Physico-chemical processes for wastewater treatment

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Lecture 46

Advanced Oxidation Processes (AOP): Introduction

Good day everyone and welcome to these lectures on Physico-chemical processes for wastewater treatment. Today we are going to start another section of wastewater treatment on which lot of research is being conducted nowadays. And these areas in which lot of research is conducted they are generally termed as AOP or advanced oxidation processes. Now, the tertiary treatment that we have studied till now are the various physico-chemical processes that we have studied till now including the aeration, adsorption, ion exchange and membrane processes etcetera.

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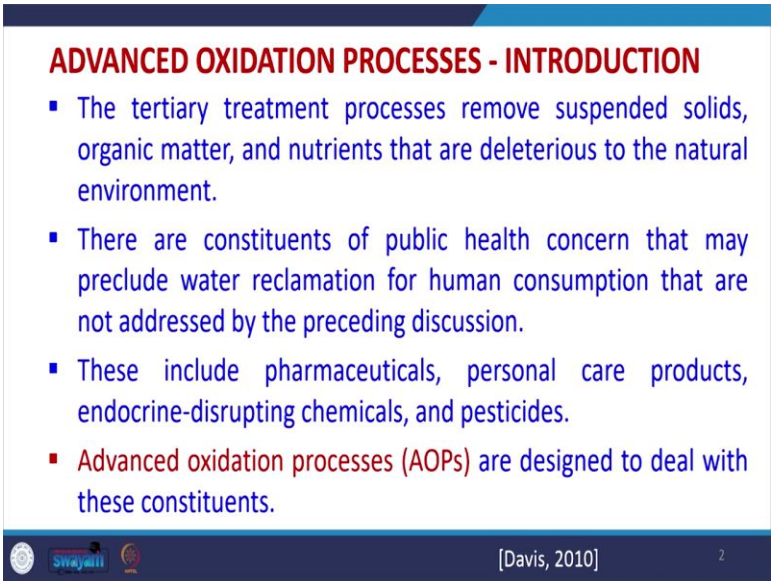

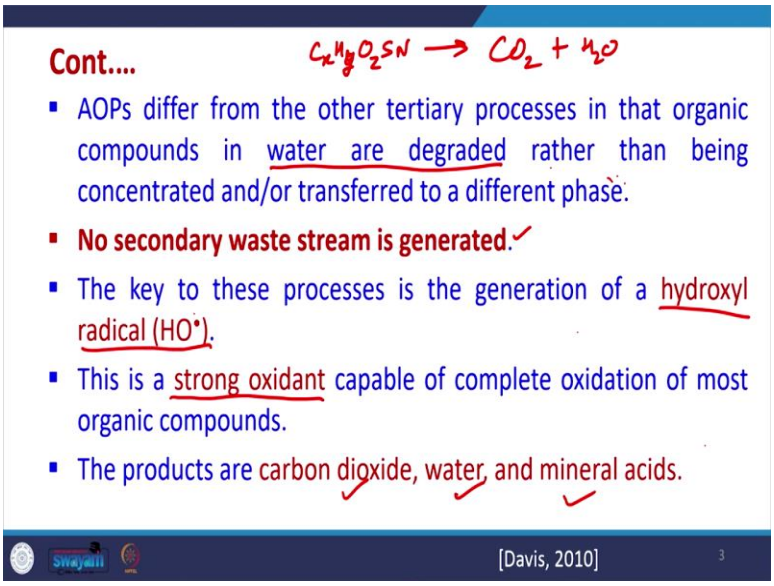

They are able to remove the suspended solids, organic matter, nutrients etcetera and that are undesirable in any of the water or wastewater. Now, with sustainability coming into the human life, as well as the growth with industrialization, there are many pollutants which are coming into the water and these pollutants include those like pharmaceutical pollutants, personal care products, many of them are endocrine disrupting chemicals.

Similarly, pesticides, insecticides and fertilizers are being used in the agricultural fields after runoff during rainy season these are getting added into the aquatic streams. Thus there are many chemicals which are getting added into the water and which cannot be treated as such by the usual physico-chemical processes that we have studied till now.

These pollutants may be presented in smaller quantity, their structure is as such that they are not being able to mineralize. So, all the wastewater treatment techniques that we have studied till now, they are not able to remove these pollutants out of the water and if we have to use that water, reuse it or recycle it, then we have to remove these water, these pollutants from the water.

In addition, if we have to discharge these water which contain these pollutants in any other aqueous streams also, then also we need to remove these pollutants because they will remain in the water for longer duration and they may go into the food chain and which will ultimately all the human beings and the aquatic life will get affected because of that.

So, we need to remove these endocrine disrupting chemicals and various other types of toxic pollutants which have been generated from the pharmaceutical, personal care products, cosmetic industries, many pesticides and insecticides etcetera. So, for removing these pollutants, new type of processes which are called as advanced oxidation processes, they are used. So, there are many categories of these advanced oxidation processes.

So, we will try to learn each of them in little detail later on. But before that, we will try to learn that how these advanced oxidation processes work. Now, the term itself is from the term AOP whose full form is like advanced oxidation processes. From here also we can learn a little bit that these processes are able to oxidize these undesirable pollutants into some innocuous products, which are not detrimental like carbon dioxide, water and mineral acids.

So, we always try to mineralize these undesirable pollutants into these things, and which do not harm us. For doing this we use some other key things during the treatment itself. So, we always desired some key things in the treatment processes. And if those things get generated, we are able to remove or mineralize the undesirable products into carbon dioxide, water, etcetera.

