Course Name: Industrial Wastewater Treatment

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Week - 02

Lecture 09: Adsorption Process

So, welcome you all. Today we are going to discuss on lecture 1, which is based on the adsorption process. So, here we will be covering about the adsorption phenomena, basic concepts of adsorption, classification. Then we will be also looking on the adsorption isotherm, various types of isotherms like the most commonly used isotherm, Langmuir and Freundlich. We will be going in more details. Then we will be also having the mass balance analysis.

So, before going into more details, let us talk about some basic terminology about the adsorption. Basically, the adsorption is a process in which atoms or molecules move from a bulk phase, that is either from solid, liquid or gas, on to a solid or liquid surface. This can occur between two phases, namely liquid to liquid, gas to liquid, gas to solid or liquid to solid interfaces. Other terminology used is basically the adsorbate.

Adsorbate is basically the substance or the pollutant which need to be separated on to the interface of other surface and adsorbent is the substance or the material on which the adsorbate is being adsorbed. For example, the activated carbon, various types of bio adsorbent, silica-based adsorbent. So, these are the terminology which we use to describe between the adsorbate and adsorbent and then there is a similarly a process which we call desorption. The desorption is the release of the adsorbate from the adsorbent surface back into the water. Desorption processes antonyms of adsorption process.

Adsorption means that is adsorption of the molecules or atoms or the pollutant on to the surface of the adsorbent, whereas desorption means that is release or separation of the adsorbed molecule on to the surface of adsorbent to the bulk phase. Let us discuss about the basic difference between the absorption and the adsorption. The two terminology we use to describe the process of separation of molecules or pollutant from one phase to another phase. So, absorption if we say that is basically the bulk phenomena where the pollutant from the bulk phase of liquid gets transferred to the another phase of solid or gases or to the liquid depending upon the type of adsorbent we use. Whereas, adsorption is a surface phenomenon where the pollutants or the molecules atoms they get adsorbed on to the surface only not on to the entire volume of the adsorbent.

So, this basically if we say this is assimilation of molecular species or the pollutant throughout the bulk of the solid or liquid which is used as the adsorption. Whereas, if the accumulation of these molecules or atoms takes place at the surface then it is called as the adsorption process. So, another difference if we see absorption is not affected by temperature whereas adsorption process could be endothermic or exothermic this depends upon the type of the adsorbent. If it is a physisorption then this could be the exothermic process whereas the chemisorption which takes place that is mostly the endothermic process. Similarly, if we talk about the rate of reaction in case of absorption it occurs at a uniform rate whereas in case of adsorption the rate of reaction increases slowly and gets equilibrium after a certain time.

So, this is a steady increase in the rate of reaction till the equilibrium is achieved. Similarly, if we talk about the concentration of the pollutant or the adsorbate so that is basically uniform throughout the mass of the material in case of absorption whereas in case of adsorption it varies and it is non-uniform. Mostly the major concentration of the pollutant takes place at the surface so surface will be different concentration whereas within the pores there will be different concentration. So, these are the basic differences between the adsorption and the adsorption process and the basic principle that takes place behind the adsorption process. The adsorption is a surface phenomenon and is basically the consequence of the surface energy.

So, this surface energy where from it comes basically if we see at every surface there is a unbalanced residual forces that exist onto the surface of the liquid or the solid that creates this high surface energy onto the surface and due to this there is a tendency of the pollutant or the molecules or the atoms that species to come out of the solution and get adsorbed onto the surface whenever it comes to the contact of other interface. So, let us discuss about the mechanism of adsorption so we will be studying here what are different mechanism through which the adsorption process takes place. So, broadly we can classify like four types of mechanism one is bulk solution transport then is film diffusion transport then is pore diffusion transport and finally this is adsorption happens. So, in bulk diffusion transport that is achieved because of the process of advection and dispersion and this happens when the pollutants they are present in the uniform concentration in the bulk liquid. So, if in this diagram if we divide different phases so if we presume this is the liquid phase where the pollutant they are dissolved at a uniform concentration in bulk liquid and then immediately to this there is a stagnant liquid which is attached to the adsorbent and then this is the interface of adsorbent where stagnant film appears on the surface and the transport of molecules since here the all the molecules they are present here in the liquid at a uniform concentration.

