Physico-Chemical Process for Wastewater Treatment
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Lecture 48
AOP: Fenton, Ozone and Catalytic Treatment

Good day everyone and welcome to these lectures on physico-chemical processes for wastewater treatment. So, in the previous lecture, we started studying advanced oxidation processes, which are referred to as AOPs. And in the previous lecture, we studied that during AOPs, the key thing is the production of the various reactive oxygen species such as hydroxyl radical during the treatment process itself.

Now, these reactive oxidation species further combined with the organic compounds which are present in the water and they mineralize these compounds into CO2 and H2O. So, these were the major techniques or the steps which are there in the advanced oxidation processes.

Now, in addition, we learn that depending upon that how this reactive oxygen species are generated, there are different types of AOPs, like Fenton oxidation processes, ozone treatment, photocatalysis, electrochemical treatment, ultrasound etcetera. Now, these advanced oxidation processes work differently and they have different mechanism how they produce reactive oxygen species, they are different combination of different processes AOPs is possible also. So, we are going to start with few of these AOPs in the today's lecture.

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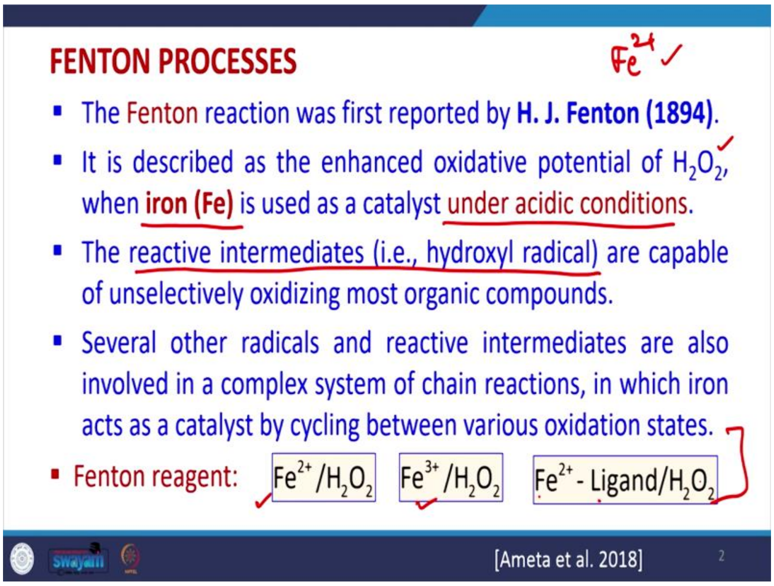

FENTON PROCESSES Fe^{2+} ✓

- The Fenton reaction was first reported by **H. J. Fenton (1894)**.
- It is described as the enhanced oxidative potential of H_2O_2, ✓ when **iron (Fe)** is used as a catalyst under acidic conditions.
- The reactive intermediates (i.e., hydroxyl radical) are capable of unselectively oxidizing most organic compounds.
- Several other radicals and reactive intermediates are also involved in a complex system of chain reactions, in which iron acts as a catalyst by cycling between various oxidation states.
- Fenton reagent: ✓ Fe^{2+}/H_2O_2 ✓ Fe^{3+}/H_2O_2 Fe^{2+}- Ligand/H_2O_2

[Ameta et al. 2018]

So, we will start with the Fenton processes which are there. So, Fenton reaction was first reported by a H. J. Fenton in 1894. And actually, this Fenton reaction has been used further for treatment of water. So, in this case in the Fenton reaction or Fenton processes, we have iron, which is used as a catalyst.

And now, this iron under acidic condition will remain in the form of Fe2 plus which is the desirability. Now, if we have some hydrogen peroxide is added beforehand then it initiates a process where lot of reactive intermediates such as hydroxyl radicals are produced and they further unselective oxidize most of the organic compounds present in the water itself.

So, several other radicals etcetera. And reactive intermediates etcetera may also get formed because of the action of Fe2 plus H2O2 and under acidic conditions with the different organic compounds, which may be the present in the water. So, the Fenton regions are Fe2 plus with H2O2, Fe3 plus with H2O2 or Fe2 plus with some ligand and H2O2. So, this is this is called as Fenton region and this is used for the treatment of the water.

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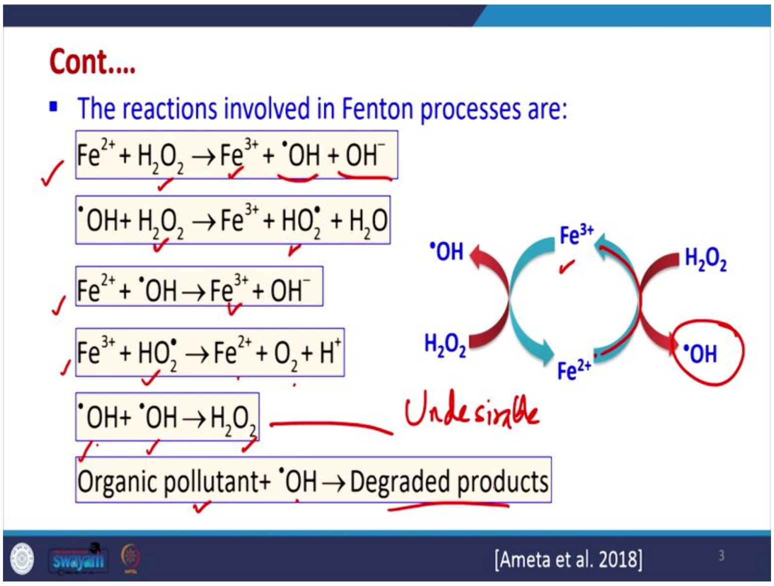

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- The reactions involved in Fenton processes are:

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$

${}^{\bullet}OH + H_2O_2 \rightarrow Fe^{3+} + HO_2^{\bullet} + H_2O$

$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^-$

$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+$

${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2$ — Undesirable

Organic pollutant + ${}^{\bullet}OH \rightarrow$ Degraded products

[Ameta et al. 2018]

Now, there are different reactions which are involved in the Fenton processes. So, these reactions are given here. So, we can see that Fe2 plus may combine with hydrogen peroxide to form Fe3 plus and OH radical and OH minus ion. So, this is possibilities Fe2 plus with H2O2 in combination may form Fe3 plus and some radicals are getting generated. So, this is there.

Now, this radical also may combine with the hydrogen peroxide itself and give back the Fe3 plus ion and some other types of radical during this process. Now, Fe2 plus itself may combine with the radical produce to form Fe3 plus. Now, this Fe3 plus can combine with the peroxy radicals to form Fe2 plus ion or O2. So, there are different and OH radicals may combine to form H2O2. So, some of these reactions are undesirable. In particular, this reaction we do not want to happen, because we want hydroxyl radical to be present in the water.

So, this is undesirable reaction and we want to avoid this possibility during the treatment. The organic compounds will combine with these radicals and produce degraded product during the treatment. This is the basic mechanism by which this Fenton process work.

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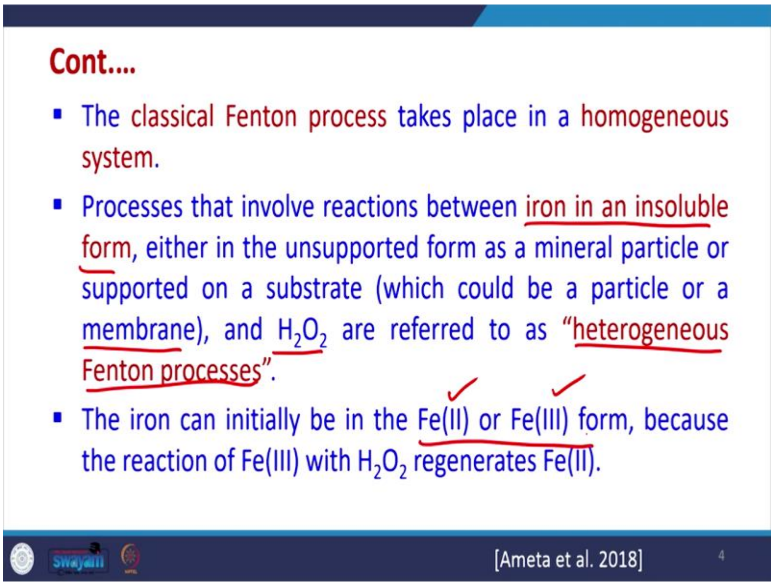

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- The classical Fenton process takes place in a homogeneous system.
- Processes that involve reactions between iron in an insoluble form, either in the unsupported form as a mineral particle or supported on a substrate (which could be a particle or a membrane), and H_2O_2 are referred to as "heterogeneous Fenton processes".
- The iron can initially be in the Fe(II) or Fe(III) form, because the reaction of Fe(III) with H_2O_2 regenerates Fe(II).

[Ameta et al. 2018]

Now, the classical Fenton process takes place in a homogeneous system and the processes that involve reaction between iron in an insoluble form either in unsupported form such as mineral particle or etcetera are they may be supported on some substrate which could be particle or a membrane etcetera. So, it is possible that iron may be supported on a substrate.

So, this is also possible along with the iron we have H2O2 and if we are using this technique, so, under that technique, it is called as heterogeneous Fenton processes, the iron can be initially in the form of Fe2 plus or Fe3 plus because the reaction of Fe3 plus with H2O2 will still generate Fe2 plus so this is iron maybe in any of this form. So, this is there.

