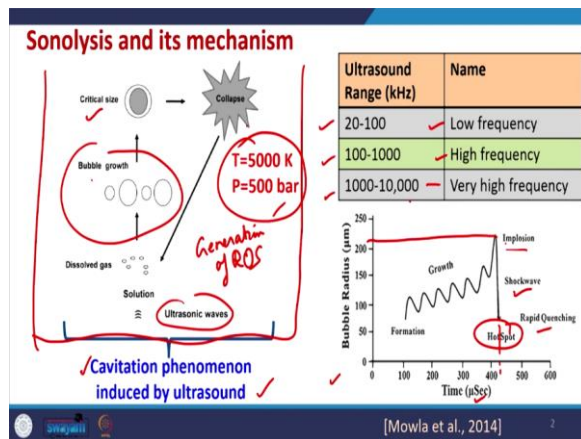


**Physico-Chemical Processes for Wastewater Treatment**  
**Professor V.C Srivastava**  
**Department of Chemical Engineering**  
**Indian Institute of Technology, Roorkee**  
**Lecture 51**  
**AOP: Sono-Hybrid Wastewater Treatment**

Good day everyone and welcome to these lectures on Physico-Chemical Processes for Wastewater Treatment. So, in the last few lectures, we have been studying the advanced oxidation processes. So, we have understood that in the advanced oxidation processes, various techniques are used for generation of reactive oxidation species.

So, these species include hydroxyl radical various are that types of radicals and we use which are used further for mineralization of organic contaminants present in the water into CO<sub>2</sub> H<sub>2</sub>O etc. So, this is done. So, we have already studied the photocatalytic water treatment, wait for oxidation method, the electrochemical treatment of wastewater which included electro coagulation ~~electro-oxidation~~ ~~electro-oxidation~~ and electro flotation in addition so, we will be continuing further and today will be learning regarding another advanced oxidation process which is called as sono-lysis. Now, in the Sonolysis, Sonolysis is like sound.

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So, we use basically ~~ultra-sound~~ ~~ultrasound~~ for creating cavitation So, cavitation means creating bubbles. So, this idea is used for generation of reactive oxidation is species and which are further used for treatment of the water. Sonolysis can be used individually also it can be used along with some other advanced oxidation processes, including electrochemical treatment and ~~photo-lysis~~ ~~photolysis~~ where via combining this Sonolysis we actually enhance the treatment

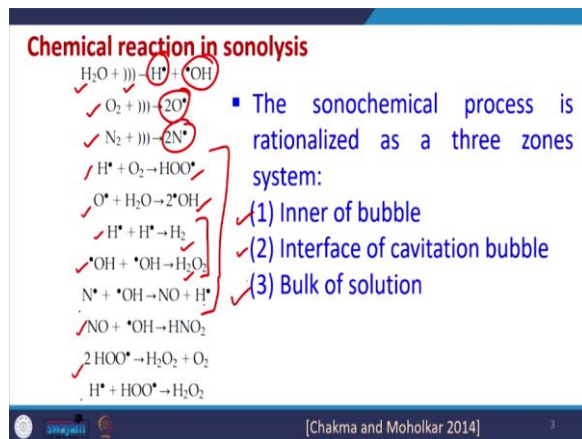
combined treatment efficiencies. So, we always observed some synergistic effect. So, let us understand the mechanism of Sonolysis first.

So, in the Sonolysis the Ultrasound is used for creating cavitation. So, we have Ultrasonic waves and this is a wastewater you can consider that everything is inside this. So, we have a wastewater and in this case, because of cavitation the bubbles are evolved. Now, this bubble will grow we can see up to a critical size and as soon as the critical size is reached, that will depend upon the height of water pressure, all those things as well. So, at the critical size, this bubble will collapse and when it collapses actually inside the bubble, the temperature and pressure may be up to this value. So, that temperature may be 5000 Kelvin and pressure maybe up to 500 bar within the bubble.

