Physico-chemical processes for wastewater treatment
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Lecture 47
AOP - Photocatalytic wastewater treatment

Good day everyone and welcome to these lectures on Physico-chemical processes for wastewater treatment. So, in the previous lectures we studied regarding the advanced oxidation processes, and we understood that in the advanced oxidation processes, the main objective is to generate various reactive oxygen species and then further use them for mineralization of various pollutants present in the water.

Considering the same there are many techniques which are available, which generate these reactive oxygen species in various ways. So, one of the techniques which is very commonly used it is called as photo-oxidation or wastewater treatment by photo-catalysis. So, we are going to learn regarding photo-oxidation or photo-catalysis in today's lecture.

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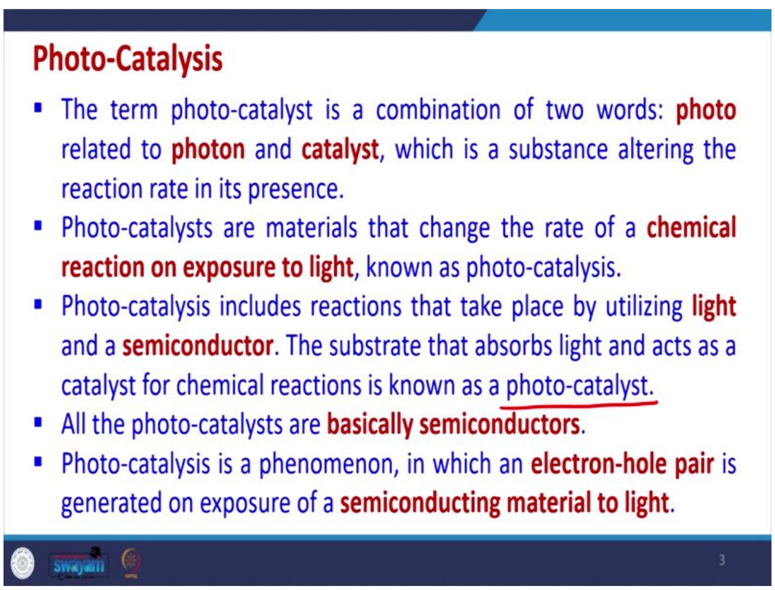

Now, photo-catalysis in general is used not only for wastewater treatment it can be used for synthesizing various chemicals etcetera also. The few things which are common in photo-catalysis for reaction engineering or photo-catalysis for wastewater treatment, certainly we use a catalyst and also certainly we use some photons to initiate the reactions.

So, this is photo-catalysis for reaction engineering and wastewater as such are similar, but how they work that we are going to learn in today's lecture regarding the use of photo-catalysis for wastewater treatment. The term photo-catalyst is a combination of two words we can see, photo, which is like related to photon and catalyst, which is substance which alters the reaction rate and thus it enhances the rate of reaction or otherwise, the reaction sometimes may not be possible also.

So, photo-catalysts are material that, change the rate of reaction chemical reaction on exposure to light and thus they are known as photo-catalysts. Photo-catalysis includes reactions that take place by utilizing light that light may be of different wavelength, and the catalyst generally is a semiconductor, which have some properties, which vai which they absorb light of some particular wavelength, the substrate that absorbs light and acts as a catalyst for chemical reaction is known as photo-catalyst.

All the photo-catalysts are basically semiconductors. So, there is a common thing that photo-catalysts are semiconductors only. And so, these semiconductors are like those substances which have an electron whole pair generation on exposure of them to a light. So, any semiconductor material, if it is exposed to light, in particular depending upon the gap which is there between the valence band and the conduction band, they will generate an electron whole pair. So, this is the common observation for all photo-catalysts.

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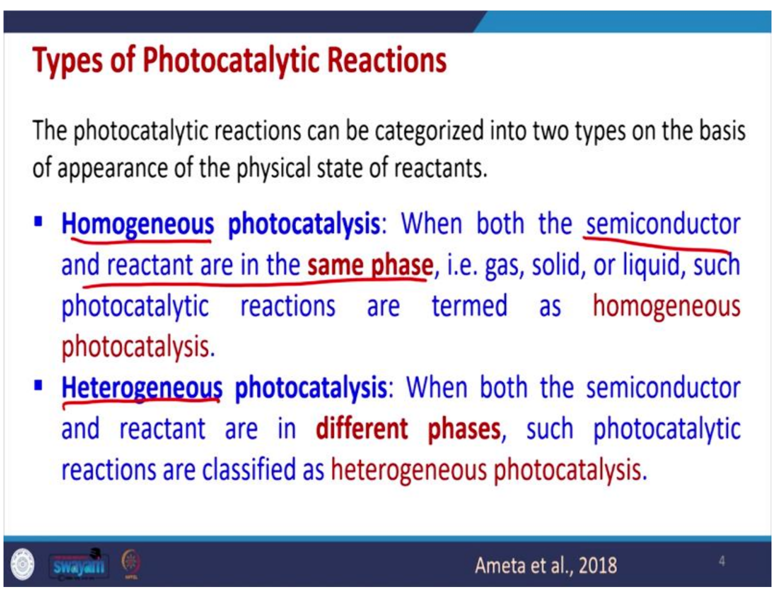

Now, there are different types of photocatalytic reactions possible and they may be categorized into two types, on the basis of appearance of the physical state of the reactants themselves. So, we have homogeneous photo-catalysis and we have heterogeneous photo-catalysis. So, we have two different photo-catalysis.

Now, in the homogeneous photo-catalysis the semiconductor and the reactant are in the same phase that is either they are in gas phase or in solid phase or in liquid phase and such reactions are called as homogeneous a photo-catalysis. Now, when thus both the semiconductor and reactants are in different phases, such photo-catalytic reactions are classified as heterogeneous photo-catalysis. So, most of the photo-catalysis reactions which are used for wastewater treatment, they are heterogeneous photo-catalysis.

