Course Name: Industrial Wastewater Treatment
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Week - 03
Lecture -5: Advanced Oxidation Processes

So, welcome back. So, we are in module 3, lecture 5 and this is the continuation of Advanced Oxidation Processes which we are discussing in the previous lecture. So, here we are going to discuss about the concepts like Electro-Fenton process. So, in the last lecture we have already talked about the Electro-Fenton process that how the electro-Fenton process can be used for generation of the species which are involved in the Fenton process. For example, the Fenton process is having the combination of ferrous as well as the H_2O_2. So, either the ferrous or the H_2O_2 it can be produced in an electrochemical system and such a process is called electro-Fenton process and this process is having an advantage that we need not to add chemicals from outside. So, this is one of the advantages of electro-phantom process. Similarly, we will talk about the ultrasound assisted advanced oxidation processes. We will also talk about the sulphate radical based AOPs. So, till now we have discussed about the hydroxyl radical based AOPs.

So, we will also talk about sulphate radical based AOPs. Then we will talk about the photocatalysis process which also leads to the advanced oxidation of the organics which are coming in contact with the photocatalysts. And similarly, we will talk about the operational problems that we generally face when we are applying the process of advanced oxidation process for the treatment of wastewater. So, as the term electro-Fenton process is it reveals that we are having a process which is having an application of electrical current, so this process is developed so that we can overcome the limitation of the classical Fenton process. So, the limitation of the classical Fenton process as we have already discussed that it involves a high cost and high risk associated with the handling, transportation and storage of the reagents.

So, we are using a number of chemicals there for example, we are using ferrous sulphate, we are using H_2O_2. So, the handling, transportation and storage of these chemicals can lead to a risk as well as the cost. And similarly, the accumulation of the iron sludge that we already discussed that when ferric is formed, ferric species are formed, so they may result in the formation of ferric hydroxide and this sludge gets deposited at the bottom and we need to get rid of the sludge so that we can dispose of the treated wastewater properly, ok. So, that is why this process has been developed so that we can get rid of these disadvantages that are related with the Fenton process. We have combined the concept of electrochemistry as well as the classical Fenton process.

So, that is why it is called the electro-Fenton process. So, this electro-Fenton process results in the generation of the Fenton reagents either or both of them. So, we can have the generation of only ferrous ions only and we can add H_2O_2 from outside or we can have the production of H_2O_2 as well as the ferrous ions in the same system. So, this is known as the electro-Fenton process. Now, here you can see that the H_2O_2 is generated via the reduction of oxygen on cathode.

So, if you have seen the electrochemical system, so we are having anode here, we are having a cathode here. So, this anode may be made up of iron for example here and this may lead to the oxidation, and this may lead to the generation of ferrous ions in the species and the electrons is released which is transferred to the cathode, right and this cathode here the ferric ions can get reduced to ferrous ions in this case. Similarly, the hydrogen ions can be reduced to hydrogen gas and we can also have the reduction of water which may lead to the generation of OH° radicals and here we can also put H_2O_2 from outside as you can see here that H_2O_2 and the ferrous that is getting generated from here at low pH values it may lead to the formation of OH° radicals and these OH° radicals can then react with the organic pollutants present in the wastewater and which can mineralize the organic pollutants which are present in the wastewater, ok. So, we can see here that the oxygen at the cathode is getting converted to the H_2O_2 hydrogen peroxide is getting generated at cathode. Similarly, at anode the iron is getting converted to ferrous ions and it is releasing two electrons from here which the two electrons are basically taken up by the oxygen for its conversion to H_2O_2 and the ferric ions also can be reduced to the ferrous ions at cathode only.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \text{ (cathode)} \qquad (8)$$

$$Fe \rightarrow Fe^{2+} + 2e^- \text{ (anode)} \qquad (9)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \text{ (cathode)} \qquad (10)$$

So, these reactions are taking place in an Electro-Fenton system. Similarly, we can have the ultrasound assisted advanced oxidation processes which is a highly efficient process for the removal of the contaminants and their degradation. This ultrasound assisted process may be generated by the ultrasound irradiation where we use the sound waves of the frequency of around 16 kHz to 100 MHz. So, this can be used, and these sound waves can basically create alternate compression and diffraction cycles inside the water, and it can lead to the three successive stages of cavity. So, cavity formation takes place, and this cavity formation may result in the nucleation that is formation of very small micro bubbles which grows up in size and then ultimately it implodes, and this implodes collapse.