So, AOP is differ from other tertiary processes in that there are organic compounds in the water are degraded rather than being concentrated or transferred. So, what does it means that here we are converting any organic compounds Cx, Hy, Oz, or anything SN etcetera. So, we want to convert them into CO2, H2O, etcetera. So, we are totally mineralizing them whereas, in some other techniques that we have studied in the tertiary processes like adsorption.

So, in the adsorption the pollutant moves from water into the solid phase. Similarly, in other techniques like coagulation flocculation it goes into the sludge. So, here there is no phase change which is occurring or we are not moving the pollutant from one phase to different phase, here we are degrading the pollutant itself. So, this is the target in the AOP. Now, thus in the AOP there is no secondary waste stream which gets generated.

So, we do not have like in the coagulation flocculation we have sludge, so that sludge has to be treated further. So, this is the difference is there that generally we use AOP which do not generate any secondary waste stream which has to be treated further. So, this is the key aspect. Now, for oxidizing different chemicals, we use our generate in-situ strong oxidants.

So, the key thing with respect to AOP is the in-situ generation of strong oxidants which are capable of completely oxidizing most of the organic compounds which are present in the water. So, this is the key thing. Now, one of the key strong oxygen which is generated it is hydroxyl radical. So, this radical there is a dot here.

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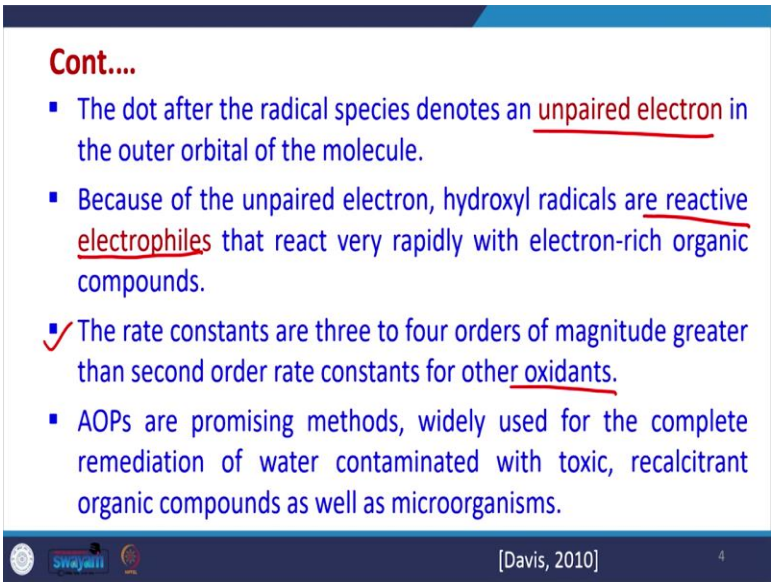

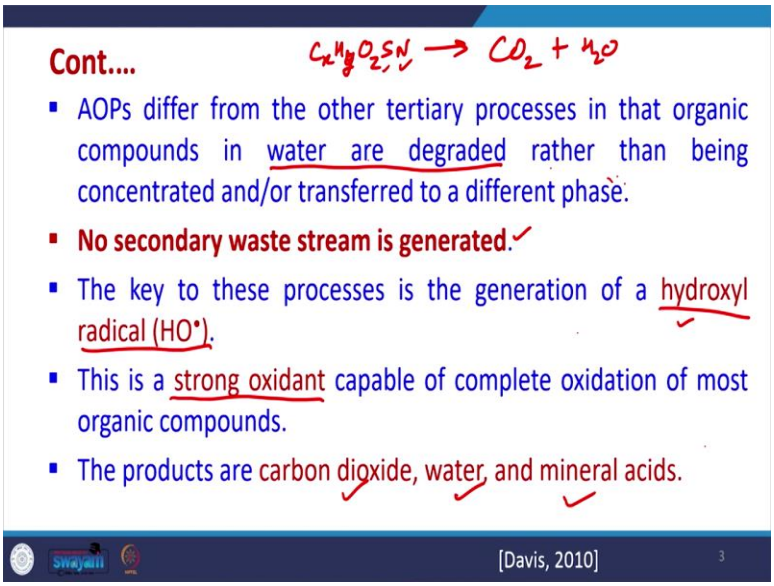

So, the dot actually symbolizes the unpaired electron. So, the dot after this radical species it denotes the unpaired electron in the outer orbit of this molecule. Now, because of this unpaired electron hydroxyl radicals are highly reactive electrophiles. So, they are highly reactive electrophiles that will react very rapidly with electron rich organic compounds.

So, because it is having a less electron, so it is always looking for that electron, so it will always attack organic compounds which are having high electron density. So, because of that it will react and it will slowly break that compound. So, this is there. The rate constants for the degradation are three to four times higher in magnitude, then the second order rate constant for other oxidants are the active oxidation species that we will try to learn within this lecture itself.

So, there are many such radicals which may get generated in the advance of these oxidation processes, and they oxidize most of the organic compounds present in the water into carbon dioxide, water and mineral acids or anything. So, depending whether nitrogen is there sulfur, so they may form some acids, otherwise, everything will get converted into carbon dioxide and water.

