**Course Name: Industrial Wastewater Treatment**

**Prof. Alok Sinha**

**Department of Civil Engineering, IIT(ISM), Dhanbad**

**Week – 04**

# Lecture-1: Advanced Oxidation Processes

So, welcome back, we are in module 4, lecture 1 and we will continue our discussion on advance oxidation processes. So, the concepts covered in this lecture will be on disinfection by UV. As you have already seen that the advance oxidation processes which results in the generation of dot OH radicals may not be feasible for disinfection of the water. So, we will discuss the disinfection by using ultraviolet rays which is very common, and it is being used currently for the disinfection of water by using ultraviolet rays. Then we will also cover the influence of the pH on the advance oxidation processes, then inhibition due to scavenger presence, the light wasting during the advance oxidation processes when we are involving the utilization of UV light and similarly we will also talk about the mass transfer limitations, we will talk about the direct ozone attack, the strategies so that we can implement the advance oxidation processes, the advantages and the disadvantages of advance oxidation processes. So, when we talk of the UV disinfection, so disinfection is considered as the mechanism for inactivation or destruction of the pathogenic organelle so that the spread of waterborne diseases can be stopped.

So, UV system it generally transfers the electromagnetic energy from the mercury arc lamp to the genetic material of the bacteria or the microorganism which come into its contact. For example, the DNA or RNA can be mutilated by using the UV light. So, UV radiation it penetrates the cell wall of an organism, and it destroys the cell ability to reproduce. So, the UV generation is generated by electrical discharge through a mercury vapor, and it penetrates the genetic material of the microorganism, and it retards their ability to reproduce.

So, we can see here that the water enters into the UV chamber, or we can say the module that is there which is having the UV disinfection process. So, here the water enters here, and we are having a UV light which is generated, and the water basically comes in contact with this UV light. It moves past the UV light for a given amount of the retention time so that the microbes and viruses which are there they can be killed by the UV light. So, the main components of the UV disinfection system are the mercury arc lamps which is there, a reactor in which the water comes in contact with the UV light and the Velas which are used for the generation of the electrical arc so that the UV light may be generated. Here the UV radiation is either the low pressure or medium pressure mercury arc lamps which is having low intensities or high intensities.

So, the low-pressure UV radiation generates low intensity whereas the medium pressure mercury lamps it generates high intensity. So, the optimum wavelength so that we can effectively inactivate the microorganism is in the range of 250 to 270 nanometers and the intensity of the radiation emitted from the lamp it dissipates as the distance from the lamp increases. So, this means that as the water depth or the thickness of the water around the UV lamp increases so the distance from the lamp also increases and which dissipates the UV intensity of the UV radiation. So, low pressure lamps they emit the monochromatic light, and which is at a wavelength of nearly 3.7 nanometers whereas medium pressure lamps they are generally used for the large facilities.

So, the disinfection by UV system it depends upon the characteristics of the water, it depends upon the intensity of the radiation, it depends upon the amount of the time the microorganism is exposed to the radiation, it also depends upon the reactor configuration. So, the medium pressure lamps have approximately 15 to 20 times more germicidal capacity in comparison to the low-pressure lamps. So, the medium pressure lamps generally disinfect faster and has a greater penetration capability because of the high intensity of the UV radiation. However, these lamps they operate at higher temperature, and they require a very high energy consumption. So, that's why they are generally used for large scale installations.

So, UV light is a type of electromagnetic radiation with a wavelength shorter than that of the visible light. So, it can be characterized based upon the wavelength, it can be characterized as UV-A, UV-B or UV-C. UV-C light which has a wavelength from 200 to 280 nanometers is the most effective for the germicidal or we can say the disinfection purposes. So, the UV-C is absorbed by the DNA or RNA of the microorganism and it forms a covalent bond between the adjacent thymine or uracil bases which are present in DNA or RNA molecules and these bonds which are also known as the thymine dimers or uracil dimers, they disrupt the normal functioning of DNA or RNA and this leads to the prevention of the replication and transcription of the genetic information by the microorganism. So, it leads to the microbial inactivation.