So, this may result in the formation of OH° radicals because this micro bubble is filled with vapor which is generated from the water and this micro bubble which when it collapses, it can immediately generate a very high temperature, and it can generate a very high pressure. So, temperatures of around 4200 to 5000 kelvins may be generated by the implosion of the micro bubble that is generated from the cavity formation and similarly we can have the high pressure generated around 200 to 500 atmospheric pressures can be generated by the implosion of such a micro bubble. So, in these conditions what happens that the water molecules which are in the form of the gas or vapor in the micro bubbles. So, they are fragmented, and they generate the hydroxyl radicals in such a case. So, you can see here that the equation that OH° radicals may be generated by the water which is present in the micro bubble in form of vapors, ok.

$$H_2O \rightarrow OH^\circ + H^\circ \qquad (11)$$

So, the benefit of this ultrasound assisted AOP is that it lowers the consumption of chemical reagents and similarly it also leads to the generation of less base sludge, ok. So, there is no sludge generation in such a case. So, these are the two advantages of the ultrasound assisted advanced oxidation processes. In addition to the hydroxyl based AOPs, we can also have sulfate radical based AOPs. For example, we can have the persulfate.

So, persulfate is already a very strong oxidant, it is having a strong oxidation potential of nearly 2.01 volts and when it this persulfate compound is activated by heat or it is activated by UV radiations or in the presence of transition metals or at elevated pH, it can form a very very powerful radical that is called the sulfate radicals which is having a very high oxidation potential which is greater than persulfate that is nearly 2.6 volts and this sulfate radical then initiate the process of the advanced oxidation. So, we can see here the equation here 28 that we can see that the persulfate ions are present and in presence of heat or in presence of UV light, it can get converted to sulfate radicals. Similarly, when the persulfate it comes in contact with the metal ions, so this can reduce the persulfate into sulfate radicals as well as the metals may be oxidized in such a case.

$$S_2O_8^{2-} \xrightarrow{\Delta/UV} 2SO_4^{*-} \qquad (28)$$

$$S_2O_8^{2-} + M^{n+} \rightarrow SO_4^{*-} + SO_4^{2-} + M^{n+1} \qquad (29)$$

So, then we can see that the sulfate radicals may convert the bicarbonates into bicarbonate radicals, the carbonates to carbonate radicals, biphosphate to biphosphate radicals and so on. So, here the elevated pH can also lead to the to activate the persulfate, but the mechanism related to the elevation of pH and generation of the sulfate radicals from persulfate ions basically is still unclear. However, the thermally activated persulfate method can also lead to the generation of sulfate radicals, and we have to apply a temperature of nearly 35 to 130 degrees centigrade in such a case. If we talk of sulfate radical generation from heat or UV activated method, so it is found that for the same molar persulfate concentration nearly 50% of sulfate yield is more in case of the heat or UV activated persulfate method rather than the metal activation method. So, metal activation method leads to the generation of sulfate radical 50% less in comparison to other methods.

So, therefore the metal activation method may not be efficient and however we use metals like ferrous and ferric ions, so that we can activate the persulfate ions, and we can also use the copper and silver which have also seen the activation capability of the persulfate ions. Now, similar to hydroxyl radicals sulfate radicals are also very highly reactive species, and they also have a very very short life span, but the reaction patterns of hydroxyl radicals and reaction pattern of the sulfate radicals, so they are quite different. For example, when we talk of the hydroxyl radicals, so we see that the hydroxyl radicals generally they add to the organic compounds which are having C double C bonds, so their hydroxyl radicals gets added to such type of organic compounds and they may lead to the formation of radicals of such organic compounds. And similarly, when we are having C single H bond, so in that case the hydroxyl radicals have been shown to abstract the H from there, right. So, these reactions we have already discussed in our previous lectures.

So, this is how the hydroxyl radicals they react, whereas in contrast the sulfate radicals they generally remove the electrons from the organic molecules, and they transform these organic molecules into organic radical cations. So, that is where the difference in the reaction patterns is visible. So, we can also see that the hydroxyl radicals which can also be produced from the sulfate radicals when we are having alkaline conditions, so we can see that the sulfate radicals they can lead to the formation of OH° radicals, in water sulfate radicals can at higher pH they can also lead to the formation of OH° radicals and sulfate ions are produced here.

$$SO_4^{\circ -} + H_2O \rightarrow OH^{\circ} + SO_4^{2-} + H^{+} \qquad (30)$$

$$SO_4^{\circ -} + OH^{-} \rightarrow OH^{\circ} + SO_4^{2-} \qquad (31)$$

So, then we can also have the advanced oxidation processes which can be initiated by using a photocatalyst. So, photocatalyst means that is we are having a combination of photo and catalyst, where photo refers to photons which are coming from the light and the catalyst is a substance that alters the rate of reaction.