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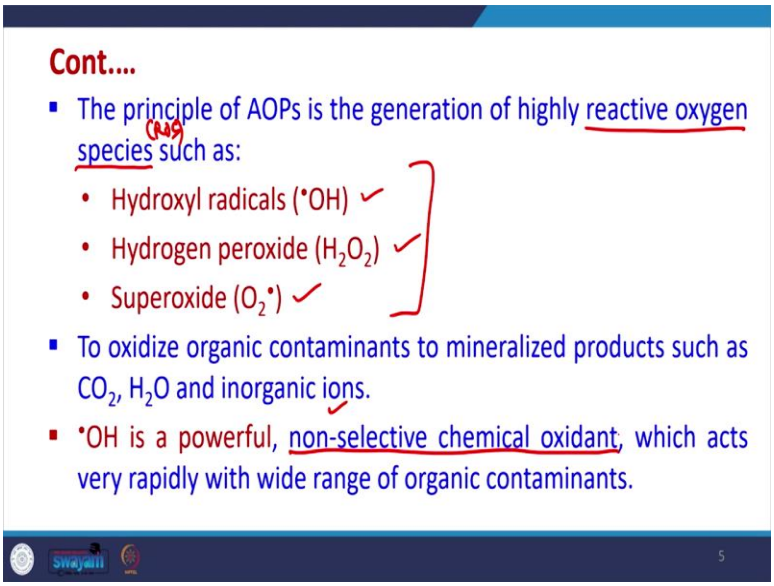

Now, the principle of AOPs is the generation of highly reactive oxygen species, they are also termed as ROS. So, this we are going to learn ROS as well. Now, the main one of the few key main species which are generated are like hydroxyl radical, hydrogen peroxide, superoxide, etcetera. So, to oxidize organic contaminants to mineral products such as CO2, H2O and inorganic acids etcetera, or inorganic ions, these radicals are used.

Among them OH is radical is highly powerful, non-selective chemical oxygen, non-selective means it will oxidize anything and everything. So, every type of organic compound it will try to oxidize, so it is not selective. So, that means, we are able to oxidize anything which is present in

the water. So, this is good, which is we require a non-selective chemical oxidant during the treatment. Now, this OH radical acts very rapidly with wide range of organic contaminants. So, this is there. So, it is highly active reactive oxygen species and which helps in the degradation of the pollutant.

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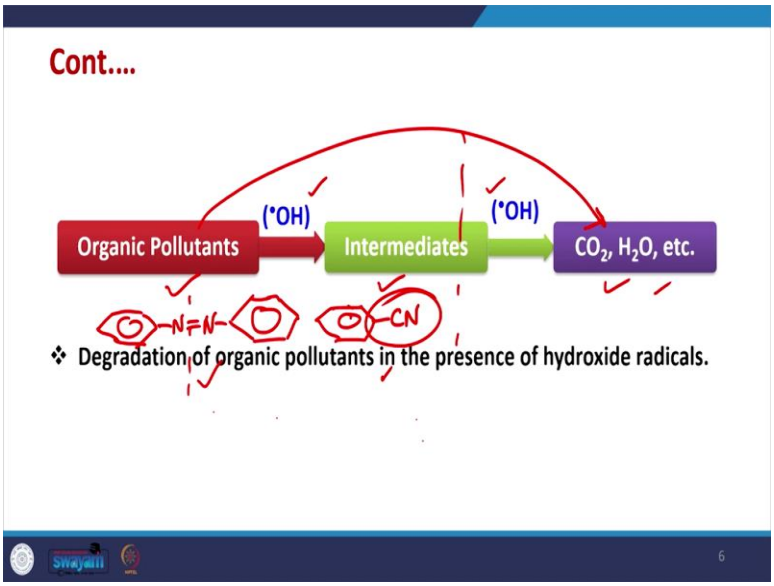

Now, how the system works? We have organic compounds. We have OH radical or any other types of reactive organic species which will be formed. Now, this will react with this organic pollutant and form intermediate. Now, this intermediate will further react with radical to form these compounds so this is the method by which most of the AOPs will work.

Now, sometimes if any of the AOP actually stops at this place only then there is a problem, sometimes like example is there many of the dyes like a azo dyes are there. So, as azo dyes have some structure similar to this. So, they will be connected by azo bond and then some other group may be present on other side. Now, this is there. Now, if it breaks only partially. So, we have some compounds which may form which will be having this CN group.

So, like we may have just tentatively writing here, we may have some group like this. Now, this if cyanide group is present or any Nitryl group are present, they are in fact more toxic than the parent compound. So, in the AOP we generally require that that complete mineralization of the organic compounds into CO2 and H2O should happen, it should not get stopped at halfway or

otherwise, because sometimes for the parent organic compound may not be as toxic as the intermediate compound which is formed after partial degradation.

So, but most of the AOPs, generally they will work very well and they may help in converting this organic pollutants into CO2 and H2O, which is what is desirable. So, this is the working principle of AOPs.

