# Basic Environmental Engineering And Pollution Abatement
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## Lecture: 39
## Tertiary Treatment- 3

Hello, everyone. Now, we will discuss on the topic Tertiary Treatment Part 3. In the last two classes, we have discussed on the adsorption based and membrane based methods for the tertiary treatment of wastewater and water. Now, we will be discussing on another type of methods which are also used for tertiary treatment. And this method is basically advanced oxidation process.

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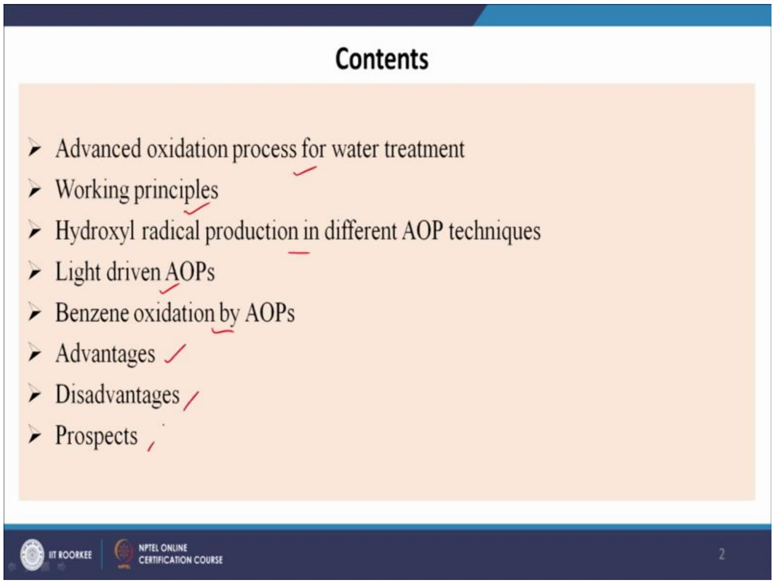

Contents

- Advanced oxidation process for water treatment
- Working principles
- Hydroxyl radical production in different AOP techniques
- Light driven AOPs
- Benzene oxidation by AOPs
- Advantages
- Disadvantages
- Prospects

Here, we will discuss on advanced oxidation process for water treatment and then working principles, hydroxyl radical production in different advanced oxidation process techniques, light driving AOPs, benzene oxidation by AOPs, that is, one example we will discuss and advantages disadvantages and prospects.

So, this advanced oxidation process includes two term, one is your advance, another is your oxidation. So, it clearly indicates that oxidation of the pollutants will be there, and it is of advanced type. That means conventional oxygen will not be used. So, here hydroxyl radical is used for this process, and hydroxyl radical is generated in situ by different methods.

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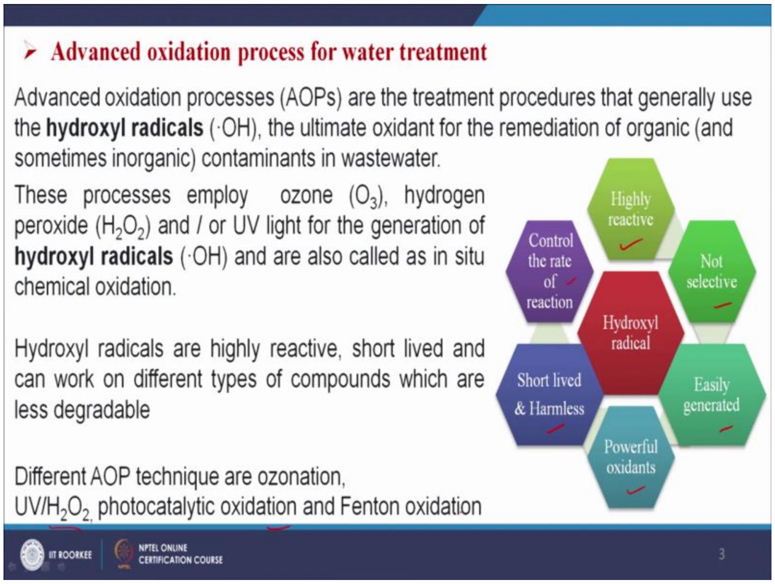

**➤ Advanced oxidation process for water treatment**

Advanced oxidation processes (AOPs) are the treatment procedures that generally use the **hydroxyl radicals** (·OH), the ultimate oxidant for the remediation of organic (and sometimes inorganic) contaminants in wastewater.

These processes employ ozone ($O_3$), hydrogen peroxide ($H_2O_2$) and / or UV light for the generation of **hydroxyl radicals** (·OH) and are also called as in situ chemical oxidation.

Hydroxyl radicals are highly reactive, short lived and can work on different types of compounds which are less degradable

Different AOP technique are ozonation, $UV/H_2O_2$, photocatalytic oxidation and Fenton oxidation

Hydroxyl radical

- Highly reactive
- Not selective
- Easily generated
- Powerful oxidants
- Short lived & Harmless
- Control the rate of reaction

By the use of hydroxyl radical or the production of hydroxyl radical, we get many advantages as shown here. Hydroxyl radical are highly reactive, these are not selective, they can work on all types of molecules, organic, inorganic etc, and easily generated. That can be generated not so easily but it is not that difficult also, it can be generated easily that way.

And we will see that hydroxyl radical is very, very powerful oxidant and this is short lived, and does not make any harm for the application of the treated water because these radicals are short lived. And control of rate of reaction is also not that difficult, it controls the rate of reactions.

The oxidation rate becomes under control, that is also not that vigorous reaction. So, we will see here, advanced oxidation processes are the treatment procedures that generally use the hydroxyl radicals, the ultimate oxidant for the remediation of organic and sometimes inorganic contaminants in wastewater. The process employs ozone hydrogen peroxide and UV light for the generation of hydroxyl radicals and are also called as in situ chemical oxidation.

The photocatalytic oxidation is also under this category. And hydroxyl radicals are highly reactive short lived and can work on different types of compounds, which are less degradable. And different AOP techniques are ozonation UV, hydrogen peroxide, photocatalytic oxidation, Fenton oxidation, etc. So, we will be discussing about all of these techniques.

