Course Name: Industrial Wastewater Treatment

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Week - 03

Lecture 3: Advanced Oxidation Processes

Welcome back. So, we are in module 3, lecture 3 and we will talk about the Advanced Oxidation Processes in this lecture. So, the concepts that we will be covering during this lecture will be on advanced oxidation processes that is what are these advanced oxidation processes, how these processes take place and then we will compare the oxidizing potential of various oxidizing agents which are involved in advanced oxidation processes. Hydroxyl radical based advanced oxidation processes will be discussed. We will also discuss that what are the compounds which can be oxidized by OH radicals, which are the compounds which cannot be oxidized by OH radicals. So, coming to the advanced oxidation processes they are also referred to as AOPs in short form and these are the processes which are used to oxidize complex organic compounds which are found in wastewater into simpler end products that is the compounds which are there they can be completely mineralized to carbon dioxide and water.

So, here when we are talking of the conventional wastewater treatment processes it is possible that there are certain compounds which cannot be degraded by the naturally occurring microbes which are used to degrade the wastewater which are being generated from domestic effluents right. So, in this case the wastewater getting generated from industries like pharmaceutical industries or we can have the wastewater coming out from tanneries etcetera. So, they can contain certain compounds which can be highly toxic to the bacteria which are used in the conventional treatment processes. So, it is necessary that we oxidize these compounds so that these compounds can be totally omitted from the wastewater, and they can be further degraded by the conventional treatment process.

So, for example, when we talk of the pharmaceutical wastewater. So, pharmaceutical wastewater may contain certain pharmaceutical compounds which can be toxic to the microbes. So, microbes cannot degrade these compounds and in turn they can also die in these pharmaceutical compounds. So, what we can do here that we can use certain advanced oxidation processes which can degrade these compounds easily and then the wastewater can become more amenable to the naturally occurring microbes and then they can degrade these compounds these wastewaters easily ok. So, the advanced oxidation process they typically involve the generation and the use of highly potential oxidizing radical which is also called as OH° radical it is also called hydroxyl free radical.

So, this hydroxyl free radical is the compound that basically can be used to oxidize certain compounds which cannot be oxidized by the conventional oxidant such as we are having oxygen or chlorine or ozone right. So, they cannot oxidize such type of compounds in that case the hydroxyl radical can be used for oxidizing these compounds and except fluorine which is having higher redox potential than the hydroxyl radical right. So, this hydroxyl radical is one of the most active oxidants and it is generally used in the wastewater treatment as the generation of this hydroxyl radical is easier in case of the water or wastewater conditions right. So, this hydroxyl radical is one of the most active oxidants and it is having a very high redox potential of around 2.8 volts.

Hydroxyl radical then reacts with different constituents and they can initiate a number of oxidation reaction so, that the constituents which are there so, they can be completely mineralized they can be converted into carbon dioxide and water. But they are having a non-selective approach that is they cannot target a particular compound and whatever the compound which can be oxidized. So, they will be oxidized by the OH° radical and they cannot select a certain compound and oxidize it. So, because of the non-selective nature of the attack and their ability to operate at normal temperature and pressure so, hydroxyl radicals they are capable of oxidizing all the materials which are present in the solution. So, if we say that there are certain compounds which are present in the wastewater matrix so, we can have compounds which cause BOD, the compounds which cause the COD in the wastewater and similarly we are having the compounds like pharmaceutical compounds are present in the wastewater.

So, the OH° radical will not only attack the pharmaceutical compounds or the complex organic compounds, but they will also try to degrade the BOD and COD causing compounds also which can otherwise be degraded by naturally occurring microbes. So, this process that is the advanced oxidation process it differs from the other treatment process in the sense that these compounds can be degraded rather they are transferred or concentrated into a different phase. For example, if we talk about adsorption process where we are having the use of activated carbon or any other adsorbent which can be used which can be put into the wastewater and the organic compounds can get transferred from the liquid phase to the solid phase. So, here what is happening in the advanced oxidation process the compounds are degraded rather than they are transferred to different phase. Now, the activated carbon then becomes a waste which is generated, and this waste needs to be further treated, or it needs to be disposed of properly.

So, there is a problem that when we are using such type of techniques or the technology where we are transferring the compounds from one phase to another phase. So, then to whichever phase it is transferred so, then we have to get rid from that waste. So, either we have to go for the disposal the proper disposal material or we have to regenerate the materials by using certain other techniques. So, here what happens that the partial oxidation may also happen. For example, suppose we are using advanced oxidation process and for a wastewater which is not being treated by biological treatment method by the conventional biological treatment method.

