Physico-Chemical Processes for Wastewater Treatment
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Lecture 50
AOP: Electrochemical Wastewater Treatment - II

Good day everyone and welcome to these lectures on physico-chemical processes for wastewater treatment. So, in the last few lectures we are studying regarding the advanced oxidation processes. And in the last lecture we started studying regarding electrochemical wastewater treatment.

So, in this today's lecture will continue further with the electrochemical wastewater treatment, this technology has lot of potential for application with respect to wastewater treatment in industries with discharge water, peculiar type of water like very high COD water or water which is having very low pH or very high pH. So, this or those wastewater which are having oil and grease surfactant etc, also in the water itself, so electrochemical technology has lot of potential for treatment of such wastewater.

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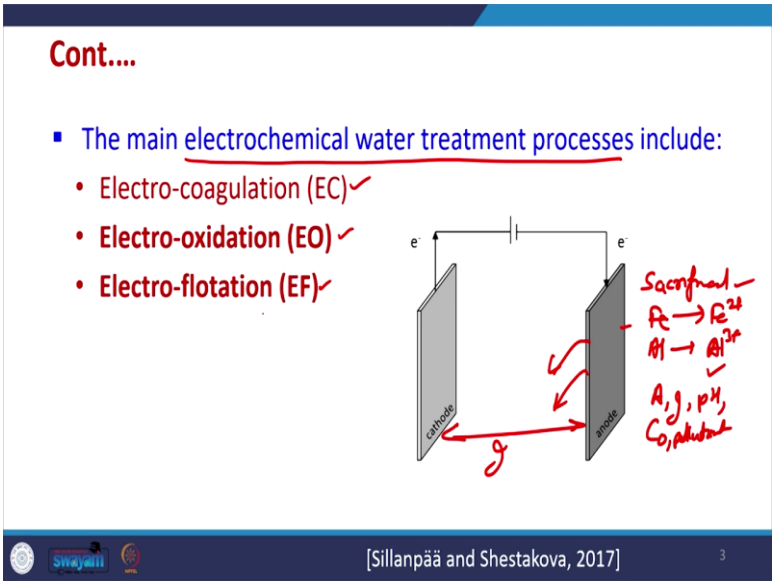

In the previous lecture, we understood that the electrochemical water treatment technology processes actually they incorporate three different methods, one is electro-coagulation, another is electro-oxidation and electro-flotation. So, we studied in detail-the electro coagulation process in the previous lecture.

Now, we will go further and study the electro-oxidation and electro-flotation methods in today's this particular lecture and understand that how they work? What are the different

mechanisms of their working? In the electro-coagulation process, we understood that the anode is there and this anode may consist of some sacrificial metals, so, that sacrificial metals included like iron and aluminum.

Now, these come out in the form of Fe 2 plus or Al 3 plus and the release of these metals from the anode that depends upon various parameters including the current the electrode gap which is between the cathode and anode. So, this is generally represented by g. Similarly, it will depend upon the pH of the water, also depend upon various other parameters including the concentration of various pollutants in the water. So, all those things depend and also the treatment depends upon the type of gases which are getting generated. So, this already we have studied electro-coagulation in detail in the previous lecture.

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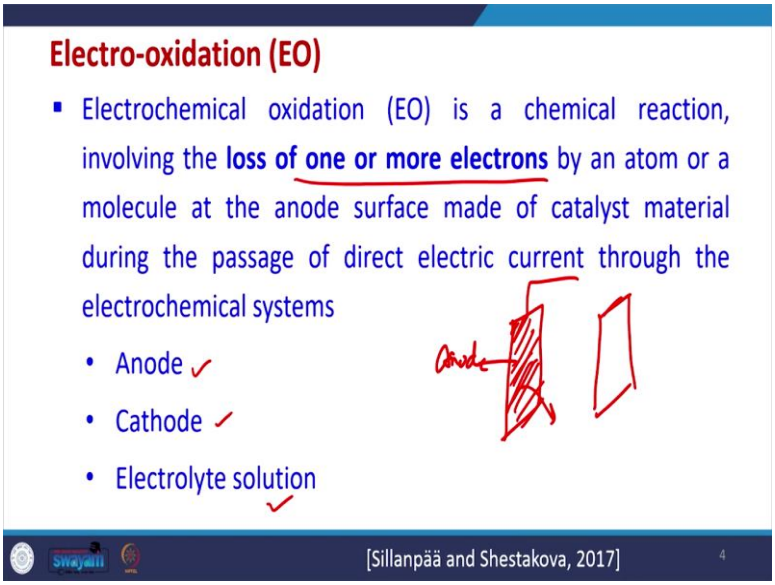

Now, we will continue the electro-oxidation and electro-flotation and understand them. Now, electro-oxidation, so, electrochemical oxidation is a chemical reaction involving the loss of one or more electrons by an atom or a molecule at the anode surface made of catalyst materials during the passage of direct electric current through the electrochemical system. So, electrochemical system will always have anode, cathode and some electrolytic solution. So, we have a anode which is there and we have a cathode which is there.

