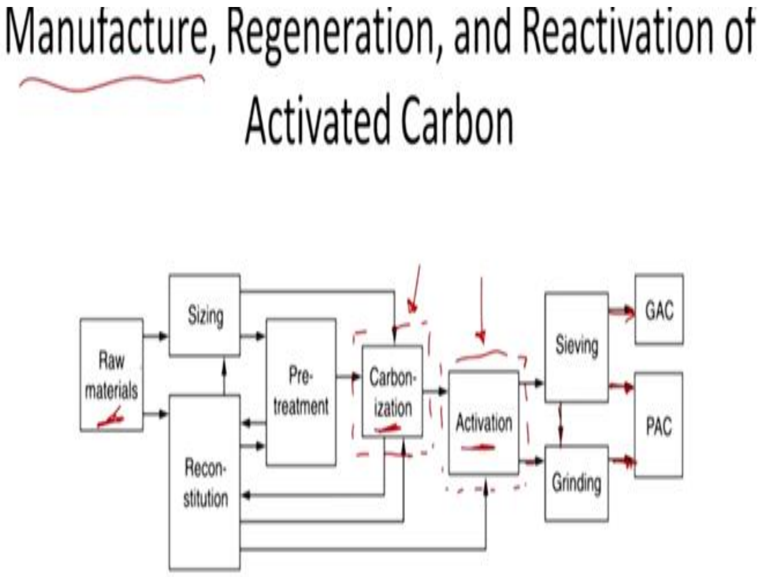
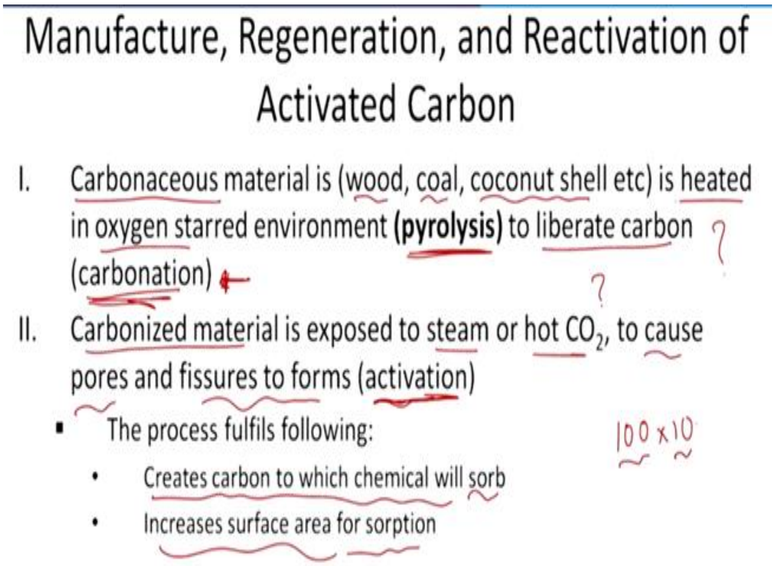


Manufacture, Regeneration, and Reactivation of Activated Carbon

How is it that you are going to manufacture this particular GAC or PAC, so first raw materials, different types of woods, coal. Sizing key aspect is that as you can see, everything comes to carbonization, that is one aspect. And after carbonization, we have what is called activation. Two aspects; carbonisation and the other one is activation and then sieving to look at the size or separating the size, the bigger ones GAC, small ones PAC. If you want PAC, you can grind it and then get PAC.

Now let us look at what this carbonization and activation is and what the raw materials are. **(Refer Slide Time: 17:55)**



Manufacture, Regeneration, and Reactivation of Activated Carbon

I. Carbonaceous material is (wood, coal, coconut shell etc) is heated in oxygen starred environment **(pyrolysis)** to liberate carbon (carbonation)

II. Carbonized material is exposed to steam or hot CO_2, to cause pores and fissures to forms (activation)

- The process fulfils following:
  - Creates carbon to which chemical will sorb
  - Increases surface area for sorption

100 x 10

Raw materials wood, coal, coconut shell etc., the key aspect is carbonaceous material. And, it is organic matter in a way. What am I trying to do? I am going to try to liberate the carbon, how am I going to do it? I am going to heat it in the absence of oxygen. It is not oxidation of the carbon and it is just liberating carbon or carbonation.