So, under that condition, when this collapse happens, because of various interaction that reactive oxygen species get generated. So, this generation of reactive oxidation species will happen, during this sonolysis and because of this the treatment of water happens, now, these ultrasonic waves are Ultrasound and it is frequency that critically affects the generation of these bubbles and what will be the bubble size critical bubble size etc. and what is the duration up to which this collapse happens after what time that also depends upon that. So, there are many frequencies. So, up to 2200 megahertz it is kilo hertz it is called low frequency 100 to 1000 kilo hertz it is high frequency then 1000 to 10,000 we have very high frequency of ultrasound.

Now, this particular figure shows the bubble radius we can observe. So, we can see the bubble radius may go up to 200 micrometers are beyond depending upon the type of our frequency of Ultrasound being used. And we can see at the how the bubble growth is happening and after a few microseconds only. So, it is like a blink of an eye, we have the collapse which happens and as soon as the implosion happens we have shock waves and rapid pinching that happens and we have a hot spot created, which has a temperature of 5000 Kelvin and 500 bar and because of this reactive oxygen species are generated.

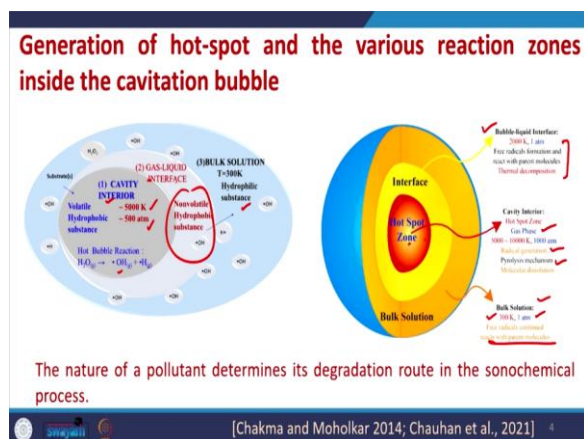
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Now, during this process, many chemical reactions happen and because of which these species get generated, these chemical reactions are listed here. So, water because of Ultrasound may release these radicals also oxygen present in the water nitrogen in the present in the water, they also generate their respective radicals, because of this Ultrasound and bubble growth and collapse mechanism, these generated radicals they further undergo interaction via these reactions, which are listed here.

And we can see here that we can generate secondary radicals, also some of the radicals may combine together to form  $\text{H}_2$ ,  $\text{H}_2\text{O}_2$ , which is not very desirable also a one radical can get converted into secondary radical and similarly, these radicals may interact with other types of species in the present in the water. So, we have lots of reactive oxygen species which can generated because of the use of sonolysis in the water treatment. Sono chemical processes is rationalized as a three zones system first is the inner of the bubble, then interface of the cavitation bubble and then the bulk of the solution. So, these three we are more interested in this zone as compared to other.

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Now, let us further understand the generation of hotspot and the inside of the cavitation bubble and their various reaction zones etc. So, this is shown. So, we have three already discussed we have three zones, we have cavity interior. So, it is a considered as a volatile hydrophobic substance a temperature and pressures are already given.

So, this is hot bobble reaction is possible where these radicals are getting generated, then we have a gas liquid interface. So, it is nonvolatile hydrophobic substances may be here and after that we have bulk of solution. So, this is hydrophilic substances and here all the radicals generated will ultimately go. So, these cavitation bubbles they are zones, these all will depend upon a number of parameters.

So, again the same thing is shown here in this particular slide. So, we have cavitation cavity interior which is gas phase, the temperature and pressures are very high here at the interface that pressure has been reduced the temperature is still high and it is where the free radical formation takes place and they react with parent molecules. So, here the thermal decomposition will also happen.

Within the hotspot zone we have radical generation certainly happening then paralyzes mechanism may also work here and in the bulk of solution where the temperature is ambient and pressure is also ambient, free radicals they come after and they collide with the parent molecules and their degradation happens. So, this is there.

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**Variable for sono-chemical Effects**

**Initial radius of the cavitation bubble**

- Smaller is the bubble size, higher is the cavitation effect
- Smaller sized bubble can expand higher with more intense than bubble with a large radius during the transient collapse.
- This is due to the higher Laplace pressure in smaller <sup>size bubble</sup> pressure, i.e. the difference between inside and outside pressure of a bubble at the gas-liquid interface
- The critical size depends on the liquid and the frequency of sound; at 20 kHz, for example, it is roughly 100-170  $\mu\text{m}$ .