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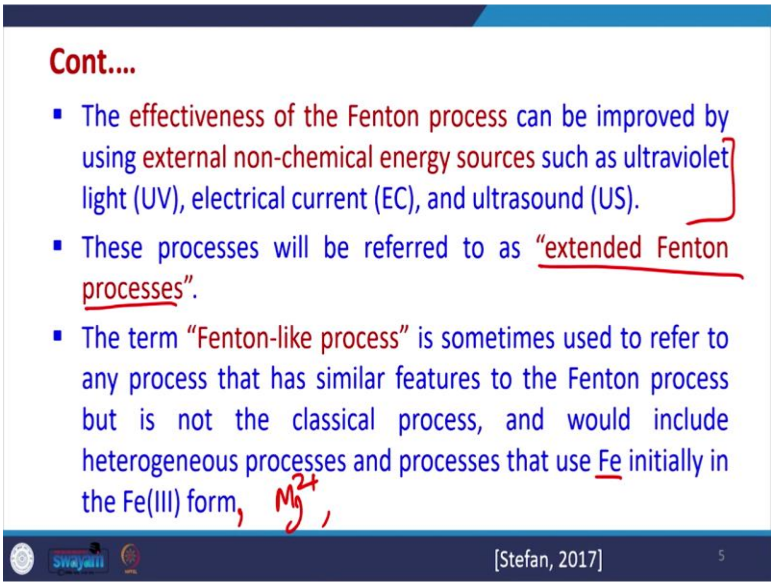

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- The effectiveness of the Fenton process can be improved by using external non-chemical energy sources such as ultraviolet light (UV), electrical current (EC), and ultrasound (US).
- These processes will be referred to as "extended Fenton processes".
- The term "Fenton-like process" is sometimes used to refer to any process that has similar features to the Fenton process but is not the classical process, and would include heterogeneous processes and processes that use Fe initially in the Fe(III) form, Mg^{2+} ,

[Stefan, 2017]

Now, going further, the effectiveness of the Fenton process, it can be improved further, if we are using some external non chemical energy sources. So, we require some if we are providing some energy sources, it will increase the possibility of formation of different types of radicals. So, these external non chemical energy sources may be ultraviolet light may be electric current, maybe ultrasound et cetera.

So, this is all any of them is possible, but whether to use them or not use them that will depend upon the wastewater to be treated some laboratory studies to be carried out beforehand, otherwise, the energy consumption may increase this is possible.

Now, these if we are combining the Fenton processes with these, these are called as extended Fenton processes. Then there is another term which is called as Fenton like processes. So, which are similar to Fenton but where iron is not being used. So, this is there.

So, that term Fenton like process is sometimes referred to any process that has similar feature to the Fenton process, but is not the classical process and will include like heterogeneous processes that use Fe initially in the Fe3 plus form classically, it was Fe2 plus form similarly, we can use other types of similar like many mg 2 plus etcetera. So, other types of catalyst having with some other metals elements etcetera can also be used. So, these are called as Fenton like processes.

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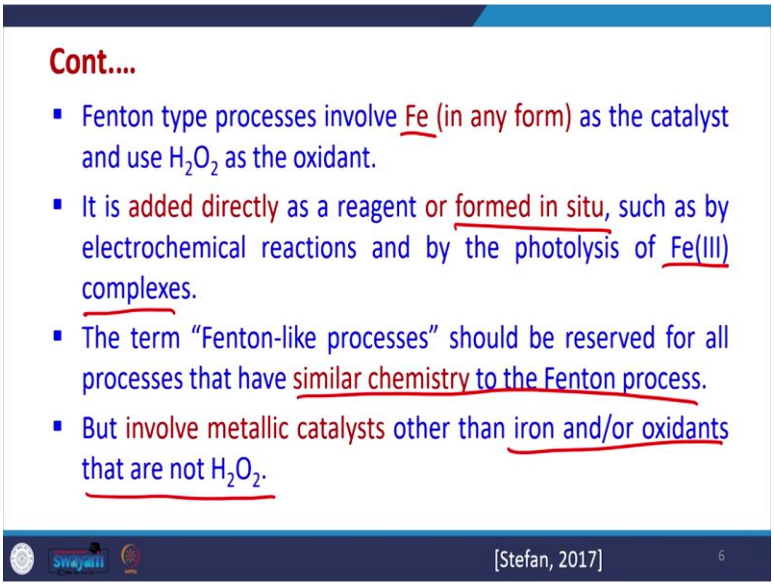

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- Fenton type processes involve Fe (in any form) as the catalyst and use H_2O_2 as the oxidant.
- It is added directly as a reagent or formed in situ, such as by electrochemical reactions and by the photolysis of Fe(III) complexes.
- The term “Fenton-like processes” should be reserved for all processes that have similar chemistry to the Fenton process.
- But involve metallic catalysts other than iron and/or oxidants that are not H_2O_2.

[Stefan, 2017]

Now, Fenton type processes involve iron in any form as a catalyst and use H2O2 as an oxidant. It is, so this H2O2 and these are added directly as a region or they may form in situ as well such as by electrochemical reaction are by the photolysis of Fe3 plus complexes. So, this is possible.

So, they may be added directly they may be generated in situ also, the term Fenton like process should be reserved for all the processes that have similar chemistry to the Fenton process. So, this is there, but they involve metallic catalyst other than the iron are also oxidants that are not H2O2. So, this is there. So, these are called Fenton like processes as discussed.

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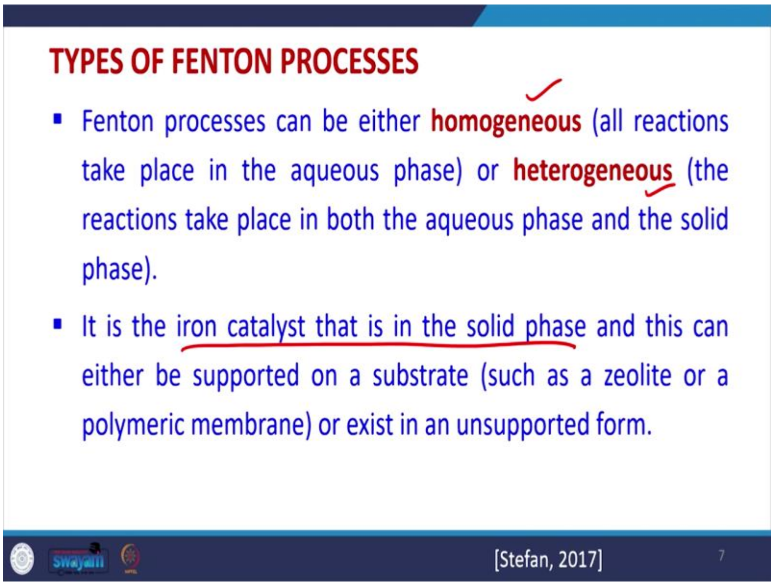

TYPES OF FENTON PROCESSES

- Fenton processes can be either **homogeneous** (all reactions take place in the aqueous phase) or **heterogeneous** (the reactions take place in both the aqueous phase and the solid phase).
- It is the iron catalyst that is in the solid phase and this can either be supported on a substrate (such as a zeolite or a polymeric membrane) or exist in an unsupported form.

[Stefan, 2017]

Now, there are different types of Fenton processes. So, already we have discussed we have homogeneous Fenton process, we have heterogeneous Fenton processes. Now, in the homogeneous Fenton processes, all the reactions take place in the aqueous phase itself. Whereas, in the heterogeneous Fenton processes the reactions take place in both the aqueous phase and the solid phase both.

So, this is the difference between homogeneous and heterogeneous Fenton processes. Iron catalyst that is in the solid phase and this can be supported on a substrate such as zeolite polymeric membrane et cetera or it may be existing in the unsupported form. So, depending upon that it may be homogeneous phase, heterogeneous phase etcetera.

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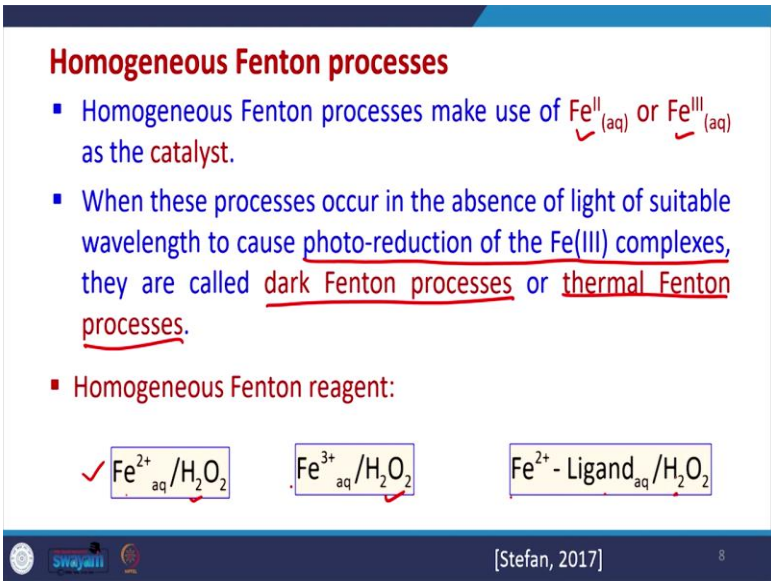

Homogeneous Fenton processes

- Homogeneous Fenton processes make use of $Fe^{II}_{(aq)}$ or $Fe^{III}_{(aq)}$ as the catalyst.
- When these processes occur in the absence of light of suitable wavelength to cause photo-reduction of the Fe(III) complexes, they are called dark Fenton processes or thermal Fenton processes.
- Homogeneous Fenton reagent:

✓ Fe^{2+}_{aq}/H_2O_2 Fe^{3+}_{aq}/H_2O_2 $Fe^{2+}\text{-}Ligand_{aq}/H_2O_2$

[Stefan, 2017]

Now, homogeneous Fenton processes they make use of iron in the aqueous phase are iron in the iron 2 or iron 3 in the aqueous phase as a catalyst when these processes occur in the absence of suitable wavelength light to cause photo reduction of Fe3 plus complexes they are called as dark Fenton processes or thermal Fenton processes. So, this is another classification of Fenton processes. Now, homogeneous Fenton region in the aqueous system we have Fe2 plus with H2O2 Fe3 plus with H2O2 or Fe2 plus with ligand in the aqueous phase with H2O2. So, this is there.