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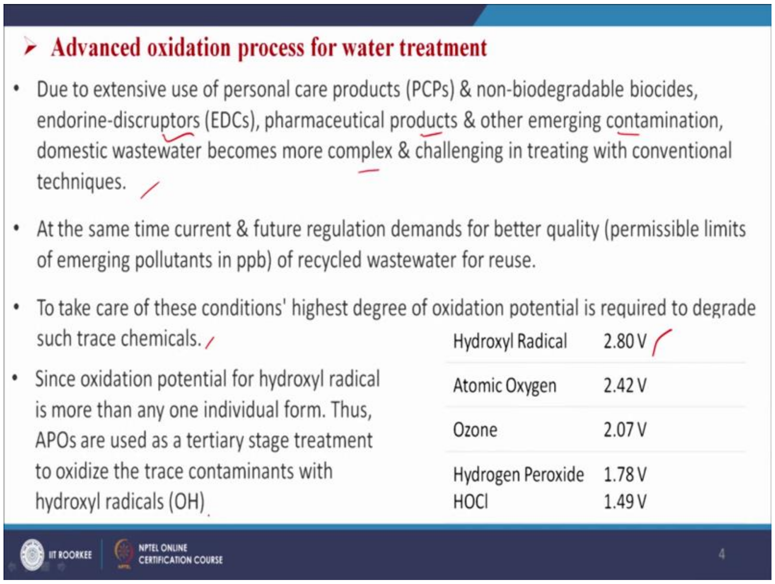

**Advanced oxidation process for water treatment**

- Due to extensive use of personal care products (PCPs) & non-biodegradable biocides, endorine-discruptors (EDCs), pharmaceutical products & other emerging contamination, domestic wastewater becomes more complex & challenging in treating with conventional techniques.
- At the same time current & future regulation demands for better quality (permissible limits of emerging pollutants in ppb) of recycled wastewater for reuse.
- To take care of these conditions' highest degree of oxidation potential is required to degrade such trace chemicals.
- Since oxidation potential for hydroxyl radical is more than any one individual form. Thus, APOs are used as a tertiary stage treatment to oxidize the trace contaminants with hydroxyl radicals (OH)

| | |
|---|---|
| Hydroxyl Radical | 2.80 V |
| Atomic Oxygen | 2.42 V |
| Ozone | 2.07 V |
| Hydrogen Peroxide | 1.78 V |
| HOCl | 1.49 V |

Before that, we will see what is the important of this advanced oxidation process. So, as we discussed that in tertiary treatment, our objective is to give the complete removal of the residual pollutants which are available after secondary and primary treatment, and in this case, the concentration of the pollutants normally, is very, very less. But the presence of some type of pollutants, even in trace amount is also not desirable. It creates different health impacts.

So particularly for the removal of this type of pollutants, this advanced oxidation system or advanced oxidation methods are very, very relevant. For example, say the personal care products which we are using, the residual is coming with the wastewater and getting entry into the water, and that remains even after primary and secondary treatment in very, very trace concentration, like say some pesticides, biocides, endocrine-disruptors, pharmaceutical products, other emerging contaminants, domestic wastewater becomes more complex and challenging.

Because of the presence of these contaminants, domestic wastewater becomes more complex and challenging in treating with conventional techniques. So, this is one major trend we are following nowadays, which needs special attention. And the other way, to ensure the good public health the future regulations are coming gradually, so the quality parameters are being monitored more closely day by day.

And so, the removal of the trace amount of the pollutants is very, very essential in today's scenario. And for this, to take care of these conditions, highest degree of oxidation potential is required to degrade such trace chemicals. Now, if we see the normally used different oxidizing agent like say, HOCl, hydrogen peroxide, ozone, atomic oxygen and hydroxyl radical out of these the maximum oxidation potential is for hydroxyl radical, that is 2.80 volt.

Since oxidation potential for hydroxyl radical is more than any one individual, as mentioned here like say, atomic oxygen, this is basically nascent oxygen. And then ozone, hydrogen peroxide, HOCl, this is highest. So, thus AOPs are used as a tertiary stage treatment to oxidize the trace contaminants with hydroxyl radicals. So, that is the reason why we expect that most efficient oxidation, we can get, if we use this hydroxyl radical, which is generated in situ in the reactor.

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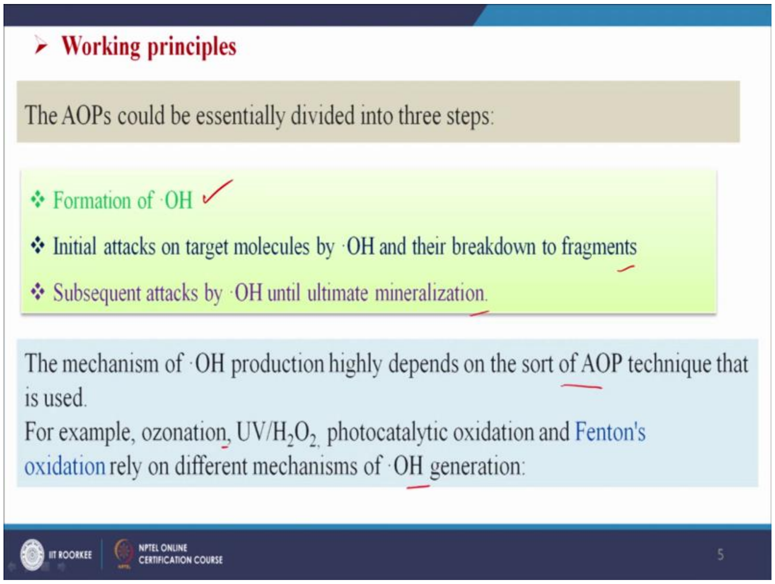

➤ **Working principles**

The AOPs could be essentially divided into three steps:

- Formation of $\cdot OH$
- Initial attacks on target molecules by $\cdot OH$ and their breakdown to fragments
- Subsequent attacks by $\cdot OH$ until ultimate mineralization.

The mechanism of $\cdot OH$ production highly depends on the sort of AOP technique that is used.
For example, ozonation, $UV/H_2O_2$, photocatalytic oxidation and Fenton's oxidation rely on different mechanisms of $\cdot OH$ generation:

Now, we will see the working principle of these AOPs. So, what we will the steps for the reactions there are number of steps and the first is formation of hydroxyl radical, then second step is initial attack on target molecules by which radical and they are break down to fragments and third is subsequent attacks by $\cdot OH$ until ultimate mineralization.

So, initially OH radical is formed, second step, it attacks that target molecules, then third step, consecutive attacks takes place until the molecule is degraded to the smallest form. Now, the mechanism of hydroxyl radical production highly depends on the sort of AOP technique that is used, that we have mentioned different types of techniques.

So, for different techniques, different mechanisms are there for the production of $\cdot OH$ or hydroxyl radical. For example, ozonation, $UV/H_2O_2$, photocatalytic oxidation and Fenton's oxidation rely on different mechanisms of $\cdot$OH generation. Here, we will see how this OH radical is generated, hydroxyl radical is generated for different process.