Now variables which affect the sono chemical effects. So, there are initial radius of the cavitation bubbles. So, what are the parameters which affect these, so, smaller is the bubble size higher is the cavitation effect. So, this is this is one thing this is very important. smaller size bubble can expand higher with more intense then bubble with large radius during the transient collapse. So, this is their So, the smaller size bubble if it collapses then the effect is different as compared to collapse of large scale large radius bubble and this is due to higher Laplace pressure in the smaller pressure that is in smaller pressure in the smaller size bubble.

So, that is there the difference between inside and outside pressure of a bubble at the gas liquid interface which is called as Laplace pressure. So, and this is because of this, the effect is different, that critical size up to which the bubble may grow will depend upon the liquid type of liquid, the frequency of the sound being used. And like for example, at 20 kilohertz, the size of the bubble may go up 100 to 170 micrometers of critical size will depend upon the type of liquid, it is the hydrophobic hydrophilic nature and the frequency of the sound we use. (10:29)

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**Presence and Nature of Dissolved Gases**

- A gas with a high specific heat ratio gives a greater cavitation effect than one with a low specific heat ratio.
- Monatomic gases, such as argon and helium, convert more energy upon cavitation than diatomic gases, such as nitrogen and oxygen, because of the larger ratio of specific heats. ✓
- Gases which are extremely soluble in the reaction mixture may reduce the cavitation effect because the bubbles formed may redissolve before collapse occurs

Now, also the presence and the nature of dissolved gases, they also affect the Sonolysis process. So, against with the high specific heat ratio gives a greater cavitation effect, then one with low specific heat ratio, so, this is there. Similarly, monatomic gases such as argon and helium convert more energy upon cavitation than diatomic gases such as nitrogen and oxygen, because of the larger ratios of a specific heat.

So, within this, this is there, now gases which are extremely soluble in reaction mixture may reduce the cavitation effect because the bubbles formed may be dissolved before collapse happens. So, this is they are so, extremely soluble gases are will actually hamper the effect of the Sonolysis.

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**Choice of Solvent**

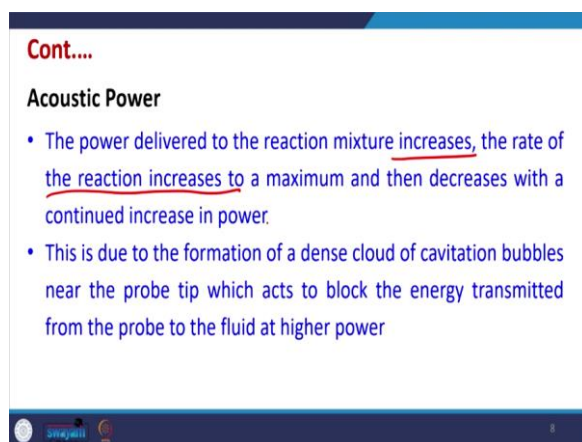
- Cavities are more readily formed when using solvents with high vapor pressure, low viscosity, and low surface tension.
- At very high frequencies, the cavitation effect is reduced because either:
  - The rarefaction cycle of the sound wave produces a negative pressure which is insufficient in its duration and/or intensity to initiate cavitation.
  - The compression cycle occurs faster than the time required for the microbubble to collapse sonochemical reactions were carried out at frequencies between 20 and 50 kHz.

So, this is there now, choice of solvents. So, depending upon what type of solvent or what type of other types of materials which are present in the water that will also affect the Sonolysis cavities are more readily found when using solvents with high vapor pressure, low viscosity and low surface tension.

So, if there are organic compounds which are present in the water, which have low vapor pressure, low viscosity and low surface tension, then that cavities will be more farmed at a very high at frequencies the cavitation effect is reduced, because the refraction cycle of the sound wave produces a negative pressure which is insufficient in its duration or intensity to initiate the cavitation.