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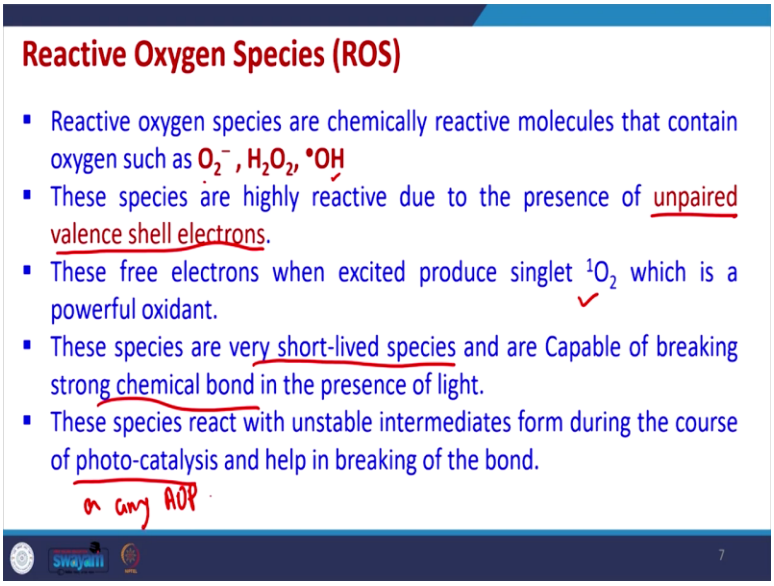

Now, we talk about reactive oxygen species. So, we will try to learn what are the different reactive oxygen species? How they work and what are their degradation potential, etcetera. Now, reactive oxygen species are chemically reactive molecules that contain oxygen such as O2, H2O2, OH radical, etcetera, these species are highly reactive due to the presence of unpaired valence shell electrons.

Now, each of these oxygen species they are highly reactive because they have unpaired valence shell electron. Now, these electrons when excited, they will produce singlet like this O2 which is again a powerful oxidant itself. So, the problem is that these oxygen species are generally very short lived species, but during that time itself, they are capable of breaking strong chemical bonds which may be present in the presence of light or otherwise as well.

So, this is how they work. So, these species react with unstable intermediate compounds or any other parent compounds also during the course of degradation. So, example could be photo-

catalysis or any other AOP. So, they may work depending upon the type of AOP. So, any other AOP also they will work. So, this is how the system works.

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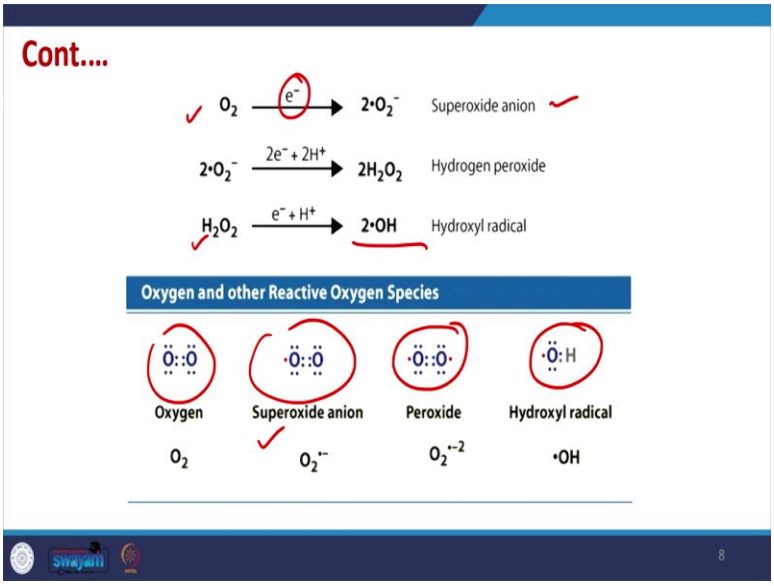

Now, you can see here how these reactive oxygen species are getting generated. So, we have oxygen whose you can see the valence is full, but superoxide may get formed via this reaction. And we see here there is a one electron is missing here. Now, peroxide which is another compound, reactive oxygen species it has two electrons missing. Similarly, hydroxyl radical again one electron which is missing from the its valence. So, this is there.

And we can see that hydrogen peroxide may form two hydroxyl radical. Similarly, oxygen may also form superoxide, but we have to remove one electron. So, how do we do this? So, how the generation of these reactive oxygen species is done in the AOP? There are different methods of that.

So, they all these, there are different types of AOPs, they work differently to produce these reactive oxygen species in situ via different methods and the contact of these species with the water and in particular the organic compounds or pollutants which are present in the water is different. So, that is how so many AOPs have been developed.

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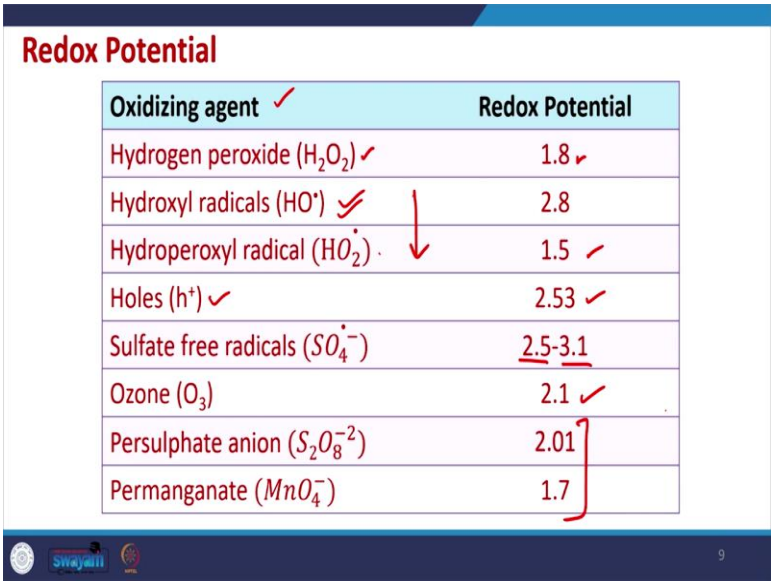

Now, these are some of the redox potential of different oxidizing agents. So, like the higher the redox potential, higher is the capability of treatment by these oxidizing agents. So, we can see here the hydrogen peroxide has a redox potential of 1.8, hydroxyl radical have a redox potential of 2.8 which is very, very high. Now, hydroperoxyl radical HO2 stars, so it has a lower redox potential as compared to hydroxyl radical and during AOPs the conversion may happen.