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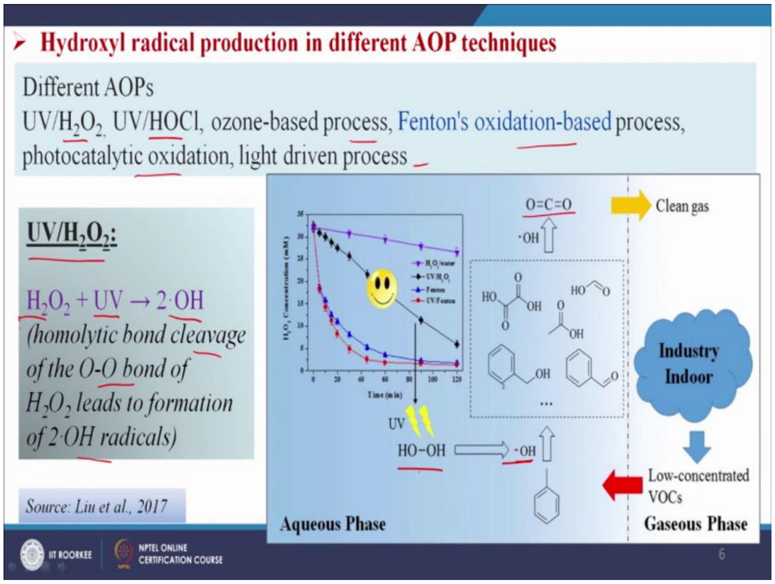

Hydroxyl radical production in different AOP techniques

Different AOPs

$UV/H_2O_2$, UV/HOCl, ozone-based process, Fenton's oxidation-based process, photocatalytic oxidation, light driven process

**$UV/H_2O_2$:**

$H_2O_2 + UV \rightarrow 2 \cdot OH$

*(homolytic bond cleavage of the O-O bond of $H_2O_2$ leads to formation of 2·OH radicals)*

*Source: Liu et al., 2017*

Different process are $UV/H_2O_2$, UV/HOCl, ozone based process, Fenton's oxidation based process and photocatalytic oxidation and light driven process. In case of $UV/H_2O_2$ that is presence of UV if we use $H_2O_2$ in the reactor, then hydroxyl radical is generated that degrades the organic compound or that oxidizes the organic compound.

So, what is the happening here we have $H_2O_2$ + UV light. So, $H_2O_2$ is dissociated into 2OH radicals, that is homolytic bond cleavage of the O-O bond of $H_2O_2$ that leads to formation of $2\cdot$OH radicals.

$H_2O_2 + UV \rightarrow 2 \cdot OH$

So this bond is broken and 2 electron is shared with each OH and that is called OH radical.

And this OH radical is reacting with this organic compound and that initially it will be attached then it will be break down continuously. So, bigger molecule to smaller and then ultimately we will be getting $CO_2$. So, this is a mechanism through which the $\cdot$OH is produced in presence of UV and $H_2O_2$, and how the compound is degraded.

So, here it is shown that these organic compound is coming from this gas stream and it is coming into the liquid phase, water phase and that is degraded by these way. Here, this graph also shows $H_2O_2$ concentration millimole for different type of system where $H_2O_2$ is available and UV is available.

So, let us say $H_2O_2$ water system, here UV is not available, UV/$H_2O_2$, UV and $H_2O_2$ both are available this is Fenton, no UV, and UV/ Fenton. In this case Fenton is also available, UV is also available. So, this graph shows in case of only UV, but this graph shows $H_2O_2$ water. So, if only $H_2O_2$ and water is remaining, then the $H_2O_2$ concentration is this much, that means the formation of hydroxyl ion is less.

But when we are using the UV or when we are using the Fenton or UV/Fenton so, when Fenton then we are getting more hydroxyl ion formation and UV Fenton both giving the maximum hydroxyl ion production because UV/$H_2O_2$ concentration is reduced, that means that is converted to this type of products, that is hydroxyl radical. So, these are the different methods where the hydroxyl radical are formed, and the extent of hydroxyl radical formation is different and that depends upon the type of methods which we are following.

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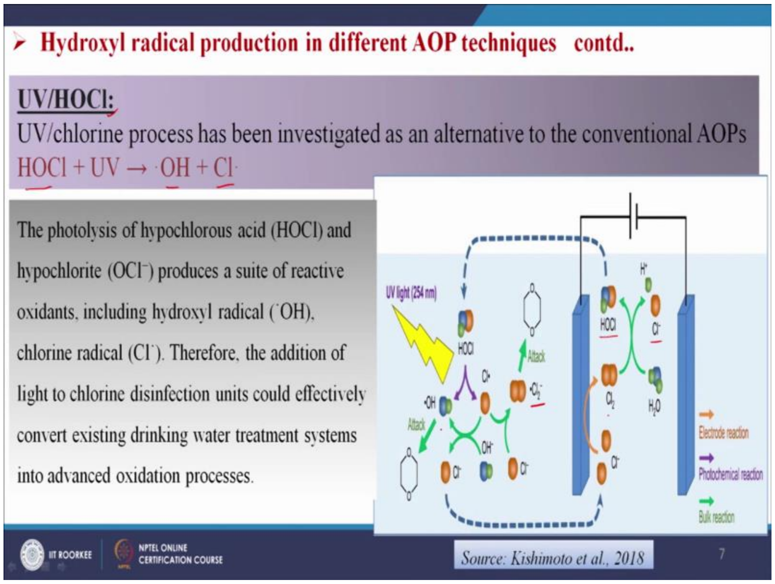

➤ **Hydroxyl radical production in different AOP techniques contd..**

**UV/HOCl:**

UV/chlorine process has been investigated as an alternative to the conventional AOPs

$HOCl + UV \rightarrow \cdot OH + Cl\cdot$

The photolysis of hypochlorous acid (HOCl) and hypochlorite ($OCl^-$) produces a suite of reactive oxidants, including hydroxyl radical ($^{\cdot}OH$), chlorine radical ($Cl^{\cdot}$). Therefore, the addition of light to chlorine disinfection units could effectively convert existing drinking water treatment systems into advanced oxidation processes.

Source: Kishimoto et al., 2018

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Now, UV/HOCl method we will see that is also in presence of UV light, say if HOCl is present in the water, that is hypochlorous acid in water, then this HOCl will be dissociated to $\cdot OH$ and $\cdot Cl$ that is hydroxyl radical and chlorine radical. So, how this can be possible? So, if HOCl is present in the water, so, under the presence of UV light, it will be dissociated to $\cdot OH$ and $\cdot Cl$. But HOCl in water, how this can be available?

We have chloride in the solution. So, if we provide some electrolytic circuit, so then if we provide some voltage, so there will be some conversion of chloride to $Cl_2$ and that $Cl_2$ will be reacting with $H_2O$ and give us HOCl and $Cl^-$. So, then, HOCl, in presence of UV light that we will be converted to $\cdot OH$ and $\cdot Cl$.

Once $\cdot OH$ and $\cdot Cl$ is converted, so, the $\cdot Cl$ can further be reacting with $Cl^-$, so that will give us $Cl_2$ this, and then that will attack organic compound and this $\cdot OH$ will also attack on the organic compound, and the similar type of attack will continue until this complete organic compound is degraded and converted to $CO_2$ and $H_2O$.

