Physico-Chemical Processes for Wastewater Treatment
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Lecture 31
Adsorption I

Good day everyone and welcome to these lectures on Physico- Chemical Processes for Wastewater Treatment. So, in the previous lectures, we have studied the various unit operations that are used in water or wastewater treatment and those unit operations included like flow, equalization basin, coagulation and flocculation, settling, then filtration. So, all these basic theories, the design aspects and some of the basic approaches which are used in the wastewater treatment via these techniques were discussed earlier.

Now, from today's lecture, we are going to start another section which is called as adsorption. And adsorption is used in virtually all the chemical industries for separations of gases as well as for separating some of the key elements or molecules out of various gaseous streams or liquid is streams.

A waste adsorption is also very common in wastewater treatment, be the treatment is being done at large scale or small scale and so, adsorption is very very common unit which is used in virtually all the water or wastewater treatment methods which are practiced. So, what is adsorption?

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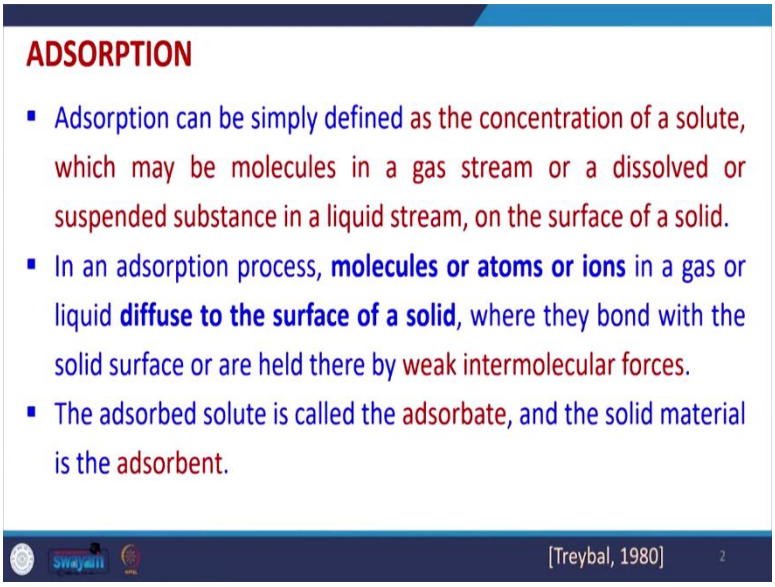

So, we can define the adsorption as the concentration of a solute and that solute maybe molecules in a gas stream or a liquid or suspended substance in a liquid stream on the surface

of a solid. So, the key thing is that, that we have a solid and on the surface of the solid we try to remove that component which is either undesirable or desirable sometimes also from a stream which may be gaseous stream or a liquid stream.

So, both separations are possible, certainly the solid which is used, that is selected in such a manner that whatever is desirable that can be achieved. So, in the adsorption processes, the molecules or the atoms or the ions which are there in the gas stream or the liquid stream, they diffuse to the surface of the solid where they bond with the solid surface either by weak intermolecular forces or strong forces also and they remain there.

So, the solute or the molecule or ion which gets actually separated out it is called as adsorbate and the solid material which is used for separating this it is called as adsorbent, so selection of adsorbent depends upon the adsorbate which has to be separated out, also it depends whether we have a gaseous stream or we have a liquid stream, how much separation has to be done, whether the solution is highly concentrated or it is highly dilute. So, depending upon various parameters, we have a selection procedure for adsorbent.

And then the system, whole system is designed which is used for doing the separation. So, in this lectures on adsorption, we are going to study all these aspects in detail and we are going to design, our ultimate aim is to have a simple design which can be used in a industry or during water treatment in any Municipal Corporation, etc. Going further, the selection of adsorbent is very very important, it has been highlighted in the previous slide. Now, there are various types of adsorbent which are there which can be used for removal of pollutants.