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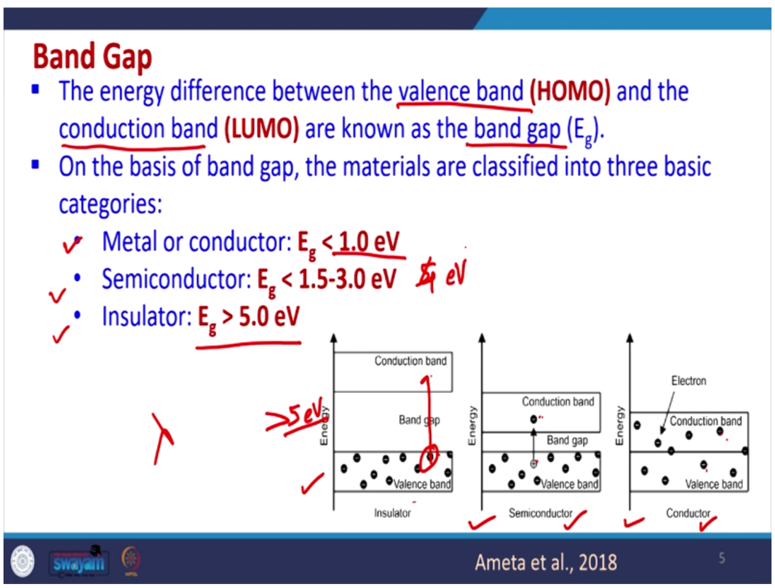

Now, there is one property of semiconductor is that they have band gap. So, that band gap is very essential for generation of electron whole pair and depending upon the band gap these semiconductors absorb light of different wavelength. So, the energy difference between the valence band and conduction band LUMO band is known as band gap.

So, on the basis of band gap the materials can be classified into three basic categories one metal or conductor, another semiconductor, and another is insulator. So, those who are having less than 1 electron bandgap, so they are called as metal or conductor. Now, semiconductor are those who are having electron gap more than 1.5 but around 3 to 4, so and up to 5 also. Insulators they have band gap more than 5 electron volts.

So, what does it mean? It means, so, here we can see here the insulator is there, semiconductor and conductor. Now, if we start with the insulator, so this is the valence band and this is the conduction band and here the gap is more than 5 electron volts. So, for providing this much energy the lambda value which actually is reachable on the earth or otherwise which can be provided the amount of energy required is very high.

So, we despite every mean it is not possible to turn it this electron into this conduction band. So, because we cannot generate any electron whole pair, so this is they are termed as insulator. In the conductors, the band gap the energy difference between the conduction band and valence band is very, very less. So, in fact very small amount of energy is also good enough to transfer the electron from valence band to conduction, but so, we have generation of electron and holes, but the problem is that that electron again will quickly fall back into the valence band.

So, electron whole pair which gets generated, that will not be stable. So, it is highly unstable though the moment is there. Now, in the semiconductors the band gap electron can move into the conduction band, the energy we can obtain using UV light, the most of the research is going towards utilizing the visible light can we create this electron whole band gap this electron can be transferred from the valence band to conduction band and still they are stable.

So, we have a whole in the valence band and electron in the conduction band. If we can stabilize this condition so that is called semiconductor. So, semiconductor are these materials which have 1.5 to up to 5 or maybe 4 electron volts. So, up to this we can use the semiconductors.

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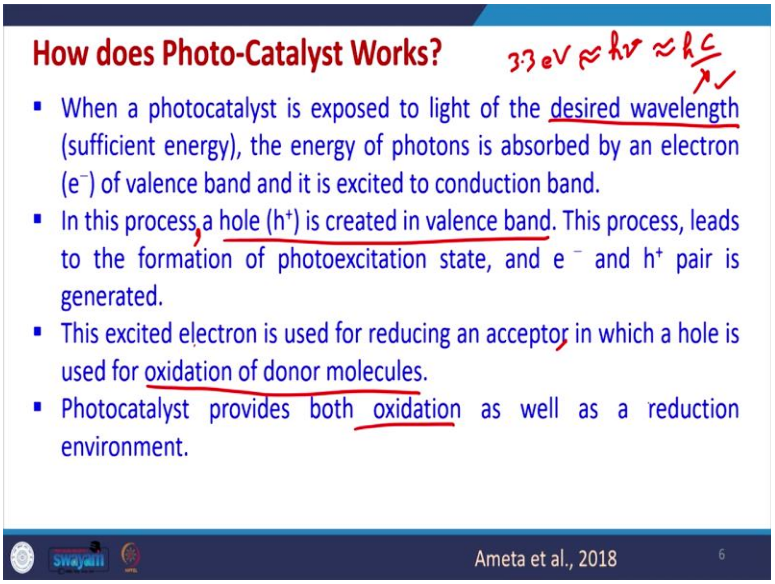

Now, going further how does photo-catalyst work. So, when a photo-catalyst is exposed to light of desired wavelength, desired wavelength is like the whatever is the band gap it should be able to excite the electron from the valence band to conduction band that must sufficient energy should be there. So, we have like suppose 3.3 electron volt, so this should be equal to h nu or we can write this should be equal to hC by lambda.

So, we can know the lambda value which will be having enough sufficient energy. So, if the photo-catalyst is exposed to this desired wavelength, which can be calculated from here, the energy of photons is absorbed by the electron of the valence band and it is excited and it goes into the conduction band. Now, in this process a hole is created in the valence band itself.

This process leads to the formation of photoexcitation state and an electron and hole pair are getting generated. This excited electron is used for reducing an acceptor in which a hole is used for whereas, a hole is used for oxidation of donor molecule. So, now this electron can be used for reduction, this hole can be used for oxidation. So this way we can perform different processes via using this electron hole pair.

Now, photo-catalysts provide both oxidation as well as reduction environment. So, through this we can work and use them for oxidation of different types of compounds in present in the water which are desirable. So, any undesirable pollutant which is like any organic pollutants, so if it is present in the water it can be oxidized via using this technique.

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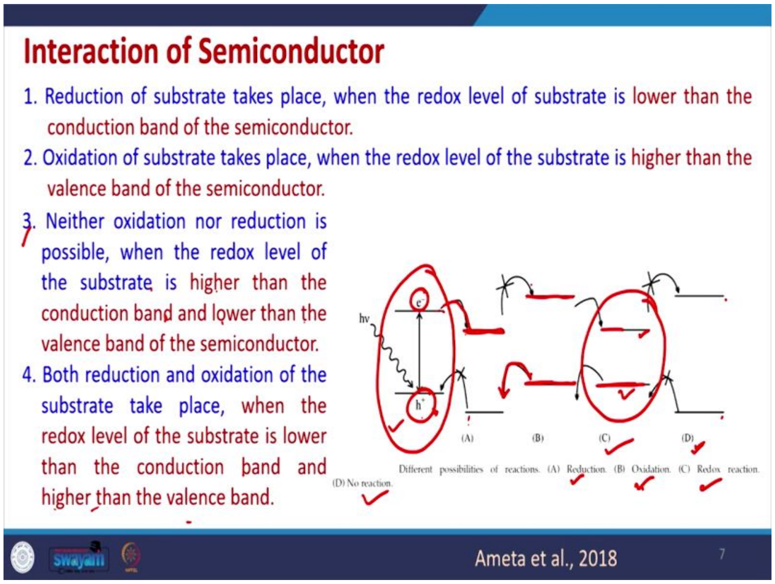

Now, interaction of semiconductor. Now, reduction of substrate takes place. So, if suppose, we have a electron, we have a hole pair which is generated here and we have a electron which is here. Now, how it will interact with different substrates? So, this is what is shown here. So, reduction of substrate takes place when the redox level of substrate is lower than the conduction band of the semiconductor. So, if the redox level of substrate is this, it is possible because electron can go into this, but if it is at higher state it is not possible. So, this is the problem.