It is heated in oxygen starved environment which is pyrolysis. This is what we have pyrolysis and we are liberating the carbon here. This carbonized material is then exposed to steam or hot carbon dioxide, why? Because I want to form these pores and fissures which will lead to increase in the surface area. And this is activation, one is carbonization or carbonation.

And the other one is activation, one to liberate the carbon and the other one to activate the relevant surface area. It is granular activated carbon, that is something to keep in mind creates carbon to which may chemically will sorb or adsorb increase the surface area. First option one is creating this carbon on towards the chemical will absorb, the other one is creating the surface area.

One aspect notice that per one gram of this activated carbon you will have maybe 1000 meter square of surface area or such, not as big as soccer field. But you can understand the surface area that will be captured in 1 gram of this activated carbon. But let us look at the data before I go forth.

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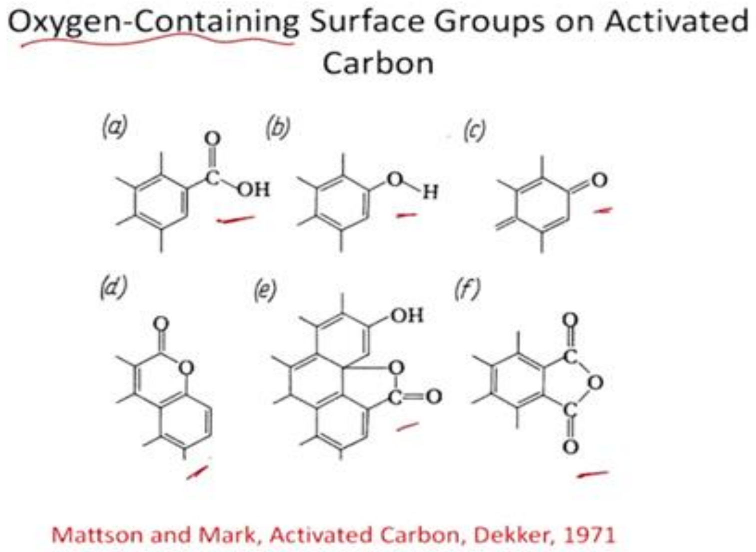

Oxygen-Containing Surface Groups on Activated Carbon

Mattson and Mark, Activated Carbon, Dekker, 1971

Depending upon the type of source, you will have different oxygen containing surface groups on the activated carbon which plays a role in this particular adsorption, so that is something to keep in mind.

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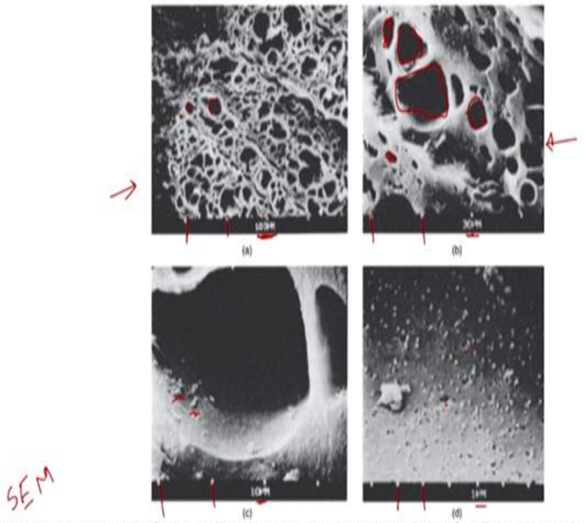

Scanning electron micrographs for lignite-based activated carbon. The scale line for all the SEMs is the interval between the white marks (clockwise starting in the upper left the scales are 100, 30, 10, and 1 μm).