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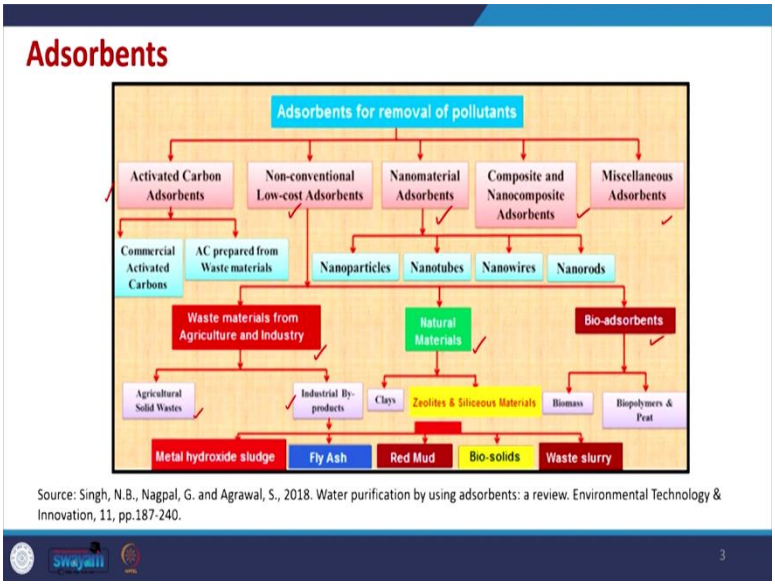

So, these may be like activated carbon based adsorbents, other type of non-conventional low cost adsorbents. There are many nanomaterial adsorbents which are getting developed. So, these may be there we may have a composite or nano composite adsorbents for various applications and then various miscellaneous adsorbents also. The activated carbon adsorbents are most common and they are commercially used in most cases for water or wastewater treatment.

In addition, other types of adsorbents like low cost adsorbents are also being developed and used in the water treatment. Now, these non-conventional low cost adsorbents can further be categorized into three categories. So, based upon their development, so, waste material from agriculture and industry can be used for development of such adsorbents.

Similarly, natural materials like clays, zeolites and silica materials all these can also be used as an adsorbent. So, depending upon the processing they may be low cost or higher cost, then bio adsorbent like biomass and biopolymer etc. can also be used further as adsorbents. Within waste materials they can be agriculture waste materials and industrial byproducts also. So, there are and within industrial byproducts there may be metal hydroxide, sludge flyers, red mud, so, many types of materials can be converted into adsorbents, depending upon the property which is gained by the adsorbents, they can be used for different applications.

So, this is going we are going to learn what are the different properties which are very, very important in judging their probable applications in different fields that maybe gas phase adsorption or liquid phase adsorption within liquid phase adsorption, whether they can be used for removing acidic materials or basic materials, whether they can be used for removal of molecules, metals, all those things we are going to discuss in these subsequent slides.

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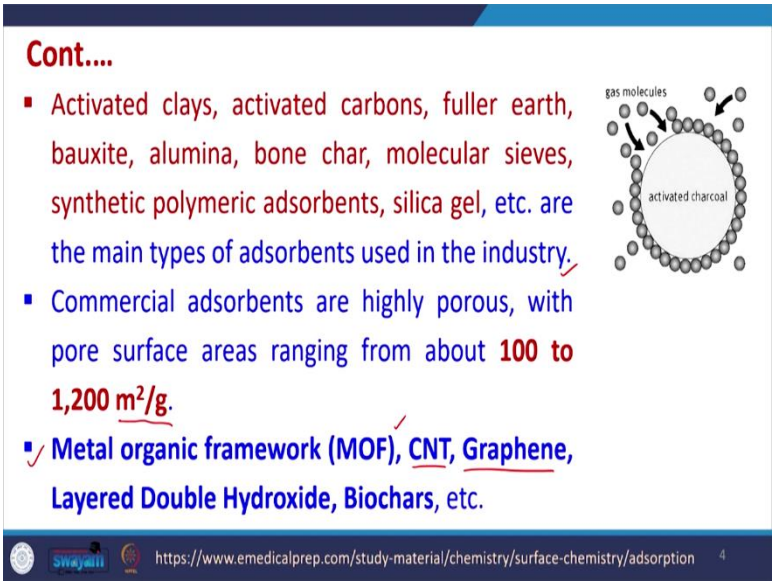

Now, activated clays, activated carbons, fuller earth, bauxite or alumina, bone char molecular sieves, synthetic polymeric adsorbents, silica gel, these are the most common adsorbents which are used in the industry. So, they are already developed up to a commercial scale and they are most commonly used in the industries. Whenever we are selecting any adsorbent, one of the foremost and important property of the adsorbent which is desirable is the surface area. So, most of the commercial adsorbents generally we require they may be having surface area in the range of 100 to 1200 meter square per gram.