Now, similarly, oxidation of substrate takes place when the redox level of substrate is higher than the valence band of the semiconductor. So, if this is the level it is possible that reduction will happen, otherwise reduction may not happen. So, under this condition as we can see, so, here it is possible that electron will move from this substrate to this hole and thus neutralize this hole.

Neither oxidation nor reduction is possible when the redox level of the substrate is higher than the conduction band and lower than the valence band of the semiconductor. So, this is the state C we can see here. So, we can see here reduction will happen when this condition is there that for substrate what are its redox level. So, one of its redox level higher redox level is lower than that of the conduction band. So, reduction is happening.

And this is not possible because this is at lower level, so it will never go like this. Similarly, in the B stage the lower redox level of the substrate is higher than that of the valence band. So, the electron can move from the valence band this lower level to this conduction band through this valence band and it can this moment is possible, but this moment is not possible because the conduction band level is lower than the highest redox level of the substrate.

So, electron can never move into this but electron can move into to this, so oxidation is possible. In the C level well, both are in between these two levels. So, we can see both are possible. So, this is totally redox reaction which is possible, so this is another condition where both the possibilities are there that oxidation and reduction both may happen.

Now, there is another condition D condition where we can see the higher level is above the conduction band lower level is below the valence band. So, under that condition, there is no possibility of any reaction which is possible. So, the key inference is that we should know the gap with respect to semiconductors also and we should know the substrate redox level as well.

So, if we can perform this calculation beforehand, we can know that whether any oxidation or reduction is possible or not. So, this is there. So, we can see here what is written in the third that neither oxidation nor reduction is possible when the redox level of the substrate is higher than the conduction band and lower than the valence band which is like D, stage D.

Now, both reduction and oxidation of substrate takes place when the redox level of the substrate is lower than the conduction band which is here and the higher than the valence band so this is here. So, in the under this condition, both oxidation reduction is possible. So, this slide gives an idea that when any reaction is possible, when we can oxidize or reduce any of the pollutant or not. So, this is there. So, we should know the level, redox level of the substrate as well which can be calculated.

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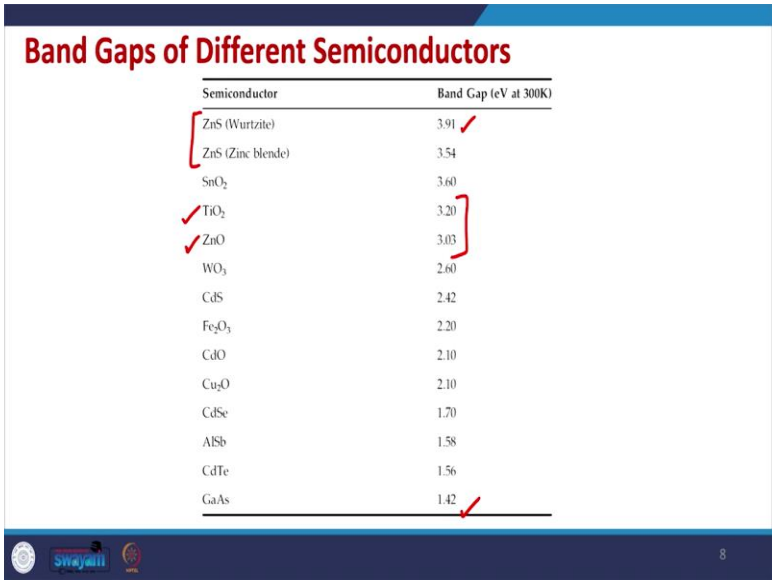

Semiconductor	Band Gap (eV at 300K)
ZnS (Wurtzite)	3.91
ZnS (Zinc blende)	3.54
SnO_2	3.60
TiO_2	3.20
ZnO	3.03
WO_3	2.60
CdS	2.42
Fe_2O_3	2.20
CdO	2.10
Cu_2O	2.10
CdSe	1.70
AlSb	1.58
CdTe	1.56
GaAs	1.42

Now these are the band gaps of different semiconductors. So, we can see here from 1.42 to 3.91. So, for zinc, ZnS these are different zinc sulfide, so they have. Similarly, common catalysts which are used in wastewater treatment they include like zinc oxide, titanium oxide, so they have this band gap So, these may vary also. So, they have been reported differently at different temperatures, how they are made, what is their morphology etcetera, so depending upon that, these are the tentative band gaps which have been reported in the literature they may vary also a little bit. So, this is there.

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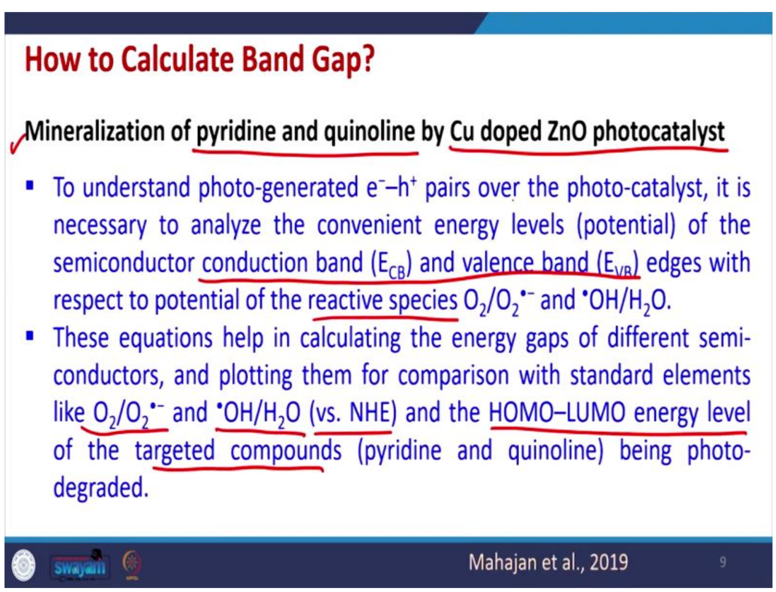