So, the efficiencies goes down. So, we always want this radical to be present in higher concentration, but if this radical is produced as well still some oxidation will happen. Similarly, whose which may get generated during photo-catalysis they also very high redox potential. The sulfate free radical SO4 minus, so also its redox potential is reported differently from 2.5 to 3.1.

Similarly, ozone has very high redox potential. So, that is why many places ozone treatment is done of the water. So, 2.1 is redox potential. Per sulfate ions, per magnet ion they also have good redox potential and they are capable of oxidizing most of the organic compounds themselves. So, this is there.

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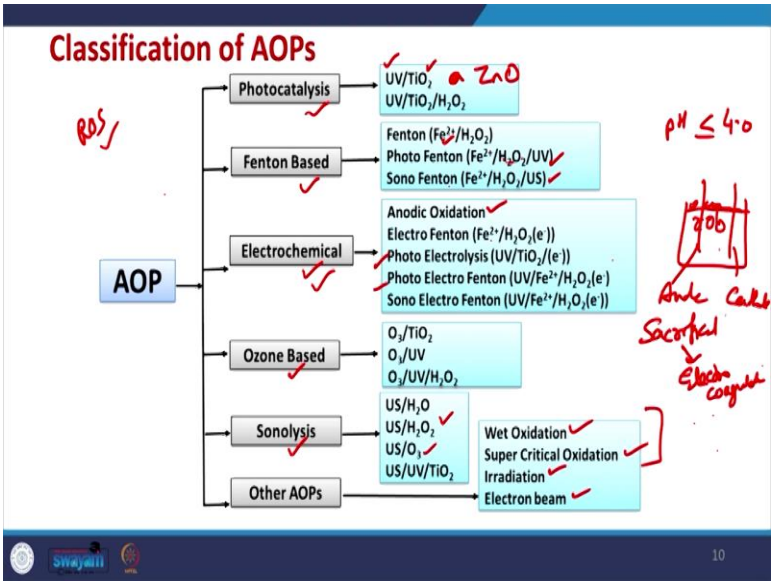

Now, we have studied that how various reactive oxygen species help in the treatment of the water. In particular the organic compounds which are present in the water they are converted into CO2, H2O, etcetera. Now, depending upon the how these ROS get produced, we have different AOPs. So AOPs may be classified here. So, they are like photo-catalysis, Fenton based method, electrochemical, ozone, Sonolysis.

So, Sonolysis uses ultrasound, then we have other AOP methods also wet oxidation, supercritical oxidation where we use high temperature and pressure, then irradiation, electron beam, etcetera where we use high energy intensity beam etcetera to produce reactive oxygen species. So, depending upon that how these reactive oxygen species are generated, we have different AOPs. Now, first of them is photo-catalysis.

So, in the photo-catalysis we use catalysts such as TiO2, or zinc oxide etcetera to produce reactive oxygen species in the presence of ultraviolet rays. So, the key thing is that they require photons for excitation. So, we require ultraviolet rays. Now, the lot of research is going on towards using or making catalyst which can work with the visible light because the intensity of UV light which is present on the surface of the earth is way less as compared to visible light.

So, if we can use the visible light, then it will be better. The problem is that the visible light have lower intensity as compared to the UV light. So, they require other types of catalyst. So, all these aspects we are going to study more when we are going to study the photo-catalysis in detail.

Similarly, Fenton based method they use iron type of catalyst and iron in its two plus valence form along with hydrogen peroxide or any of the other techniques like UV rays, US ultrasound, etcetera may be used, but generally they will essentially require iron type of catalyst which are in Fe2 plus form.

Now, for any catalyst to be present iron catalyst to be present in the Fe2 plus form the pH needs to be lower than this around 4 or 4.5. So, this system works only in the low pH wastewater. So, this is the problem. So, lot of research is also going on these type of treatment by Fenton based method.

Similarly, electrochemical methods are used. So, in the electrochemical methods we have two electrodes one is the anode and another is cathode.

Now, depending upon the type of anode, which is being used and the type of wastewater being treated, different possibilities are there. So, one of the key possibilities that if anode is sacrificial. So, that means, it will dissolve into the water itself. So, if it is sacrificing itself then we have the process which is called as electro coagulation. So, this is well known process and it is, but it is not like advanced oxidation processes because we are using, doing the coagulation by adding the coagulant in-situ during the wastewater treatment and that coagulant is coming from the anode. So, this process is called electro coagulation.

Now, if this anode is not oxidizing itself, where, though it is oxidizing the pollutants in the water then it is called anodic oxidation or electrochemical oxidation. So, this is possible. Similarly, gases get generated during the treatment at both anode and cathode. So, these gases may take the organic compounds present into the water into the surface, so that electro flotation may also work.