So, here in this bulk phase because of this advection and dispersion process they will be in the uniform concentration and if we see there is a concentration here and the here there is a decrease in the concentration. So, this concentration gradient is established and because of

this concentration gradient the pollutant or the adsorbate that moves from bulk liquid phase towards the interface of solid and liquid that is within the stagnant liquid film the pollutants they will move and they will come to the surface of the adsorbate. If we see the concentration of particle if we measure that concentration will be decreasing. So, again here if we see the concentration at the surface is high whereas the concentration within the pore if we see that is having no solute so here there will be again a concentration gradient will establish and because of this concentration gradient the pollutant will move from surface within the different types of pores here, here and finally the pollutant when it reaches to its interior surfaces so they will get adsorbed because of the two process that is because of either to the electrostatic attraction because of unlike charges that attacks each other or maybe because of the Van der Waals forces that is basically the intermolecular forces which holds this adsorbent together on to the adsorbent surface. So, this is basically the different mechanisms of adsorption.

So, here this is basically the different mechanism of adsorbent step one that is diffusion of adsorbate onto the adsorbent surface. So, here this is the surface all the particles they get adsorbed onto the surface and then this is the step two where migration of the pollutant takes place within the pores and the micro pores. So, here from the surface if again you see there is a lot of concentration gradient will be there within this pore. So, because of this concentration gradient the pore diffusion occurs and pollutants from surface they moves inside the pores and they get accumulated in and finally get adsorbed onto the different pores of this adsorbent. So, in step three there is a buildup of concentration of this adsorbate onto the surface.

So, this can be the monolayer adsorption this can be multi-layer adsorption that depends upon the nature of the adsorbate and the nature of the adsorbent surfaces. Then let us talk about what are the different types of adsorption occur what are the different phenomena. So, broadly if we see the adsorption process we can divide into two process that is physio adsorption and another is chemisorption process. So, physio adsorption process if we say it arises because of the Van der Waals forces whereas chemisorption process that is because of the formation of a new chemical compound by breaking the bonds onto the surface of the adsorbent. So, this is basically the chemical bond formation occurs in case of chemisorption whereas in case of physio adsorption.

So, this is simply the Van der Waals forces which attracts the molecules to remain stick and attached with the surface. Physio adsorption if we say that is basically the reversible process because this is not having the strong chemical bond. So, the pollutants they are reversible in nature they can be detached easily from the surface of the adsorbent whereas in case of chemisorption process because there is a new compounds are formed new chemical bonds are formed. So, the pollutants are the adsorbate they cannot be dissolved easily from the surface of the adsorbent because they have different chemical bonding.

Another difference so the adsorbate do not react in case of this physio adsorption process whereas in case of chemical adsorption process the adsorbate reacts with the adsorbent and form a new compounds.

Similarly, if we see the enthalpy so enthalpy in case of physio adsorption process that is very low that is around 20 to 40 KJ/mol whereas in case of this chemisorption process the enthalpy is high and that is ranges from 80 to 240 KJ/mol. So, if we talk about the heat of exchange so in case of physio adsorption process normally the exothermic process, favorable at low temperature whereas in case of chemisorption process this is endothermic process where it favors with the increase in the temperature the rate of adsorption increases. Similarly, if we see no appreciable activation energy is required in case of physio adsorption process whereas the chemisorption process that requires high activation energy to start with the process. Then if we look into the type of adsorption like monolayer adsorption, multilayer adsorption. So in case of physio adsorption process there could be multilayers of adsorbate get adsorbed onto the surface whereas in case of chemisorption process so this is basically the monolayer adsorption process where there is a single layer of adsorbate that is being adsorbed onto the surface. Then let us talk about different types of adsorbents we use in case of adsorption process so most commonly used adsorbent that is activated carbon then there are other adsorbents also like activated alumina there is a clay there is a synthetic zeolites there are polymers there are resins there are silica gels so even nowadays number of bio-absorbents are evolved among these if we see the synthetic polymers and silica based adsorbents they are basically very costly and they are seldom used because of their high cost. Whereas activated carbon that is not very costly and is mostly used in the industry and nowadays even low cost of bio-absorbents are available and which are extensively used to in treatment process to reduce the overall cost of this adsorption process.