So, in that case we can go for the combination of advanced oxidation processes and the combination of the conventional biological treatment process, where we can partially oxidize, or we can make the wastewater more amenable to the bacteria and these bacteria can further degrade the non-toxic wastewater that has been produced from the partial oxidation by advanced oxidation process. Because advanced oxidation process may be costly and if we want to reduce the cost if we want to improve the economics of the wastewater treatment, we can also go for the combination of advanced oxidation process and the biological treatment processes. So, the advanced oxidation process will reduce the toxicity, and it will make the wastewater more amenable to the subsequent biological treatment process and the AOPs which are used so, they can utilize the powerful hydroxyl radicals also as well as the sulfate radicals also as an oxidizing agent and this was first proposed in 1980s for the potable water treatment process. And so, the AOPs are strong oxidants which can degrade the recalcitrant organic pollutants which are basically generated from the industrial wastewater, and they can also remove the inaugural pollutants from the wastewater which are getting generated again from the industries. So, we can have different common oxidants such for example, chlorine or ozone.

So, they are used as an oxidant so, they are serving dual purposes that is they are not only decontaminating the water, but they are also helpful in the disinfection process also. For example, we generally use the chlorine and ozone for disinfection purpose right. So, the AOPs which are used here which we are discussing so, they are primarily used for destruction of organic and inorganic contaminants in water and wastewater, and they are generally not used for inactivation or destruction of the pathogens which are present in water or wastewater. Because it has been studied earlier that AOP can be used for inactivation of the pathogens, but they are rarely used for the disinfection process because they are having very short half-life that is the of the order of around microseconds. So, they require a large, huge retention time may be required for the disinfection purpose and that is why it is not used for the inactivation of pathogens or for the disinfection purpose ok.

So, similarly when we AOPs are being applied for the wastewater treatment so, they are very powerful oxidizing agents they sufficiently destroy the wastewater pollutants, and they transfer these pollutants into less or even non-toxic products. So, the oxidation of the specific compounds can be characterized by the extent of the degradation that happens in the final oxidation products. For example, we can have primary degradation, we can have acceptable degradation, we can have ultimate degradation, we can have unacceptable degradation. When we talk about the primary degradation it means a structural change in the parent compound that is the parent compound is there it is getting oxidized it is getting converted to another compound or basically it is breaking into a simpler product. So, that is called the primary degradation and if we take it further then we can also have acceptable degradation that is called defusing.

So, the structural change in the parent compound to the extent that the toxicity is reduced so, that is called the acceptable degradation. So, that is what we are talking about that if we take, we can use the AOPs for acceptable degradation and later on when the toxicity is reduced, we can go for the conventional treatment process. Ultimate degradation means the mineralization that is the conversion of organic carbon into inorganic carbon dioxide. So, that is known as the mineralization that is the organic compound is completely converted into carbon dioxide and water. So, that is called the ultimate degradation.

Similarly, we can also have unacceptable degradation, or it is also called fusing where the structural change in the parent compounds takes place in such a way that it may induce toxicity it may increase the toxicity of the wastewater. So, that is called the unacceptable degradation also called the fusing. For example, let us say we are having chromium 3 in the wastewater and if we are oxidizing it may get converted to chromium 6 hexavalent chromium which can be more toxic which can be highly toxic it can be carcinogenic in the wastewater ok. So, we have to keep in this in mind that when we are using the AOPs advanced oxidation processes then we should always look for what are the daughter products that are being formed and whether they are less toxic or they are more toxic than the parent compound. So, that needs to be seen.

So, we always talk of oxidation reduction potential when we are talking of the AOPs. So, the redox potential or it is also called the oxidation reduction potential it is called also termed as ORP in the short form or PE or EH. So, they all represent the redox potential. So, it is the tendency of the chemical species either to acquire electrons or to lose the electrons. So, when they acquire the electrons, so it is called reduced right and when they lose the electrons, so they are called oxidized ok.

So, this redox potential is generally expressed in volts, or we also express it in terms of millivolts ok. So, the positive redox potential means that the oxidizing conditions are there whereas, the negative values represent the reducing conditions. For example, if we talk of water flowing where a lot of oxygen it is coming in contact with lot of oxygen. So, it may have a positive redox potential whereas, if we talk of wastewater which is there in a condition where anaerobic conditions are prevailing. So, you will find that a lot of negative values are reported when we are having the anaerobic degradation taking place in the wastewater ok.