So, this is also one of the techniques for water treatment and it will be highly useful where oil and grease etcetera are present in the water. So, oil and grease is taken to the top. So, this is more of a separation technique as compared to oxidation, but it may work in conjunction with the anodic oxidation itself. So, this is also possible.

So, there are different types of electrochemical techniques which are possible like electro fenton, photo electrolysis, photo electro fenton, sono electro fenton, so we will discuss this hybrid

electrochemical technique, which has lots of potential for uses, in particular for treatment of wastewater generated from those industries, which have peculiar characteristics. So, the electrochemical has a lot of potential for treatment of those wastewater.

Similarly, ozone based wastewater techniques can also be used. So, in the ozone based we generate ozone in-situ or it is generated outside using different methods and then it is send diffused into the water and after that these ozone molecules they combined with different organic contaminants present in the water and convert them into CO2, H2O etcetera. So, this is there.

Now, similarly ultrasound along with H2O2 or ozone or any other technique can be used for generation of reactive oxygen species and then these reactive oxygen species are able to degrade the compound. Now, this sonolysis can work very well with the electrochemical treatment techniques because the passivation of electrode which happens during the treatment of water that passivation does not occur if we are using ultrasound along with the electrochemical technique.

So, there is we can combine many of the AOPs together thinking in similar manner. So, thus many a times if the individual techniques are used like suppose any wastewater is there, an electrochemical technique we are using and it is able to treat or remove 70 percent of the COD and if we are using sonolysis alone, it is possible that it may only be able to remove only 15 percent of the COD.

Now, if we combine them together, they add, adding them together it will account for only 85 percent of the COD removal, but actually they may be able to remove more than 95 percent of the removal of the COD. So, this is called synergistic effect of two AOPs. So, hybrid AOPs are also coming into picture.

So, those things we are going to discuss later on within this section itself. So, similarly wet oxidation, supercritical oxidation, where use high pressure and temperature conditions. Many times with catalysts without catalysts etcetera for treatment of water, so we will study them later on.

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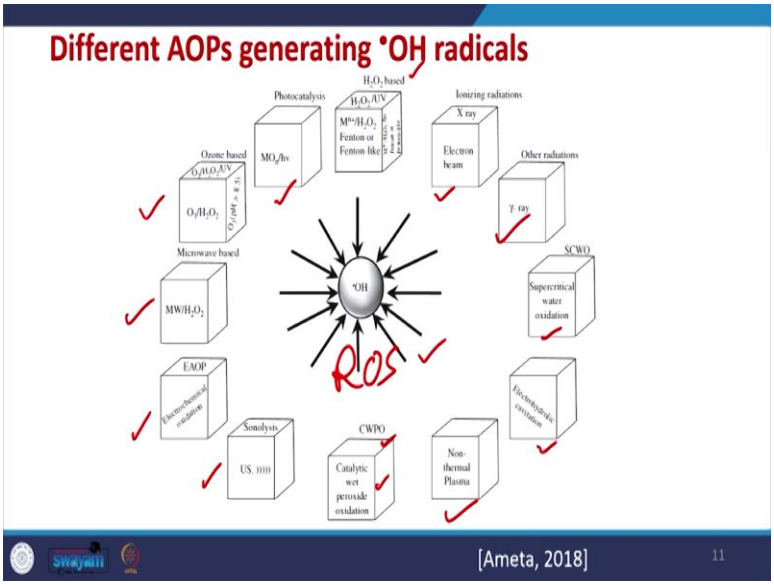

Now, these are different AOP generating OH radicals, AOPs, which generate OH radicals or any other reactive oxygen species by different means, the same we can use photo-catalysis, we can use lot of hydrogen peroxide based techniques which is called as per oxidation. So, we can use hydrogen peroxide along with some catalyst. So, they will always produce reactive oxygen species.

Similarly, X-rays ionization ionizing radiations like X-ray can be used for producing this species, other types of gamma ray, supercritical water oxidation we use very harsh technique conditions of temperature and pressure for producing reactive oxygen species. Similarly, ultrasound that means, like electro hydraulic cavitation techniques can also be used.

So, ultrasound may be used some other methods of cavitation generation can be used and they will be able to produce these hydroxyl radical. Non thermal plasma can be used. Similarly, catalytic wet per oxidation, where we use H2O2 or we may use H2O2 along with some very high temperature and pressure conditions, through this technique.

Similarly, sonolysis can be used electrochemical oxidation, micro wave based methods etcetera can be used and ozone can be used for this. So, already we have discussed little bit of this. And we are going to discuss these methods in detail further on. So, we will be studying the principle, we will be studying the key advantages, disadvantages, many times reactor configurations,

etcetera, how they are able to teach the water and how what are the challenges associated with these techniques for their application in actual field.

The AOPs are still in the developing stage, and not all the AOPs are being used for actually for water or wastewater techniques, only are in they are in developing a study. So, there are still many challenges which are there with respect to their utilization for industrial wastewater treatment or otherwise.