So, in the presence of a photocatalyst it is possible that our advanced oxidation system may be quite efficient in the sense that the OH° radical production is enhanced when we are having a catalyst and light is induced on it, ok. So, what happens that here that the energy state in any catalyst material, so it has got two bands where we are having the valence bands and the conduction band. So, this I think we have already discussed in our previous lectures also that these two bands are there where these two bands are having a band gap, or we call it as energy gap. So, here you can see that the electrons which are present in the valence band when the energy is induced on it, so these electrons may jump to the conduction band, ok. So, you find that a number of holes they become visible in the valence band and the electrons they basically go into the conduction band.

So, conduction band may lead to the reduction processes whereas the valence band in presence of the holes it may lead to the oxidation processes, ok. Here the holes then basically react with the water, so they generate the OH° radicals, so which is highly oxidizing in nature. Similarly, the electrons they can react with the oxygen, and they can form a superoxide anion radical in this case and here we can see that the generated pair of electrons and holes, so they can react with the adsorbed molecules also, they also can basically prompt a redox reactions because the electrons and holes they basically can lead to the reduction and oxidation of the organic compounds directly. And it can also lead to the formation of H_2O_2, so this H_2O_2 can also basically lead to the generation of OH° radicals and this will lead to the formation of more OH° radicals.

So, we can see here that the conduction band is there where number of electrons are present, so the light is basically present here, this in the presence of catalyst is there and this catalyst is having a valence bond here and this valence bonds are having a number of holes as the light is basically getting induced on it.

So, the electrons basically they are going to the conduction band, so electrons when they come in contact with the oxygen, so it can basically lead to the superoxide radicals, right, by reduction process. Similarly, when the water it comes in contact with the valence band holes, so these it may lead to the oxidation of water, and it may lead to the Cambria (Body)radicals. Now, this is OH° radicals which are present or the superoxide radicals which are present, so they may lead to the mineralization of the organic compounds which are present and then basically we can get rid of such type of organic compounds by the photo degradation process. So, we can have different type of reactions that are taking place during the photo catalysis that is we are having the photo catalyst for us the light that is induced on it, it produces the holes and the electrons, right, and this may lead to the generation of heat also and where the H^+ or we can say here holes, so they basically when they combine with OH^- or water, so they can lead to the formation of OH° radicals, the oxygen can basically combine with electrons and it can leads the superoxide radicals in turn, right, then the superoxide radicals can then combine with H^+ that is at low pH it can forms the hydro peroxide radicals, these hydro peroxide radicals can then combine and they can form H_2O_2 and then H_2O_2 may further lead to the production of OH° radicals, right, and these OH° radicals or the superoxide radicals which are generated from this photo catalysis process, so this can lead to the mineralization or the degradation of the organic compounds.

$$\text{Photocatalyst} + h\nu \rightarrow h^+ + e^- \quad (1)$$

$$h^+ + e^- \rightarrow \text{heat} \quad (2)$$

$$h^+ + OH^- \text{ (or } H_2O) \rightarrow OH^\circ \quad (3)$$

$$O_2 \text{ (free)} \rightarrow O_2 \text{ (ads)} \quad (4)$$

$$e^- + O_2 \text{ (ads)} \rightarrow O_2^{-\circ} \quad (5)$$

$$O_2^{-\circ} + H^+ \rightarrow HO_2^\circ \quad (6)$$

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

$$H_2O_2 + e^- \rightarrow OH^\circ + OH^- \quad (8)$$

$$O_2^{-\circ} + \text{pollutant} \rightarrow \text{products} \quad (9)$$

$$OH^\circ + \text{pollutant} \rightarrow \text{product} \quad (10)$$

So, then we can have a number of operational problems that can happen when we are having the advanced oxidation systems.