So, the formation of thymine or uracil dimers they interfere with the microorganism or ability to replicate or perform essential cellular functions as they are not able to reproduce. So, their population declines, and they are inactivated. So, that's how the inactivation of the microorganism by using UV light can take place. Similarly, if we are prolonging the UV exposure, it may result in the inhibition of DNA synthesis as we have already seen, and it may lead to the death by apoptosis process. So, the UV light on the longer duration of exposure it may result in the death of the microorganism.

So, the application of this UV disinfection is commonly in the water treatment, it can also be used in the air purification, it can be used for the surface disinfection also because of its capability to disinfect anything which comes in contact with the UV light. So, that's why it may be used for the not only water treatment, but it can be used for air purification as well as the surface disinfection. So, UV lamp or UV-C LEDs are also employed for these purposes and the UV disinfection is generally utilized in hospitals, laboratories, in water treatment plants and other settings where the control of microbial contamination is really critical. So, we can see here that the UV-C range of the light it basically penetrates the cell wall of the microorganism, it can lead to the inactivation of the microbes as well as it can lead to the death of the microbes if the longer duration of exposure is there, or the intensity of the UV light is high. So, the advantages of the UV disinfection may be it inactivates most of the viruses, spores and cysts.

It eliminates the need to generate, handle or transport or store the toxic or hazardous corrosive chemicals as we can see that when we are using the conventional process like chlorination. So, in that case we require to handle and transport the toxic or hazardous chlorine gas which can be generated through the chlorine cylinders. So, they are quite toxic and hazardous. So, they need to be handled properly. So, here the need of those handling basically reduces.

Similarly, there is no residual effects that can harm the aquatic life, and it requires a lesser space also as you have seen, and it has a shorter contact time when we compare the other disinfectants. So, it has got a shorter contact time for the inactivation or killing of the microbes. So, the disadvantages of UV disinfection may be the low dosage may not be highly efficient for some of the cysts and the viruses and similarly there can be the microorganism can sometimes they can repair or reverse the destructive effects of UV and through a repair mechanism which is known as the photoactivation, or it is called the dark repair. So, they can again reactivate it and because of which the chances of water contamination may increase and similarly it does not also have the capability to provide the protection again when we are transporting the water from one place to another place. So, that may be one of the disadvantages of the UV disinfection process.

So, now if we compare different type of AOP techniques which are commonly applied for example, we can have UV/$H_2O_2$, we can have $H_2O_2$/UV, we can have ozone/UV. So, the influence of pH may play a very important role because we know that the pH influences the rate of the radical generation for the system of ozone or $H_2O_2$, $H_2O_2$/UV or ozone/UV. So, that is why it is very necessary that we choose a proper pH so that we can apply these processes effectively and the destruction of the organic compounds can take place at an optimum pH value. Similarly, we also know that the photo oxidation process may result in the decline of the pH because of the generation of the acidic species. So, it is very necessary that we adjust the pH of the treated water, and this can be done by using some laboratory tests by performing certain tests at the in the laboratory so that we can achieve the highest efficiency of the pollution abatement.

As we know that we can achieve a certain target degradation at an optimum pH value. So, that is why it is very important that we find out that what is the optimum pH values and if the pH of the water which is getting treated by advanced oxidation processes it increase or decrease then basically we have to adjust the pH so that the optimum pH may be reached and we can get the highest efficiency for the pollution abatement and these values of the pH may commonly be between 3 to 5 for most of the common pollutants that we encounter for the destruction by advanced oxidation processes. So, we can also have the inhibition of the advanced oxidation processes by the scavengers as we have already studied that the advanced oxidation processes it results in the generation of raw 2H radicals and these raw 2H radicals it results in the indiscriminate oxidation of the organic compounds. So, similarly it does not differentiate between the type of the species that are present and it generally oxidize anything which is in the reduced form. So, we can see that bicarbonates and carbonates they are present.