Remember it is meter square per gram. So, that is very, very huge amount of area in very small per unit mass of the adsorbent and this is what is desirable. So, surface area increasing the pore surface area is one of the most important features which all the scientists are targeting and they want to have the material which can have largest surface area possible, so, that they can increase the capacity of these adsorbents with respect to removal of pollutants out of the water.

So, many researchers all over the world are trying to develop or use new type of adsorbents for various water treatment as well as for gas separation etc. So, some of these adsorbents include metal organic framework, which may have surface area beyond 5000 or 6000 meters square per gram. Similarly, carbon nanotubes, graphene, graphene oxide, layered double hydroxides, etc. are also being used and being developed by various researchers and industries for various applications.

Similarly, biochars which can be developed from the agriculture materials, biomass or industrial waste materials, they are also being targeted because they are of low cost and in those development actually we are using waste materials. So, in a way we are recycling them, so, biochars etc. are also highly focused area of research we are many people are working all around the world. So, first and foremost, we always tried to develop some adsorbent which must have very high pore surface area. So, this is the most important feature that is looked in any adsorbent.

Now, there are many types of activated carbons, zeolites, polymeric adsorbent. So, some of the different adsorbent types, their characteristics, advantages and disadvantages are discussed in this slide and subsequent slide. So, activated carbon is the most adsorbent, which is used everywhere in particular and that activated carbon we can be made from various sources, some of the common sources include like coconut shell, the choir pit, etc. So, any waste material which has lot of carbonaceous content, so, that can be used for development of any adsorbents. So, this is possible.

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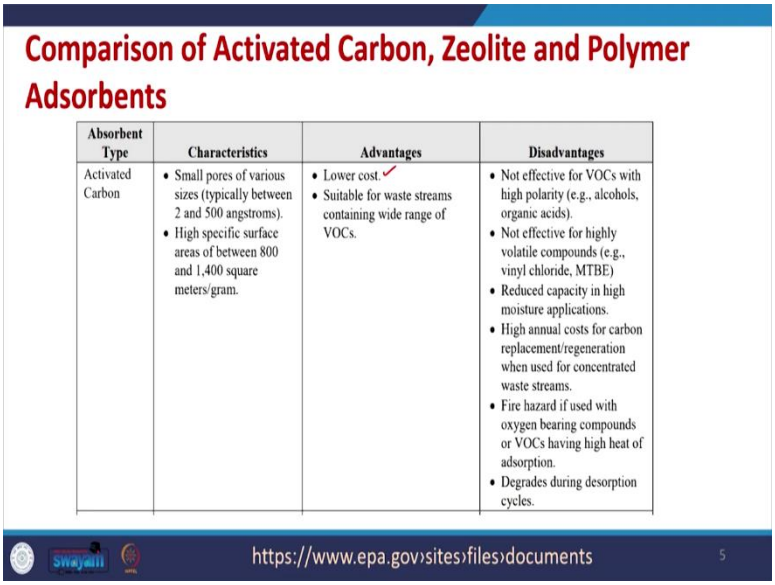