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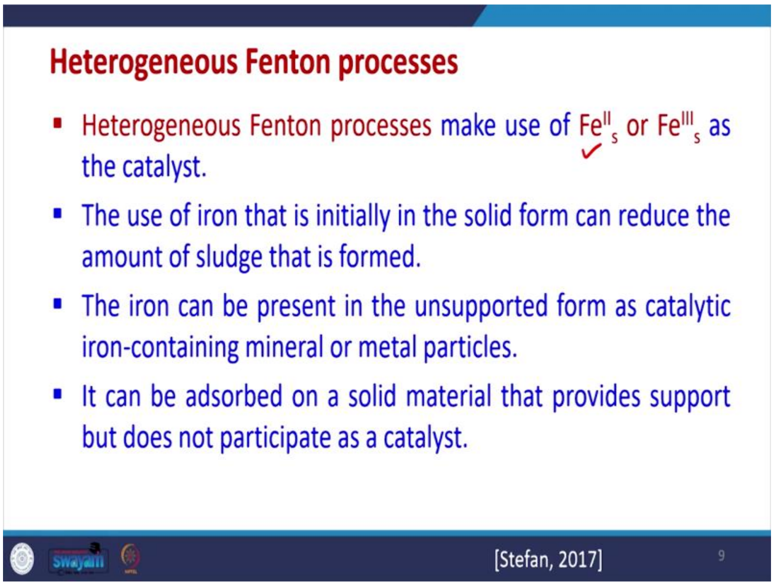

Heterogeneous Fenton processes

- Heterogeneous Fenton processes make use of Fe^{II}_s or Fe^{III}_s as the catalyst.
- The use of iron that is initially in the solid form can reduce the amount of sludge that is formed.
- The iron can be present in the unsupported form as catalytic iron-containing mineral or metal particles.
- It can be adsorbed on a solid material that provides support but does not participate as a catalyst.

[Stefan, 2017]

In the heterogeneous Fenton process, they use iron in Fe2 plus or 3 plus form in the solid form as a catalyst, the use of iron that is initially in the solid form that reduces the amount of sludge that is formed and iron can be present in the unsupported form or it can be supported on any of the polymer any of the zeolite are membrane metrics as well.

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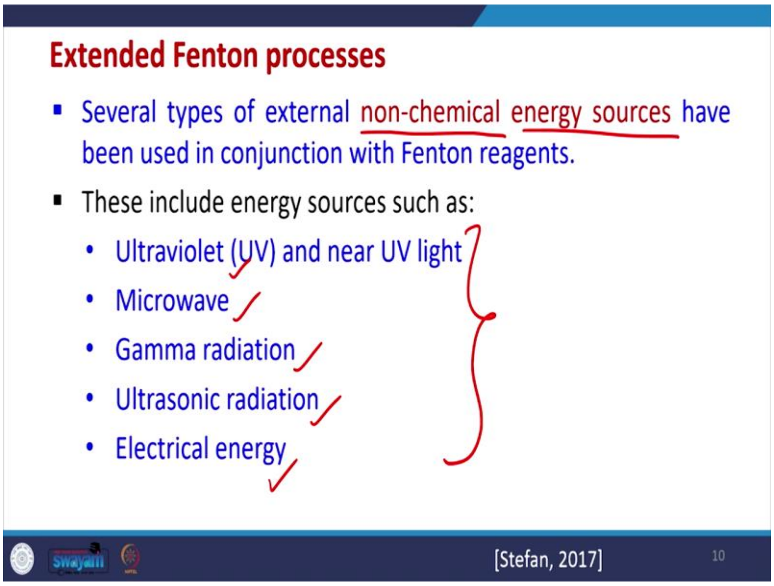

Extended Fenton processes

- Several types of external non-chemical energy sources have been used in conjunction with Fenton reagents.
- These include energy sources such as:
  - Ultraviolet (UV) and near UV light
  - Microwave
  - Gamma radiation
  - Ultrasonic radiation
  - Electrical energy

[Stefan, 2017]

Now, there is another thing which is called an extended Fenton process. So, several types of non-external non-chemical energy sources have been used in conjunction with the Fenton regions. So, any of these energy sources if they are used along with the Fenton processes, they are referred to as extended Fenton processes these energy sources may include ultraviolet, microwave, gamma radiation, ultrasonic radiation, electrical energy etcetera. So, these are called as extended Fenton process.

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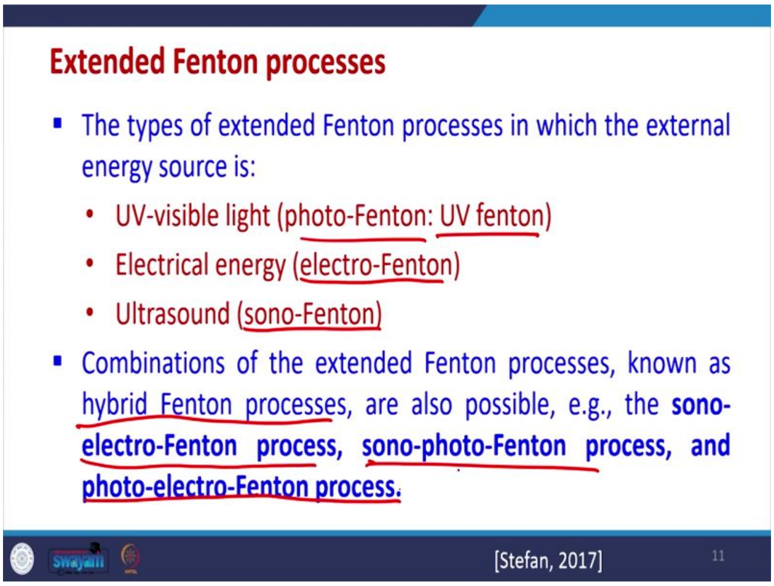

Extended Fenton processes

- The types of extended Fenton processes in which the external energy source is:
  - UV-visible light (photo-Fenton: UV fenton)
  - Electrical energy (electro-Fenton)
  - Ultrasound (sono-Fenton)
- Combinations of the extended Fenton processes, known as hybrid Fenton processes, are also possible, e.g., the **sono-electro-Fenton process**, **sono-photo-Fenton process**, **and photo-electro-Fenton process.**

[Stefan, 2017]

Now, within extended Fenton processes that types of extended Fenton process in which external energy is used or like UV-visible light, so, it is called as UV Fenton or photo Fenton. Electrical energy we have call it electro Fenton then ultra sound it is called as sono Fenton. So, combination of these extended Fenton processes is also possible and they are referred to as hybrid Fenton processes. And so, these are like sono photo electro so, all 3 are combined. Sono photo Fenton processor two more possibilities photo electro Fenton processes there is this is another possibility.

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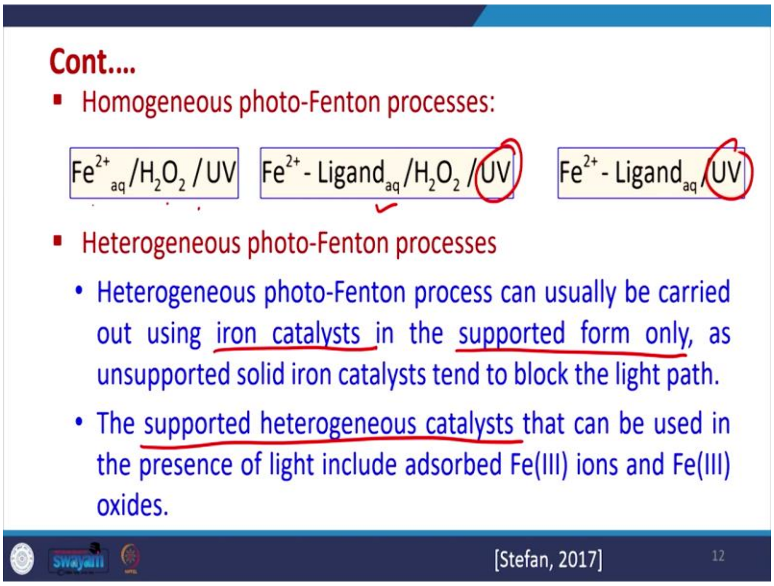

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- Homogeneous photo-Fenton processes:

$Fe^{2+}_{aq}/H_2O_2/UV$ $Fe^{2+}\text{-}Ligand_{aq}/H_2O_2/UV$ $Fe^{2+}\text{-}Ligand_{aq}/UV$

- Heterogeneous photo-Fenton processes
  - Heterogeneous photo-Fenton process can usually be carried out using iron catalysts in the supported form only, as unsupported solid iron catalysts tend to block the light path.
  - The supported heterogeneous catalysts that can be used in the presence of light include adsorbed Fe(III) ions and Fe(III) oxides.

[Stefan, 2017]

So, in this case we are using Fe2 plus with H2O2 in the aqueous form or in the solid form also we can use. So, this is there we are using ultraviolet here you can see then we have heterogeneous photo Fenton processes. So, heterogeneous Fenton process can be used carried out using iron catalyst in the supported form only as unsupported solid iron catalyst will block the light path. So, this is possibility.

So, in this case it is called heterogeneous photo Fenton process. The supported heterogeneous catalyst that can be used in the presence of light include like absorbed iron third or iron ions or iron third oxides on different types of supports, including geo lights and membranes.

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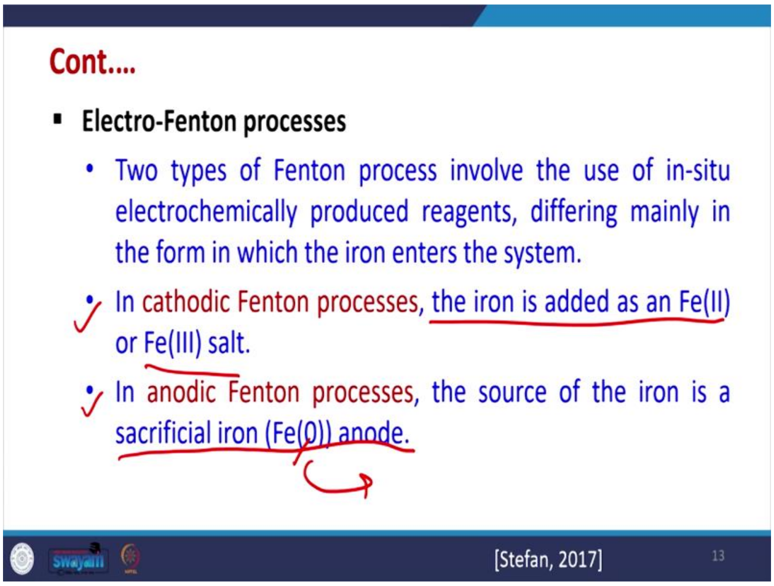

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- **Electro-Fenton processes**
  - Two types of Fenton process involve the use of in-situ electrochemically produced reagents, differing mainly in the form in which the iron enters the system.
  - In cathodic Fenton processes, the iron is added as an Fe(II) or Fe(III) salt.
  - In anodic Fenton processes, the source of the iron is a sacrificial iron (Fe(0)) anode.