So, this is the mechanism of the UV/HOCl process and the photolysis of hypochlorous acid. And hypochlorite OCl produces a suite of reactive oxidants including hydroxyl radical chlorine radical, therefore, the addition of light to chlorine disinfection units could effectively convert existing drinking water treatment systems into advanced oxidation process.

We have already discussed that in case of conventional treatment or after tertiary treatment we go for disinfection. So, when we use both chlorine and UV in that time, this type of reaction can take place and disinfection also takes place. So, automatically disinfection and advance oxidation is taking place in the system when we use this UV and chlorine for the disinfection purpose.

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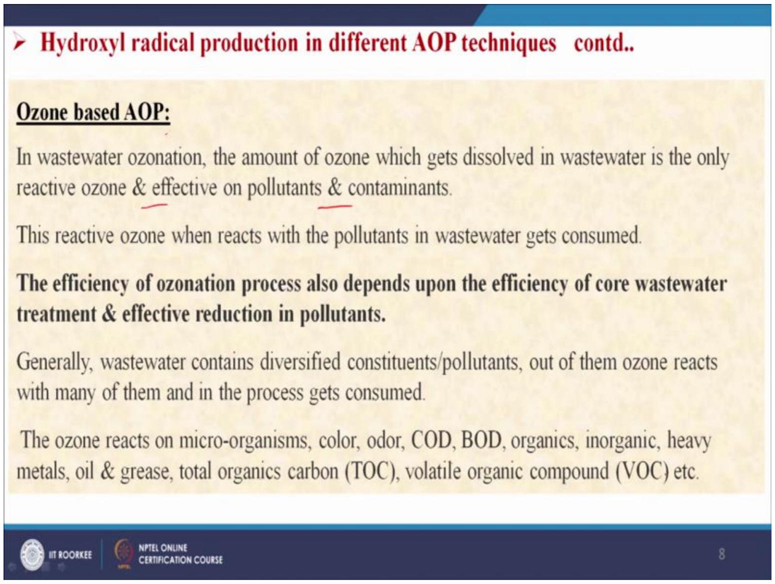

➤ Hydroxyl radical production in different AOP techniques contd..

**Ozone based AOP:**

In wastewater ozonation, the amount of ozone which gets dissolved in wastewater is the only reactive ozone & effective on pollutants & contaminants.

This reactive ozone when reacts with the pollutants in wastewater gets consumed.

**The efficiency of ozonation process also depends upon the efficiency of core wastewater treatment & effective reduction in pollutants.**

Generally, wastewater contains diversified constituents/pollutants, out of them ozone reacts with many of them and in the process gets consumed.

The ozone reacts on micro-organisms, color, odor, COD, BOD, organics, inorganic, heavy metals, oil & grease, total organics carbon (TOC), volatile organic compound (VOC) etc.

Now, we will discuss on AOP with ozone, advanced oxidation process based on application of the ozone. So ozone based AOP, so, in wastewater ozonation, the amount of ozone which gets dissolved in wastewater is the only reactive ozone and effective on pollutants and contaminants. So, ozone which is coming into the water phase that will be reacting and that will be generating nescent oxygen.

So, we have seen that nascent oxygen is also having very high oxidation potential, which is more than the ozone. So, this is considered as very effective agents for the oxidation purpose. So, the reactive ozone when reacts with the pollutants and wastewater gets consumed also, the efficiency of ozonation process also depends upon the efficiency of core wastewater treatment and effective reduction in pollutants. So, whether this ozone only or it is there are, some UV or $H_2O_2$ or Fenton etc

So, depending upon the environment the efficiency of the hydroxyl radical formation will be wearing. So, generally wastewater contents diversified constituents pollutants out of them ozone reacts with many of them and in the process gets consumed and the ozone reacts on microorganisms color, odor, COD, BOD, organics, inorganic heavy metals, oil and grease, total organic carbon, volatile organic compound, etc.

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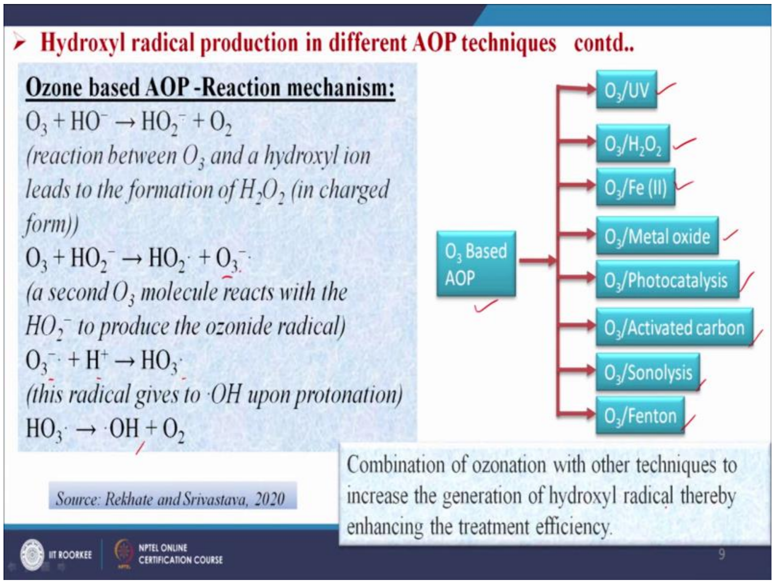

- **Hydroxyl radical production in different AOP techniques contd..**

**Ozone based AOP -Reaction mechanism:**

$O_3 + HO^- \rightarrow HO_2^- + O_2$

*(reaction between $O_3$ and a hydroxyl ion leads to the formation of $H_2O_2$ (in charged form))*

$O_3 + HO_2^- \rightarrow HO_2^{\cdot} + O_3^{-\cdot}$

*(a second $O_3$ molecule reacts with the $HO_2^-$ to produce the ozonide radical)*

$O_3^{-\cdot} + H^+ \rightarrow HO_3^{\cdot}$

*(this radical gives to ·OH upon protonation)*

$HO_3^{\cdot} \rightarrow {}^{\cdot}OH + O_2$

*Source: Rekhate and Srivastava, 2020*

Combination of ozonation with other techniques to increase the generation of hydroxyl radical thereby enhancing the treatment efficiency.

And ozone can we used in different way like say ozone based AOP maybe like ozone in presence of UV ozone in presence of $H_2O_2$ ozone in presence of Fe (II) and ozone in presence of metal oxide, ozone in presence of photocatalysis, ozone with activated carbon, ozone with sonolysis and ozone with Fenton.

So, different methods, we can adopt using ozone for the advanced oxidation purpose. And in this case, we will see the mechanism for the hydroxyl radical formation and oxidative agents, formation. So,

$O_3 + OH^- \rightarrow OH_2^- + O_2$.

So, reaction between ozone and hydroxyl ion leads to the formation of $H_2O_2$ in charged form.