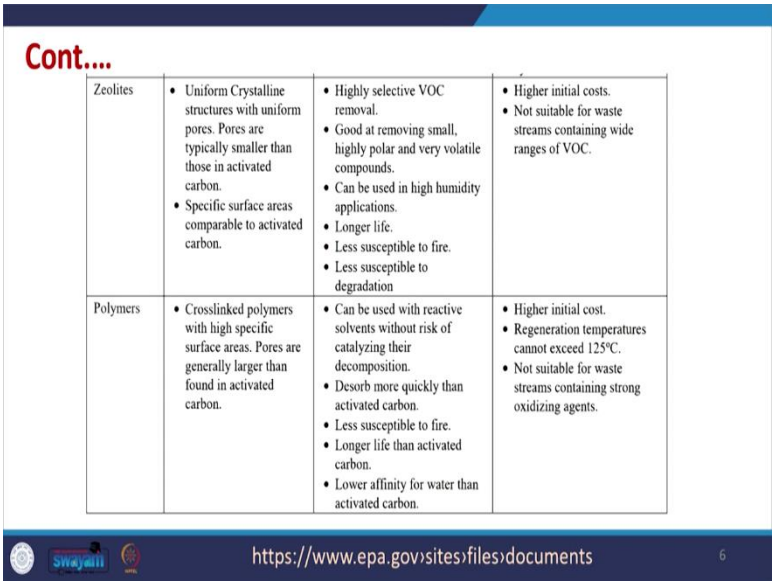

Now, the characteristics which include for activated carbon include the various size of pores, so, they may range from 2 to 500 angstrom, so, they are very wide range. So, that is why their applications are also wide and they have very high surface area which is desirable as compared to other low cost adsorbents. So, they have the main advantage is they are low cost and they are very suitable for removing various pollutants including wide range of VOCs, etc. And they cannot be used for like removal of VOCs with high polarity other types of compounds etc.

So, they may have certain disadvantages also many times but they are generally the most common adsorbent which is used everywhere. Similarly, zeolites etc. are also very common and zeolites, the good thing with zeolite is that they have very uniform crystallized size, structure with very uniform pores. So, that means if they have very uniform pore, we can design the pore size also. And that is how we can select a zeolite with different pore sizes. So, that is why if suppose we have a stream which is having molecules of different size ranges, so we can easily separate them out using the zeolite of different pore sizes.

Now, a specific surface area is higher generally as compared to activated carbon. So, they can be used for various purposes. Similarly, polymers are also there. So, crosslinked polymers with high surface area, they have very large larger pore size as compared to activated carbon or zeolite. So, they can be used for wider application, they have certain pores in the range of mesopores and other things.

Generally, they have very high initial cost, which is the disadvantage with respect to polymeric types of adsorbents which are there. The regeneration temperature for these

polymers is also an issue because they cannot be heated beyond a certain temperature otherwise, degradation in the polymer may happen. So, that is one of the key aspect that we have to take care whenever we are selecting any polymeric adsorbent. So, there are various advantages and disadvantages with respect to polymers also.

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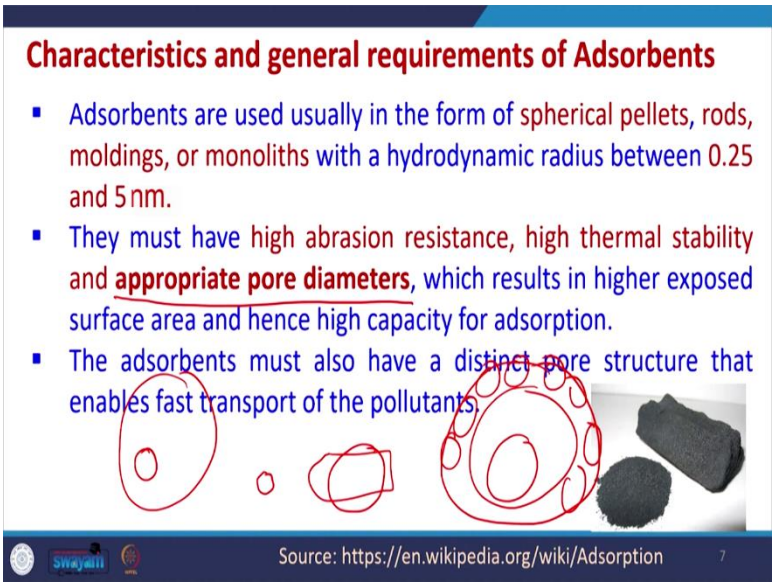

Now, going further, there are always some characteristics and general requirements of adsorbent, we came to know that surface area is one of the important properties that we always look in any adsorbent. There are many other properties also that may be there. Now adsorbents may be in the form of spherical pellets, rods, moldings, monoliths with hydrodynamic radius between 0.25 to 5 nanometer and also along with that. So, we always try to select those adjustments, which when used in the packed bed, they should have a lesser pressure drop when the liquid or gaseous stream is moving through that bed.

