Course Name: Industrial Wastewater Treatment

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Lecture 4: Advanced Oxidation Processes

Okay, so welcome back and we are in module 3, lecture 4 and we are discussing the advanced oxidation processes. So, the concepts covered in this lecture will be on technologies which are used to produce hydroxyl radicals. So, OH° radicals are very oxidative species which can oxidize anything which comes in its contact. So, these OH° radicals will not only degrade the compounds of interest but it will also degrade the compounds which are causing the BOD or COD into the wastewater. So, OH° radical production can lead to the destruction of the organic compounds which are present in the wastewater indiscriminately. So, it does not discriminate what type of organic compounds are present and whatever the things that can be oxidized whether it is organic in nature or inorganic in nature so it can be oxidized by the OH° radicals.

So, they are highly reactive species which can lead to the oxidation of any recalcitrant compound also present in the wastewater systems. So, these OH° radicals can be produced by a variety of techniques. For example, it can be ozone based advanced oxidation processes where ozone is used for the treatment of the wastewater for the degradation of the compounds which are present in the wastewater, and they are not being degraded by the conventional processes. Similarly, we can have the UV based AOPs where the ultraviolet irradiation is used for the degradation of certain organic compounds depending upon how much UV irradiation it is absorbing and what is the rate of degradation in presence of UV light for such compounds.

So, then the efficiency of these technologies can also be enhanced by using the combination of these technologies. For example, we can have ozone and UV combination so ultraviolet rays, and the ozone can be combined in a reactor and that can also lead to the degradation of organic compounds by the production of OH° radicals by this method. Similarly, we can also combine ozone and hydrogen peroxide. So, hydrogen peroxide is also a very highly oxidizing agent, and it can combine with ozone so that the OH° radical production can be enhanced and we can get a higher degradation rate in comparison to ozone alone. Similarly, we can also combine hydrogen peroxide and ultraviolet rays so that we can get the degradation of organic compounds at a higher rate and lastly, we will discuss about the Fenton’s process and in the Fenton's process we will be seeing that how hydrogen peroxide can get activated by certain metal species so that OH° radicals can be produced by this process.

So, the technologies which are used to produce OH° radicals can be classified into three types. For example, we can have ozone here, we can have UV here, we can have H_2O_2 here. So, these technologies which can be individually used as well as they can also be combined together so that we can produce OH° radicals by using these technologies. So, we can have ozone based AOPs where ozone and UV can be combined, or we can combine ozone and hydrogen peroxide which is a combination of these three technologies. Similarly, we can have UV based AOPs where the hydrogen peroxide and UV can be combined as well as ozone and UV can be combined.

We can have the Fenton related AOPs where we can have the reaction of ferrous salts with the H_2O_2 so that we can lead to the generation of OH° radicals. Similarly, we can have the photocatalysis based AOPs where the photocatalysis are in the presence of catalyst and in the presence of UV light or in presence of light so it can lead to the generation of OH° radicals and oxidation of the organic compounds. Similarly, ultrasound can also lead to the oxidation of the organic compounds by the production of OH° radicals which we will discuss in our coming lectures. So broadly we can classify the advanced oxidation processes into two parts. One is called the ozone-based processes and other is called the non-ozone-based processes.

For example, when we are using ozone at elevated pH so that can lead to the oxidation of compounds, so this is called the ozone-based process. Similarly, the ozone and UV can be combined. We can combine ozone and H_2O_2. We can also have a combination of ozone UV and H_2O_2 where the efficiencies of all these three systems can be combined in one and we can lead to the higher oxidation of organic compounds. Similarly, ozone can also react in presence of a titanium dioxide which is semiconductor, and this can also enhance the process of oxidation by production of higher amount of OH° radicals.

Similarly, we can combine the ozone titanium dioxide and H_2O_2 and we can also have the combination of ozone and electron beam irradiation which can also be used for the enhancement of the OH° radicals. Similarly, the ultrasonics can be used in combination with the ozone so that the production of OH° radicals can be enhanced and we can enhance the efficiency of the degradation. The non-ozone-based processes as the name says that it does not involve ozone into it so we can have the combination of H_2O_2 and UV. We can have the combination of H_2O_2, UV and pentons reagent that we have just now discussed. We can have the simple electron beam irradiation which can also cause the degradation of the organics by production of OH° radicals in such a case.