So, this $OH_2^-$ this is nothing, but if we add $H^+$ then it will be giving us $H_2O_2$. So, this is $H_2O_2$ in charged form. So, that is the first step and then

$O_3 + HO_2 \rightarrow \cdot HO_2 + \cdot O_3^-$, So, a second ozone molecule reacts with the $OH_2^-$ to produce the ozonide radical this is and this ozonide radical further reacts with $H^+$ and gives us $\cdot OH_3$. This radical gives to OH upon protonation.

So, $HO_3$ that will give us $\cdot OH + HO_2$. So, this is if one oxygen is coming out and $\cdot OH$ we are getting hydroxyl radical we are getting. So, this is a mechanism through which $\cdot OH$ is produced in presence of ozone. And we see here ozone in combination with other agents gives better performance combination of ozone with other techniques to increase the generation of hydroxyl radical thereby enhancing the treatment efficiency.

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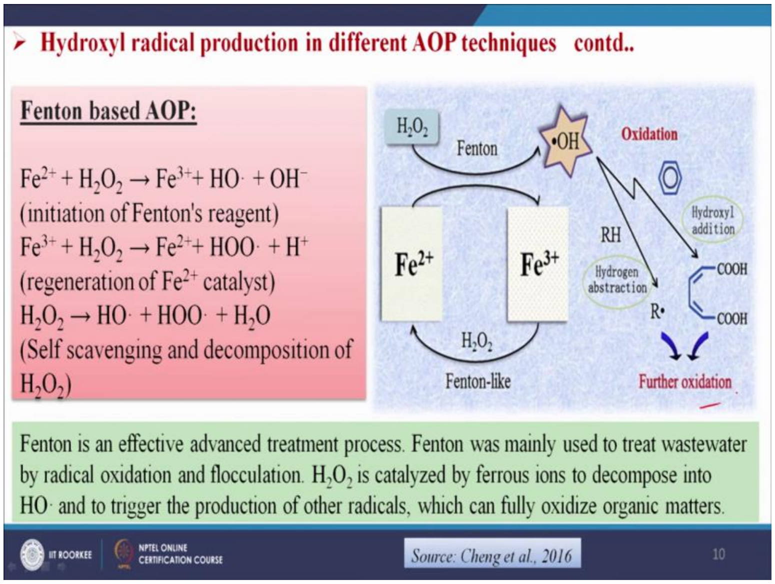

➤ Hydroxyl radical production in different AOP techniques contd..

**Fenton based AOP:**

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\cdot + OH^-$
(initiation of Fenton's reagent)
$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\cdot + H^+$
(regeneration of $Fe^{2+}$ catalyst)
$H_2O_2 \rightarrow HO\cdot + HOO\cdot + H_2O$
(Self scavenging and decomposition of $H_2O_2$)

Fenton is an effective advanced treatment process. Fenton was mainly used to treat wastewater by radical oxidation and flocculation. $H_2O_2$ is catalyzed by ferrous ions to decompose into HO· and to trigger the production of other radicals, which can fully oxidize organic matters.

Source: Cheng et al., 2016

Now, Fenton based AOP, we will see. So, here $Fe^2$ is converted to $Fe^3$ in presence of $H_2O_2$. So, this is the Fenton's reagent $H_2O_2$ and $Fe^2$, it will be available in the media. So, then $Fe^2$ will be converted to $Fe^{3+}$ and $\cdot OH$ radical plus $OH^-$. So initiation of Fenton's reagent, this is. And then regeneration of $Fe^2$+ catalyst So $Fe^3$ which is produced in the first step that will be converted to again $Fe^3$ to $Fe^{2+}$.

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\cdot + H^+$

$H_2O_2 \rightarrow HO\cdot + HOO\cdot + H_2O$

So, self scavenging and decomposition of $H_2O_2$ basically. So this is the mechanism of Fenton based AOP where we see here $\cdot OH$ is generated by this reactions $H_2O_2$, and once so $\cdot OH$ is generated, that will be reacting on organic compounds.

So, hydroxyl additions and that will be degrading this like this, and further degradation will come and it will be giving us $CO_2$ an $H_2O$ like this. And if it is RH, hydrogen abstraction can take place here. So, then $R\cdot$ and $H_2O$ will form, so that $R\cdot$ will further be reacting with this so $\cdot OH$ like this and further oxidation will be carried out. So, that way this method will work.

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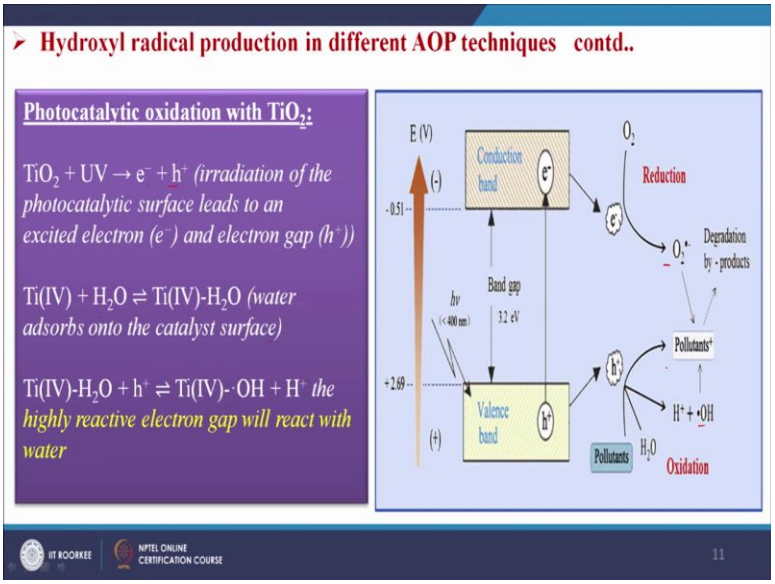

➤ Hydroxyl radical production in different AOP techniques contd..

**Photocatalytic oxidation with $TiO_2$:**

$TiO_2 + UV \rightarrow e^- + h^+$ *(irradiation of the photocatalytic surface leads to an excited electron ($e^-$) and electron gap ($h^+$))*

$Ti(IV) + H_2O \rightleftharpoons Ti(IV){-}H_2O$ *(water adsorbs onto the catalyst surface)*

$Ti(IV){-}H_2O + h^+ \rightleftharpoons Ti(IV){-}\cdot OH + H^+$ *the highly reactive electron gap will react with water*

Now, we will see Photocatalytic oxidation with $TiO_2$.

$TiO_2 + UV \rightarrow e^- + h^+$

So, in this method, in presence of UV $TiO_2$ keeps one electron and produces one $H^+$. So, that is your gap that is called irradiation of the photocatalytic surface leads to an excited electron and electron gap. So, this is electron gap it is generated and this is giving us a valence band $H^+$ and another electronic generated that is conduction band.

So, these two bands have some energy gap band gap, that is called. Now, both, this e- will be reacting with oxygen and it will be generating $\cdot O_2^-$ and $\cdot H$ which is available with this $TiO_2$, that will be helping to produce $OH^-$, as shown here. The $TiO_2$ will be absorbing $H_2O$.