So, that is very, very important consideration in selection of any adsorbent. So, this is one of the features that we always take care of, we select that adsorbent in such a manner that our these the pressure drop criteria is met. They must also should have high abrasion resistance, high thermal stability and appropriate pore diameter. The thermal stability criteria is more important for gas phase separations, where because the gases may be at high temperature.

For liquid cases where temperature for water or wastewater treatment, the temperature is not that much important, but abrasion resistance may be important for those waters which may be highly acidic or highly basic. So, under those conditions, the adsorbent selected should be chemically stable also. And that is one of the important features we always look for. Now, in

addition to abrasion resistance and thermal stability, appropriate pore diameter is very, very important.

And if we have appropriate pore diameter, it will result in highly exposed surface area and hence high capacity of adsorption. So, what is the appropriate pore diameter, I will just give you an example. So, suppose we have a gaseous systems and we have some gas that has to be separated out of the other gases. Now, the gas molecular size are lower as compared to liquid molecules suppose, suppose any dye molecule is there.

So, for dye molecules the pore size maybe the its molecular size may be larger, whereas, for gaseous molecules if the molecular size will be smaller, so under that condition, if we select suppose an adsorbent which is having a pore size, which is less than the molecular size of the dye molecule and so suppose the pore sizes something like this, so this dye molecule cannot go inside the average pore diameter which is there of the adsorbent. So, under that condition, the selection of adsorbent has not been correct.

Because the molecule dye molecule cannot go inside that adsorbent which is having pore diameter lower than the molecular size of the adsorbent itself. Now, that particular adsorbent it is possible that it is having a very high surface area, but still it is not able to adsorb the liquid dye molecules in the liquid phase. The same adsorbent it is possible that it may separate the gaseous molecules because the size range of the gaseous molecules will be much smaller than the dye molecules.

So, the same adsorbent may work very well for the gas phase adsorbent, but it may not work for the liquid phase adsorbent. Now, if we select suppose in a second case, if we select a size molecular size range is again same and we are selecting a proper appropriate pore diameter adsorbent which is having the size molecular size like this. So, it is possible that the molecules will now go inside and they will reside like this on the pores, side of the pores. So, this is possible.

Now, suppose we use this adsorbent for gas phase separation, so, and only mono layer separation is occurring or mono layer formation is occurring. So, in that condition most of the space in between the pores will be unutilized. So, under those conditions, the same size, same pore diameter adsorbent is working very well for the dye molecule, but its capacity may not be that good for the gas phase separation, though the guys is always is going inside that pore

of the adsorbent and getting separated, but the capacity or the amount of gas separation is not proper.

So, selection of appropriate pore diameter adsorbent is one of the very, very important consideration in selection of the adsorbent. The adsorbents must also have should have a distinct pore structure that enables fast transport of the pollutants. So, in this condition what is it is meant that is suppose the molecular size is this. So, the pore size of the adsorbent should be at least 5 to 10 times more than that. Otherwise, that diffusion of the adsorbate into that adsorbent will become sluggish or very slow and kinetic issues will come into picture.

So, that means, if there is a kinetic regime which is controlling this pore diffusion, then the overall it will take a lot of time for adsorption to occur and overall the system may become very huge for the same separation. So, these aspects we are going to discuss more in later. Now, most of the industrial adsorbents fall into one of the following classes like oxygen containing compounds, carbon based compounds and polymeric based components.