So, they can also be oxidized by the 2H radicals so it can be converted to carbonate radicals here we can see here that bicarbonates when it combines with the .2H radicals. So, it can be converted to carbonate radicals similarly carbonate may also be converted to carbonate radicals and carbonate radicals they are much less reactive than 2H. So, this means that if the carbonates of bicarbonates or if the If the alkalinity of the water or the waste water is high then it may result in the species which are less reactive and that is why basically the efficiency of such a process may be decreased and that is why it is very important that we remove the scavengers which are present so that we can enhance the efficiency of the advanced oxidation processes. So then when we are having ozone for example, when we are having a combination of ozone and H2O2 or we are having the combination of ozone and UV so it may require that the ozone molecule transfer from the gas stream to the liquid bulk. So, it is very necessary that whatever the ozone when it comes in contact with the water so it may be diffused into the water so that it can degrade the organics which are present in the water. So here the mass transfer limitations play a very important role and the rate of ozone consumption per unit volume can be so high that the mass transfer limited regime for ozone absorption is established and which results in the decrease of the quantum efficiencies and an increase in the operating cost. As the mass transfer limitation, it limits the absorption of the ozone into the water and basically the degradation of the compounds so it remains unutilized, it goes in the effluent without reacting and this may lead to the reduction in the quantum efficiencies as well as it may also lead to the very high operational cost as we require a higher amount of ozone for the degradation.

So, we can see that the ozonation is an absorption process and the mass transfer it depends upon the physical properties of the phases, what type of phases are there for example, we are having the liquid phase, we are having the gas phase so from the gas phase it is getting transferred to the liquid phase. So, we can see here that we are having the gas phase here where the concentration of ozone is here in the gaseous phase, and we are having a certain concentration in the liquid phase and these two phases are separated by the interfaces where we are having the gaseous film is there and we are having the liquid film at the interface of the liquid. So, this may result in the decline in the absorption, or we can say the diffusion of the ozone gas and you can see that as it diffuses through these two layers the mass transfer plays a very important role and the concentration of the ozone in the liquid it declines. So, this may depend upon the physical properties of the different phases that are there, it may also depend upon the concentrations at the two interfaces which are there, and it may also depend upon the degree of turbulence. So as the degree of turbulence may increase so the diffusion process may be enhanced, and we can get a higher efficiency of the oxidation by advanced oxidation process, and this may also overcome the mass transfer limitation in that case.

This means that the design of the mixing or contact system for attaining a transfer efficiency is very important and we want that the mixing basically the different type of mixing systems have basically been applied so that we can get a higher efficiency of the transfer from the gaseous phase to the liquid phase. Similarly, we can find that when we are having the fine bubble diffusers so the flow pattern through the contact vessels and the depth of the diffusers, so they play a very important role in the transfer efficiency of the ozone from the gaseous phase to the liquid phase. So it is very important to understand that what are the mass transfer limitations that can be encountered and depending upon that we can decide the depth of the contact towers or we can say the fine bubble diffusers similarly the flow pattern that basically is there in the contact vessel so that we can get a higher retention time and we can get a higher diffusion for the ozone from the gaseous phase to the liquid phase. So, the transfer efficiency may be defined as the ozone feed minus the ozone out divided by the ozone feed. So the transfer efficiency depends upon a number of factors for example it may depend upon the bubble size, it may depend upon the temperature, it may also depend upon the pressure similarly it will depend upon the gas to liquid ratio, it will depend upon the concentration of ozone in the feed gas that is it is related to the ozone generator output similarly it will also depend upon the water chemistry.

So, we can see that where the transfer efficiency decreases as the applied ozone dose increases. So, as we increase the dose, so the transfer efficiency declines, similarly the transfer efficiency increases as the water quality decreases. As the ozone demand increases as the water quality decreases so ozone demand will increase, and which will result increase in the transfer efficiency. Similarly, the transfer efficiency will also increase as the formation of the hydroxyl radicle, so the transfer efficiency increases as the water chemistry favors the formation of the hydroxyl radical for example, when we are having a high pH or low alkalinity water, so in that case the transfer efficiency increases. Similarly, the transfer efficiency decreases as the gas to liquid ratio increases.