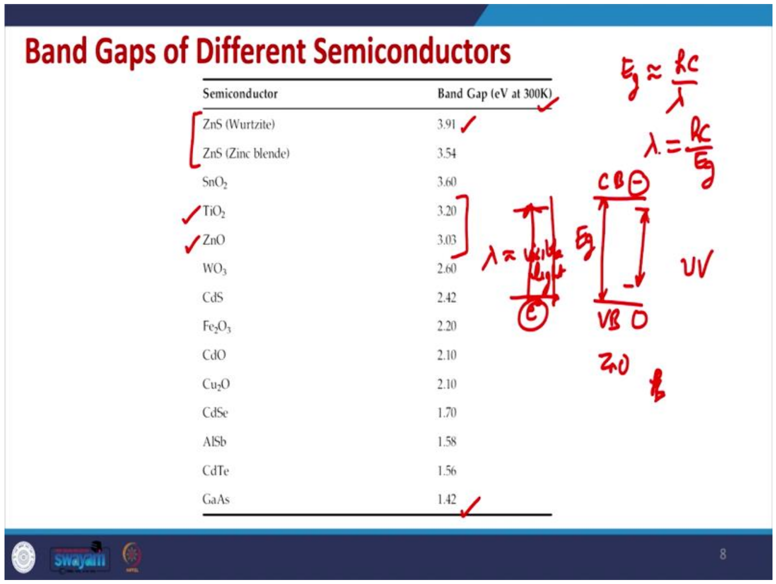

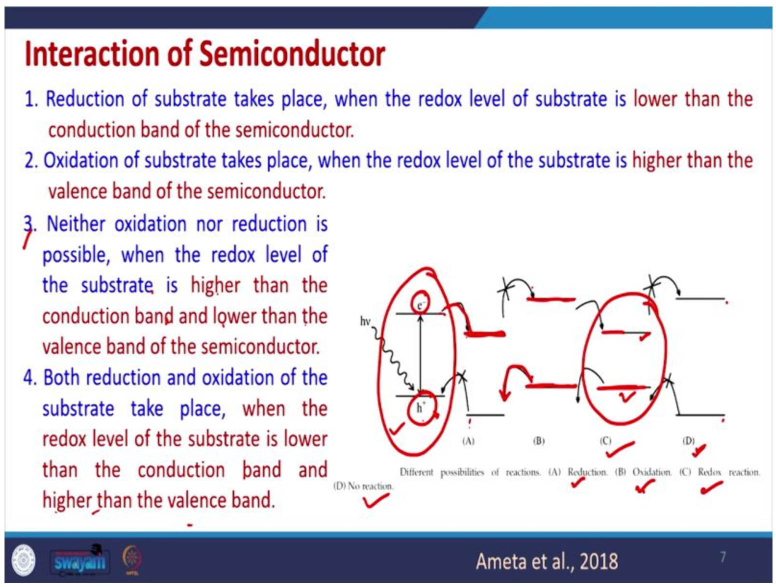

How do we calculate the band gap of any new semiconductor material or any new photo-catalyst suppose we synthesize. So, in this example has been given for mineralization of pyridine and quinoline by copper doped zinc oxide photocatalyst. So, this is there. Now, people are working to use different types of photo-catalyst and now to reduce the band gap. So, why they want to reduce the band gap and how they can do this.

So, they can reduce the band gap by a doping or using any localized state there are many possibilities in that, but here we will try to understand that how why they are going for reduction in the band gap in particular for TiO2 and zinc oxide. So, if we actually perform the calculation for with respect to valence band and conduction band of like zinc oxide. So, whatever is this band gap Eg value. So, we can know this Eg value.

Now, this Eg value is equated to hC by lambda. And from this we can calculate the lambda value by proper unit convergence. So, after putting the values in proper unit, so that they are reduced so we can find that lambda value. Now, we will find that the lambda value which is required for performing the this electron whole pair that will be equal to, that we require the light in the UV range that means, we require very high intensity light.

Now, the amount of light UV light which is available at the surface of Earth is much, much lower as compared to visible light. So, people want to reduce this band gap, so they want this valence band to be here, but maybe the conduction band to be here, so that we can have the lambda which is in the visible light range. So, this is the objective.

Now, there is a problem if the band gap gets reduced. So, whenever there is any electron which is moving from here to here, it falls back also very quickly. So, there is a dilemma between how to go ahead and stabilize the system is still used the visible light. And we can reduce this band gap of suppose, this is zinc oxide, so we can reduce it by doping. So, we have some localized conduction band or valence band created either here or here.

So, if we can do this, so this is the reduction in the bandgap which is there. So, that is why here copper doped zinc oxide photo-catalysts was created and that is been used for pyridine and quinoline which are difficult to oxidize compound, so, far then mineralization. So, to understand photo-generated electron whole pairs were the photo-catalysts it is necessary to analyze the convenient energy levels or potentials of the semiconductor that is in between conduction band and the valence band edges with respect to potential of the reactive species.

So, with respect to reactive species, what is the potential and also we have to know what are their levels the valence band and conduction band. So, these equations help in calculating the energy gaps of different semiconductors plotting them for comparison with the standard elements like we can any of these NHE, this you can plot and then we can know. Similarly, we can calculate the HOMO-LUMO energy levels of targeted compounds like pyridine, quinoline etcetera. So, though, so, we can understand whether this interaction is possible or not the way it is shown here in this slide.

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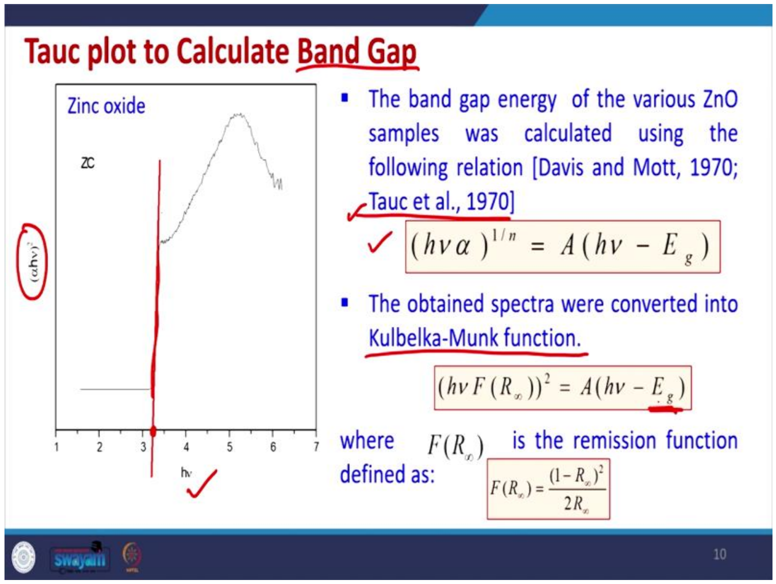

The band gap energy of the various ZnO samples was calculated using the following relation:

$$(h\nu\alpha)^{1/n} = A(h\nu - E_g)$$

The obtained spectra were converted into Kulbelka-Munk function:

$$(h\nu F(R_\infty))^2 = A(h\nu - E_g)$$

So, going further, so, what we do is that first we try to get the UV versus lambda value and from that we use this particular equation. So, band gap energy of various zinc oxide sample or any other sample can be calculated using the following relationship which is called as tauc relationship or tauc plot.