Then let us see in a simple photograph of this is like the white color activated alumina oxide and then this is zeolite then this is kind of resins we used and then these are the synthetic ion based adsorbents so these are the typical photographs of different types of adsorbent material we use in the process of adsorption and then let us talk about how these adsorbents they are prepared as we have seen there are types of adsorbent wherein the activated carbon is most commonly used in the industry so let us discuss more about its preparation and its properties what are the methods by virtue of which we can prepare the activated carbon so let us talk about the different process so the first of all we have to select a base material so base material could be the wood it could be the nutshell it could be coconut it could be cell material it could be lignin it could be coal it could be bones or any any carbon containing material which can be taken as a base material so first of all we need to select a base material, then preparation of the base material is also important because this base material that contains various types of impurities which we need to clean it out before it goes for carbonization which is the second step in production of this activated carbon so carbonization is essentially a pyrolysis process which results into carbonization

of base material that converts it into a char material which is very rich in carbon content and this process is carried out by heating the base material to a red heat at a temperature of around 700 °C and essentially it is done in absence of oxygen so this is done because if there is a lot of oxygen present it will oxidize the carbon materials so when this base material is heated to a temperature of 700 °C in absence of air and gets converted in the form of a char and then we need to go for activation. Activation means basically the development of porous structure within this char material which is produced as a result of carbonization so this is essentially done by adding the steam or carbon dioxide gases or any oxidizing gases at temperature of around 800 to 900 to so this char material is further kept into the muffle furnace and it is heated to around 800 to 900 °C and after this this is exposed to a oxidizing gases like steam or carbon dioxide which develops a porous structure in the char material and thus creates a number of pores, micro pores, nano pores, different size of pores within the char material which enhances its internal surface area so this is the process of activation which is basically very important to increase the specific surface area of the adsorbent. So finally this activated carbon is produced and then if we see during this activation process the following chemical reaction takes place the carbon is there in the char material when it is exposed to the water vapor so it will form the carbon monoxide and it will form this hydrogen so these gases are eluted out and then creates the porous structure. So properties of this activated carbon which is generated out of this activation process that basically depends upon the type of the base material we have used and also on the kind of methodology we have used to prepare this activated carbon. So even after this activated carbon is prepared then we can have its surface modification we can add different types of surface charges functional material which comes under this surface modification and how this is done we will be looking into the further slides.

So similarly we discuss about the synthesis of other natural adsorbent using the chemical activation process. So here we will be described about the SANA basically is the full form if we see that is super adsorbed natural adsorbent which is derived from non-usable bale fruit cells so that is called a BFS for drinking water treatment so this kind of adsorbent how it was prepared this is the simple methodology just to illustrate this is like the virgin bale fruit cells so we have collected it then the chemical activation process is done by adding phosphoric acid and this phosphoric acid when it is added into this this will dissolve all types of impurities present into the bale fruit cell and after this activation further we give the thermal treatment at around 500 °C we prepare this activated char and this char then can be used as a super adsorptive natural adsorbent that is SANA and this is basically used for removal of natural organic matter present in the water so when we add this SANA (super adsorptive natural adsorbent) into the water so it will remove out the pollutant and the water will get free from the different types of pollutants so this is the FESEM image before and after the process of activation so this is FESEM image of virgin bale fruit cell whereas this is the FESEM image of the chemically activated bale fruit cell so here we can see after chemical activation the pore size the internal pores they have been developed of larger size as compared to the virgin fruit cell so this is how the process of developing the natural adsorbent is carried out and the process of its chemical activation so this is basically