So, higher redox potential means that the compound is having a higher affinity for the electrons and the tendency to be reduced in this case. So, we can measure the oxidation reduction potential by using an electrode and where the standard hydrogen electrode is used as the reference electrodes which is having a half cell potential of around 0 volts, but standard hydrogen electrode is fragile and impractical for the routine laboratory use. So, that is why we may use a silver chloride and saturated calomel electrode as the reference electrode. So, you can see here that this is the reference electrode that we are using Ag and AgCl and here KCl is the solution the electrolyte that is being filled and another electrode here is made up of noble metals like platinum or gold right and the potential difference between these two things is known as the oxidation reduction potential. If we compare the oxidizing potential of various oxidizing agents for example, you can see here that the list of the oxidizing agents is given.

So, fluorine is having the topmost position with the electro chemical oxidation potential EOP of 3.06 volts right and similarly we are having the hydroxyl radical after that is 2.8 volts and similarly the atomic oxygen then ozone right then hydrogen peroxide hypochlorite chlorine, chlorine dioxide and oxygen. So, these are the ORP values of different type of oxidizing agents which are there, and this is given in the decreasing order and similarly the EOP is with related to the chlorine where you can see that the normalized values with respect to chlorine are given. So, here also you can find that the fluorine is having the highest EOP relative to the chlorine, but it is not generally used in the wastewater treatment as the hydroxyl radical generation is more important in the wastewater treatment.

So, when we talk of the hydroxyl based AOPs. So, here we see that the oxidation potential may vary from 2.8 volts to 1.95 volts depending upon the pH right and the OH° is having a very non-selective behavior and it can rapidly react with the number of species and the rate constants may be very high it may be of the order of $10^8 - 10^{10}$ per molar per second right. So, the versatility of AOP is enhanced by the fact that they offer different possible ways for OH radical protection.

Thus, they allow the better compliance with respect to the specific treatment requirement. So, we can have different type of processes which we will be discussing in the coming lecture and these processes can be used for the specific removal of certain specific compounds. So, when we talk of the hydroxyl radicals, so they are having the properties like they are non-selective, they are very very short-lived as we already discussed, they are harmless right, they are very very powerful oxidants, they control the rate of the reactions as we have seen that the rate constants are very very high and they are highly reactive and they can be easily generated by using different techniques. So, the hydroxyl radical attacks the organic pollutants in three basic pathways. So, these are for example, one of the pathways the radical addition where the hydroxyl radical they add to an unsaturated compound or aliphatic or aromatic compound to form a free radical product ok.

So, in addition for example, suppose we are having the aromatic compounds, so it can result in the formation of cyclohexadenyl radicals here for example, you can see here this reaction that OH° radical when they are reacting with benzene, so it is forming a cyclohexadienyl radical ok.

$$OH^\circ + C_6H_6 = (OH)C_6H_6^\circ$$

Similarly, another pathway can be hydrogen abstraction that is the hydrogen can be extracted from that compound and it can form the free radical is generated and similarly the water is generated from such hydrogen abstraction.

$$OH^\circ + CH_3OH = {}^\circ CH_2OH + H_2O$$

So, OH° radical may take the H^+ ions from here and it may form the radical of methanol in this case right and the water is basically formed here. Then we can also have the electron transfer that is where the electrons can be transferred from the OH° radicals and they can lead to the formation of the higher valence state or atom or the free radical for example, we can see here that the ferrous can be oxidized to ferric ions and OH^-ions get released in this process ok. So, this is because of the electron transfer, so for example, suppose we are having chromium 3, so chromium 3 can be oxidized to chromium 6 in this case and that may lead to the resultant of a highly toxic compound.

For example, we can have the oxidation of chromium going to chromium 3 going to chromium 6 that is highly toxic in that case, or we can also have conversion of ferrous to ferric. Similarly, we can have the radical combinations where the hydroxyl radical it reacts with the other hydroxyl radicals right and they can form they can combine to form a stable product. For example, here OH° radicals and OH° radicals may combine and they can form H2O2, or hydrogen peroxide and this hydrogen peroxide may be again a highly oxidizing agent. So, it may result in the further oxidation of the compounds ok. So, we can see here that the hydrogen abstraction when we are having OH° radicals the hydrogen abstraction pathway is being followed.