So, this is the refraction cycle of the sound waves that affects the cavitation effect. Similarly, the compression cycle occurs faster than the time required for the microbubble to collapse. So, Sonochemical reactions are carried out generally in frequencies in this range 20 to 50 kilo hertz. So, this is the reason mostly the most of the pseudo chemical reactions will be carried out under this condition.

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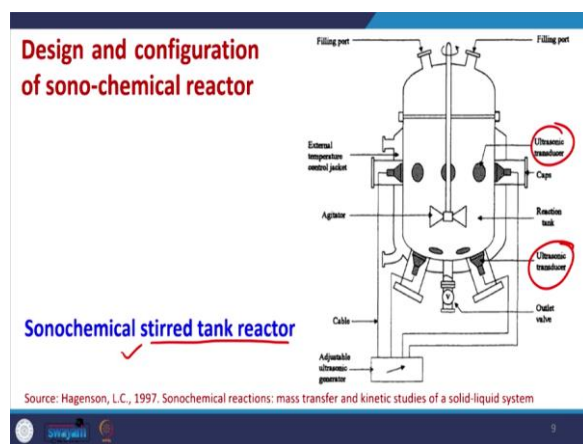
**Acoustic Power**

- The power delivered to the reaction mixture increases, the rate of the reaction increases to a maximum and then decreases with a continued increase in power.
- This is due to the formation of a dense cloud of cavitation bubbles near the probe tip which acts to block the energy transmitted from the probe to the fluid at higher power

So, a Acoustic power also affects the cavitation So, what is the power delivered to the reaction mixture that is very important, so, as power increases the rate of reaction also increases to a maximum. So, we have to see that we have to use the power in such a manner that the rate of reaction is maximum, if we use the power beyond that value, at least will not be used. So, our energy consumption will increase.

So, we have a critical power that we should analyze beforehand and use in the wastewater treatment using Sonolysis and this is this critical power is because of the formation of dense cloud of cavitation bubbles near the probe tip which acts as a block to the energy transmitted from the probe to the fleet at very high power beyond the critical power. So, this is there. Now, there are many types of Sonochemical reactors have been reported in the literature some of them are being shown here.

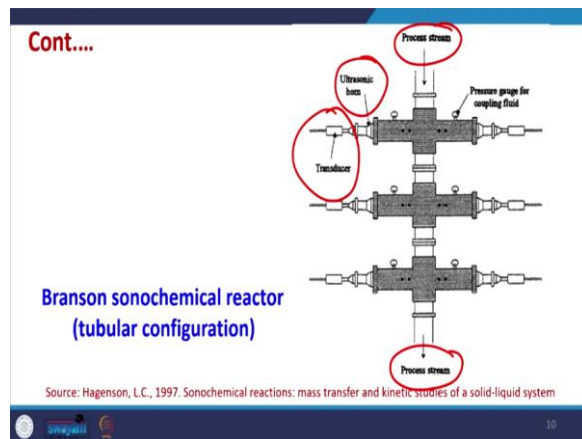
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So, Sonochemical stirred tank reactor this is this technology is not much practice react in large scale reactors, but these are the different types of reactors which have been reported. So, we can see here this is a stirred tank reactor, but along with some Ultrasonic transducers which are fitted for generating the bubbles and then the using that cavitation effect. So it is very common a stirred tank reactor but it is fitted with Ultrasonic transducer.