[Stefan, 2017]

Then we have electro Fenton processes. So, two types of Fenton process that involve in-situ electrochemical production of reagents. So, that may be cathodic Fenton processes and anodic Fenton processes. So, iron is added in this case as Fe2 plus or Fe3 plus salt and in this case, the sacrificial anode will generate the iron in the 0 valance. So, it has no valence but it will get converted into Fe2 plus Fe3 plus for further uses. So, this cathodic Fenton and anodic Fenton both are possible.

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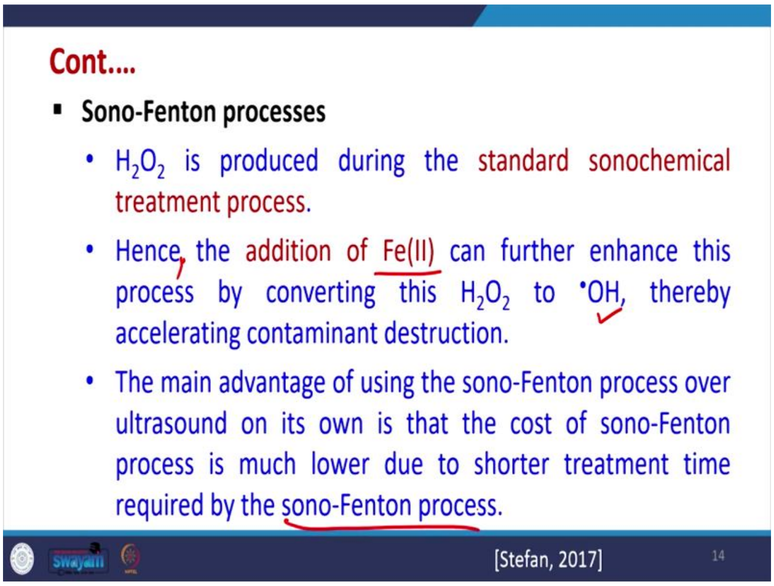

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- **Sono-Fenton processes**
  - H_2O_2 is produced during the standard sonochemical treatment process.
  - Hence, the addition of Fe(II) can further enhance this process by converting this H_2O_2 to $^{\bullet}OH$, thereby accelerating contaminant destruction.
  - The main advantage of using the sono-Fenton process over ultrasound on its own is that the cost of sono-Fenton process is much lower due to shorter treatment time required by the sono-Fenton process.

[Stefan, 2017]

Then there is a sono Fenton process also in which H2O2 is produced during standard sono chemical treatment process. So, hence the addition of Fe2 plus can further enhance this process by converting this H2O2 to OH radical. So, this is there and thereby it accelerates the contaminants destruction and we are able to mineralize the contaminant very quickly, the main advantage of using the sono Fenton process is that, that the cost of sono Fenton processes it may be much lower due to shorter treatment time which is there with respect to sono Fenton process. So, this is a possibility and that is how the sono Fenton process work.

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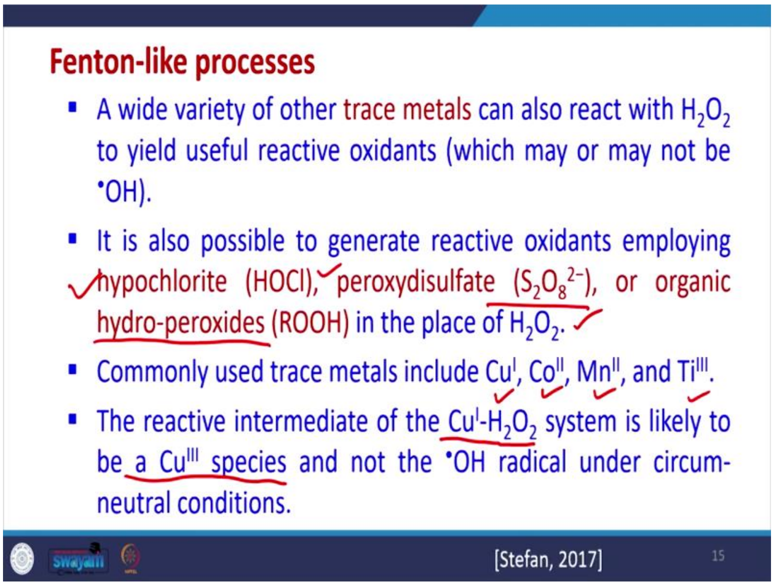

Fenton-like processes

- A wide variety of other trace metals can also react with H_2O_2 to yield useful reactive oxidants (which may or may not be $^{\bullet}OH$).
- It is also possible to generate reactive oxidants employing hypochlorite (HOCl), peroxydisulfate ($S_2O_8^{2-}$), or organic hydro-peroxides (ROOH) in the place of H_2O_2.
- Commonly used trace metals include Cu^{I}, Co^{II}, Mn^{II}, and Ti^{III}.
- The reactive intermediate of the Cu^{I}-H_2O_2 system is likely to be a Cu^{III} species and not the $^{\bullet}OH$ radical under circum-neutral conditions.

[Stefan, 2017]

Then, we have discussed Fenton like processes. So, this is another key thing. So, with a large number of transmitters can also react with H2O2 to use very highly reactive oxidants. So, this is possible they may be OH radical, they may not be OH radical, but they can react and it is possible to generate hypochlorite peroxidized sulfate. So, this is another type of reactive oxygen species. Then, we have hydroperoxides which may be formed in addition to or in place of H2O2.

And so, we can use many trace metals these may be copper, cobalt, manganese, titania etcetera. The reactive intermediate of these systems may include like this Cu1 H2O2 system is maybe a this copper 3 species, it may be possible to produce OH radical under certain condition, it is also possible that other types of radicals are getting generated.

Now, all these radicals, they will combine together they will react with the organic compounds present in the water and thus they will mineralize these organic compounds into CO2 H2O2 etcetera. So, these are called Fenton like processes.

So, there are different possibilities of Fenton processes. And the key thing is that in the Fenton process, we have H2O2 which is used along with the iron catalyst, so, that iron is either in the Fe2 plus form and Fe3 plus form. Fenton system works more very well for water which is having low pH around 4 or less. So, these are the key observations that have been reported in the literature with respect to treatment of water by Fenton like processes. So, this is there.

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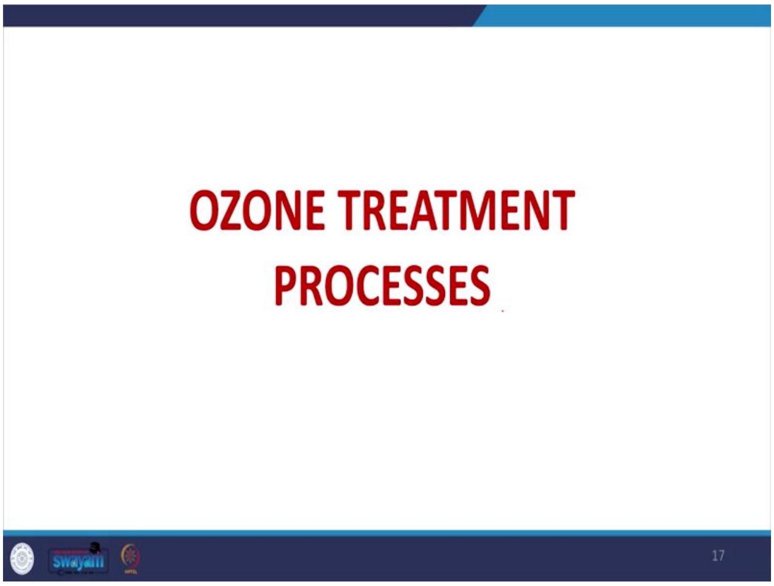

OZONE TREATMENT PROCESSES

OZONE TREATMENT PROCESSES

- Ozone (O_3) has been used in drinking water applications to meet multiple objectives including:
  - Disinfection, minimizing taste and odor
  - Reducing the formation of disinfection byproducts
  - Oxidizing organic contaminants
- Ozone (O_3) has ability to provide inactivation of pathogens and oxidation of organic contaminants.

[Stefan, 2017]

Now, we will go further and study another AOP technique which is called as ozone treatment process. So, in the ozone treatment process ozone is used in drinking water applications to meet multiple objectives. So, ozone can be used various ways. So, it can be used for disinfection, for minimizing taste and odor.

So, if any water is containing odor or any of the pathogens are also present, so, it will be able to distract all those things which are presented the water, so it will reduce the formation of disinfectant byproducts, thus oxidizing in addition, these will oxidize the organic compounds present in the water. So, ozone has the ability to produce to inactivate the pathogens and to oxidize most of the organic contaminants present in the water. So, ozone can be used differently.

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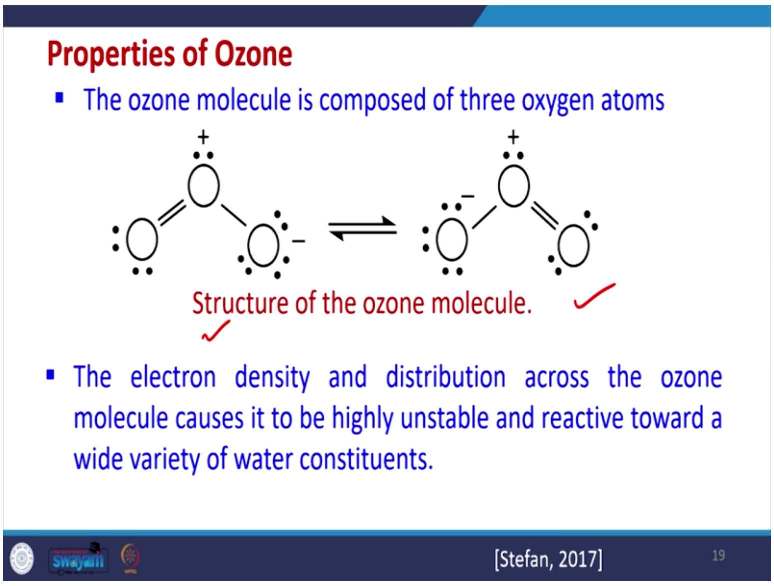

Properties of Ozone

- The ozone molecule is composed of three oxygen atoms

Structure of the ozone molecule.