And this is what it looks like when we look at it close up and how are we doing that? We are doing with scanning electron microscopy or micrograph. Scanning electron micrographs for lignite based, it is based on lignite based activated carbon. Here we have 100-micron, 30-micron scale, 10 micron and 1 micron. This is the scale, this is 100 microns, this is 30 microns, this is 10, progressive magnification.

Here you can look at the heterogeneity with respect to the pore sizes. And you can see how many pores are there in this particular 100-micron, magnified surface. You can see the number of surfaces available or number of sites available for absorption. And this is pretty clear when I magnified further the bigger, smaller pores all this inside also you will have the surface available for adsorption.

This is something that we looked at earlier. Much more magnified you see this. And you have other smaller groups or pores out here, further magnification you see that it is remarkably heterogeneous and it is not homogeneous. That is something to keep in mind. This is what we looked at earlier or this is the figure. We saw the bigger pores, we saw the smaller pores, and so forth.

Depending upon the pore size and the time available, you are going to have the compounds of interest being adsorbed all over this activated carbon. Over time, the relevant surface area is going to be completely taken up by this particular adsorbate, adsorbate which is going to be accumulating on the surface of this adsorbent which is the GAC.

And then what do you need to do? You will need to typically dispose it and put in fresh one. In general, in water or at least with respect to water treatment, they do not use regenerated activated carbon. That is one thing to keep in mind.

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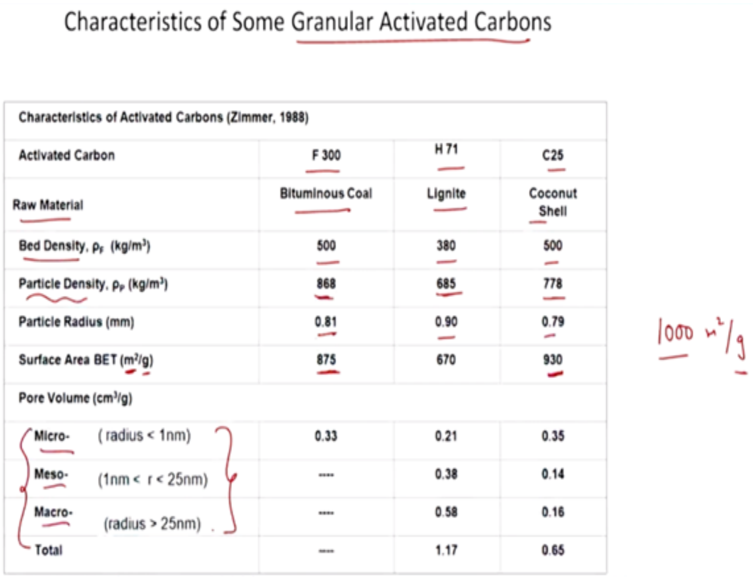

Characteristics of Some Granular Activated Carbons

Characteristics of Activated Carbons (Zimmer, 1988)

Activated Carbon		F 300	H 71	C25
Raw Material		Bituminous Coal	Lignite	Coconut Shell
Bed Density, ρ_F (kg/m^3)		500	380	500
Particle Density, ρ_P (kg/m^3)		868	685	778
Particle Radius (mm)		0.81	0.90	0.79
Surface Area BET (m^2/g)		875	670	930
Pore Volume (cm^3/g)				
Micro-	(radius < 1nm)	0.33	0.21	0.35
Meso-	(1nm < r < 25nm)	----	0.38	0.14
Macro-	(radius > 25nm)	----	0.58	0.16
Total		----	1.17	0.65

1000 m^2/g

Let us look at the characteristics of some GAC. Raw material, different types of raw material and the kind of code for the accurate carbon. Bed density is different and particle density is different, bed density packing will play a role. Particle density, different particles have different densities, radius also differ slightly and surface area as you can see 875 meter square per gram.

My earlier estimate of 1000 meters square per gram was not way off. Per just 1 gram of activated carbon, you are having almost 1000-meter square of the relevant area. And one other aspect to keep in mind is that the pore volume is taken up by pores of different sizes, micro and macro, you would want to find balance between these kinds of pore sizes, why?