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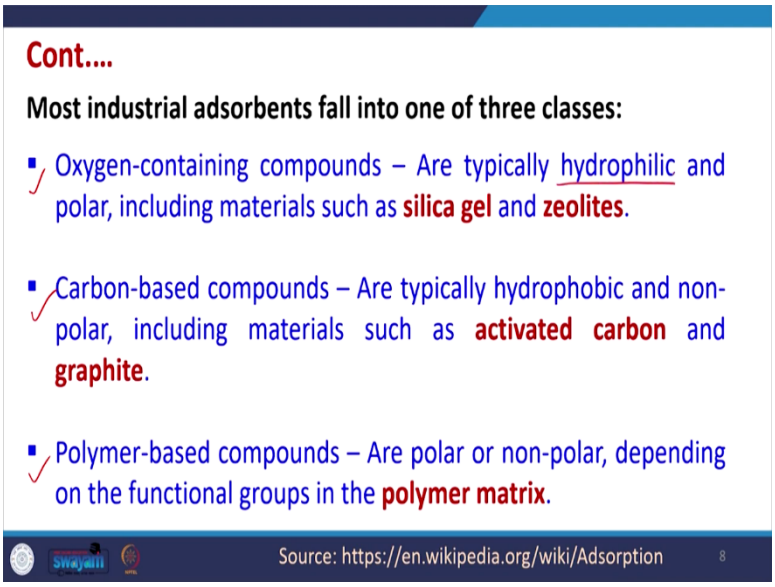

Now, oxygen containing components are typically hydrophilic and polar, so, they do not generally prefer the water to be adsorbed. So, this is what you desirable in the water treatment. So, these may include silica gel, zeolites and other types of material. So, we may have a proper selection whether it is hydrophilic, hydrophobic or any other thing. So, this aspect we have to see that it should be there like hydrophilic but sometimes we do not require hydrophilic, we require hydrophobic.

So, carbon based adsorbents can be better because they are hydrophobic, but they are nonpolar. So that means, they will be able to adsorb everything and anything; for polar bass compounds, then we preferably better adsorb in a polar bass adsorbent. So, that possibility is there. So, we always look whether it is hydrophobic, hydrophilic, etc. So, that aspect is very important that is why activated carbon is highly used in the industry for wastewater treatment. Now, silica gel can very well working in the gas phase adsorption because it will able to separate out the any moisture which is there in the steam.

So, that is possible, similarly, zeolites can also work very well, then there are polymer based components also which are used as adsorbents, they may be polar, they may be non-polar depending upon the functional groups which are important in the polymer matrix. So, this is the now, it this slide shows that there is a lot of importance of the functional groups which are there in the adsorbent. Now, suppose, we have to use an polymeric adsorption, polymeric base adsorbent for wastewater treatment and that wastewater has some particular compounds which are toxic or it may be containing some pathogens.

So, under those conditions, if we can impart some functional groups in the polymer itself, which may be deterrent towards those toxic compounds. So, those toxic components will be attracted or they may be broken by these functional groups or attracted by these functional groups and they may be separated out easily. So, suppose any adsorbent is basic in nature. So, it will be very good in the adsorption of any acidic compounds.

Similarly, if that adsorbent is acidic in nature, it will remove basic components. So, in this way, we can take an adsorbent, we can impart some 10 properties, which may be acidic or basic, we can impart certain functional groups within the adsorbent materials. And in this way, we can specifically design the adsorbent with respect to functionalities, so, that they can easily remove the targeted pollutants are removed most of the pollutants, so, that means, the third important property is the functional group.

So, along with the surface area, pore size, the functionality of the different functional groups, which are there on the adsorbent that becomes very, very important. Now, how to compare different adsorbents for water treatment or for wastewater treatment. Suppose, we have 10 or 5 adsorbent, now, how to select out of that, which is working very well. So, there are certain parameters based upon which we test them.