So, if we are having RH compound here, so it may form R° radical right and it may also lead to the formation for example, ROH is there, so RSH is there it may lead to the formation of RO° radicals or RS° radicals and because of the hydrogen abstraction the water is formed as a byproduct ok. Similarly, this OH° radical can be added to the organic compounds for example, we can see here that $R_1 - CH(OH) - C^*H - R_2$. So, this organic compound the OH may be added to this compound, and we can have the centralized C° coming here. Similarly, we can have the centralized radical compound forming and OH getting added to this compound ok. So, this may be due to the OH addition that takes place because of the OH° radical reaction with the compound.

Similarly, we can have the conversion of ferrous to ferric as we are talking about when we are having the electron transfer.

$$OH° + [Fe(CN)_6]_4 = [Fe(CN)_6]^{3-} + OH^-$$

So, electron transfer process may happen the oxidation of ferrous to ferric may happen. Similarly, we are having a compound like $R_1 - S - R_2$. So, this compound may form the radical right in this case and ultimately, hydroxide ions are getting generated from such a reaction. So, these are the processes by which the degradation of organic compound may take place.

So, the radical combination is not the process where the degradation is taking place for the organic compound, but it is rather a combination of two OH° radicals and they can form H2O2 right.

$$OH° + OH° = H_2O_2$$

Though it is having a lesser oxidation potential but is still having an oxidizing potential which can further react with the organic compounds ok. So, when we talk of the reactions of the organic compounds. So, they produce a carbon centered radicals for example, we are having R° radical is there or ROH° radical is there. So, we can see here that when we are having the initiators like H2O2 is present or ozone is present, or water is present.

So, then in the presence of certain catalyst or in presence of UV or in presence of ultrasonics right semiconductors or metals. So, it can lead to the generation of OH° radicals. So, we can have different type of reactions that we will be discussing in the coming class. So, these OH° radicals are produced right in this case and when the organic pollutants they come in contact. So, the reaction happens, and it may form the R° radical in this case which is again the carbon centered radical which may form, and this may further lead to the mineralization, and this can happen that this R° radical is again mineralized to H2O and CO2 in presence of oxygen which is there.

So, when we are having this reaction with the oxygen it is there that the dissolved oxygen may present in the water or the wastewater. So, these carbon centered organics they may again form organic peroxide radicals that is ROO°. So, these radicals may be formed which can further react and they can lead to the formation of H2O2 right they can lead to the formation of a more highly reactive species. For example, superoxide can result from here right and this may lead to the further degradation of the organic compound, and it can even lead to the mineralization of these organic compounds ok. So, these are the reactions which happens when we are having the water or wastewater when they come in contact with the OH° radicals and these OH° radicals are always generated in situ.

The reason for the generation of in situ is that because they are having a very short half-life right. So, they have had a half-life, or we can say the lifetime of around microseconds. So, they must be generated in situ because we cannot produce it somewhere and then we can transfer it to other place because they are having a very short life. So, that is why it is necessary that when we are treating water or wastewater by using advanced oxidation process. So, the in-situ generation of the hydroxyl radical is necessary.

So, that they can lead to the oxidation of the targeted compounds. So, there can be number of compounds that can be oxidized by OH radicals for example, we can have acids like formic acids, gluconic acid, lactic acid, malic acid, propionic acid and tartaric acid ok. Similarly, we can have alcohols like benzyl, tert-butyl, ethyl, ethanol, ethylene glycol, glycerol, isopropanol, methanol and propanediol ok. So, we can have number of aldehydes like acetaldehyde, benzaldehyde, formaldehyde like black sol and is butyraldehyde and trichloroacetaldehyde. So, these are the some of the compounds that can be degraded easily which cannot be degraded by the conventional treatment process.

For example, you can see the aromatics like benzene, chlorobenzene, chlorophenol, creosote, then dichlorophenol, hydroquinone, phenol, toluene, xylene. So, these are very highly reconsidering compounds which are present, and they cannot be degraded by naturally occurring microbes and it is very very difficult for the removal of these compound during the conventional process. For example, when we talk about the phenols which are present in the domestic wastewater also right. So, they are very difficult to degrade by these conventional processes ok. So, that is why we can use advanced oxidation processes for degradation of such compounds.