- The electron density and distribution across the ozone molecule causes it to be highly unstable and reactive toward a wide variety of water constituents.

[Stefan, 2017]

Now, for doing this, we need to produce the ozone. Now, the ozone molecule is composed of 3 atoms you can see here. So, it can resonate in different forms. These 2 forms depending upon the pH and other conditions, so it may be there. So, this is the ozone molecule, the electron density and the distribution across the ozone molecule causes it to be highly unstable so it will always be highly unstable. It may deteriorate very quickly and form oxygen. So, this is there, but before it happens, we have to use the oxygen molecule or ozone molecule for distracting the contaminants present in the water.

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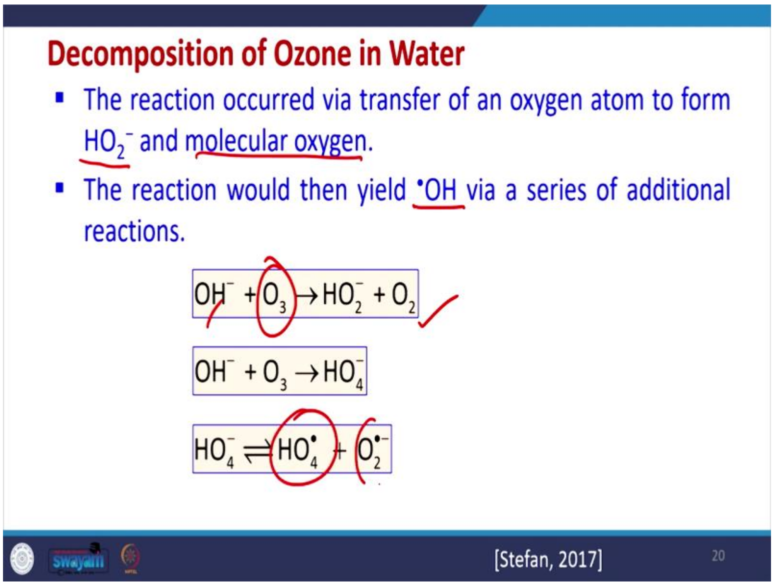

Decomposition of Ozone in Water

- The reaction occurred via transfer of an oxygen atom to form HO_2^- and molecular oxygen.
- The reaction would then yield $^{\bullet}OH$ via a series of additional reactions.

$$\boxed{OH^- + O_3 \rightarrow HO_2^- + O_2}$$

$$\boxed{OH^- + O_3 \rightarrow HO_4^-}$$

$$\boxed{HO_4^- \rightleftharpoons HO_4^{\bullet} + O_2^{\bullet -}}$$

[Stefan, 2017]

Now, decomposition of ozone how it happens in the water, the reaction occurs via transfer of an oxygen atom to form HO2 minus and molecular oxygen. So, this is this is how the ozone will decrease very quickly, the reaction would then yield OH radical via series of additional reactions. So, it is possible that ozone will form different types of OH radical are peroxy radical etcetera. So, this is possible during ozone treatment.

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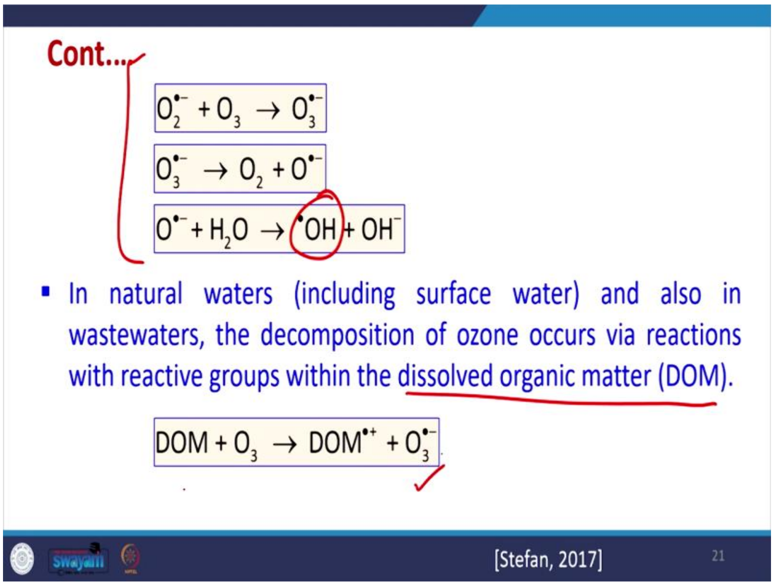

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$O_2^{\bullet-} + O_3 \rightarrow O_3^{\bullet-}$

$O_3^{\bullet-} \rightarrow O_2 + O^{\bullet-}$

$O^{\bullet-} + H_2O \rightarrow {}^{\bullet}OH + OH^-$

- In natural waters (including surface water) and also in wastewaters, the decomposition of ozone occurs via reactions with reactive groups within the dissolved organic matter (DOM).

$DOM + O_3 \rightarrow DOM^{\bullet+} + O_3^{\bullet-}$

[Stefan, 2017] 21

We can see here different series of reactions are happening before the OH radical is getting formed in natural waters including surface water and also in the usual wastewater that decomposition of ozone occurs via reaction with reactive groups within the dissolved organic matter. So, many dissolved organic matters may be present in this natural water. So, ozone will combine with them and form degrade. So, which is undesirable we want ozone to react with the organic compounds and convert them or mineralized them.

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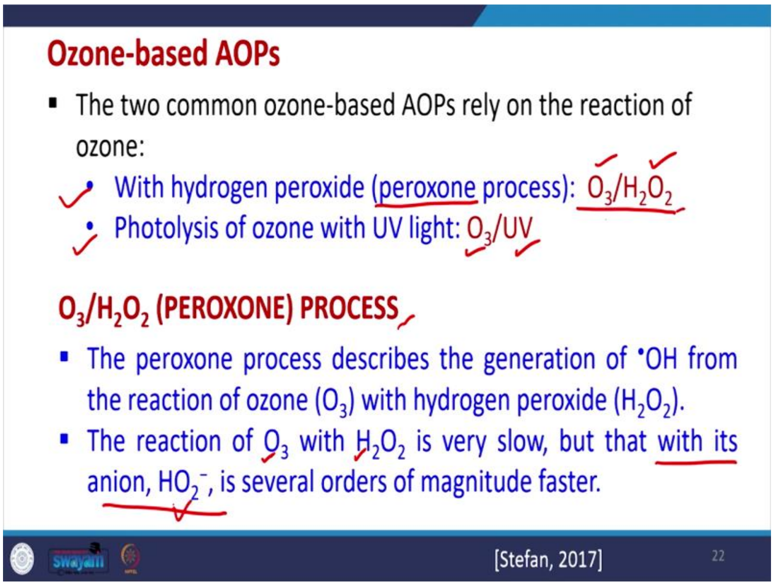

Ozone-based AOPs

- The two common ozone-based AOPs rely on the reaction of ozone:
  - With hydrogen peroxide (peroxone process): O_3/H_2O_2
  - Photolysis of ozone with UV light: O_3/UV

O_3/H_2O_2 (PEROXONE) PROCESS

- The peroxone process describes the generation of ${}^{\bullet}OH$ from the reaction of ozone (O_3) with hydrogen peroxide (H_2O_2).
- The reaction of O_3 with H_2O_2 is very slow, but that with its anion, HO_2^-, is several orders of magnitude faster.

[Stefan, 2017] 22

Now, ozone based AOP there are different ozone based AOPs which are used for wastewater treatment, the two common methods include hydrogen with hydrogen peroxide and with photolysis. So, this is there. So, if with hydrogen peroxide it will called as O3 H2O2. So, this is where we can see here, the peroxide is there and ozone is there. Similarly, Ozone in combination with UV is also possible. Now, this, the first process is called as peroxone process as well. So, we are going to study this process in detail here.

So, this process describes the generation of OH radical from the reaction of ozone with hydrogen peroxide, the reaction of O3 with hydrogen peroxide is slower, but, that can be but with its anion H2O2 minus ion it is several orders of magnitude faster. So, if it reacts with H2O2 directly it will be slower, but it can react very quickly with this anion of hydrogen peroxide.

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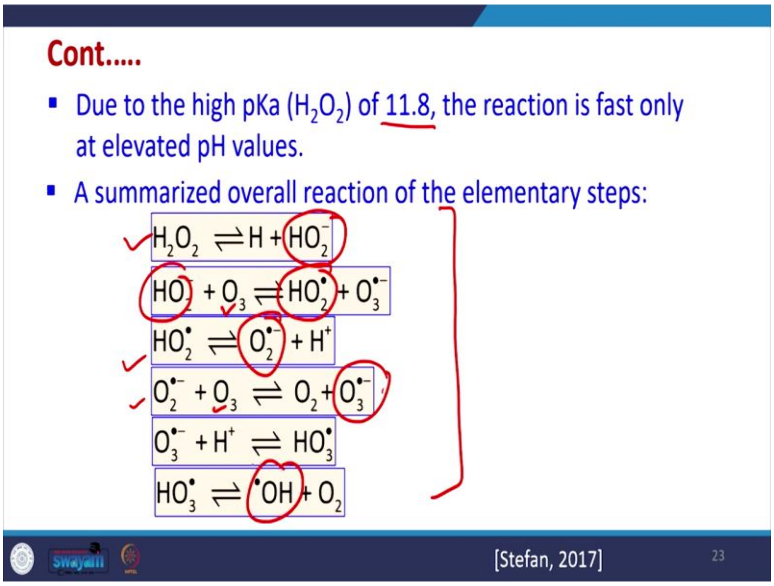

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- Due to the high pKa (H_2O_2) of 11.8, the reaction is fast only at elevated pH values.
- A summarized overall reaction of the elementary steps:

$$H_2O_2 \rightleftharpoons H + HO_2^-$$
$$HO_2^- + O_3 \rightleftharpoons HO_2^\bullet + O_3^{\bullet-}$$
$$HO_2^\bullet \rightleftharpoons O_2^{\bullet-} + H^+$$
$$O_2^{\bullet-} + O_3 \rightleftharpoons O_2 + O_3^{\bullet-}$$
$$O_3^{\bullet-} + H^+ \rightleftharpoons HO_3^\bullet$$
$$HO_3^\bullet \rightleftharpoons {}^\bullet OH + O_2$$

[Stefan, 2017]

Due to high pKa value of H2O2 which is around 11.8, the reaction is fast only at elevated ph. So, if any wastewater is there, which is having pH around 10 Or 12 then under those conditions the reaction of ozone with H2O2 will be very quick. So, this is there as summarized overall reaction of various elementary is stressed which are they are during ozone reaction with H2O2 are given here.