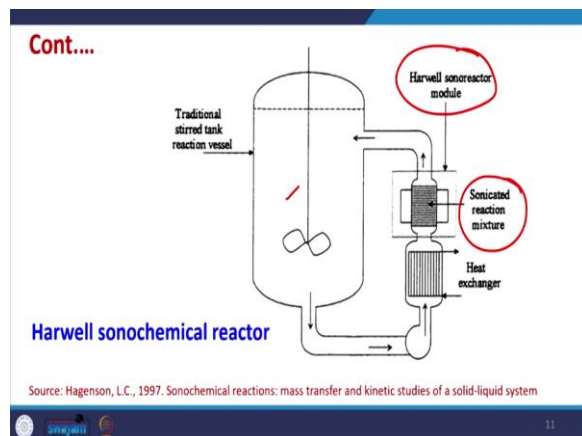


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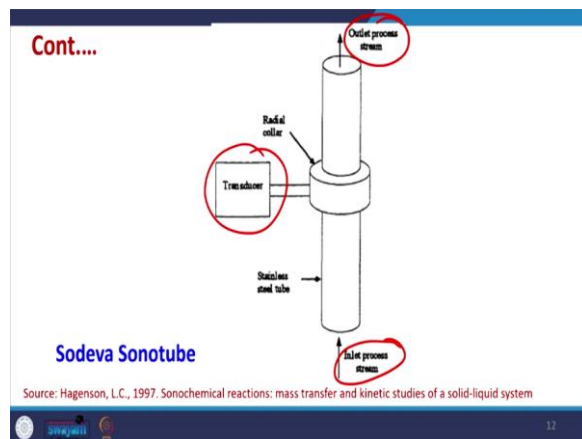
Similarly, this Branson Sonochemical reactor has been reported. Again we can see that transducers and Ultrasonic horn here the process is stream to the water to be treated is coming in after treatment it is going like this. So, this is again a tubular configuration of Sonochemical reactor, which has been reported.

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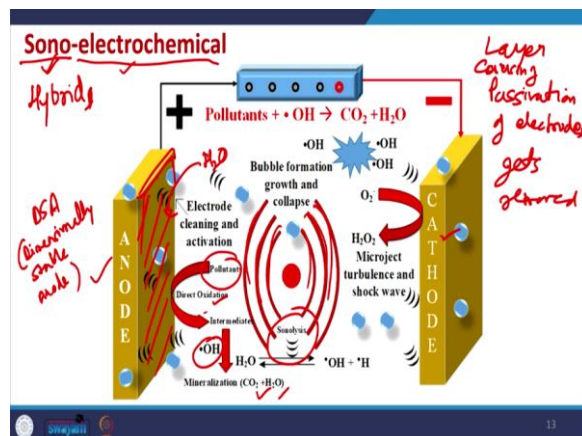
Similarly, a harvest, Sono chemical reactor has been reported where the recycling is being done and the water from the stirred tank vessel is coming and then it the reaction is being done separately out of the reactor and here the Sonochemical reaction mixture here this Harwell Sonoreactor module has been acted and water is further edit and treatment is being done in the usual CSTR method.

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This is another Sonotube where transducer is fitted. So, again a simple transducer is being fitted in the line itself. So, here we have inlet processes team and here the outlet processes stream is there where the water is coming out after the treatment. So, these are the various configuration of Sonochemical reactor.

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Now, Sono chemical reactor have few benefits. So, they generally treat the water up to a certain labor, they do not have that much capability to overall treat the water fully remove the cod etc. So, Sonolysis has been combined with a number of other AOP methods this will be called as hybrid AOP methods. Now, Sono electrochemical is one such method and what are the benefits that are being shown here in this slide. So, electrochemical treatment we have already studied

in the previous lecture. So, here we will try to understand that if we combine sono Electro what are the benefits, so, let us understand are recollect the electrochemical treatment.

So, in the electrochemical treatment we understood that depending upon the type of anode are cathode being used, so, we suppose we are using DSA type of electrode, DSA means Dimensionally Stable electrode, So, dimensionally stable electrode we are using anode. So, under that condition the anode will be highly stable not only with respect to anodic oxidation, but also with respect to corrosion.

Now, on this surface the pollutants may come and direct oxidation may happen, similarly the OH, H<sub>2</sub>O may go on the surface and these radicals may get form and these radicals may react with the pollutants and then mineralize them and convert them into CO<sub>2</sub>, H<sub>2</sub>O etc. So, this is there. Now, the problem with electrochemical technology is that, after a certain time, what happens is that that a passive layer gets formed on the anode surface.

So, this the organics will get attached, but they are not coming out. So, actually the surface which is available for this interaction for direct oxidation or for generation of reactive oxygen species that decreases and the resistance in the system increases with time. So, the efficiency of electrochemical treatment method decreases with prolonged use of these this particular method.