Similarly, electrohydraulic cavitation can also result in the production of OH° radicals which can lead to the degradation of organic compounds. We can also use ultrasonics so that we can generate OH° radicals here and the non-thermal plasma can also lead to the oxidation of the organic compounds. Similarly, the pulse corona discharge can also lead to the degradation of organic compounds. Photocatalysis that is when we are having the combination of UV and titanium dioxide so this can also result in the higher amount of the OH° radicals produced in comparison to the single entities. Similarly, the gamma radiation can also lead to the destruction of the organic compounds.

Catalytic oxidation and similarly we can have the supercritical water oxidation can also lead to the oxidation of organic compounds. So, these are all the non-ozone-based processes. So, when we talk of ozone based AOPs, so the ozone itself is a very strong oxidant. So, it is having an oxidation potential of nearly 2.07 volts versus the standard calomel electrode and the direct oxidation by ozone can also take place and direct oxidation of ozone is a highly selective reaction in the sense that it can only attack it can only react with the ionized and dissociated forms of the organic compounds rather than the neutral form.

But it is having rate constants of nearly 1 to 1000 per mole per second of the reaction rate. So, this reaction rate constant is quite small in comparison to the case where OH° radicals are produced. So, in presence of ozone the OH° radicals may be produced by certain mechanisms if we are having in combination of UV, if we are having in combination with H_2O_2. So, then there may be production of OH° radicals can take place. Similarly, OH° radicals may also be initiated from the ozone directly at higher pH values.

So, we can have OH° production which is an indiscriminate oxidation that is it does not discriminate between the type of compounds which it will oxidize either it is present in the neutral form, or it is present in the ionized form it will oxidize whatever the organic things or whatever the inorganic things which can be oxidized are present in the wastewater. So, such type of mechanism is called also known as the indirect mechanism where the OH° radicals are not getting produced from the ozone directly. So, that is why it is called indirect mechanism where we are using certain other technologies like UV or H_2O_2 or Fenton etc. So, they are generating the OH° radicals by using the indirect mechanism. So, we can have OH° generation where the overall reaction with the ozone can involve that is the production of OH° radicals here that is OH° radicals can be produced and the oxygen can be produced.

$$^\circ 3O_3 + H_2O \rightarrow 2OH^\circ + 4O_2 \qquad (1)$$

So, such type of reaction can happen at high pH. So, the rate constant that is there for the reaction with the target compound with the hydroxyl radicals is nearly several order of magnitude higher than the rate of reaction of the target compound with the ozone. So, that is why it is preferred that hydroxyl radicals are produced during the reaction with ozone. So, that the rate of reaction can be enhanced. Similarly, when it is the ozone is present in combination with certain oxidants or irradiation.

So, OH° yield can be significantly improved. For example, when we have a system where ozone and H_2O_2 are combined. So, it is also known as peroxone system. So, in that case the hydroperoxide can be produced from the H_2O_2 decomposition and this hydroperoxide can later cause the production of the OH° radicals. As you can see in the reaction 2 that H_2O_2 may decompose to form the hydroperoxide ions and these hydroperoxide ions can decompose the ozone to hydroxyl radicals and oxygen is produced.

$$H_2O_2 \rightarrow HO_2^- + H^+ \quad (2)$$

$$HO_2^- + O_3 \rightarrow OH^{\circ} + O_2^- + O_2 \quad (3)$$

Similarly, ozone can be present in combination with ultraviolet irradiation where H_2O_2 is generated as an additional oxidant. So, for example, you can see here the equation number 4. So, ozone when it is present in combination with the ultraviolet radiation. So, this may generate H_2O_2 and oxygen.

$$O_3 + H_2O + hv \rightarrow H_2O_2 + O_2 \quad (4)$$

And then later on the OH° radicals can be generated by three pathways as you have discussed by the direct ozonation also at elevated pH it can be generated by ozone and H_2O_2 combination it can be generated as seen in equation 2 and equation 3.

Similarly, the photolysis of H_2O_2 will give the generation of the OH° radicals. As we have seen that when ozone and ultraviolet irradiation are present. So, in that case the ozone may be converted to H_2O_2 and this H_2O_2 may be further photolysed to give the OH° radicals which results in the degradation of the organics present in the wastewater.

$$H_2O_2 + hv \rightarrow 2OH^{\circ} \quad (5)$$

So, then we can have UV based AOPs where the UV photolysis is a process in which the compounds, they adsorb photons and the energy that is released it drives the oxidation process. So, the photolysis rate can be estimated based on the light absorption rate by the compound as well as how much quantum is getting yielded that is how much degradation is taking place.