And in this what we do is that we plot this particular value with respect to h nu. So, if we can plot this we can perform the calculation and we this plot is done and here we take the tangent and wherever this tangent intersects the X axis that value is equal to the Eg value or the band gap. So, here we can see it is tentatively between 3 and 3.5. So, we can take like 3.25 or something.

So, this is how we plot them and thus we can calculate. So, you can go into the literature and study regarding this paper. So, you can use tauc equation and then also this function is used further for plotting this particular equation and from here we can calculate the band gap. So, this is the band gap value that we obtained from this plot.

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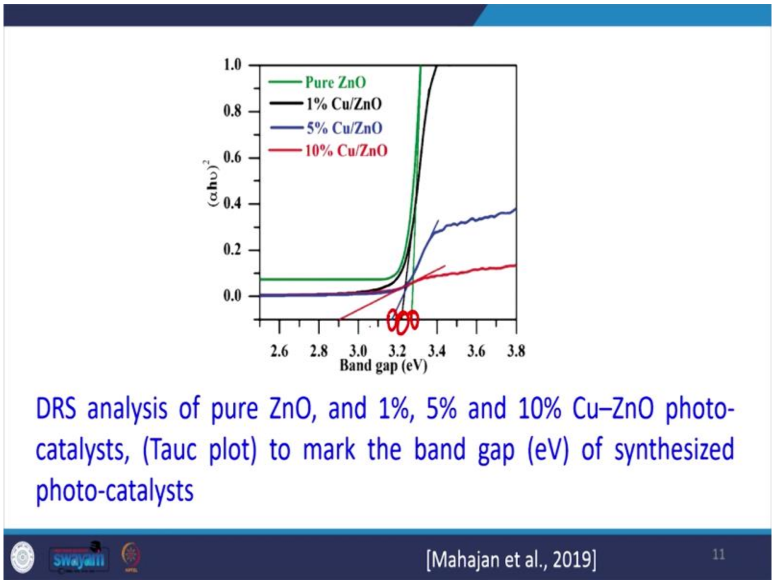

So, we can see here different tauc plots are plotted for different dope 1 percent, 5 percent dope copper on zinc oxide and these values can be used for knowing the band gap. So, we can see that with doping the band gap is decreasing. So, there is some optimum doping which will help in reducing the band gap up to a desirable value so that the semiconductor can be used for mineralizing any compound or otherwise.

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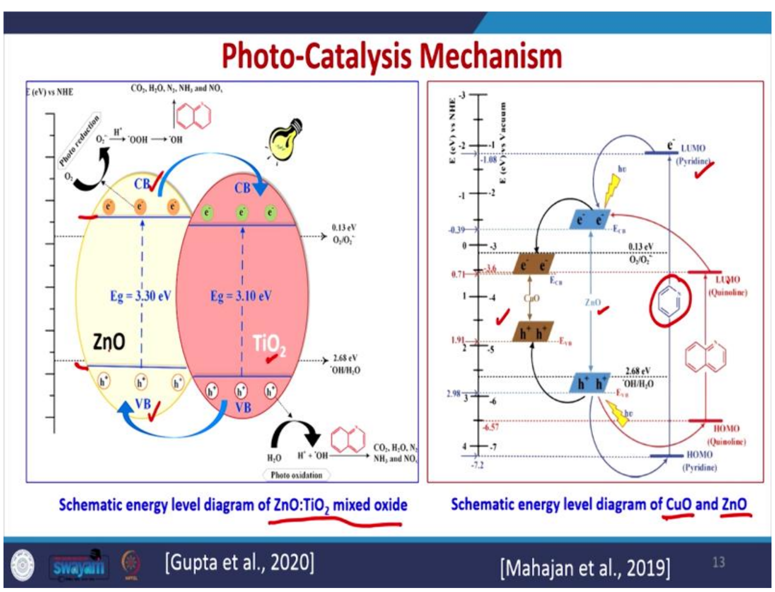

So, how we know then what is done is that the interaction how to understand the interaction that can be done using these particular equations. So, we can see here for zinc oxide, the valence band and the conduction band, the levels are given here. So, the band gap is 3.3 electron volts. Similarly, for TiO2 also this is given here. So, we can see whether interaction between them is possible. So, this is for some zinc oxide, titanium mix oxide.

So, we can know the band gap levels. Similarly, we can hear in another condition for Copper Oxide and Zinc Oxide, for copper oxide the band gap levels are shown, for zinc oxide the band gap levels are shown and then for pyridine we can see here for pyridine their LUMO and HOMO levels are shown.

And similarly, for quinoline their LUMO and HOMO levels are shown. So, if Copper Oxide and Zinc Oxide are mixed together, so we have different levels which are created. And similarly for pyridine, so there are different possibilities of interactions which are possible. So, movement of electron from one place to another. So, using these calculations we can understand the basic mechanism by which overall interaction is happening.