Similarly, we can have amines like anilines, cyclic amines, diethyl amine, dimethyl formaldehyde and EDTA etcetera. So, this can be degraded by using advanced oxidation process. Similarly, the dyes are there, anthraquinone or we talk about diazo dyes or mono-azo dyes. So, they may contain N double N bonds right which are also known as the iso-bonds, and they are very very difficult to degrade they are really recalcitrant and that is why it is said that we have to degrade these dyes before we can put the effluents to the certain water bodies. Because the recalcitrant nature of these dyes, so they cannot be degraded in the natural environment they will also impart lot of color to the water which is receiving these types of effluents, and they are highly toxic to the aquatic life which are present in the water ok.

So, that is why it is very very necessary that we first of all degrade these dyes right and then only we can put such effluent which is then colorless and also non-toxic to the water stream ok. Similarly, we can have ether which can be removed by using hydroxyl radicals, similarly we can have number of ketones which can be removed by using the hydroxyl radicals ok. There can be certain compounds which cannot be oxidized by OH radicals. For example, we can have acetic acids right, we can have chloroforms, we can have tetrachloroethane, we can have methylene fluoride, acetone, malic acid, trichloroethane, oxalic acid, carbon tetrachloride, malonic acid and paraffins. So, these are the some of the compounds that cannot be further oxidized by the OH° radicals.

They are already in the oxidized state right. So, that is why it is very difficult for oxidizing these compounds by using the OH° radicals. So, it is very necessary that when we are going for the advanced oxidation process, we should understand that what is the characteristics of the wastewater, what type of organic compounds are present in the wastewater and whether our ° OH radicals or the advanced oxidation process will be able to remove such type of compounds or not. So, it is really necessary that we first of all characterize the wastewater before treating it by using advanced oxidation processes. So, one important application of the advanced oxidation process is the enhancement in the biodegradability. For example, let us say that having wastewater getting generated from pharmaceutical industries ok.

So, these pharmaceutical industries may contain the certain compounds which are highly toxic to the microbes which are used for the degradation of the wastewater ok. So, if we are using such type of techniques for degradation of the wastewater that is the conventional techniques for degradation of the wastewater then it is it becomes very very difficult for degradation or treatment of such type of wastewater by using conventional treatment system because the pharmaceutical compounds which are present in the pharmaceutical wastewater so they may be toxic to the microbes and the microbes may even die in the presence of the such pharmaceutical compounds ok. So, you will find that if we are having the pharmaceutical wastewater if you check that the COD values may be very high right, but it is possible that the BOD values are very very low because BOD is the biodegradable fraction of the wastewater the toxic compounds are present. So, this biodegradable fraction may not come out in the BOD studies because the microbes they will not be able to survive in such type of wastewater ok. So, what happens that we have to first of all remove these compounds from our wastewater and then only the biodegradability of such type of wastewater can be enhanced.

For example, you can see here a very good example is given that as we are increasing the current density. So, current density here is increasing the enhancing the OH° radicals getting generated. So, we are using the electrochemical process for generation of the OH° radical and the OH° radicals are getting enhanced as the current densities are increasing right ok. So, you find that the COD of the wastewater is going down COD of the wastewater is going down because the organics which are there though they may have the biodegradable organics also as well as the non-biodegradable organics also right and the organics are going down. So, these are mainly the recalcitrant organics also or they are going down and the toxicity of the water may be getting reduced and because of which you find that the BOD values are increasing.

As the water is getting treated by the advanced oxidation process, so the COD values are going down, but the BOD values are increasing. The BOD values are increasing because now the toxicity which is there in the pharmaceutical wastewater is getting reduced and because of which the BOD the biodegradation of such type of wastewater is getting increased right and that is why you see that the BOD by COD ratio is increasing and BOD by COD ratio is a very important measure for checking the biodegradability of a wastewater. For example, we say that when we are having the BOD by COD ratio greater than 0.5 then it is very very easy for the biodegradation of such type of wastewater and we can use conventional processes for treating such type of wastewater, but when we are having the BOD by COD ratios less than 0.2 or so then it becomes very difficult for treating such type of wastewater by using the conventional biological treatment methods.

So, we can see here that we can reduce the toxicity of the wastewater, we can enhance the biodegradability of the wastewater and then after that we can combine the partially treated wastewater also when the biodegradability is enhanced to a limit where we can use it, where we can degrade the wastewater by using the conventional biological systems. So, then it can be taken to those systems and then we can get rid of the wastewater pollutants which are there, and we can treat the wastewater to the desired effluent standards. So, we stop here, and we will be discussing about techniques for the AOPs in our coming lecture. So, these are the references that I have used in this lecture.

Thank you.