Well, if you have everything to be small pores that is not going to be beneficial because your compounds of interest might be relatively across a diverse range with respect to size and also if you have to find pores, they can be? I should not use the term choke but that is the layman's term. That is so you want to have heterogeneity or greater diversity here. That is what you have out here.

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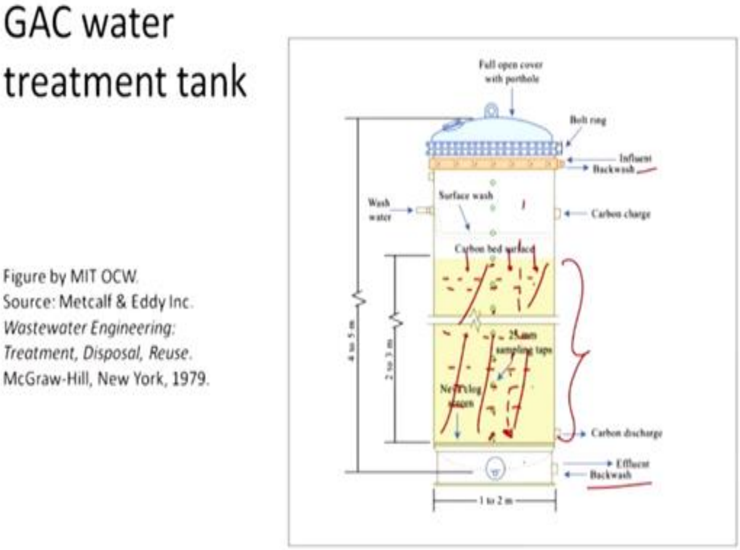

GAC water treatment tank

Figure by MIT OCW.
Source: Metcalf & Eddy Inc.
Wastewater Engineering: Treatment, Disposal, Reuse.
McGraw-Hill, New York, 1979.

And this is the activated carbon tank, typical activated carbon tank. There are different ways; bottom up or top bottom. Here you have top to the bottom influent and then some head and it is coming out of here. Or sometimes it is going to be pressured and pumped up. And you can know there are different ways to look at or understanding when this activated carbon has been exhausted, this is my media here.

As the water is passing through that the compounds are the adsorbate in the relevant solution is being adsorbed onto the adsorbent which is the granular activated carbon. After time, this will be exhausted. There can be indications if you are actually paying attention to the plant and the plant manager or operator is taking samples at regular intervals, you see the different sampling ports.

For example, here this water is coming in contact, here most of this will first be exhausted and then this exhausted layer will come down and down and then you will have breakthrough, we will look at this. Sampling ports will give you an idea about when this might happen. Sampling ports will give you an idea about where this particular active or mass transfer zone is and then you can predict when that is going to be exhausted.

Or one other way to look at the amount of pressure or head that is head loss that is occurring. That will also give you an idea about when you need to backwash or if it is already exhausted. Typically, we look at head loss for looking at how frequently you need to backwash the relevant surface not surface the media. That is what you see backwash setup.

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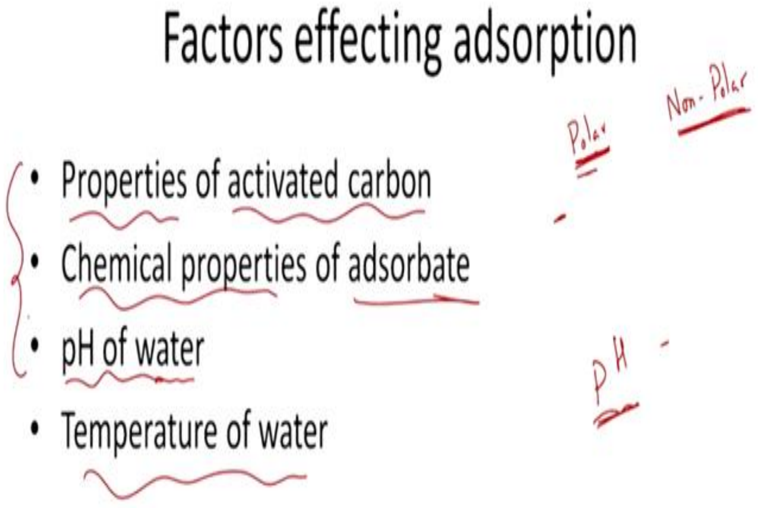