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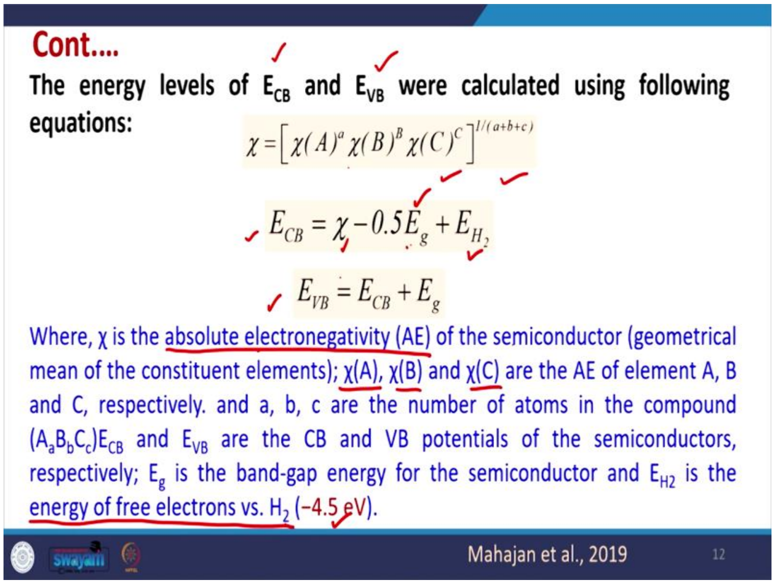
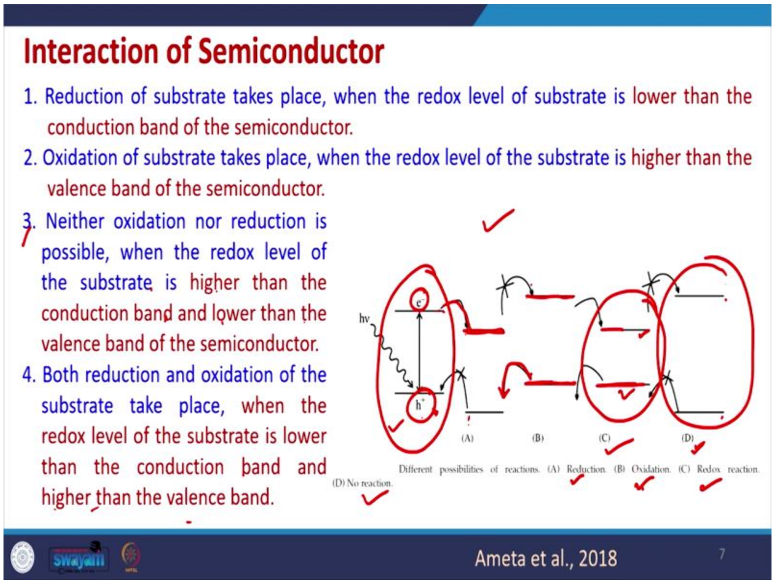


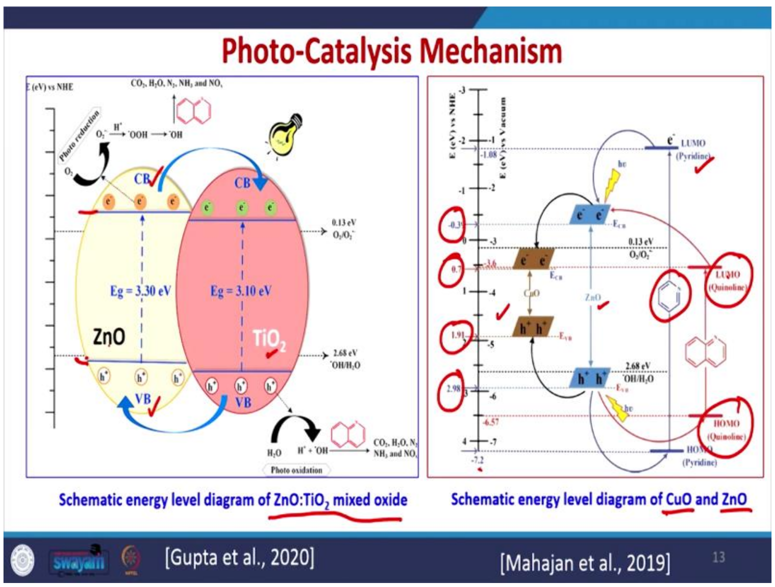
The energy levels of E_{CB} and E_{VB} were calculated using following equations:

$$\chi = \left[\chi(A)^a \chi(B)^B \chi(C)^C \right]^{1/(a+b+c)}$$

$$E_{CB} = \chi - 0.5E_g + E_{H_2}$$

$$E_{VB} = E_{CB} + E_g$$





Now, the energy levels of the conduction band and the valence band can be calculated using this equation. So, these equations are used to calculate the values. So, how do we know that what is the exact value of conduction band and the valence band? So, for doing this what we do is that first we calculate the absolute electronegativity of the semiconductor. So, this is done.

And this is done using this equation. And here we require the value of A, B, C etcetera of the absolute electronegativity of the elements present in the semiconductor as well. So, using this we can calculate the absolute electronegativity of the semiconductor. Now, once this is known and the band gap is known. So, and also the EH2 value the energy of the free electron at versus H2 this value minus 4.5 electron volts this is known to us.

So, if this value is known, this value is known from the top plot, this value we have calculated above, so we can calculate the ECB, so conduction band. Then we can calculate for valence band, so which is equal to ECB plus Eg. So, using this equation, we can know the exact point like here for copper it is 1.91 and 0.71. Similarly, for zinc oxide we can calculate 2.98 minus 0.39, but this will we can see this depends upon the band gap value as well.

So, through these calculations, we can know the energy levels of the substrate energy levels of the mix oxides, its different composition, its different oxides within the mix oxides or doped oxide. So, through this we can understand the basic mechanism as well. Vice versa if suppose, we want to mineralize some key compound.

So, we can know calculate the HOMO level itself. And from the literature we can know how which photo-catalyst we should select so that we have that desired interaction possible via all these four possibilities. So, we will select because we will be knowing the HOMO LUMO level of some targeted compound. So, we should select this photo-catalyst in such a condition that interaction is always possible. So, these are the possibilities with respect to use of photo-catalysts.

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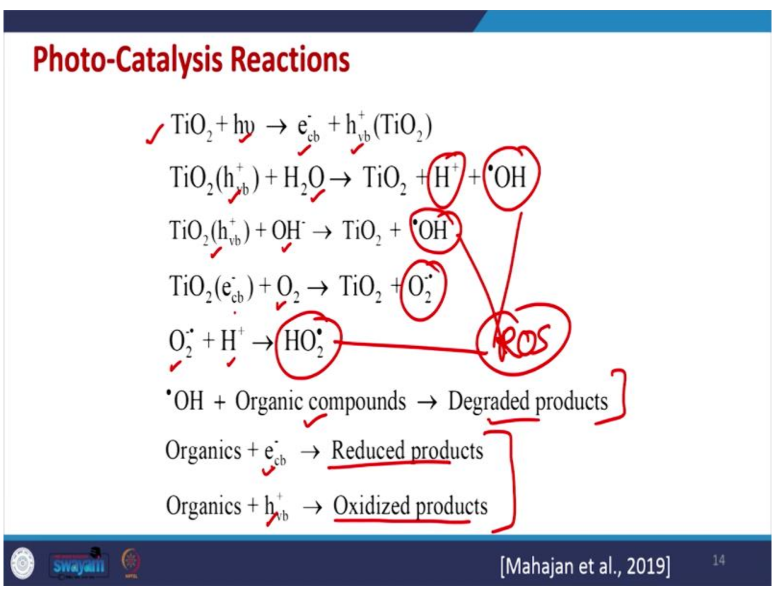

These are the some of the photo-catalysis reactions which are given here. So, like a titanium oxide interacting with the desired photon and then we have electron and hole pair which is getting generated. Now, this hole is again interacting with the water present in the wastewater sample and then we have H plus and hydroxyl radical which is getting generated. Similarly, this hole is interacting with OH minus and again a hydroxyl radical is getting generated.