So, hydrogen peroxide may form this anion this anion further reacts with ozone to form peroxy radical, this peroxy radical may give another oxygen radical, oxygen radical may combine with ozone to form other types of oxygen reactive oxygen species, which further react to form hydroxyl radicals. So, the steps are number of elementary steps are involved before hydroxyl radical gets formed from the ozone and hydrogen peroxide. Now, this is there.

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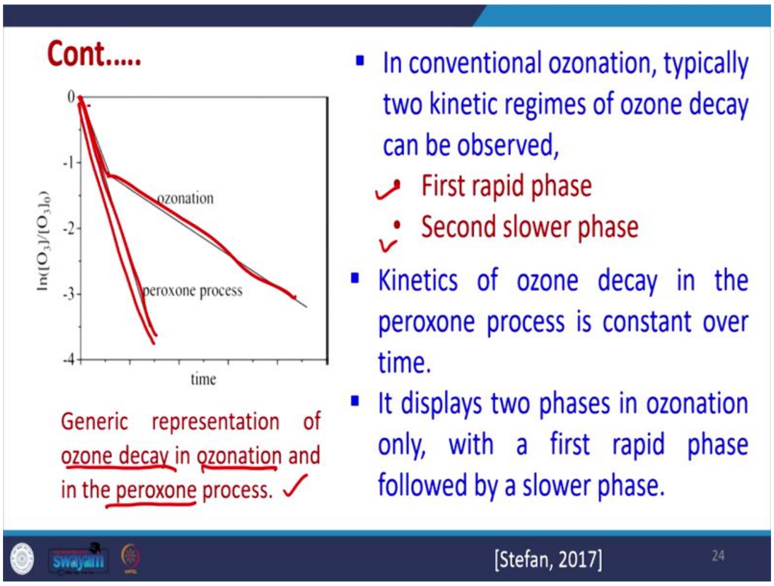

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Generic representation of ozone decay in ozonation and in the peroxone process. ✓

- In conventional ozonation, typically two kinetic regimes of ozone decay can be observed,
  - First rapid phase
  - Second slower phase
- Kinetics of ozone decay in the peroxone process is constant over time.
- It displays two phases in ozonation only, with a first rapid phase followed by a slower phase.

[Stefan, 2017]

In conventional ozonation, typically, two kinetic regimes of ozone decay are observed. So, if we have used utilizing the ozone of how the ozone decreases this is the representation of ozone decay in ozonation as well as peroxone process is given here. So, in the ozonation, there will be one step then there is will be a second step. Whereas, in the peroxone process, there will be a single step degradation only. So, in the usual ozonation conventional ozonation the first rapid step is there than there is a slower second step.

The kinetics of ozone decay in the peroxone process is constant over the whole range we can see here it is overall constant, so it displays two phases in the ozone only, whereas, it shows only one phase in the peroxone process. So, this is there.

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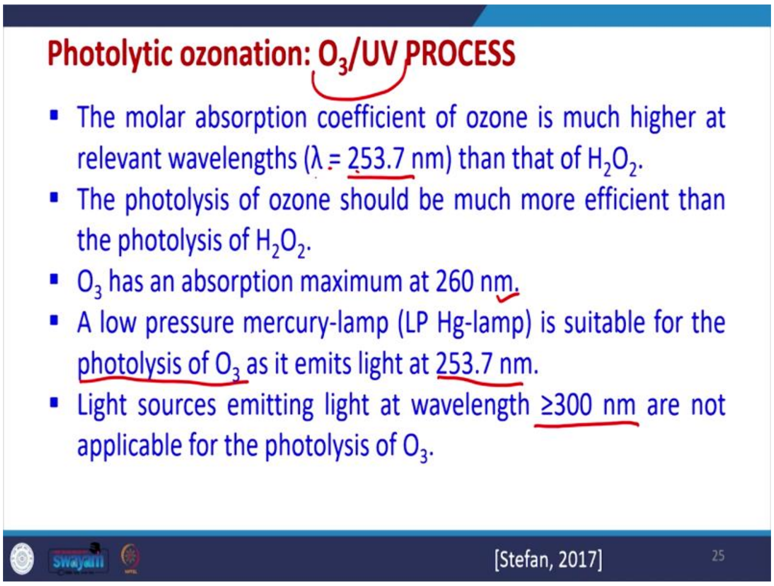

Photolytic ozonation: O_3/UV PROCESS

- The molar absorption coefficient of ozone is much higher at relevant wavelengths (λ = 253.7 nm) than that of H_2O_2.
- The photolysis of ozone should be much more efficient than the photolysis of H_2O_2.
- O_3 has an absorption maximum at 260 nm.
- A low pressure mercury-lamp (LP Hg-lamp) is suitable for the photolysis of O_3 as it emits light at 253.7 nm.
- Light sources emitting light at wavelength ≥300 nm are not applicable for the photolysis of O_3.

[Stefan, 2017]

Now, photocatalytic ozonation is also possible we are we are not using H2O2. So, we are not using any hydrogen peroxide, here the treatment is being done without hydrogen peroxide, but in the presence of ultraviolet light, the molar absorption coefficient of ozone is much higher in the relative UV wavelength range. So, like if the lambda is 253.7 which is one of the key wavelengths for destruction of pathogens.

So, under that condition, the molar absorption coefficient of ozone is very high as compared to that of H2O2 to itself. So, the photolysis of ozone is much more efficient than photolysis of H2O2 itself. So, this is the reason that O3 in combination is UV can be highly, highly beneficial as well as highly efficient process for wastewater treatment.

Now, O3 has an absorption coefficient absorption maximized 260 nanometer and where the lambda here for usual pathogen destruction is 253.7. So, the difference is not much a low-pressure mercury lamp is suitable for photolysis of O3 as it will emit this 253.7 nanometer wavelength UV light.

So, this low-pressure mercury lamp along with ozone can be used for treatment of water, light sources emitting light at wavelength greater than 300 nanometers are not able not applicable for this ozone UV process. So, we have to use this mercury lamp low pressure mercury lamp etcetera.

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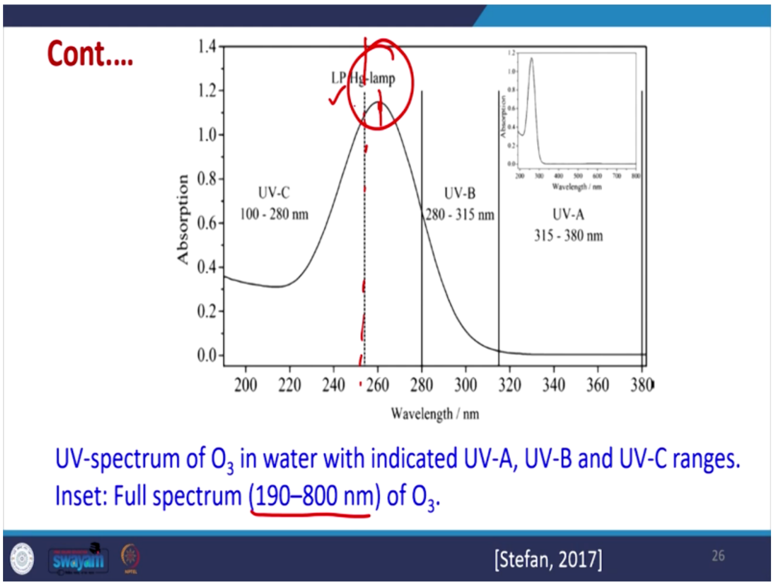

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UV-spectrum of O_3 in water with indicated UV-A, UV-B and UV-C ranges.
Inset: Full spectrum (190–800 nm) of O_3.

[Stefan, 2017]

So, we can see the UV spectrum of ozone in water with different phases like UV A, UV B, UV C ranges, so, this is there and in the inset the fullest spectrum is given from 190 to 800 nanometer. So, you can we can see here that the low-pressure Hg lamp emits UV in this wavelength. Whereas, the maxima for ozone spectrum is at 260. So, that means in the UV C range near to this range, we have the highest efficiency and there is a good possibility that we can combine together. So, this may ozone along with UV is a good combination for further use in the wastewater treatment and for degradation of pollutant in the wastewater.