the expanded view of the internal structure of the adsorbent material like activated carbon if we see if we see this a small piece of this if we further enlarge it we will see there are number of pores, different size of pores, hair size pores then comparatively bigger size of pores. So this depending upon the diameter of the different pores developed within the activated carbon we can classify like micro pores which have the diameter more than 50 nm whereas mesopores which have the diameter varies between 2 nm to 50 nm whereas the micro pores they are basically having size <2 nm so the micro pores they have the size having the diameter <2 nm then let us see the various properties of the granular and activated carbon derived from this process so if we see these are the parameters like if we see the particle size surface area bulk density there are number of properties if we see so if we compare this is granular activated carbon and then this is powder activated carbon the basic difference both are activated carbon one is having a smaller size one is having bigger size so the size range > 0.1 mm they comes under granular activated carbon whereas the size having <0.074 mm they are called as powder activated carbon. similarly if we see the surface area is very high that is 700 to 1300 m^2/g whereas in case of the powdered activated carbon the surface area is much higher compared to the surface area of granular activated carbon that is 800 to 1800 m^2/g so similarly here we can see the bulk density that is 400 to 500 kg/m^3 in case of granular activated carbon whereas it is 360 to 740 in case of powder activated carbon basically if we see this is the typical example of the various characteristics of granular and powder activated carbon which is normally used in the industry for removal of various pollutants using this adsorption process. So then let us talk about the various factors how this adsorption process is affected what are the different factors so let us talk about the nature of the adsorbate so nature of the adsorbate if we see if there are liquefiable gases like NH_3, HCl, Cl, SO_2 they are basically readily adsorbed than the other gases like O_2, N_2, and H_2. The adsorption process also depends upon the solubility of the adsorbate so if the solubility of adsorbate is more the adsorption process is less like the rate of adsorption will be less if the adsorbate is insoluble solubility is less than the adsorption of that pollutant is more. So similarly if we see the nature of the adsorbent and the surface area it is highly dependent upon the surface area of the adsorbent so this adsorbent is basically as I told there is a different types of adsorbent there are costly adsorbent, there are low cost adsorbent, there is activated carbon which is mostly used so this is very selective in nature which is based on the its cost its efficiency its adsorption capacity so this is very selective and basically if we see the adsorption and the surface area that is basically in direct proportion more the surface area more is the adsorption. Similarly the presence of active groups on the adsorbent surface like if there is a polar or activated groups present so it will increase the process of adsorption then let us see another factor that is temperature as we have discussed there is two types of adsorption that is video adsorption process there is a chemisorption process so in case of physisorption process normally the adsorption process is not affected but it if we see overall this is inversely proportional to the temperature so physisorption process with increase in the temperature will decrease whereas it is favored in case of low temperature whereas in case of chemisorption process so this chemisorption process again is the temperature dependent up to the equilibrium limit is reached then it is inversely proportional to the temperature.

So chemisorption process basically if we see that is endothermic in nature so it will increase if the temperature increases and if the temperature decreases the rate of adsorption will also decrease and this happens till the equilibrium is not achieved and after the equilibrium this chemisorption process again it is inversely proportional to the temperature. See the pressure this is another important factor which affects the process of adsorption as we discuss pressure in case of chemisorption process the adsorption is not affected by the pressure whereas in case of physisorption process it increases with increase in the pressure so this is like the illustration here if we see the rate of adsorption if we plot the pressure onto the x-axis we will get a kind of this curve so it demonstrate that the increase in the pressure will increase the rate of adsorption till the equilibrium is achieved and after that there is a no further increase in the rate of adsorption even after increasing the pressure. So then let us we discuss about the various types of adsorption isotherms let us discuss about what is adsorption isotherm. So adsorption isotherm if we say that is a mathematical model or the functional expression this depicts the distribution of solute between the solid and the liquid surface at the equilibrium at a constant temperature. So this basically gives the quantity of adsorbate that can be absorbed per unit weight of the adsorbent at a constant temperature and the relation showing between the quantity of adsorbate that can be absorbed per unit weight of adsorbent at a constant temperature is called as the adsorption isotherm. So if we see the equation $q_e = \frac{(C_0 - C_e) \times V}{m}$. So if we see q_e is basically the adsorbent phase concentration after the equilibrium means how much adsorbent is being absorbed per unit weight of adsorbent so this we can get by multiplying with the volume of liquid so the adsorbate phase concentration of the after the equilibrium can be computed by this equation whereas q_e is the adsorbate phase concentration after the equilibrium is achieved it means the milligram of adsorbate that is absorbed per unit weight of the adsorbent and C_0 is basically that is the initial concentration of the adsorbate that is in milligram per liter similarly C_e if see that is the equilibrium concentration of adsorbate after the adsorption process occurred and this V is the volume of the liquid that was taken in the batch study and then M is the mass of the adsorbent that is being added to the solution for adsorption to occur so we can say this q_e value that can be find out by using this equation so this is how this equation came that is simple a mass balance analysis of the adsorption process suppose we take a sample having certain initial concentration we add some adsorbent into that and then after the adsorption process is occurred we take out the sample and again measure the concentration of that adsorbate in the solution so we can have a mass balance of how much is being absorbed how much is being there in the liquid phase so this all the analysis comes under mass balance analysis so if we see to find out this amount of adsorbate that is being absorbed that will be equal to initial amount of adsorbate in the solution minus final amount of adsorbate after the adsorption is over if we say $C_0 \times V$, C_0 is the initial concentration and V is the volume of the solution taken so this will multiply $C_0 \times V$ will give you the amount of adsorbate initially present into the solution and similarly $C_e \times V$ that will give the amount of adsorbent that is now present into the solution after the adsorption process is done so this will be equal to that will be the amount of adsorbate being absorbed onto the adsorbent so this will be q_e e if q_e is the mg of adsorbate being absorbed per gram of adsorbent m is the weight of the adsorbent that is being added so multiplying this will