Similarly, the electron in the conduction band is interacting with oxygen which may be dissolved in the water to get this particular ion and this particular ion again the reating with H plus to form another radical. So, these are the different possibilities of radical formation. So, all these radicals which are getting formed, so all these are called reactive oxygen species. And now these will react with organic compounds and degrade them. So, this is possible.

Also there is a direct organic compound may interact with electron and holes. So, we may have reduced product we may have oxidized products. So, this is direct reaction of the organics with electron and hole pair and this is like indirect oxidation where first radicals are getting generated and then they are reacting with organic compounds. So, these are the, this is the how the wastewater treatment happens via advanced oxidation processes using photo-catalysis.

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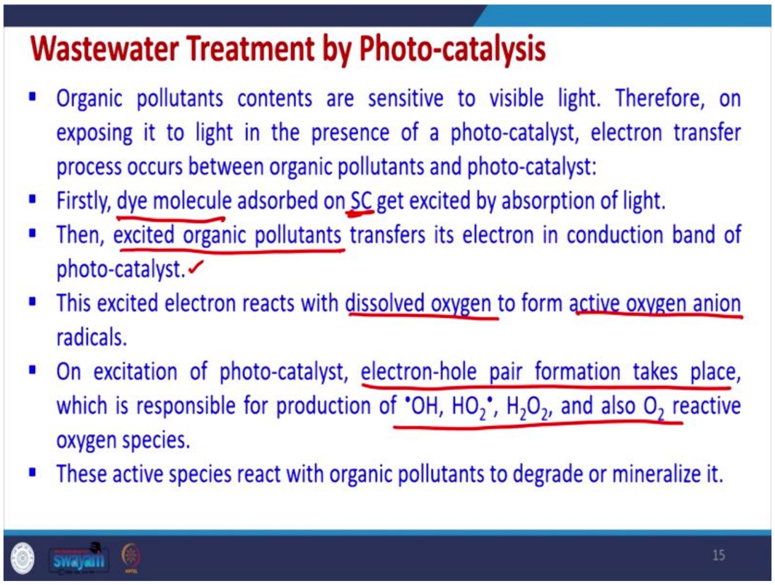

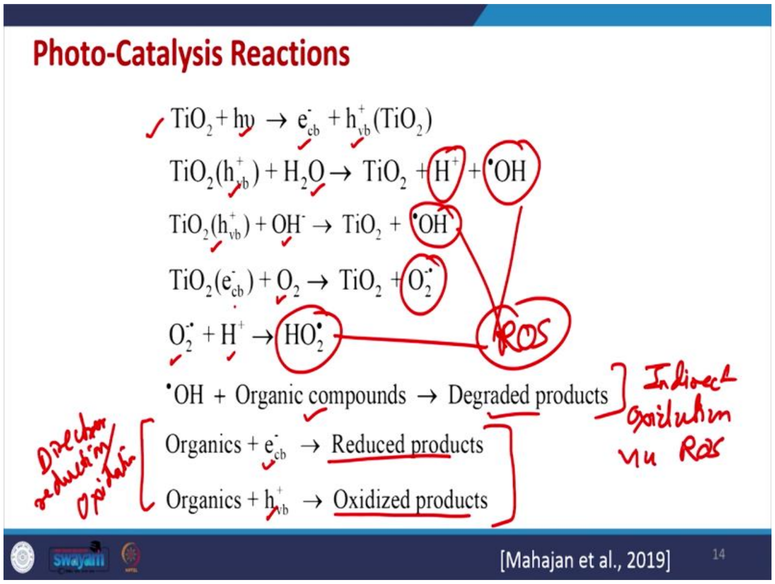

Now, wastewater treatment by photo-catalysis, there are few key things to understand. So, organic pollutants they are sensitive to visible light, therefore, on exposing it to the light in the presence of some photo-catalyst electron transfer will occur between the organic compounds and the photo-catalysts. So, firstly suppose we take any dye molecule.

So, suppose dye molecule adsorb on any of the compound or semiconductor will get excited by absorption of light then excited organic pollutant or dye molecule will transfer it is in a turn in the conduction band of the photo-catalyst. This excited electron then reacts with the dissolved oxygen to form active oxygen anion radicals on excitation of photo-catalysts electron hole pair formation will take place and which is responsible for production of any of these reactive oxygen species and these species react with organic pollutant to mineralize them.

So, the basic mechanism is very similar, there may be, as given here there may be this is called direct reduction or oxidation. So, this is there. So, this is direct reduction or oxidation, so any of these possibilities are there then we have indirect oxidation, indirect oxidation via reactive oxygen species. So, this is also possible.

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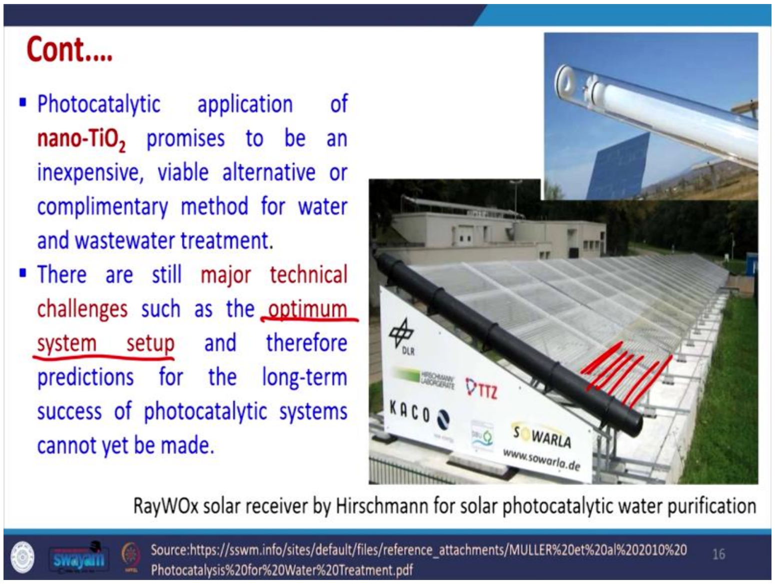

Now, going further the photo-catalytic application of like nano-titanium oxide promises to be inexpensive via alternative complementary methods for water and wastewater treatment. But there are many challenges which are there with respect to utilizing photo-catalysts for large scale application.