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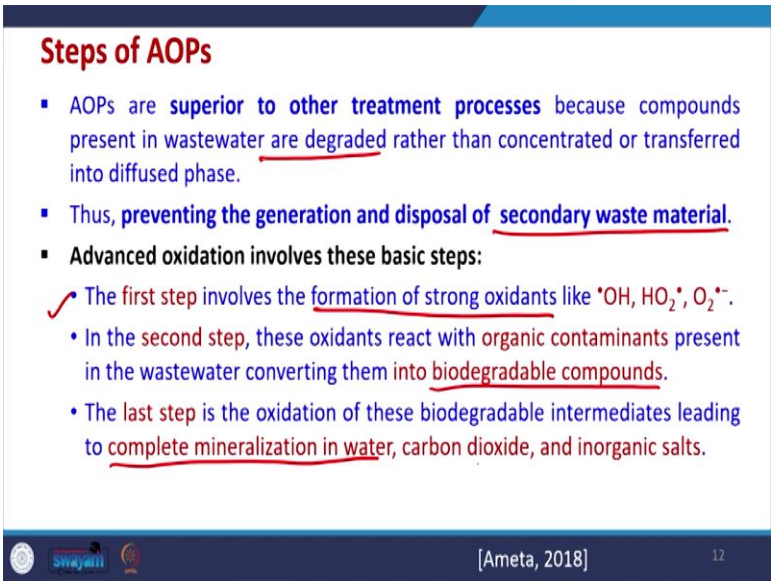

Now, what are the different steps which are involved in the AOP method of treatment? So, AOPs are superior to other treatment techniques, because here the compounds are degraded rather than concentrated. So, this is one thing that we are totally removing the compound itself, we are degrading it not separating it out or concentrating it or transferring it into a different phase. So, this is there. So, we do not have any secondary waste which is getting generated.

Now, there are basically many steps which are involved in the advanced oxidation processes. So, the first step is to form strong oxidant, so first step involves formation of strong oxidants like different reactive oxidation species, hydroxyl radical, peroxy radical, superoxide etcetera. In the second step, these oxidants react with organic contaminants present in the wastewater and converting them into biodegradable compound.

So, it is possible that we can use these ROS to convert the recalcitrant pollutants into biodegradable compound. So, in the last step, the oxidation of these biodegradable intermediates leading to complete mineralization into carbon dioxide, water, inorganic salts etcetera happen. So, this is the last step. So, this is there.

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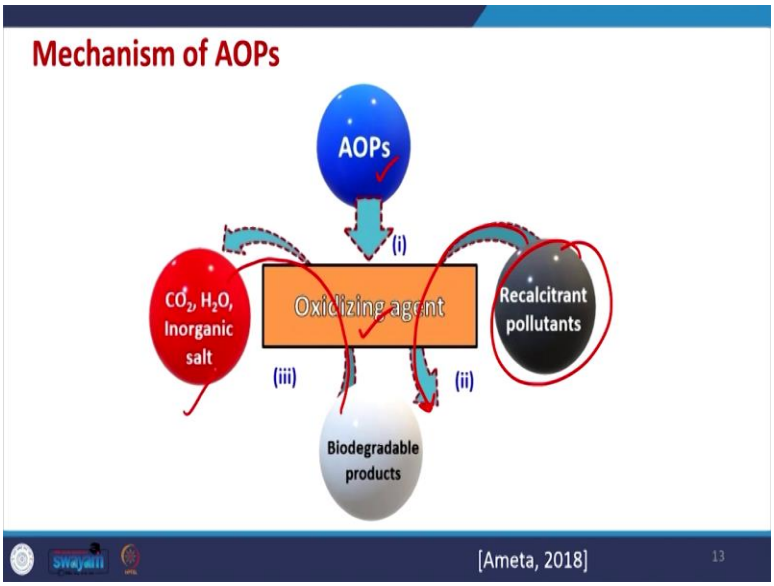

So, we have recalcitrant pollutants. So, various AOP techniques are there. So, they will get converted into biodegradable products in the presence of oxidizing agents, which are getting generated because of these AOPs. And then these biodegradable pollutants are converted into these CO2, H2O, inorganic salts etcetera. So, this is the mechanism of AOP and how it works.

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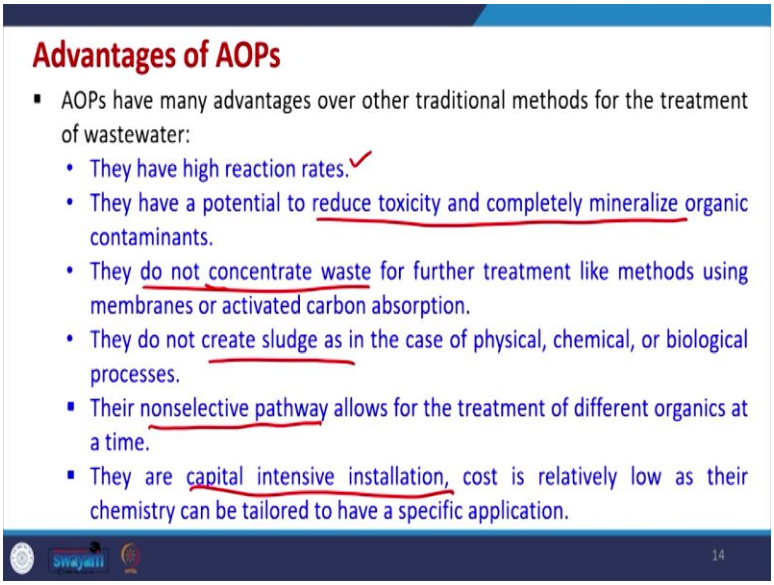

The advantages already we have discussed few of them, but there are other advantages also over traditional methods for the water treatment. So, these AOPs generally have high reaction rates. So, that means, the reactor configuration will be smaller. So, higher the reaction rate the faster will be the treatment. So, within a reactor volume, we can treat more amount of water or if the amount of water is fixed per unit hour how much it is generated, we can reduce the reactor volume.