$Ti(IV) + H_2O \rightleftharpoons Ti(IV){-}H_2O$

That is water adsorbs on to the catalyst surface and then

$Ti(IV){-}H_2O + h^+ \rightleftharpoons Ti(IV){-}\cdot OH + H^+$

So, on this solid catalyst or $TiO_2$ one $\cdot OH$ radical is generated. So, that $\cdot OH$ radical will help to further oxidize the pollutants to the more elemental form. So, this is the mechanism for the photocatalytic oxidation with $TiO_2$, the highly reactive electron gap will react with water.

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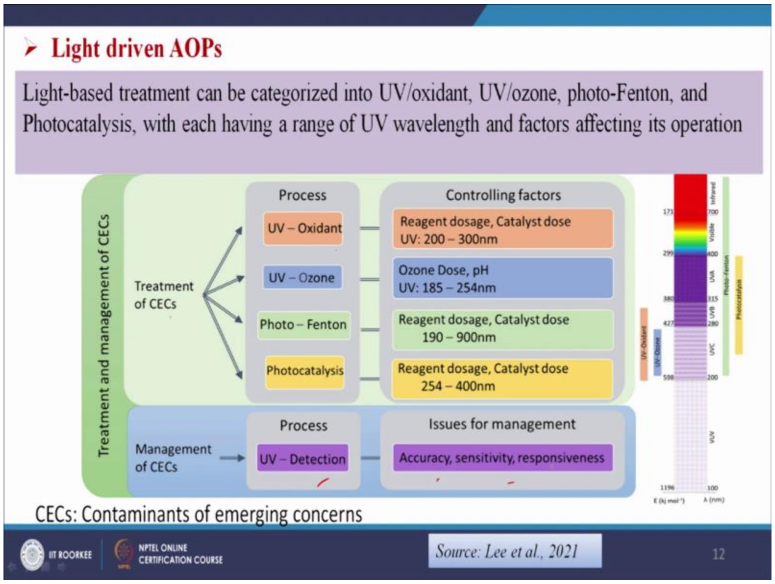

## Light driven AOPs

Light-based treatment can be categorized into UV/oxidant, UV/ozone, photo-Fenton, and Photocatalysis, with each having a range of UV wavelength and factors affecting its operation

Treatment and management of CECs

Treatment of CECs

| Process | Controlling factors |
|---|---|
| UV – Oxidant | Reagent dosage, Catalyst dose<br>UV: 200 – 300nm |
| UV – Ozone | Ozone Dose, pH<br>UV: 185 – 254nm |
| Photo – Fenton | Reagent dosage, Catalyst dose<br>190 – 900nm |
| Photocatalysis | Reagent dosage, Catalyst dose<br>254 – 400nm |

Management of CECs

| Process | Issues for management |
|---|---|
| UV – Detection | Accuracy, sensitivity, responsiveness |

CECs: Contaminants of emerging concerns

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Source: Lee et al., 2021

Now, light driven AOPs. So, in case of light driven method, certainly light will be used, and different wavelengths of light will be used, we will see here in this slide. So, you see, that is contaminants of emerging concern that is CECs. So, treatment of CECs, there are number of process like UV oxidant, UV ozone, photo Fenton, photocatalysis, so, all these methods use light somewhere we use UV and somewhere we use the visible light.

So, that way different types of wavelength have been used for different types of methods. And for this, the extent of OH radical production or generation is varying in this methods. And some controlling factors are given for this methods like say UV oxidant, reagent dosage, catalyst dosage are very important, and UV is used, that is, 200 to 300 nanometer wavelength, these rays are used, and UV ozone, we use, that is ozone dose, and pH is important UV 185 to 254 nanometer.

And then reagent dosage catalyst dosage both are very important for photo Fenton reactions and in that case light, 190 to 900 nanometer is used. And photocatalysis reaction, that is reagent dose and catalyst dose are very important, and light used is 250 to 400 nanometer. Then, there are some management concern on this process also, like the detection of light. So, what will be the wavelength, what is the intensity and there are some issues also accuracy, sensitivity and responsiveness of this methods. So, these are the challenges or issues we need to address for the successful application of these methods.

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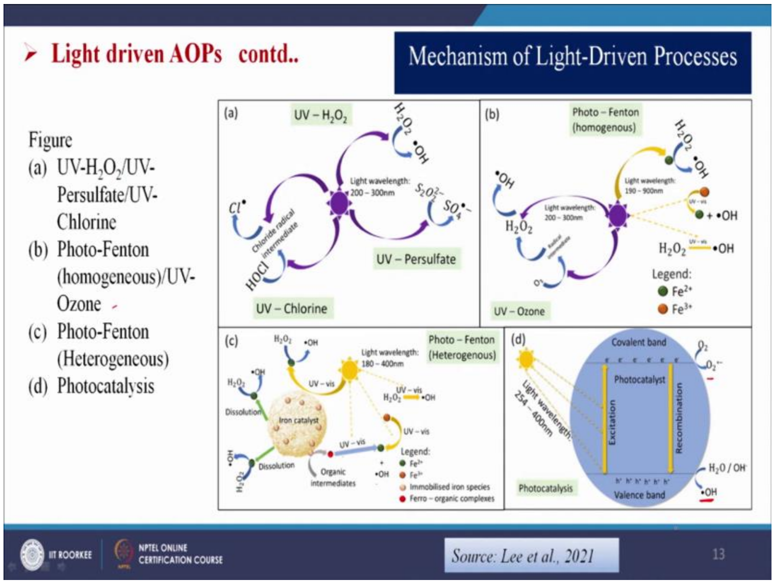

➤ Light driven AOPs contd..

Mechanism of Light-Driven Processes

Figure
(a) UV-$H_2O_2$/UV-Persulfate/UV-Chlorine
(b) Photo-Fenton (homogeneous)/UV-Ozone
(c) Photo-Fenton (Heterogeneous)
(d) Photocatalysis

Source: Lee et al., 2021

Now, light driven AOPs, we will be seeing the mechanism. So, here, we have seen that some light is used of different wavelength and then we will see the UV-$H_2O_2$, UV-persulfate UV-chlorine, any methods we have discussed about and photo Fenton homogeneous UV ozone another type of method, and photo Fenton heterogeneous and photocatalysis.

All those mechanisms are applicable in presence of light in these methods or in light driven methods, all these mechanisms are applicable. So, this figure a shows the, these three mechanisms UV-$H_2O_2$, so, that in presence of UV-$H_2O_2$ will be converted to $\cdot$OH. So, UV-persulfate in presence of UV-$H_2O_2$ minus will be converted to a $SO_4$ dot and then in UV chlorine HOCl will be converted to $\cdot$Cl and $\cdot$OH.