So, there are many major technical challenges such as optimum system setup. How much water we can process so that the availability of light is still there? So, that is one difficulty. So, we can see your pipes are there. So, in this the titanium may be coated and the water while flowing through this pipe gets treated. So, this is there. Also there are many challenges with respect to utilization of photo-catalysts for large scale application, but slowly then slowly modules are coming.

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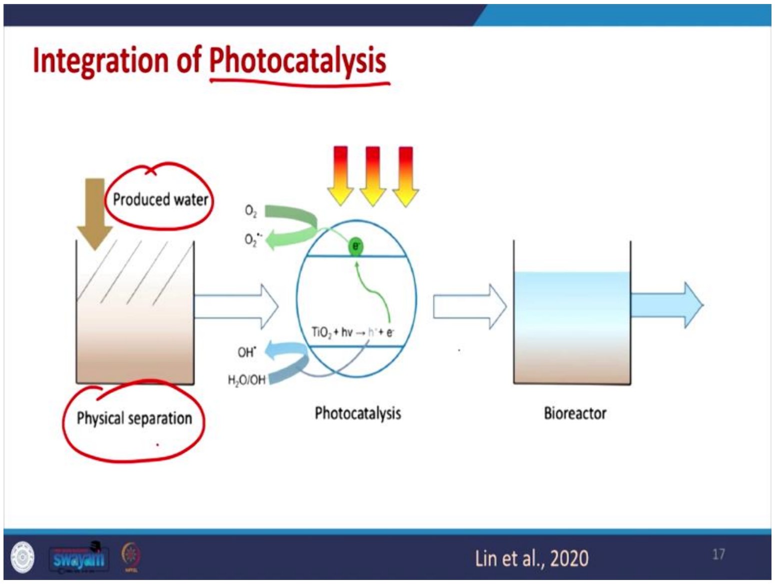

Now, similarly, the photo-catalysis may be integrated with other traditional wastewater system is this manner and suppose any water is produced which is like it has to be treated. So, we have some physico-chemical treatment here after that the some photo-catalysis is performed so that we can degrade some targeted compounds. And once that targeted compounds are there degraded the simpler compounds will also get degraded. So, this is possible and after this treatment there, it may go to bioreactor for further treatment. So, there are many integration feature possible of photo-catalysis along with the traditional treatment.

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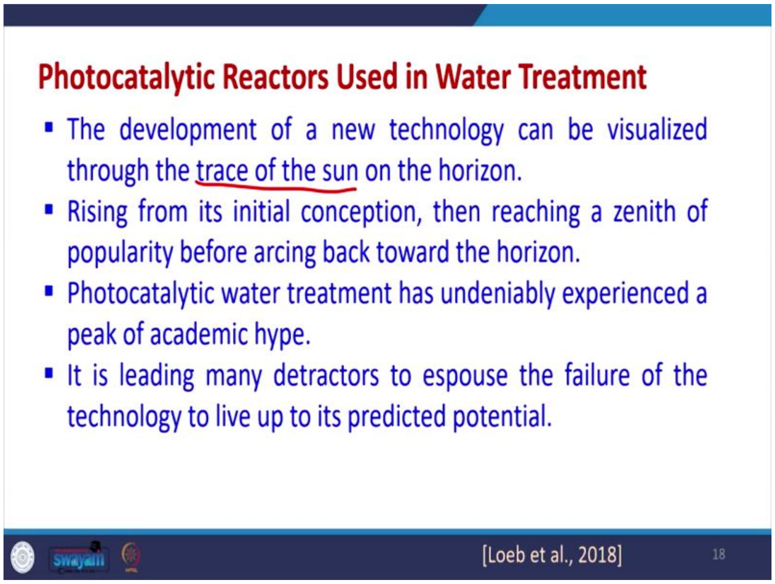

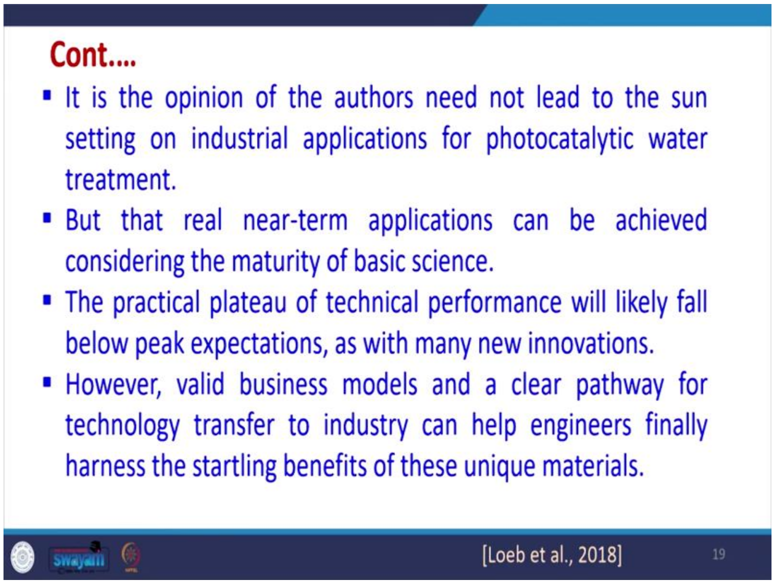

Now, photo-catalytic reactors, which are used in the water treatment. The development of new technology can be visualized to the taste of the sun on the horizon. So, we have lots of availability of light from sun. And the problem is that from rising from initial stages during that in the morning. So, there is lots of problem and challenges with respect to photo-catalytic water treatment because, like the water treatment using photo-catalyst will work only during the daytime and also only between 4 to 6 hours depending upon the availability of sunlight.

Second thing the availability of UV light is not that much. So, we have to see that photo-catalysts which are developed, they should be able to work in the visible zone. So, this is a challenge with respect to development of photo-catalysts. Then there are other challenges that we cannot treat highly murkier water because the sunlight will not penetrate into that water. So, that is another challenge which is there. So, there are many challenges with respect to water treatment and we need to understand all these things.

So, there are a lot of studies going on all these aspects will not discuss into this, but there you can study many papers and other thing to further understand this. A photo-catalysis has a lot of prospects, we understood that it can be used for wastewater treatment, already lot of research has been carried out. The only challenge is that it will work only during daytime otherwise, we will have to create a simulated atmosphere where the treatment can be done using some artificial lights.

Second thing is that we have to use some photo-catalysts which can work in the visible light. So, we need to develop those, then only our system can work without utilizing the artificial energy. Otherwise, we will be requiring UV light from other sources. So, that will make the overall system highly energy intensive. So, with this we will end that today's lecture. We will continue further with advanced oxidation treatment processes, different type and understand how they work. Thank you.