So, we what we can do is that we can combine the sono method along with there. So, if we use Sonolysis, So, it will generate these shock waves during bubble formation and collapse and because of this bubble formation and collapse, the layer which gets formed, which actually does the passivation of electrode, this layer gets removed.

So, layer causing passivation of electrode that gets removed because of this shock waves, so, layer causing passivation of electrode gets removed. So, what happens is that we have we can do the treatment for longer duration and also the efficiency increases. So, both aspects are there. So, we have a parameter which is called as synergistic effect. So, because of Sonochemical effect the synergy of treatment increases.

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**✓ Sono-electrochemical and its mechanism**

- Sono-Electrochemical technology is combined method of sonolysis and electrochemical treatment.

**Advantage**

- ✓ In-situ clean the electrode surface.
- ✓ Reduce electrode passivation problem.
- ✓ Increase the life of electrode.
- ✓ Ultrasound wave accelerate the diffusion of ion and pollutants increase the mass transfer.
- ✓ Decreases the diffusion layer thickness.
- ✓ Enhanced •OH radicals generation ✓
- ✓ Speed up the electron transfer at the electrode area by creating agitation.

**Synergy index** =  $\frac{E_{US+EC} - 0.95}{E_U + E_{EC} - 0.11 + 0.7}$

$E_U \rightarrow 0.11$  or 11%  
 $E_{EC} \rightarrow 0.70$  or 70%  
 $E_{US+EC} \rightarrow 0.95$  or 95%

**SI > 1**

[Thokchom et al., 2015] 14

So, will understand this also the So, Sono electro chemical is a combined method of Sonolysis and electrochemical treatment, the advantage is that in this institute cleaning up the electrode surface happens and this is because of the south wave this reduces the electrode passivation problem. So, again efficiency will increase, this also increases the life of electrode there is another benefit because of the use of Ultrasound, Ultrasound waves accelerate the diffusion of ions and pollutants because of the increased mass transfer, so this aspect is also there, because of Ultrasound diffusion layer thickness decreases.

So, we have overall increase in the mass transfer and also because, now we are using two techniques we are using, Sonochemical, sono method along with electrochemical So, we have more amount of OH radical formation happening and because of that, the overall treatment efficiency increases a lot also, because of these shock waves collapse etc. the agitation the more amount of agitation is created.

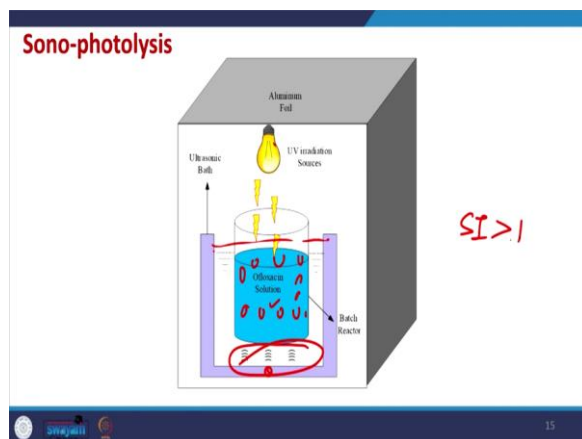
So, many times we do not need a separate mixer in the electrochemical treatment. So, Sono electrochemical treatment may why with that, we may not have to use a separate mixing a pretest. So, in this way we are saving on that. So, overall there are lots of benefits are there with by using Sono electrochemical method together. So, that is why these two technologies are being merged together also.

Now, within this I discussed about the synergy index there is one parameter which is called as synergy index. So, suppose we are using Sonolysis alone US alone. So, under that condition, suppose the efficiency is 0.11 we are just assuming that means, or 11 Percent treatment

deficiency. Now, if we are using electrochemical method alone, and we have supposed 70 Percent efficiency or 70 Percent treatment deficiency now, in the synergist synergetic index, what we do is that we try to find out the efficiency when both US and EC are combined together. So, generally will be finding that this efficiency will be more than the efficiency of both of them combined together.