So, this we have discussed already. In case of photo Fenton, homogeneous and UV ozonation we see the UV ozone. So, ozone is there and that will give us this $\cdot$OH, and in case of homogeneous photo Fenton, we have $Fe^2$ and $Fe^3$ in the media. So, that conversion takes place $Fe^2$ to $Fe^3$ and $Fe^3$ to $Fe^2$.

So, that conversion will take place and we will get the $\cdot OH$ formation. So, $H_2O_2$ will give us $\cdot OH$ formation at the same time, this conversion will also take place. And so these type of reaction, which you will already have discussed are also applicable for light driven AOPs when the photo Fenton homogeneous phase is used.

When photo Fenton heterogeneous phase, it is used, that means iron is not in a homogeneous in a liquid solution it is in heterogeneous phase, that mean a solid are immobilised and iron species, when it is used. So, this is our iron species, immobilized, and this is our base. So, in that case what will happening? Will we happening that different $H_2O_2$ will be converted to $\cdot OH$ in the presence of this active sites. And this will be dissolution will be there and then $H_2O_2$ formation, $H_2O_2$ will be converted to $\cdot OH$.

Similarly, this metal which is immobilised here, that will help to capture the organic intermediates, so, then Ferro organic compounds and then that will be further converted to $\cdot OH$, and this type of conversion will be there, $Fe^3$ to $Fe^2$. And UV, visible light $H_2O_2$, $\cdot OH$ formation will also be possible. So, different types of reactions will be involved in this type of light driven AOPs.

And photocatalysis, already we have discussed that there will be some valence band and some covalent band, covalent band will help to produce this mighty, and valence band will be helping to produce $\cdot OH$ mighty, and these free radicals very, very powerful, that is nascent oxygen and then $\cdot OH$, all are very, very powerful agent for the oxidation and organic compounds will be oxidized.

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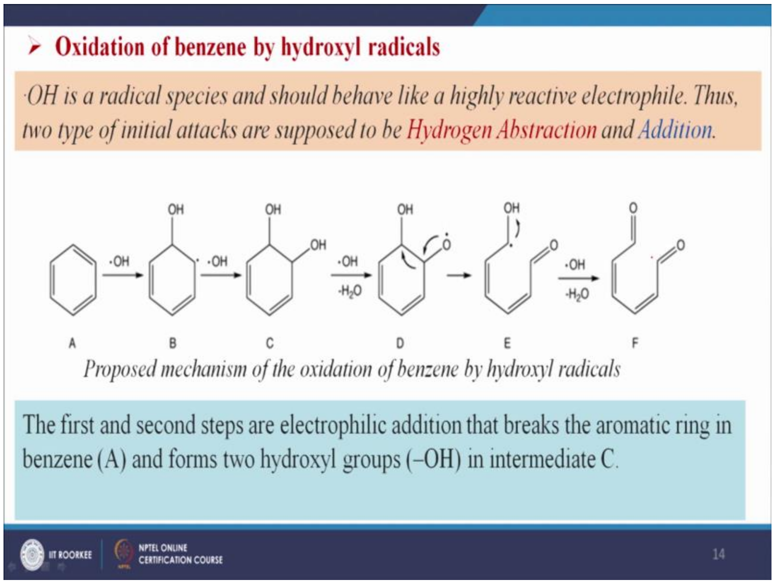

**Oxidation of benzene by hydroxyl radicals**

*·OH is a radical species and should behave like a highly reactive electrophile. Thus, two type of initial attacks are supposed to be Hydrogen Abstraction and Addition.*

*Proposed mechanism of the oxidation of benzene by hydroxyl radicals*

The first and second steps are electrophilic addition that breaks the aromatic ring in benzene (A) and forms two hydroxyl groups (–OH) in intermediate C.

Now, one example we will see here, oxidation of benzene by hydroxyl radicals. So, in this case say this is our benzene hydroxyl radicals is produced so it is attached the first attachment another is attached as a side by side, we are getting this one. Further attachment of the, that will abstraction OH, so $H_2O$ will form and these radical, it will help to break it so they are breaking of this bond. So, this might will form further attack of OH dot it will give this type of compound so further attack will continue until we are getting $CO_2$ and $H_2O$, this type of mighty.

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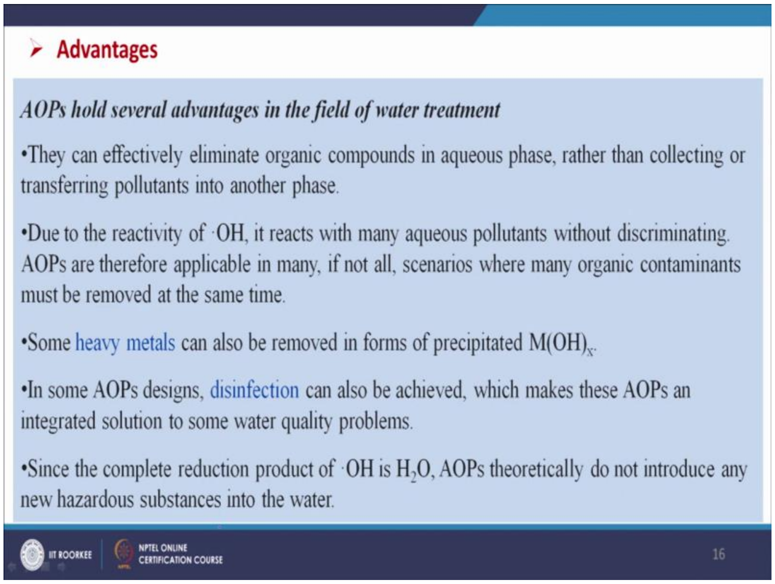

**Advantages**

***AOPs hold several advantages in the field of water treatment***

•They can effectively eliminate organic compounds in aqueous phase, rather than collecting or transferring pollutants into another phase.

•Due to the reactivity of ·OH, it reacts with many aqueous pollutants without discriminating. AOPs are therefore applicable in many, if not all, scenarios where many organic contaminants must be removed at the same time.

•Some heavy metals can also be removed in forms of precipitated $M(OH)_x$.

•In some AOPs designs, disinfection can also be achieved, which makes these AOPs an integrated solution to some water quality problems.

•Since the complete reduction product of ·OH is $H_2O$, AOPs theoretically do not introduce any new hazardous substances into the water.

Now, this methods the advanced oxidation processes have some advantages and disadvantages, we will discuss those. So, advantages, is that this can work on all types of pollutants, even in very small concentration, the pollutants are available not that can be effective. So, there is one major advantage. And most important is that they are not producing any pollutants. Basically the organic compounds are being oxidized to $CO_2$ and $H_2O$. So, secondary pollutants are not being generated.

So, they can effectively eliminate organic compounds in aqueous phase rather than collecting or transferring pollutants into other types of reactions into another phase. Due to the reactivity of $\cdot OH$, it reacts with many aqueous pollutants without discriminating AOPs and therefore, applicable in many, if not all scenarios, where many organic contaminants must be removed at the same time.