So, depending upon that if suppose this anode is have made of iron aluminum, so, it will come out, it will slowly get released into the water, but if it is made of some material which is highly stable, so, then it will only release the electron but the material will not come out and also depending upon the coating which has been done which type of oxide, so, depending

upon the redox conditions and other thing, so, they will lose the electron but the metal will not get dissolved, so, this is there.

And depending upon this electron which comes into the water, different types of species reactive oxygen species get generated and treatment of water happens.

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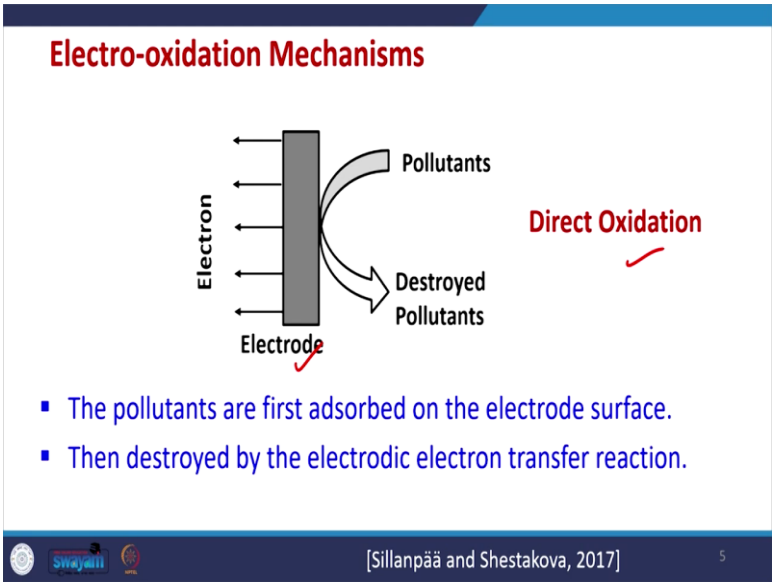