They have a potential to reduce toxicity and completely mineralized organic contaminants which is the key advantage. Second key advantage is that they do not concentrate waste. So, that means, there is no secondary pollution which is happening or we have to further think about how to discard the adsorbent, suppose, we are using adsorption technique, how to discard or reuse the sludge etcetera during coagulation flocculation.

So, these challenges are not there. So, these techniques do not create sludge as in the case of physical, chemical or biological processes. So, this is there. During treatment generally, they are non selective that means, they are able to degrade any type of organic compound or pollutant present in the water. So, this is there.

These are, these techniques are capital intensive installation, but cost may be relatively lower as compared to other techniques depending upon the type of technique we are using. Many times these techniques may be energy intensive as well. But if we can use photo-catalysts, so that

energy intensive nature goes out. So, this is. So, depending upon the requirement etcetera, different types of AOPs can be used.

Many times the water which is generated in a industry itself or many other places, they cannot be treated at all by the usual treatment methods. So, like if pH is around 1 or pH is more than 10. So, under those conditions, some of the AOPs become highly beneficial and they can treat the water and in fact they can balance the pH. So, sometimes if the pH is supposed 2.

So, during treatment, they will reduce the remove the COD etcetera, but they will increase the pH also to 5, 6 etcetera. So, this is possible. Similarly, for higher pH wastewater they may reduce the pH also along with the treatment. So, these are the advantages of AOPs.

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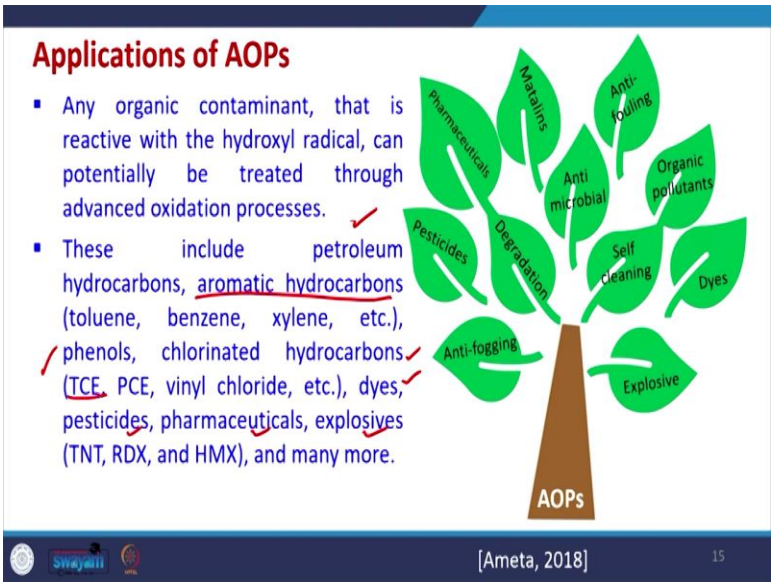

Now, AOPs can be used for treatment of many types of organic contaminants. So, this is here. And they are, since they are non selective they can be used at many places. So, the type of wastewater which can be treated using AOPs include like petroleum hydrocarbons, aromatic hydrocarbons (toluene, benzene, xylene, etcetera). Since, phenols, chlorinated hydrocarbons like PCE, TCE, vinyl chloride, etcetera.

Similarly, they can be used for removing dyes, pesticides, pharmaceutical explosives, high energetic materials, etcetera. So, they can be used for treatment of various types of wastewater which contain various types of organic compounds, which may contain pH varying in different

range. So, all these compounds etcetera or the contaminants can be mineralized by AOP technique. And different AOPs techniques have been developed. We will try to study these AOP techniques in detail in further lectures onward.

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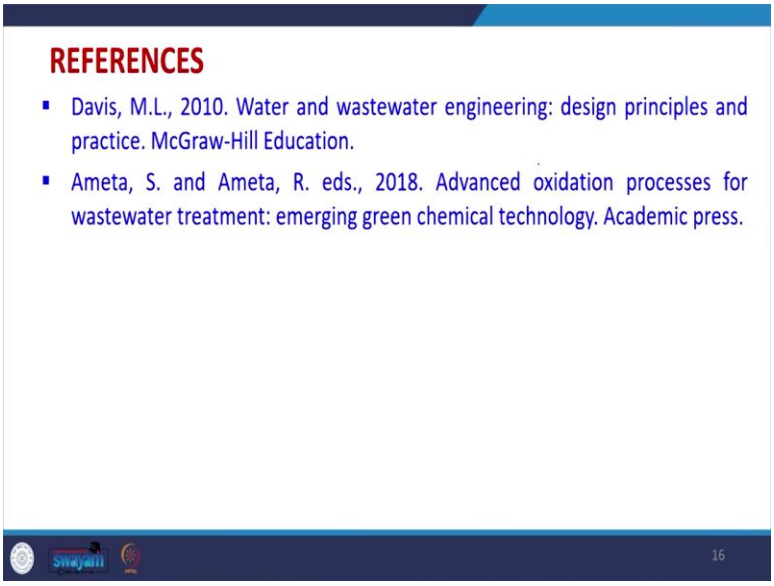

In this today lecture, we have used only few references which are given here. You can go and further study if you wish. So, thank you very much.