And some heavy metals can also be removed in forms of precipitate. And then in some AOPs design, disinfection can also be achieved which makes the AOPs and integrated solution to some water quality problems. And since the complete reduction product of $\cdot OH$ is $H_2O$, AOPs theoretically do not introduce any new hazards substances into the water.

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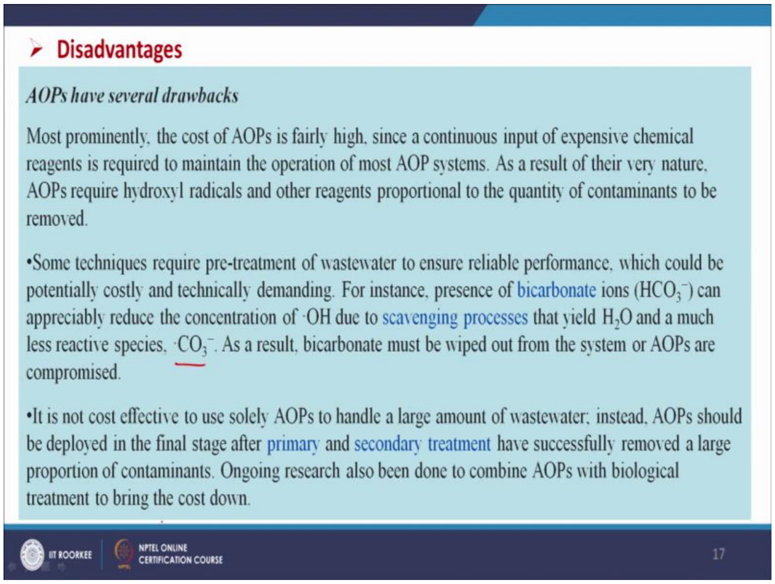

## ➢ Disadvantages

*AOPs have several drawbacks*

Most prominently, the cost of AOPs is fairly high, since a continuous input of expensive chemical reagents is required to maintain the operation of most AOP systems. As a result of their very nature, AOPs require hydroxyl radicals and other reagents proportional to the quantity of contaminants to be removed.

- Some techniques require pre-treatment of wastewater to ensure reliable performance, which could be potentially costly and technically demanding. For instance, presence of bicarbonate ions ($HCO_3^-$) can appreciably reduce the concentration of $\cdot OH$ due to scavenging processes that yield $H_2O$ and a much less reactive species, $\cdot CO_3^-$. As a result, bicarbonate must be wiped out from the system or AOPs are compromised.
- It is not cost effective to use solely AOPs to handle a large amount of wastewater; instead, AOPs should be deployed in the final stage after primary and secondary treatment have successfully removed a large proportion of contaminants. Ongoing research also been done to combine AOPs with biological treatment to bring the cost down.

So, these are the advantage and AOPs has some disadvantages also. Like most prominently, the cost of AOPs is fairly high, since a continuous input of expensive chemical reagent is required to maintain the operation of most AOPs system. As a result of their nature AOPs require hydroxyl radicals and other reagents proportional to the quantity of contaminants to be removed. So, the selection on the dose, etc. that is also an issue.

And some techniques require pretreatment of wastewater to ensure reliable performance which could be potentially costly and technically demanding. For instance, the presence of bicarbonate ion, can appreciably reduce the concentration of $\cdot$OH due to the scavenging processes that yield $H_2O$ and a much less reactive species, this one, carbonate radical. As a result, bicarbonate must be wiped out from the system or AOPs are compromised.

So, in presence of bicarbonate the system may not be effective, it is not cost effective to use solely AOPs to handle a large amount of wastewater. Instead AOPs should be deployed in final stages after primary and secondary treatment have successfully removed a large portion of contaminants. Ongoing research also been done to combine AOPs with biological treatment to bring the cost down.

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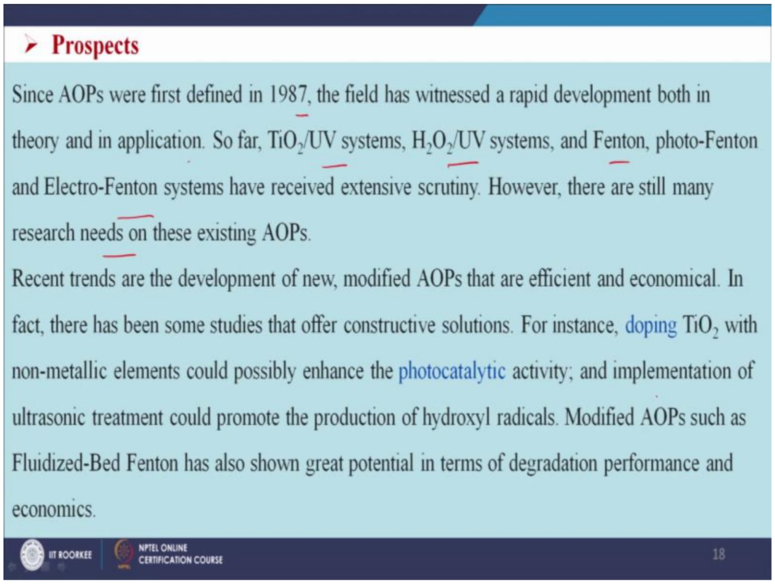

## ➤ Prospects

Since AOPs were first defined in 1987, the field has witnessed a rapid development both in theory and in application. So far, $TiO_2$/UV systems, $H_2O_2$/UV systems, and Fenton, photo-Fenton and Electro-Fenton systems have received extensive scrutiny. However, there are still many research needs on these existing AOPs.

Recent trends are the development of new, modified AOPs that are efficient and economical. In fact, there has been some studies that offer constructive solutions. For instance, doping $TiO_2$ with non-metallic elements could possibly enhance the photocatalytic activity; and implementation of ultrasonic treatment could promote the production of hydroxyl radicals. Modified AOPs such as Fluidized-Bed Fenton has also shown great potential in terms of degradation performance and economics.

And if we think about the prospects of this process, then you will see the AOPs were first defined in 1987. The field has witnessed a rapid development both in theory and in application. So, far $TiO_2$/UV system $H_2O_2$/UV system and Fenton, photo Fenton, electro Fenton systems have received extensive scrutiny.

However, there are still many research needs to on these existing AOPs. These are basically on development stage and good amount of research is going on in this area. Recent trends are the development of new modified AOPs that are efficient and economical. In fact, there has been some studies that offer constructive solutions.

For instance, doping $TiO_2$ with nonmetallic elements could possibly enhance the photocatalytic activity and implementation of ultrasonic treatment could promote the production of hydroxyl radicals. Modified AOPs such as fluidized bed Fenton has also shown great potential in terms of degradation performance and economics.

So up to this in this class. Thank you very much.