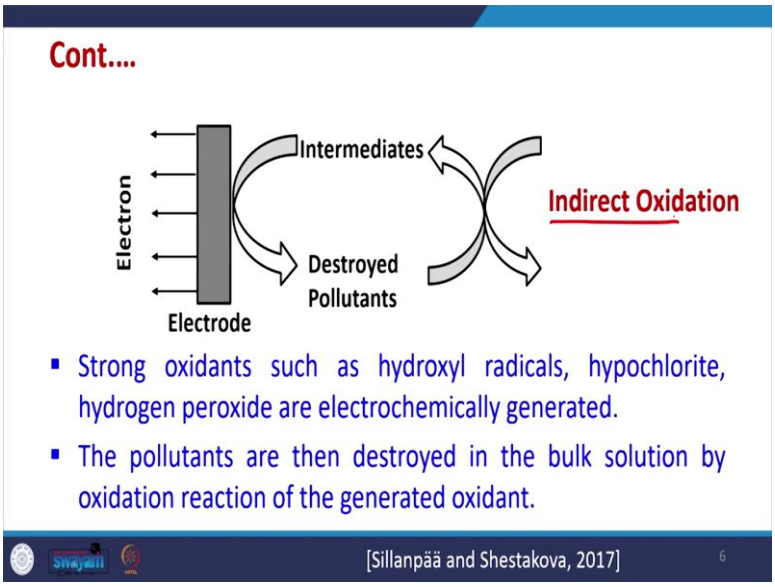

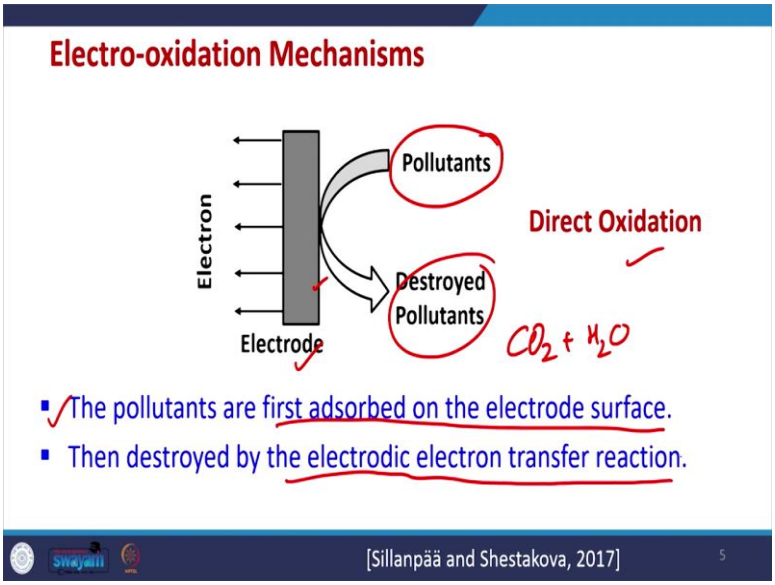

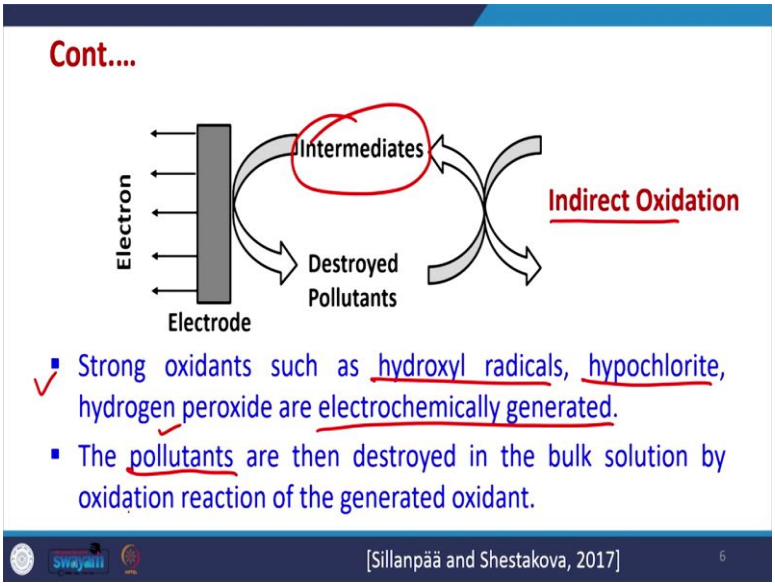

Now, this is the electrode. So, this is the anode which is there, and from here we can see the electron is coming. Now, there is a possibility of direct oxidation there are two oxidation mechanisms in the electro-oxidation process, one is called direct oxidation and other is called indirect oxidation which is given in the next slide. Now, in the direct oxidation, the pollutants which are present in the water, they directly come in contact with the electrode surface and they get destroyed. So, this is direct oxidation and we have CO2, H2O etc, which gets released.

The pollutants, so, in this condition the pollutants are first adsorbed on the electrode surface and then they are destroyed by the electrodic electron transfer reactions. So, this is the direct oxidation. Then there is a second mechanism which is called as indirect oxidation. So, in the indirect oxidation, we have some intermediates which get formed. So, that intermediates will

be reactive oxygen species which are getting generated. So, strong oxidants such as hydroxyl radicals, hypochlorite, depending upon whether the water contains chloride or not NaCl or not, hydrogen peroxide, which are electrochemically generated in situ inside the water.

So, these strong oxidants then they oxidize the pollutants which get destroyed in the bulk solution by oxidation reaction with the generated oxidants, this is how the indirect oxidation takes place. So, we have first strong oxidant which are generated and then we have the degradation which happens the pollutants are destroyed in the bulk of the solution. So, this is called indirect oxidation.

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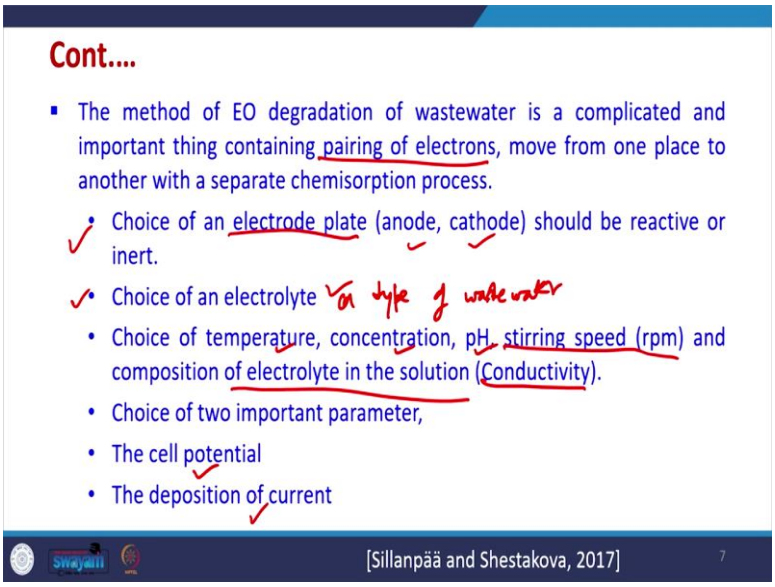