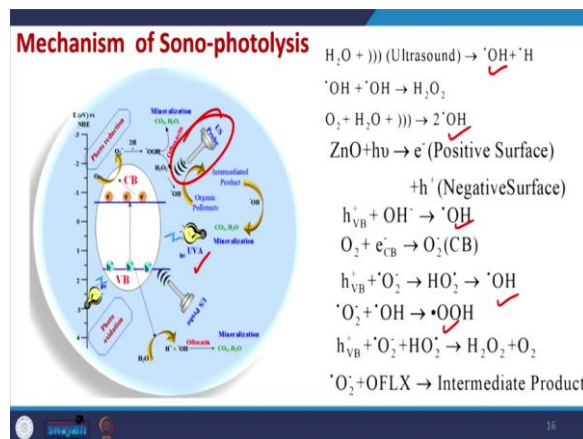
So, it is most likely this efficiency may go up 0.95 or 95 percent. So, that synergy index will be calculated as  $E_{us} + E_{ec}$  divided by  $E_{us} + E_{ec}$ . So, that means, here it will be 0.95 divided by 0.11 plus 0.7. So, that means, the synergy index SI generally has to be greater than 1. So, the higher the value the better it is. And so, this with hybrid AOP is, we always look for these parameters to cross check whether they are doing well or not. This is there.

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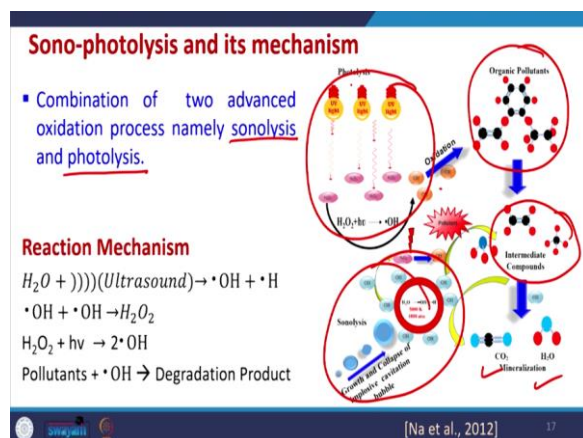
Now, Sono-photolysis is another technique. So, here we can see this treatment is being done in a batch reactor Ofloxacin solution and we have this it contains already photocatalysis and UV light is being provided. So, we have photocatalyst which are here and then the photo oxidation is happening, but if we use Ultrasound, so it will increase the efficiency and SI value is likely to be greater than 1. So, this is also possible in Sono photolysis.

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So, this is how the Sono photolysis works. Generally, it will combine along with the  $H\nu$ . So, we have both light and sound transducers both are there. So, because of that, there is increased formation of radicals and because of quick formation of radicals, we have more treatment, which happens and because of which that treatment efficiency becomes very, very high.

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So, this is the Sono photolysis and its mechanism, it is a combination of two advanced processes, mainly sonolysis as well as photolysis. So, we have photolysis happening here. And similarly, we have Sonolysis which is happening here, and because both are combined together, so we have enhanced formation of radicals and which act actually oxidized the organic pollutants.

So, we have these radicals which are there. So, the photolysis radicals will oxidize the major Organic Pollutants, other radicals which get generated the oxidized the intermediate compounds and ultimately, we have CO<sub>2</sub> and H<sub>2</sub>O, which is getting generated. So, we have increased the treatment efficiency because of the combination Sono photolysis.

So, we have till now, studied a number of AOPs in this course, and these included photolysis catalytic wastewater treatment Fenton process Ozone treatment, then electrochemical treatment we studied in detail thereafter in the today we have studied Sono lysis alone and sono lysis in combination with electrochemical treatment and Sonolysis in combination with photolysis. So, hybrid AOP are also becoming very very common, and they have a lot of potential for use in different industries for wastewater treatment.

And in particular in those industries where peculiar type of wastewater is getting discharged, we have which have some key pollutant parameter which are not common. And these key parameters cannot be treated by the conventional physicochemical treatment methods. So, then we have to use these AOP. So, with today's lecture, will end the section AOP.

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We have used a number of references, you can refer to them. And so with that, will end that today's lecture. Will continue with another section on disinfection and which actually they use the AOP methods only with little bit different. So will continue with the disinfection section from this lecture onwards. So, thank you.