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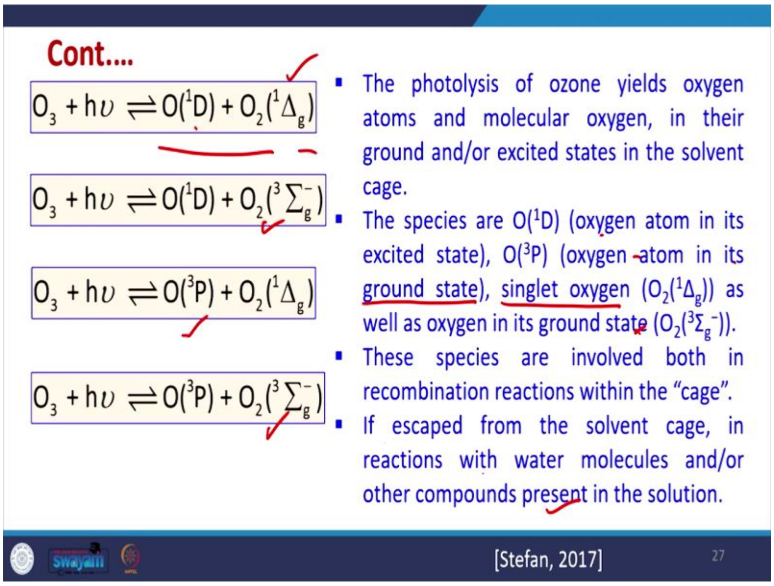

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$O_3 + h\upsilon \rightleftharpoons O(^1D) + O_2(^1\Delta_g)$

$O_3 + h\upsilon \rightleftharpoons O(^1D) + O_2(^3\Sigma_g^-)$

$O_3 + h\upsilon \rightleftharpoons O(^3P) + O_2(^1\Delta_g)$

$O_3 + h\upsilon \rightleftharpoons O(^3P) + O_2(^3\Sigma_g^-)$

- The photolysis of ozone yields oxygen atoms and molecular oxygen, in their ground and/or excited states in the solvent cage.
- The species are $O(^1D)$ (oxygen atom in its excited state), $O(^3P)$ (oxygen atom in its ground state), singlet oxygen ($O_2(^1\Delta_g)$) as well as oxygen in its ground state ($O_2(^3\Sigma_g^-)$).
- These species are involved both in recombination reactions within the "cage".
- If escaped from the solvent cage, in reactions with water molecules and/or other compounds present in the solution.

[Stefan, 2017]

The photolysis of ozone yields oxygen atoms and molecular oxygen, in their ground or excited states in the solvent case. So, this is possible. Now, the species are like here, O1D oxygen atom in its excited state, then O3P, this is also possible, this is oxygen atom in its ground state, then we have singlet oxygen, which is produced here, then as well as in its ground state also. So, this is also possible that these may be getting produced.

Now, these species are involved both in recombination reactions within the cage. So, this is also possible, but we always wish that recombination within themselves it should not occur, they should react with the contaminant first and they should be able to degrade these contaminants into CO2 H2O2. So, this is more desirable, if escaped from the solvent cage in the reaction the water molecules or other components present in the solution, so, this is there. So, we want this reaction to happen. So, these species should combine with the contaminants, which is desirable.

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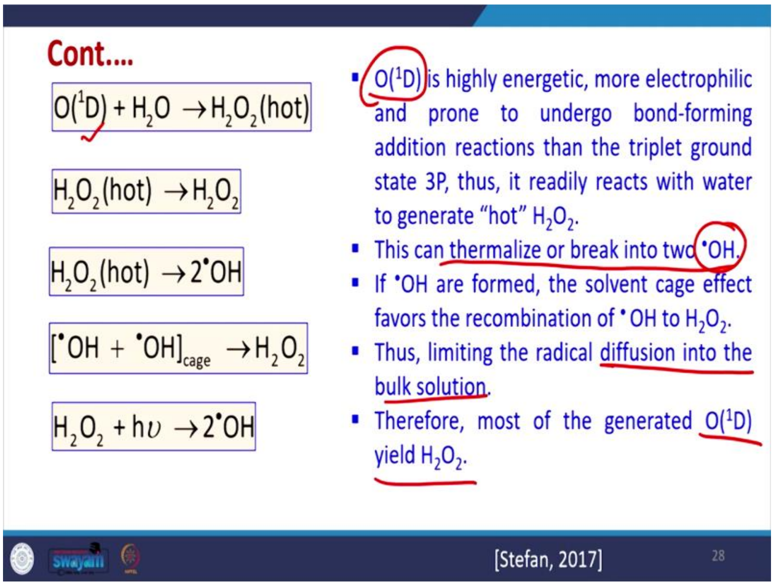

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$O(^1D) + H_2O \rightarrow H_2O_2(hot)$

$H_2O_2(hot) \rightarrow H_2O_2$

$H_2O_2(hot) \rightarrow 2^{\bullet}OH$

$[^{\bullet}OH + {}^{\bullet}OH]_{cage} \rightarrow H_2O_2$

$H_2O_2 + h\upsilon \rightarrow 2^{\bullet}OH$

- $O(^1D)$ is highly energetic, more electrophilic and prone to undergo bond-forming addition reactions than the triplet ground state 3P, thus, it readily reacts with water to generate "hot" H_2O_2.
- This can thermalize or break into two $^{\bullet}OH$.
- If $^{\bullet}OH$ are formed, the solvent cage effect favors the recombination of $^{\bullet}OH$ to H_2O_2.
- Thus, limiting the radical diffusion into the bulk solution.
- Therefore, most of the generated $O(^1D)$ yield H_2O_2.

[Stefan, 2017]

Now, out of these O1D is highly energetic and more electrophilic and more prone to undergo bond formation, addition reactions, then the other types of compounds which are getting formed. So, this particular compound in more active in degrading the compound. So, this, but this can thermalize or break into two OH radicals, and these two OH radicals can further react with the contaminant. So, this is there.

So, thus the overall limiting this particular reaction is the diffusion into the bulk solution. So, how they come out of the cage and go into the bulk solution and react with the contaminants present there. So, if we can enhance this diffusion reaction the overall treatment time will further goes down, so this is there. So, the most other genetic O1D they yield H2O2 and which can further be used for generating radicals etcetera.

So, this is how the ozone treatment processes work, ozone treatment processes have become very common and in fact a household type of simple ozone generators have been developed recently, and they are used for cleaning of the surfaces of vegetables, fruits etcetera also. So, they are low intensity ozone generator, the key aspect with respect to using these ozone generators is that they should not be combining with our body or our body system because then they will be degrading some of the cells etcetera in our body.

So, that ozone as such at the ground level is detrimental to human health as well as to the plants, but if it is used in the water, for contaminant removal, without any ozone coming out of the water, then it is good. Now, if some amount of ozone comes out of the water, but it reacts very quickly or it degrades into oxygen species then there is no issue. So, we have to be a little bit careful when we using ozone.

So, we have to see that none of the ozone is coming out of the water and it should get converted into oxygen before being released into the atmosphere. So, this is the key aspect, but overall, the Fenton processes along with the ozone treatment processes are becoming very common and lots of research and other design aspects of the studies are going on towards using these processes for common wastewater treatment techniques as well.

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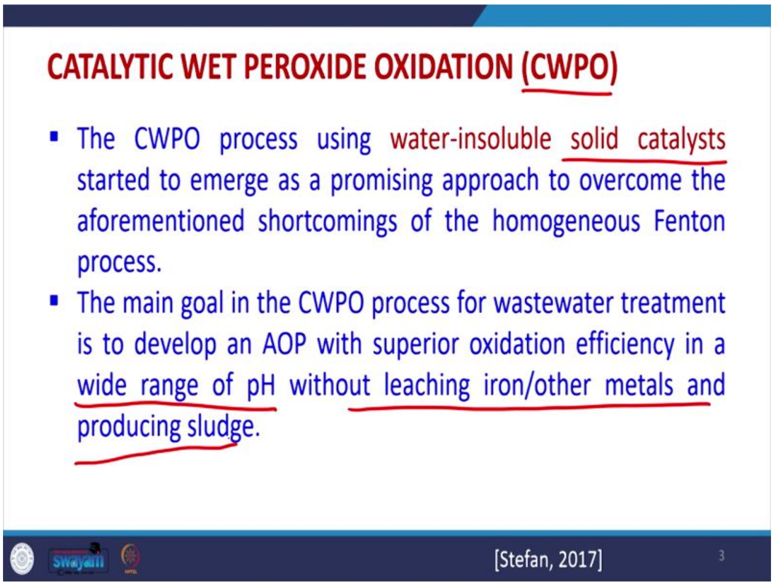

CATALYTIC WET PEROXIDE OXIDATION (CWPO)

- The CWPO process using water-insoluble solid catalysts started to emerge as a promising approach to overcome the aforementioned shortcomings of the homogeneous Fenton process.
- The main goal in the CWPO process for wastewater treatment is to develop an AOP with superior oxidation efficiency in a wide range of pH without leaching iron/other metals and producing sludge.

[Stefan, 2017]

So, one of the techniques which is, which is well reported in the literature it is called catalytic wet peroxide oxidation. So, in this technique, what we do is that, we use peroxides along with some catalysts for wastewater treatment.

So, the CWPO which is the abbreviation of this technology. So, this process uses water insoluble solid catalyst. So, we can use some catalysts, which can form radicals and using this water insoluble solid catalysts, we can generate lot of radicals in the reactive oxygen species in the wastewater and this is to this technique actually overcomes all the shortcomings of homogeneous Fenton reaction. Similarly, in the homogeneous and heterogeneous Fenton reaction also only we can use the Fenton technique up to a certain pH and generally it is applicable in the acidic range.

So, we can, this technique can be used at the other pH conditions also. So, this is there. So, it has it may be used for treatment of water at other pH wide range of pH, so this is possible without leaching of iron or any other metal are producing sludge. So, all the three aspects we are benefiting by using this technique and also it may be having superior oxidation efficiency. So, this is possible depending upon the type of wastewater we are treating the type of catalyst that we are using. So, this is there.

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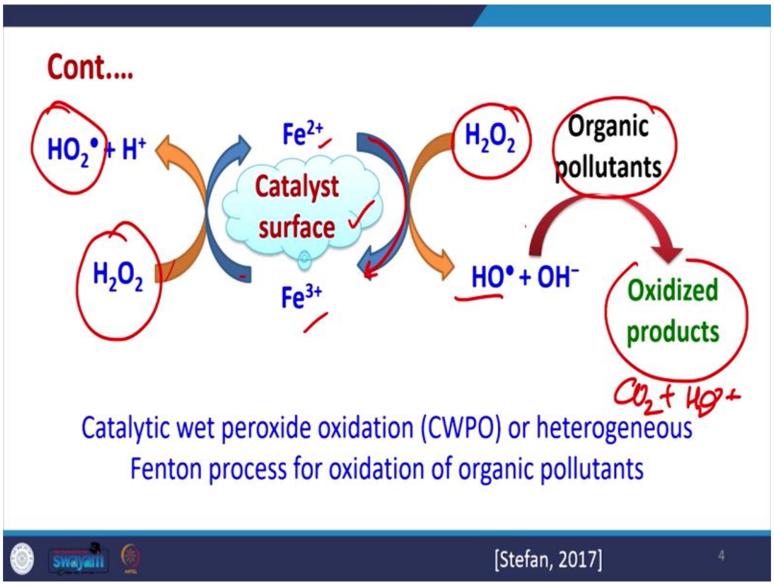

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$HO_2^{\bullet} + H^+$

H_2O_2

Fe^{2+}

Catalyst surface

Fe^{3+}

H_2O_2

Organic pollutants

$HO^{\bullet} + OH^-$

Oxidized products

$CO_2 + H_2O +$

Catalytic wet peroxide oxidation (CWPO) or heterogeneous Fenton process for oxidation of organic pollutants

[Stefan, 2017]

In the wet peroxidation method, we always use H2O2, so we always use hydrogen peroxide and actually it is converted into some radicals using some catalyst surface, so here example is given for Fe2 plus, Fe3 plus, but it can be used for other types of catalyst also. So, this is possible so, we can we can see here this particular reaction will happen when Fe3 plus is getting converted into Fe2 plus.