For example, we can have the high concentrations of carbonates and bicarbonates in the wastewater. So, all of you know that carbonates and bicarbonates, so they are a part of the carbonic acid cycle, so they also impart to the alkalinity to the water, they are also basically having, they are also providing the buffering capacity to the water against the pH, so low pH values. So, that is why the carbonates and bicarbonates will be a part of the water or wastewater. So, what happens that these OH° radicals, so they can also react with the carbonates and bicarbonates, right, and they can reduce the efficiency of OH° radicals and thus the advanced oxidation treatments process can be less effective when we are having high concentrations of carbonates and bicarbonates present in wastewater. So, this can be one of the problems that people encounter when they are treating, when they are utilizing the or when they are applying the advanced oxidation process to wastewater systems.

Similarly, wastewater systems can also contain, or water systems can also contain the natural organic matter. So, this natural organic matter when they are present in the water matrix, so they can also scavenge the hydroxyl radicals. As we have already studied that the hydroxyl radicals, so they are non-selective oxidizers that is they will not select that what type of the material is present which can be oxidized. So, they will oxidize indiscriminately whatever the reduced elements are present which can be oxidized by the hydroxyl radicals. So, now what happens that this may reduce the rates with the target compounds, suppose we want to target a certain compound and high natural organic matter is present in the water or wastewater system, this natural organic matter may scavenge the hydroxyl radicals, and it may reduce the efficiency.

Similarly, when the metal ions like for example, ferrous or manganese they are present in the water, so they also can scavenge the hydroxyl radicals and when they scavenge the hydroxyl radicals the number of hydroxyl radicals which are reacting with the target compounds, so this may reduce and in turn it will reduce the efficiency of the process. Similarly, there can be other factors also which can lead to the reduction in the efficiency of the treatment process. For example, we can have suspended materials present in the water or wastewater systems. Similarly, the pH can also affect the treatment process efficiency depending upon the type of reactions we are having in such a system. Similarly, the type and nature of the residual TOC, so that also can lead to the reduction in the efficiency and other wastewater constituents which are not the targeted compounds, so they also can consume the 2H° radicals and they can it can reduce the efficiency of the treatment process.

So, that is why it is very important that the chemistry of the wastewater matrix may be studied before we go for the application of advanced oxidation systems. Otherwise, the cost of the advanced oxidation systems may go very high because then it will lead to the reduced efficiency if the matrix is complex or if there are lot of scavengers which are present in the water or wastewater, so then the efficiency of the AOPs will go down. So, that is why it is always required that before we go for the full scale AOPs for the treatment of water or wastewater a pilot testing is required, so that we can test that what is the feasibility of the process, so that we can generate certain data that the compounds of interest how much degradation rate we are getting by using the AOPs and what is the operating cost, what is the capital cost that can be involved for such a AOPs application. So, the oxidation of refractory compounds can take place we are having the application of these AOPs for hydroxyl radical generation and these hydroxyl radicals can target the refractory compounds by a different type of reaction that happens we have already discussed these reaction that is by radical addition or by hydrogen abstraction by electron transfer also as well as by the radical combination which leads to the formation of H_2O_2. So, the refractory compounds can be easily degraded by these processes, but the application of the AOPs for disinfection may not be feasible.

So, the hydroxyl radical generation can lead to the oxidation of refractory organic compounds. So, we are having the hydroxyl radicals having very small lifetime. So, because of such a small lifetime the hydroxyl radicals may not be very useful for the conventional disinfection systems, but they are most commonly used for the oxidation of trace amounts of refractory organics which are present in the highly treated effluents. Why are we saying highly treated effluents? In the sense that if we are having a wastewater which contains a very high amount of DOD or COD and in addition to it may also contain certain refractory organic compounds which cannot be treated by our conventional wastewater treatment system. So, in that case the amount of the hydroxyl radicals which will be used for the degradation of the compounds causing BOD, COD or there are certain reduced compounds which are there.

So, they basically will scavenge a higher amount of hydroxyl radicals. So, that is why it is better that we use this technology we have removed such type of compounds by using conventional treatment systems. So, that the hydroxyl radicals they are basically targeting the compound of interest that is the refractory organic compounds ok. So, the oxidation of refractory organic compounds can take place by hydroxyl radicals and here we are not using the hydroxyl radicals for the conventional disinfection process because we know that the lifetime of the hydroxyl radicals is very very small and using it in the conventional disinfection process may require a higher detention time or we may require a higher doses so that we can get the generation of higher amount of hydroxyl radicals. So, that is why it is generally used for the oxidation of trace amounts of refractory organics which are found in the highly treated effluents.