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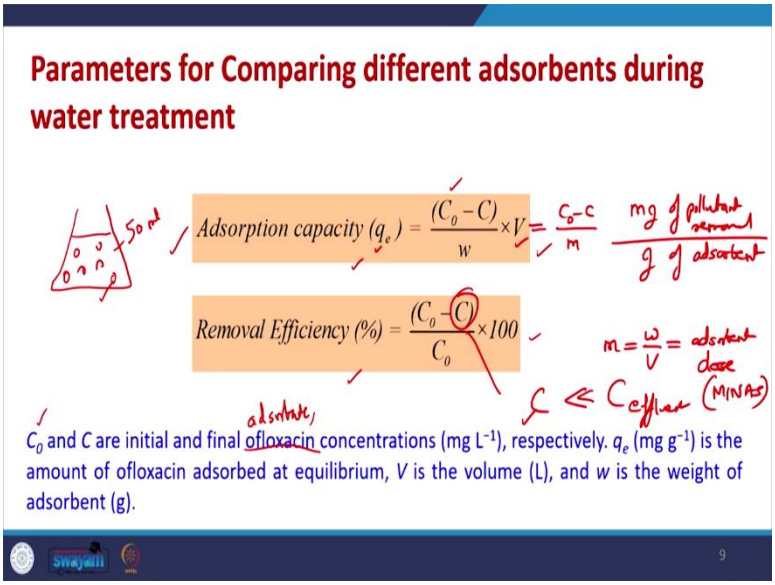

So, that details will be given in the next lectures, but the basic idea is that the that any of the adsorbent should have very good adsorption capacity. So, this is very important and that it is defined by this equation which is there. So, and it is generally given like this in milligram of pollutant or any pollutant removed per unit mass of the adsorbent or per gram of adsorbent. So, this unit may be used for comparing different types of adsorbent. And we tried to find out this via conducting some batch studies what. So, what we can do is that we can take the water in simple beaker which has to be treated and which is containing that particular compound or undesirable components.

And in that water what we do is that we mix the adsorbent certain amount so, these details we will discuss later and we shake these beakers for certain durations. Larger the duration it is better, we can save them for 24 hours or 48 hours. And after that, we initially check the concentration. So, C0 is like the initial concentration of the any ofloxacin or any other adsorbate in the solution and then we cross check the final concentrations, the example is for ofloxacin, suppose ofloxacin is there in the wastewater.

So, we check the initial ofloxacin concentration, we check the final ofloxacin concentration and this way we can find out C0 and C, W is the mass or weight of the adsorbent which has been added. So, we take different beakers and we try to see that what is the maximum amount which has been adsorbed and V is the volume. So, V is the volume of the solution suppose, it is 50 ml of the sample that has been taken in the water. So, we can by carrying out this test, we can find out 2 parameters, one is that adsorption capacity and another is the removal efficiency.

So, we can easily find out the removal efficiency and we can also find out the maximum adsorption capacity which is possible. So, and this we can find out using different approaches which is called like isotherm approach is there. So, we will discuss those in the next lectures. So, adoption capacity which is measured in milligrams of pollutants removed per gram of adsorbent is the property which is useful in finding out or comparing different types of adsorbents.

Remember this formula this is this is adsorption capacity is generally in wastewater treatment is noted by q. So, q we will be discussing in detail sometimes this formula is also reported like C0 upon minus C upon m. So, m is the adsorbent dose which is like W upon V and this is called the adsorbent dose which has been used. So, higher the adsorption capacity better is the, better it is the to select that particular adsorbent and for our uses. So, we can always compare a using the adsorption capacity as well as the removal efficiency, the same adsorbent may have different capacity for different targeted compounds.

So, it is possible similarly, sometimes that removal efficiency becomes not that much important parameter because we want to see that the final concentration the C should be below the concentration limits which have been set in the effluent by the different agencies which are there because the concentration of the pollutant in the effluent should be as per the MINAS standard if suppose water is being discharged from an industry. So, we always want the C should be less than the C effluent.

It is possible that it is not less than this value. So, under that condition, we may have to use multiple batches or otherwise or me we may have to further treat the water. So, we have to properly judge whether adsorption is good enough, whether we require further treatment or not. So, all these aspects are there. So, adoption capacity and removal efficiency both are important. Many times the final residues concentration also becomes very important. So, through that also selection is possible. So, I will end this lecture and we will continue with our theories and then basic understanding of the adsorption in the next lecture.