So, that will determine the photolysis rate for any single compound. So, hydroxyl radicals can also be initiated by the photons which are induced by the UV. So, in the presence of catalysts or oxidants can initiate the hydroxyl radicals. So, one of the most common catalysts that is used is the titanium dioxide and it is a semiconductor, and it may induce the production of hydroxyl radicals which can ultimately lead to the degradation of the organic compounds in the UV based AOPs. So, titanium dioxide particles they are excited, and they produce the positive holes in the valence band which have got oxidative capacities and the negative electrons at the conduction band which are having a reductive capacity.

$$T_iO_2 + hv \rightarrow e_{cb}^- + hv_{vb}^+ \quad (6)$$

For example, here we can have two bands here one is called the valence band where we are having the electrons, and these electrons are present in the valence band and there is an energy gap, or we can say the energy band that is there, and this is called the conduction band. So, as soon as the light basically gets induced onto this such type of catalyst. So, what happens that these electrons may jump to the conduction band and the conduction band basically now contains electrons here and the holes are generated in the valence bands. Okay. So, you can see that as the titanium dioxide in presence of the UV light so this may result in the formation of the electrons in the conduction band, and it may result in the formation of the holes in the valence band.

Okay. So, now these holes and these electrons can lead to the oxidation and reduction of certain compounds for example when it is present in contact with the water so hydroxyl ions H_2O and O_2 so they also can lead to the formation of hydroxyl radicals. So, here you can see that when the OH^- ions they go to the surface on the valence band so there we are having a number of holes present because of the excitation of the electrons to the valence to the conduction band so the OH° radicals are generated through this process. Similarly, we can see that when the water is adsorbed onto such catalyst and it reacts with the holes present in the valence band so it can also lead to the formation of OH° radicals and the oxygen can be adsorbed onto the conduction band and where the electrons are present and they may result in the formation of superoxide radicals which can also lead to the oxidation of organic compounds.

$$hv_{vb}^{+} + OH^{-}(\text{Surface}) \rightarrow OH^{\circ} \quad (7)$$

$$hv_{vb}^{+} + H_2O(\text{Absorbed}) \rightarrow OH^{\circ} \quad (8)$$

$$e_{cb}^{-} + O_2(\text{Absorbed}) \rightarrow O_2^{\circ -} \quad (9)$$

So, now in presence of strong oxidants such as H_2O_2 or ozone additional OH° may also be yielded under UV irradiation for example the H_2O_2 molecule is there when it is irradiated by the UV radiation so it can generate two hydroxyl radicals.

$$H_2O_2 + hv \rightarrow 2OH^{\circ} \quad (10)$$

and similarly in addition when we are having a wavelength less than 242 nanometers so in that case OH° radicals may also be resulted to the photolysis of the water. So, you can see that the water is present and if the UV radiation less than 242 nanometers is present so it can also result in the formation of OH° radicals.

$$H_2O + hv \rightarrow OH^{\circ} + H^{\circ} \quad (11)$$

So, then we can have a system where ozone and UV can be combined so we can have the production of free radicals of OH° so with the UV light and it can be represented by the equation 12. And it can be represented by the equation 12 where we can see that ozone and UV when they combine and the UV having wavelength less than 310 nanometers so in that case oxygen may be generated and a $O(^1D)$ excited oxygen atom is also generated in this case and this excited oxygen atom then reacts with water and it can form the OH° radicals in wet air and similarly if the this excited oxygen can also react with water and then it can lead to formation of H_2O_2 and which can lead to the formation of OH° radicals and this reaction happens in water and the first the third reaction-13 happens in air the reaction-14 happens in water. So, in this way we can have the generation of OH° radicals from the ozone which is present in the water when it is irradiated by the UV light.

$$O_3 + UV\ (\text{or } h\nu,\ \lambda < 310\ \text{nm}) \rightarrow O_2 + O\ (^1D) \qquad (12)$$

$$O\ (^1D) + H_2O \rightarrow HO^\circ + HO^\circ\ (\text{in wet air}) \qquad (13)$$

$$O\ (^1D) + H_2O \rightarrow H_2O_2 \rightarrow HO^\circ + HO^\circ\ (\text{in water}) \qquad (14)$$

So, we can see that the photolysis of ozone in wet air it can result in the formation of hydroxyl radicals directly whereas when it is present in water it first leads to the formation of the hydrogen peroxide and then later the hydrogen peroxide can be fertilized for the formation of the hydroxyl radicals so use of ozone in water may not be very cost effective. So, in air it can basically get directly ozonated also when we are having the reaction in air with ozone and UV so it can lead to the degradation of the compounds through direct ozonation as well as photolysis as well as the reaction with the hydroxyl radicals.