give you the total amount of adsorbate that is being absorbed so by balancing this the amount of adsorbate initially present in the solution then after deducting with the amount of adsorbate present in the solution will give us the amount of adsorbate that is being absorbed and that can be finally calculated by $\boldsymbol{q_e} = (\boldsymbol{C_0} - \boldsymbol{C_e}) \times \frac{\boldsymbol{V}}{\boldsymbol{M}}$ that is the concentration different before and after the adsorption multiplied by volume and then divided by the mass of the adsorbent. So this is basically the mass balance analysis this is required to develop the various isotherms as we have discussed there are various isotherms number of isotherms but in this course we have taken the two important isotherms which are most widely used in the industrial wastewater treatment process. So this is Langmuir isotherm and the second one is Freundlich isotherm so we will be discussing one by one in more detail of all these isotherms. So let us discuss about the first isotherm which is the Langmuir isotherm so this is the equation $q = \frac{q_m K_A C}{1 + K_A C}$ and if we see q_m basically this denotes the maximum adsorption capacity which the unit will be mg/g of adsorbent now this K_A basically that is the Langmuir constant which is the function of the enthalpy of the adsorption and the temperature whereas C is basically the concentration of the pollutant and q is basically the adsorption capacity so before going into the more details let us see about the various assumptions that are made during derivation of this Langmuir model so one important assumption that is reversible process means adsorption is reversible the molecules attached onto the surface can be detached it can be dissolved back to the solution and there is a monolayer adsorption and then the enthalpy of adsorption process is same for all so these are few assumptions that we take while derivation of this Langmuir isotherm so if we see the linearized form of the Langmuir equation we can rewrite it as $\frac{1}{q} = \frac{1}{q_m} + \left(\frac{1}{K_A q_m}\right)\frac{1}{C}$ so this is basically the equation which is used as a linearized equation of Langmuir model so in this equation if we see equation of straight line if we see this is m if you see this is taken as x and if we see this is taken as c and if we take this as y so this will give as a straight line equation in the form of y = mx + c so if we plot x versus y means $1/q_e$ on to the y axis and $1/C_e$ on to the x axis we will get a curve so this curve basically will define the value of different parameter of Langmuir model so if we measure the slope of this equation that will give you value of m so this m value will basically give the value of m will give $\frac{1}{K_A q_m}$ so this is basically the slope of the line that will give us the value of $\frac{1}{q_m}$ if we extend this line here so we will get certain intercept value so this intercept value if we measure so this will be equal to $\frac{1}{q_m}$ so this is basically the determination of various model parameters of Langmuir isotherms similarly the Freundlich isotherm if we talk about the Freundlich isotherm this can be explained by this equation $\frac{x}{m} = K_f C_e^{1/n}$ so whereas K_f is basically the Freundlich capacity factor which is equal to mg of adsorbate into liter of water that per milligram of adsorbate to the power 1/n so this is the unit of K_f that is Freundlich capacity factor whereas x/m if we see this is the mass of adsorbate that is being adsorbed per unit mass of adsorbent similarly if we see c_e is the equilibrium concentration of adsorbate in to the solution after the adsorption is over and then 1/n that is the Freundlich intensity factor so if in this equation again if we plot the linearized form if we take log of the equation on

right hand side left hand side both so we will get its linearized form and so if its linearized form will be $\log\frac{x}{m} = \log K_f + \frac{1}{n}\ logC_e$ that will be equal to $\frac{1}{n}\ logC_e$ this is again is in the form of a straight line relationship so if we plot this log of x/m on to the y-axis and this logc on to the x-axis we will get a straight line equation whose intercept will give the value of logk whereas the slope will give the value of 1/n so this is how we can determine the Freundlich model parameter for describing the Freundlich isotherm concepts mechanism of adsorption various types of isotherms then how these isotherms are developed using batch and column studies what are the different design parameters for designing a column adsorption column so this all the topics we will be studying in the next lecture that is lecture 2 on module 2.

So, thank you.