But if Fe2 plus is getting converted into Fe3 plus is still the H2O2 will generate hydroxyl radical and they will oxidize any organic pollutants present in the water and convert them into oxidized products, which are like CO2, H2O or other mineral acids. So, this is the what is desirable using catalytic wet per oxidation technique.

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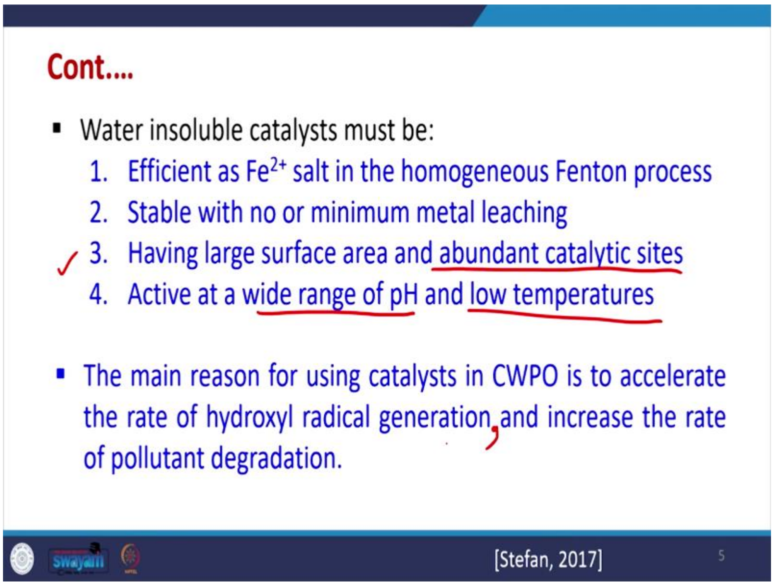

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- Water insoluble catalysts must be:
  1. Efficient as Fe^{2+} salt in the homogeneous Fenton process
  2. Stable with no or minimum metal leaching
  3. ✓ Having large surface area and abundant catalytic sites
  4. Active at a wide range of pH and low temperatures
- The main reason for using catalysts in CWPO is to accelerate the rate of hydroxyl radical generation, and increase the rate of pollutant degradation.

[Stefan, 2017]

Now, some water insoluble catalysts that are used for treatment, they should have following desirable characteristics, they should be as efficient as iron salt in the homogeneous Fenton process, but stable with minimal metal leaching. So, if we are using any catalysts, it should not leach into the water or if it is leaching it should be within the desirable metal concentration limit as set by Minhas one thing and it should be usable for very long duration. So, this is there.

The catalyst should have large surface area and a large number of catalytic sites for performing this step which are shown in the previous slide, they should be active in the wide range of pH and at lower temperatures. So, many times the catalyst may work but we may require the temperature to increase. So, it is desirable that these catalysts should work at lower temperature. The main reason for using catalyst in CWPO is to accelerate the rate of hydroxyl radicals generation and thus increase the rate of pollutant degradation. So, this is they are using this technique.

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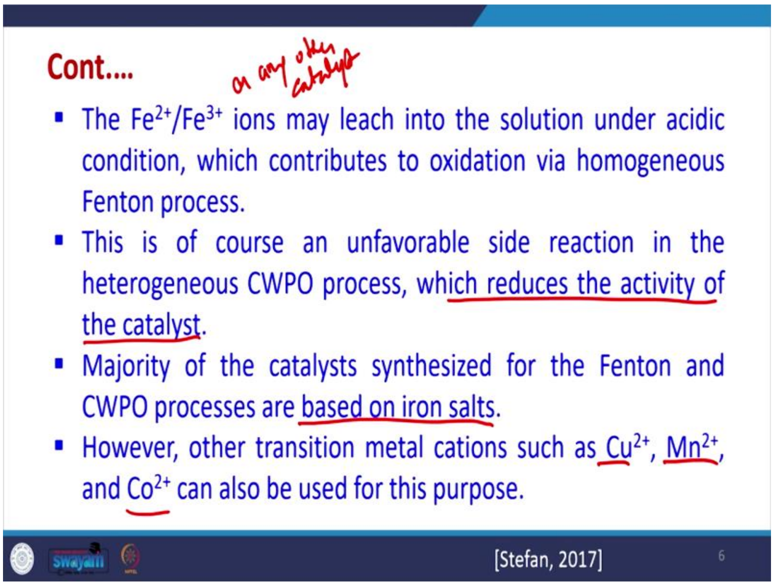

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or any other catalyst

- The Fe^{2+}/Fe^{3+} ions may leach into the solution under acidic condition, which contributes to oxidation via homogeneous Fenton process.
- This is of course an unfavorable side reaction in the heterogeneous CWPO process, which reduces the activity of the catalyst.
- Majority of the catalysts synthesized for the Fenton and CWPO processes are based on iron salts.
- However, other transition metal cations such as Cu^{2+}, Mn^{2+}, and Co^{2+} can also be used for this purpose.

[Stefan, 2017]

Now, the Fe2 plus ion are Fe3 plus ion are any other catalysts are any other catalyst may leach into the solution under acidic condition and that will contribute to the oxidation via homogeneous Fenton process. This is of course, an unfavorable side reaction in heterogeneous CWPO, which reduces the activity of the catalyst, because with time the catalyst amount will decrease the activity will also reduce because the leaching is happening and in addition the metal is going into the water which may not be desirable.

So, majority of the catalysts synthesized for Fenton or CWPO processes are based upon iron salts, but any other salt can also be used. So, other salts include like copper, manganese, cobalt etcetera, they also have been reported for CWPO to process.

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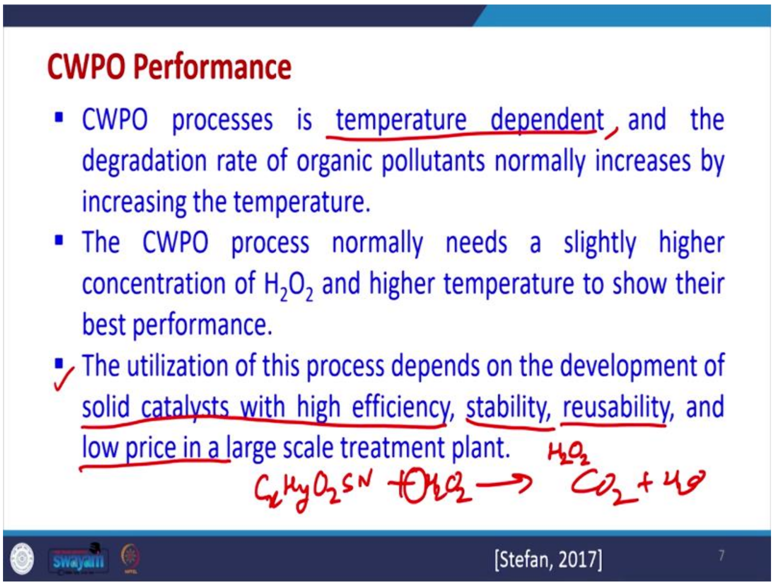

CWPO Performance

- CWPO processes is temperature dependent, and the degradation rate of organic pollutants normally increases by increasing the temperature.
- The CWPO process normally needs a slightly higher concentration of H_2O_2 and higher temperature to show their best performance.
- ✓ The utilization of this process depends on the development of solid catalysts with high efficiency, stability, reusability, and low price in a large scale treatment plant.

H_2O_2

$C_xH_yO_zSN + H_2O_2 \longrightarrow CO_2 + H_2O$

[Stefan, 2017]

Now, CWPO performance how it works? So, it is a temperature dependent one thing and the degradation rate for organic pollutant generally we know it increases by increasing the temperature. So, the CWPO process normally needs a slightly higher concentration of H2O2 and a slightly higher temperature than the ambient temperature to show their best performance. So, what we do is that we generally try to find out the amount of H2O2 require and that H2O2 requirement is done with respect to tachometric H2O2 requirements.

So, we can always perform some calculation beforehand like suppose the compound is CxhyOz or any other sulfur nitrogen etcetera is there. So, we can perform some calculation that what is the requirement for converting this into CO2 H2O etcetera. So, we know from here the whatever is the value that what is the tachometric H2O2 requirement. So, we test that with respect to tachometric H2O2 requirement, what is the actual is H2O2 requirement.

So, that can this optimization can be done by performing the lab scale studies. So, and after that we can use the usual catalytic reactor design approach for using the catalysts for wastewater treatment.

The utilization of the CWPO process depends upon the development of solid catalysts with high efficiency this is desirable. What is the stability of the catalyst? How much water we can treat per unit amount of catalyst? What is the reusability once the activity goes down so, can we reuse it after maybe some treatment of the catalyst? So that its activity is generated back and what is the price in large scale treatment? So, it will depend upon all these parameters.

So, catalytic wet per oxidation technique is also being studied a lot in literature, it is being used mostly for degradation of those organic compounds which cannot be treated otherwise by simple techniques. So, this is where they are being used. So, like for peredine, quilinine, many studies are being done for difficult to degrade compounds are which are called as recalcitrant compounds. So, they are being targeted to be treated by this technique. So, with this today we will end this lecture. We will continue with further AOP methods in the next lecture. Thank you.