So, ozone UV is more effective when we are having the degradation of the compound through the absorption of the UV irradiation as well as through the reaction with the hydroxyl radicals. So, when we are having both the reactions that is the compound is also absorbing the UV radiation and getting degraded similarly the hydroxyl radicals which are getting generated by ozone UV process so that also reacts with the compound so then it becomes more effective and more efficient. So, then we can also have a combination of ozone and hydrogen peroxide for example the compounds that do not absorb UV so in that case ozone and H_2O_2 may be quite effective. For example, when we talk of trichloroethylene perchloroethylene so these are the compounds that have been shown to degrade by H_2O_2 ozone system and the H_2O_2 ozone system it generates OH° radicals and this may result in the degradation of trichloroethylene as well as perchloroethylene. For example, the overall reaction that is there when ozone and H_2O_2 are combined so it results in the formation of OH° radical and oxygen.

$$H_2O_2 + 2O_3 \rightarrow 2HO^\circ + 3O_2 \qquad (15)$$

Similarly, hydrogen peroxide and UV can also be combined as we can see that hydroxyl radicals are formed when water containing H_2O_2 is exposed to UV light and UV light from 200 to 280 nanometers so this can result in the formation of OH° radicals. So, we can see the equation number 16 where we can see that H_2O_2 and UV when they combine, they can result in the formation of two atoms of hydroxyl radicals.

$$H_2O_2 + UV\ (\text{or } h\nu, \lambda = 200\text{-}280\,nm) \rightarrow HO^\circ + HO^\circ \quad (16)$$

Similarly, in some cases it has been found that the hydrogen peroxide and UV process has not been feasible because H_2O_2 is having a very small molar extinction coefficient that is it absorbs the absorption rate of H_2O_2 is less for the UV irradiation. So, it requires a very high concentration of H_2O_2, and it is also not using UV efficiently, so this system becomes less feasible in comparison to the other system because the H_2O_2 is having a very less rate of UV absorption. So, it has been seen that the combination of hydrogen peroxide and UV process can be applied to the oxidation of trace constituents which are found in the treated wastewater.

So, when we are treating the wastewater by using some conventional system and if we find that there can be certain trace contaminants certain trace organic compounds which needs to be removed from that system. So, in that case we can go for the treatment by using hydrogen peroxide and UV process otherwise if the organics will be higher so then the efficiency of such process may be hampered and similarly this process has been used for the removal of N-nitro-dimethane and other compounds which are present in the treated wastewater. So, we are stressing here on the treated wastewater so because the efficiency of such a system is low so if we are having the less organics present in the wastewater like the treated wastewater so there it can be quite effective. Similarly, we can have the Fenton diluted advanced oxidation processes where the Fenton's oxidation is one of the best-known metal catalyzed oxidation reactions of the water miscible organic compounds which are targeted compounds here so they can be oxidized by using the Fenton's reactions. So, in Fenton's reaction the hydroxyl radical is generated by the reaction between the ferrous ions and hydrogen peroxide.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\circ + OH^- \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\circ + H^+ \quad (2)$$

$$OH^\circ + H_2O_2 \rightarrow HO_2^\circ + H_2O \quad (3)$$

$$OH^\circ + Fe^{2+} \rightarrow Fe^{3+} + OH^- \quad (4)$$

$$Fe^{3+} + HO_2^\circ \rightarrow Fe^{2+} + O_2H^+ \quad (5)$$

$$Fe^{2+} + HO_2^\circ + H^+ \rightarrow Fe^{3+} + H_2O_2 \quad (6)$$

$$2\ HO_2^\circ \rightarrow H_2O_2 + O_2 \qquad (7)$$

If the reaction of ferrous ions and hydrogen peroxide it may result in the formation of OH° radicals and that can oxidize different type of pollutants which are present in the wastewater. So, the Fenton's method of oxidation it improves the degradation rate of the targeted pollutants through UV visible part of the electromagnetic spectrum also so if we are having a combination of Fenton's as well as UV visible electromagnetic spectrum is irradiated on such a wastewater so then it can result in the enhancement of the degradation rate. The mixture of ferrous sulfate and or other ferrous complex that can be there so and when it is combined with H_2O_2, so this leads to the formation of a reagent which is called Fenton's reagent. So, when we are having the Fenton's reagent when we applying it to the wastewater at low pH values so it may result in the catalytic decomposition of H_2O_2 by ferrous ions and it can lead to the formation of free radicals and these free radicals and because of the production of the free radicals a chain process starts and because of which the degradation or the decomposition of the targeted organic compounds take place. So, we can see here that the metals are able to activate H_2O_2 in which iron is the most frequently used metal so that it can activate H_2O_2, and it can get converted to OH° radicals.