The transfer efficiency also increases when we are having the bubble size, smaller bubble size. So, when we are having smaller bubble size, we are having the larger surface area. So that's why the transfer efficiency may increase in that case, and it may result in the higher diffusion from the gas surface to the liquid phase. Similarly, the transfer efficiency will also increase with the increasing concentration of ozone in the feed gas. So, whatever the feed gas obviously we are supplying, so that if the ozone concentration in that gas increases, then the transfer efficiency will also increase.

So, when we are applying the advanced oxidation process by using UV irradiation, so there may be, it may be possible that a light wasting process may take place. For example, the light-based processes, it can be severely penalized by the light absorption by the substrate molecule. For example, when we are having ozone or H2O2, when they are present in combination with UV light, so that may result, the UV light when absorbed by ozone or H2O2, so that may result in a higher dot OH radical generation. So that may result in a higher efficiency of the degradation process. But if the light is being absorbed by the substrate molecule, so it may result in the lower efficiency.

As the organic substrates, they undergo photochemical reactions and as a consequence of the light absorption, they can be degraded by such a process, but it may result in the less TOC reduction. Therefore, it is necessary that, so the light absorbed by the organic molecules can generally be considered as the wasted light because the organic molecules, so they are absorbing the light, but they are not contributing to the TOC reduction. So that's why it is necessary that when we are having the waste water or the water which contains organic compounds, if they are absorbing the light, so the light basically becomes wasted as we are having the lesser degradation of the organic compounds in comparison to if the light is absorbed by ozone and H2O2 which results in a higher generation of dot OH radicals and which in turn results higher degradation of that organic compound. And similarly, if the suspended solids are present in the water, so they may also lead to the wasting of the light in the sense that the suspended materials, so they can basically scatter the light, and it may not reach to the ozone or H2O2 that is present in the water or wastewater, and it may result in the lesser efficiency of the degradation. Similarly, we have also seen that when we are having the ozone at higher pH, so it may result in the formation of dot OH radicals, but ozone may also lead to the direct attack.

For example, when we are having ozone H2O2 system or ozone UV system, so the direct ozone attack can also lead to the degradation of the organic compounds. For example, when we are having the system of ozone and H2O2 and we are having a system of ozone and UV, so in that case the part of the organic load can be reduced by the direct attack of the ozone. But the ozone basically attacks a particular intermediate, for example, when the aromatic substrates are there, so in that case it may be directly attacked by the ozone and similarly when we are having the hydroxylated form of this aromatic compound, so this may be directly attacked by the ozone, but the value of K2 is much higher than the value of K1. So, this means that the direct attack of ozone is basically specie based and it generally attacks the hydroxylated form more than the non-hydroxylated form in such a case. So, the strategy is to implement advanced oxidation processes.

So, the cost of AOPs is relatively high and that's why it is very important that the efficiency and the operational time of the process basically should be monitored so that we can optimize these things so that we can reduce the cost of the advanced oxidation process systems. Similarly, the simultaneous applications of the different AOPs, for example, when we are having the UV or H2O2 combination of UV or H2O2, we are having the combination of UV/H2O2 and TiO2 or UV-Fenton, ultrasound, UV/TiO2. So, these are the systems which can lead to the synergistic effect. This means that they can enhance the efficiency of the system rather than the individual treatments alone. So, efficiencies are much higher as it can result in the higher generation of dot OH radicals when they are present in combination rather than being alone because a synergistic effect may be induced when the different type of advanced oxidation systems, they are present in combination.

So sequential application of AOPs can treat effluents which contains a mixture of organics. So that's why also so it is very important that when we are having a different type of compounds present in the water or the wastewater then different systems like UV or H2O2 so they may have different reactivity towards a different type of compounds which are present. So, it is better that we use a sequential application of various AOPs, or we use the combination of various AOPs so that it can treat a mixture of organics which is present in the water or wastewater system. When we are treating the organics by using advanced oxidation processes, so it is very necessary that we reduce the cost of the treatment. So, it is very necessary that we go for the separation treatment before we go for the advanced oxidation process system.