Factors effecting adsorption

- Properties of activated carbon
- Chemical properties of adsorbate
- pH of water
- Temperature of water

Factors affecting adsorption, different kinds of activated carbon and different properties, chemical properties of the adsorbate- aromatic, aliphatic, is it hydrophobic, hydrophilic, pH of the water. Certainly, as you can see some cases the pH will decide the charge on the relevant NOM or such. But in general, at pH neutral range, we are fine with respect to it, most of it will be negatively charged.

But one aspect I want to note here is that we talk about polar compounds and non-polar. Polar compounds which are hydrophilic will not be removed by adsorption, typically why is that? They have relatively negative and then water, polar solvent and they have a liking for each other. And this compound that has charge on it will not leave or find it difficult to leave the aqueous phase and be adsorbed onto the adsorbent.

That is something to keep in mind but if the compound is relatively nonpolar and then that is going to be adsorbed onto your relevant surface. In these cases, sometimes the pH will also play a role. That is something to keep in mind. Temperature of water too but mostly we are looking at these three aspects, let us move on. For example, humic acid- huge compounds, humic and fulvic acids, parts of the natural organic matter.

And these can have charge typically. But with respect to their solubility, they are relatively less soluble, why? Because of the structure- aromatic, aliphatic. Typically aromatic, they have a lot of these aromatic rings. They are thus not very much soluble in water. One other aspect to look at whether a compound will be easily adsorbed onto the media or not is looking at solubility of the compound of interest.

If the compound of interest has low solubility in water that will typically indicate that it will be relatively easily absorbed or more adsorbed, or wants to be adsorbed onto your adsorbent. That is something to keep in minds, so let us move on.

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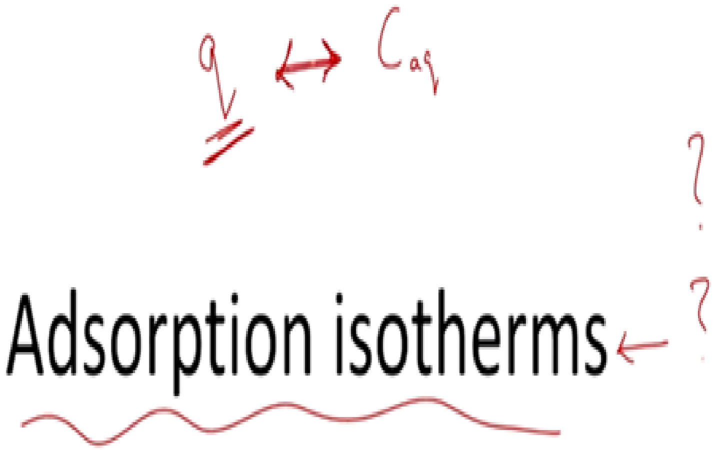

$q \leftrightarrow C_{aq}$

?

Adsorption isotherms ← ?

We are now going to move on to adsorption isotherms, what is this? And why is this relevant? Here we are talking about understanding the relationship between the concentration in the water or the bulk liquid phase, concentration in the aqueous phase and the concentration of the relevant compound of interest on the adsorbent. There is going to be equilibrium between them.

Assuming that we have a limited number of sides and you have relatively more concentration of your particular compound in the relevant water at equilibrium, the concentration, this q is also going to be relatively higher. It is going to be an equilibrium relationship between the two phases. Allowing for mass transfer to be relatively immediate, let us use a relatively effective mass transfer.

Here I want these isotherms to be able to predict what will be the equilibrium concentration in the aqueous phase. If I use this adsorbent, will I be able to achieve the level of desired compound concentration at the effluent that I want? And also, how much is the adsorbent that I need to keep for this or use for this volume of liquid? And these are the questions which will be or can be answered by these adsorption isotherms. That we will get it done in the next session. Thank you.