So, when we talk of the applications so based on the numerous studies it has been found that the combined AOPs are more effective rather than the individual agents. So, for example, if we are having ozone, we are having UV or H_2O_2 so when they are used alone so then their efficiency may not be as high as you have already discussed earlier also. So, that is why they are generally used in combination for example we can use ozone or UV in combination ozone hydrogen peroxide, or we can use all three in combination so that we can enhance the process of the degradation by AOPs. Similarly, the AOPs are generally applied for the low COD wastewater because the cost of ozone or the H_2O_2 which is required to generate the hydroxyl radicals so that may increase manifold. If we are having a high strength wastewater or if we are having the untreated wastewater so in that case, you may require a higher amount of ozone and H_2O_2 which are precursors to OH° radicals so that we can generate higher amount of hydroxyl radicals so that they can treat the refractive organics or the treat the compound which we are targeting.

So, that is why they are generally applied to the low COD wastewater, and it may also be applied in the systems which can enhance the degradation of the wastewater by conventional processes. For example, suppose we are having a pharmaceutical wastewater so in that case it may be applied earlier also so that we can first of all bring those compounds to a biodegradable level and so that we can increase the biodegradability of the wastewater and later on it can become amenable to the biological treatment. So, this we have already discussed in our first lecture for advanced oxidation process. We have discussed that how BOD by COD ratios can be enhanced by using AOPs so that can become feasible for the conventional process to degrade such type of wastewater. So, disinfection as we have already talked about that the free radicals which are generated the disinfection process that already discussed about that it is recognized that the free radicals which are generated from the ozone, they are more powerful oxidants than the ozone alone.

So, it is the reason that hydroxyl free radicals they can be used effectively to oxidize microorganism, and they can be also used for the degradation of refractory organics. We can utilize ozone for generation of hydroxyl free radicals so they also can oxidize the microorganism, but because we are having a very short half-life of these free radicals. So, in that case it is not possible we can use this process for the disinfection purpose as it may require a high concentration of the precursors, or we may require high concentration of the 2H° radicals so that this can happen this may also require the high retention times, or it may require a very large reactors so that the disinfection by the advanced oxidation process can take place. So, that is why generally we do not use the advanced oxidation process for the disinfection purposes rather we use it for the destruction of the refractory organics or for the destruction of non-bio reducible organics or for the destruction of the organics which are causing toxicity to the bacterias which are present in our conventional wastewater treatment systems. So, we can see here that the ozone and UV irradiation can be used that is ozone can be passed in the reactor from the bottom and it may lead to the very fine bubbles which basically increase in size as they go upwards because of the lesser pressure in upwards and these fine bubbles they can diffuse and they can increase the contact area of the ozone with the wastewater and here the influent wastewater that we need to treat is coming and the ozone is getting out of the system and it goes to a destruction unit thermal destruction unit because it is very important that the ozone may not go into the atmosphere otherwise it can cause lot of harm to the people come in contact it may cause harm to the flora and fauna which is coming in contact with this ozone gas which is not utilized during the degradation process and such type of reactors are known as ozone contact reactors.

After treating it with the ozone then we take the water or the wastewater which is written with the ozone into the UV systems where we are having UV reactors and the number of UV lamps basically, they are placed and here we get the water which is now the treated effluent. Similarly, we can have ozone and H_2O_2 systems where we again pass the ozone gas in the upflow mode and you can see that the ozone very fine bubbles of ozone they form and they diffuse into the reactor and they come in contact with the water and here we are also adding H_2O_2 influent only so that the H_2O_2 can also react with the along with the ozone so that we can get higher generation of the tortoise radicals then ozone is again which is not utilized is again sent to the thermal destruction unit and we get the treated effluent out of it and similarly we can also use certain packing materials which can encourage the column to become the plug flow system basically can form and it can lead to the higher diffusion of ozone into the water. Similarly, we can also have H_2O_2 and UV systems where we can apply the H_2O_2 to the influent and we can have a high energy UV lamps which are engaged in the crisscross pattern and this is a vertical reactor and the water is being water or waste water is being passed in the upward direction and we get the treated effluent out of here we have basically the effect of H_2O_2 and UV it can produce a higher amount of 2H° radicals which can lead to the destruction of the outages. So, we these are the references that I have used in this lecture, and we will discuss we will continue our discussion in our next lecture for regarding the advanced oxidation processes.

Thank you.