For example, we can utilize the treatments, the pretreatments which are called like stripping, we can go for coagulation flocculation, we can go for the sedimentation, we can go for the filtration, adsorption process etc. so that we can remove the non-targeted compounds or non-targeted species which are present in the water or wastewater so that we can be left with the species which we want to treat by using the advanced oxidation process. So, it is very important that we use a pretreatment or a separation treatment before we go for the advanced oxidation processes. Similarly, AOPs can also be applied as a pretreatment stage so that it can enhance the biodegradability, and it can reduce the toxicity which can then become amenable to the biological treatment after the advanced oxidation processes. So this type of approach basically is very important in the sense that it becomes less costly and it becomes environmentally friendly so it reduces not only the cost of the advanced oxidation processes as if we apply the advanced oxidation process for the complete degradation or complete removal of the contaminants so the cost may become very very high but if we enhance the biodegradability of the wastewater or the water that we want to treat and then we take it to the conventional processes like we take it to the conventional biological processes so then it becomes quite cost effective which again reduces the cost.

So, we can see that we can implement the advanced oxidation processes for the wastewater treatment system so we can see that the sewage is coming here, and we are going for the primary treatment like for example we are going for the primary sedimentation after primary sedimentation we can basically also go for ozonation or advanced oxidation processes before it goes to the biological treatment system. So whenever we are having water which is having highly toxic materials for example the pharmaceutical base water which may contain pharmaceuticals which can be toxic to the microbes which cannot be treated by the secondary treatment processes so in that case we can go for the advanced oxidation processes before the secondary treatment system and it can basically increase the biodegradability and it can increase the efficiency of the biological treatment systems or we can also use these advanced oxidation processes during the tertiary treatment system the wastewater is being treated by the secondary process easily and then there may be certain compounds which we do not want to release in the groundwater or the surface water so then it is necessary that we go for the treatment by using advanced oxidation systems. So here in this case the tertiary treatment as the BOD and COD values have reduced a lot so this may basically reduce the cost of the treatment by using advanced oxidation processes. Similarly, we can have the drinking water treatment systems where the pre-oxidation may be done before we go for the coagulation, flocculation or sedimentation and then we can also use the advanced oxidation processes during the filtration or disinfection process also after which we can take the water to the distribution systems. So, we can apply the advanced oxidation processes depending upon the requirement that whether the pre-oxidation is required or the post-oxidation is required.

So accordingly, we can decide, and we can basically go for the implementation of the advanced oxidation processes so that we can reduce the cost of the treatment. So, if we look the concept at a glance so we see that the working principle of the advanced oxidation process is mainly the production of the reactive oxygen species dot OH radicals or the superoxide radicals so that we can target the toxic compounds or the contamination that is present in the water or wastewater. So, it requires a very high-tech equipment is required and the performance wise it is having a very high efficiencies except for few chemicals which may not be degraded which may not be oxidized further. Similarly, the cost of the operation is quite high in this case and engineers are required for the design of such type of processes. Similarly, the operational and maintenance cost is generally high as it requires a regular supply a continuous supply of the chemicals like ozone or $H_2O_2$ is required.