So, H_2O_2 reacts with ferrous and basically it can lead to the formation of OH° radicals you can see the reactions happening in this figure where you find that the ferrocyanes they are activating the H_2O_2 which leads to the production of OH° radicals and ferrous in turns gets converted to ferric ions and these ferric ions can again be converted to ferrous ions in presence of UV light and it can basically also lead to the generation of OH° radicals . So, we can see these equations where ferrous and H_2O_2 they are combining it results in the formation of ferric and it can result in the formation of OH° radicals. Similarly, this ferric which is produced this can also combine with H_2O_2 and it can lead to the formation of ferrocyanes and hydroperoxide radicals which are there that are generated in this reaction. Now, OH° radicals may also combine with H_2O_2 to form the hydroperoxide radicals as well as the OH° radicals can also combine with the ferrous which lead to the formation of ferric. Similarly, ferric can combine with HO2 radicals that is hydroperoxide radicals which are produced in the above reactions.

So, it can get converted to ferrous ions and similarly the ferrous ions can also combine with the hydroperoxide radicals to form the ferric ions. So, this is a cyclic process that continues, and it leads to the formation of a number of radicals, free radicals which are there, and they can lead to the degradation of the organic compound which we are targeting and similarly these hydroperoxide radicals can also combine together to form H_2O_2 which is again a strong oxidant. So, we can see here that the OH° radicals are generated through the equation 1 where ferrous and H_2O_2 they are combining so it can lead to the formation of OH° radicals. Equation 2 can also lead to the formation of the ferric ions that is the ferric ions can also lead to the formation of reduced ferrocyanes with the reaction with the H_2O_2.

However, the rate constant of this equation 2 is several orders of magnitudes less than the equation 1. So, that is why the equation 1 is predominant and equation 2 may be less effective in such a case and the OH° radicals which are produced from the above reactions so they can also be scavenged by the phantom reagent as you have seen in the equation 3 and equation 4. For example, here in this equation 3 and equation 4 so these equations are representing the scavenging of the OH° radicals by the phantom's reagents itself. For example, H_2O_2 is there and ferrous is there which are the part of the phantoms reagent so they can again lead to the scavenging of the OH° radicals destruction of the OH° radicals. So, that is why there is a need that we determine experimentally the optimal molar ratio of iron to hydrogen peroxide so that we can minimize the unwanted scavenging that is taking place in such a reaction. Similarly, ferric ions which are generated so they can be precipitated out as ferric hydroxide and they can form the typical iron sludge which is there formed in the water and wastewater treatment conditions and that is why we need to separately dispose of such type of sludge so that we can get rid of such a sludge we can dispose the wastewater safely and this basically increases the complexity as well as the operational cost of such a process.

So, this means that the hydroxyl radical generation in the phantom reaction is most effective at the acidic pH conditions and as a result the application of the pentons reaction for wastewater treatment is restricted because of the above complexities. So, based on the classical phantom treatment scheme that is classical phantom treatment scheme means that is we are having the ferrous and we are having the H_2O_2. So, we can also have a certain modified phantom process which are proposed which can enhance the efficiency of pentons system. For example, we can have a penton like system we can have photo Fenton system we can have electro penton system. In penton like system, we are having the ferrous is replaced by ferric ions that is the equation 2 is now taking the lead and equation 2 leads to the formation of the OH° radical in rather than the equation 1.

So, this happens in the system which is called the model the penton like reactions where ferric ions they react with the H_2O_2 for the formation of OH° radicals. Similarly, we can have a photo penton induced reaction where we are having the UV radiation taking place and this UV radiation enhances the conversion of ferric to ferrous and which in turn enhances the efficiency of such a system because now the ferric ions which leads to the formation of the sludge. So, they also basically get converted to ferrous ions. So, this is a cyclic process that goes on by the induction of the UV irradiation and that may enhance the efficiency and the production of OH° radicals in such a system. Similarly, we can have an electro penton system where the pentons reagents the basically we are talking about ferrous as well as the H_2O_2.

So, they are produced by the electrochemical method. So, either or both of them can be produced by electrochemical method. So, this means that we do not need to add these chemicals into the water for the reaction to happen and that is possible by using the electro penton reaction and that is why this reaction can be highly efficient in the sense that the use of chemicals can be limited in such a reactor. So, these are the references that I have used in my presentation. So, then we will also talk about the electro penton process in our next lecture.

Thank you.