It is quite reliable as it can be basically when we take it to the waste water when we scale it to the operating conditions so it is a quite a reliable process and the main strength is that destroys almost all the organics without the pollution being transferred from one phase to another phase as we have already discussed also and the main weakness is that it is having a very high operational cost. So, when we come to the advantages so advantages include that it basically degrades the organic contaminants without being transferred for this from one phase to another phase and there is no need of treating or disposing of for example when we are having reverse osmosis process so in that case a very high amount of brine basically may be generated which again needs to be disposed of properly. Similarly, when we are having granular activated carbon so adsorption may happen on to the GSE media, but again it may require the regeneration or basically safe disposal of such type of material which is having a high concentration of the toxic compounds which are present in the water which have been transferred to these media from the water or wastewater. So, the advantage is that it may convert most of the refractive organic contaminants into the biologically treatable form. Similarly, it is very effective in treating the most micropollutants so nowadays we are having a lot of problem which is being generated of the presence of the emerging contaminants, the presence of the priority pollutants which are there in the water, so it is highly effective in degradation of such type of compounds at a very small or nano scale levels also. And similarly, it is non-selective, and it can treat a broad range of contaminants because of its non-selective nature. During the treatment process it can also oxidize the taste and water causing compound from the drinking water. And similarly, it can also be used for the water reuse purposes so if we are having a lot of contaminants which are there so they can be removed from the system and then the water basically can become safe for reusing. Similarly, the reactions are very fast and requires less contact times and because of the less contact times it requires less volume of the reactor which again may decrease the capital cost for the reactors. And similarly, it can also result in the microbial disinfection also while it is degrading the contaminants which are present in water or wastewater so it can also lead to the disinfection process also simultaneously.

So, the disadvantage is that it can lead to a very high capital cost as well as annual operation and maintenance cost as a lot of power is required, and we require lot of chemicals for its implementation so it may result in a very high capital as well as operation maintenance cost. Similarly, the treated water can be tested for the potential regulated and under-regulated product as the treated water may contain a very small amount of the micro pollutants which may be left if it is not treated properly. So, we have to test the water or the wastewater before it is being used or it is being disposed of in a certain water body. And similarly, we should also quantify if we are using hydrogen peroxide so we should also see that the hydrogen peroxide residuals are not remaining in the water, and they must be properly quenched before the water goes to a potable water distribution system or before the water goes into the disposal system. So similarly, when we use the UV reactors so it is possible that UV lamps may break, and it contains a very hazardous material that is the mercury, and this mercury may go into the water.

So, it is very important that when we are using UV lamps so we should also see that there are no possible concentrations of the mercury being leached into the water. Similarly, the power interruption may also play a very important role in the sense that the power interruption may reduce the efficiency of the system, and it may also require as we need a regular power supply so it may also require expensive power conditioning equipment so that the power can be given continuously to the advanced oxidation processes systems.

And it is possible that if we are not having such an expensive power conditioning equipment system and the power is not being supplied continuously so it is possible that the water may not be treated for a certain period of time, and it may result in the contaminated water into the effluent. So, we have to see that the power is continuously supplied to the advanced oxidation process systems. So now we take a problem and here the electrical energy input per log reduction, so it is given by this formula that is EE by O which is basically written as in the short form as EE by O.

So, EE by O is equal to electrical energy input in kilowatt hours, and this is divided by the volume of the liquid that we are treating and divided by the log of the initial concentration of the contaminant that we are targeting and the final concentration of the contaminant that we are targeting. So, it is in the volume is in cubic meter the initial concentration nanograms and it is final concentration is the nanogram present in the given volume of the water. So let us take the problem here the water treatment plant it uses H2O2 or UV process and so that it can oxidize the trace constituents in the water. So hydroxyl radicals are formed when the water is exposed to the UV light and UV light is from 200 to 280 nanometers and the plant treats a volume of around 50 cubic meter of the water and we find that the concentration of trace constituent which we are treating in the water is was 5 nanogram and after the treatment the concentration decreases to 1 nanogram and during this process the electrical energy input is around 650 kilowatt hours. So now we have to calculate the electrical energy required for the reduction per unit volume in kilowatt hours per cubic meter.

So, we can apply this formula which we have already discussed, and we can see that the electrical energy input is around 650 kilowatt hours and the volume that we are treating is 50 cubic meters and the reduction the initial concentration was 5 nanograms and the final concentration is around 1 nanogram. So, by calculating these values we get the value of the electrical energy input per log reduction around 18.6 kilowatt hours per cubic meter per log reduction. So now we end the topic here and we will discuss in the next lecture about the membrane processes.

Thank you.