Now, the method of electro-oxidation or electrochemical oxidation degradation of wastewater is a complicated and there are many parameters which are associated. So, the pairing of electron movement from one place to another with a separate chemisorption process all these parameters affect, there are a number of parameters which affect the electro-oxidation efficiency these are, which type of electrode plate is used for anode and cathode. So, it should be sometimes like it should be reactive or is it anode depending upon the type of pollutants which are present in the water.

Then choice of an electrolyte, so, electrolyte many times the wastewater may be there, but it may not contain ion. So, under that condition we may have to add some ions from outside maybe some salt. So, that will depending upon choice of electrolyte or type of wastewater, so, we can right here that type of wastewater also. So, this is there. Also the choice of temperature, concentration of wastewater pollutants, then pH what is the mixing or stirring

speed etc so, stirring speed for batch, so, how quickly the mixing is happening? All those things.

The composition of electrolyte in the solution or its important thing is conductivity. If sufficient conductivity is there, because of the presence of salts, we do not need to add salt from outside otherwise, we need to add salt from outside and also choice of other parameters like cell potential and whether deposition is happening or not on the anode surface cathode surface, because of this reduction in current etc, is happening or not all these things are important.

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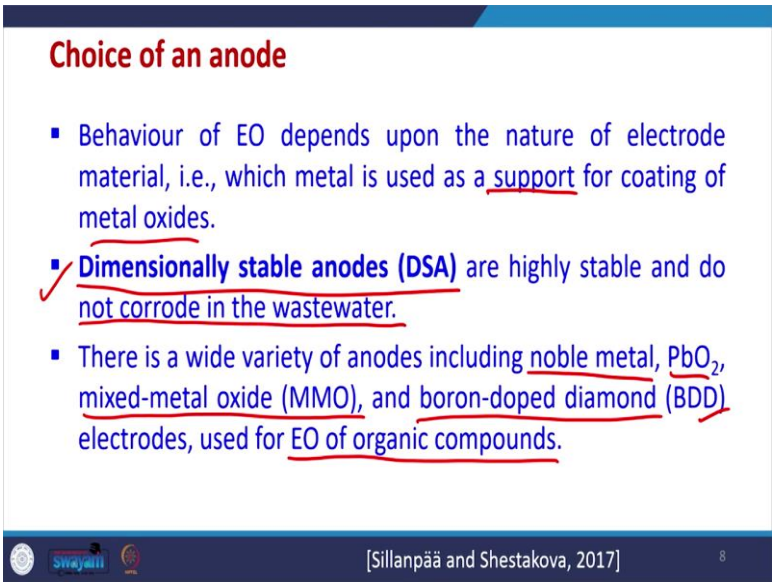

So, behavior of electro oxidation depends upon the nature of electrode material, which metal is being used as a support for coating of some oxide. So, both support and the coating are important. The important thing is that, in the electro-oxidation generally we use dimensionally stable anodes these are called DSA, there is another term which is called as dimensionally stable electrode DSE. So, this is DSA will fall on that category only.

So, these DSA electrodes are highly stable and they do not corrode in the wastewater. So, they will corrode very, very slowly, so that means, that life of dimensionally stable electrodes is or dimensionally stable anodes is very very large and, they are able to treat large amount of wastewater, so, this is there.

There are a large wide variety of anodes or DSA anodes which are available. So, they may be made of noble metals some like lead oxides, mixed metal oxides. So, any of them mixed metals maybe there, one of the metal may be support another metal oxide will be coated on

the same, then boron-doped diamond electrode have been well reported and they have these anodes are used for electro-oxidation of organic compounds present in the water.

So, the any of them can be used for treatment of water depending upon the pH, various other materials present in the water. So, all those thing will decide which type of electrode material has to be used, so, generally they will classify under dimensionally stable anodes.

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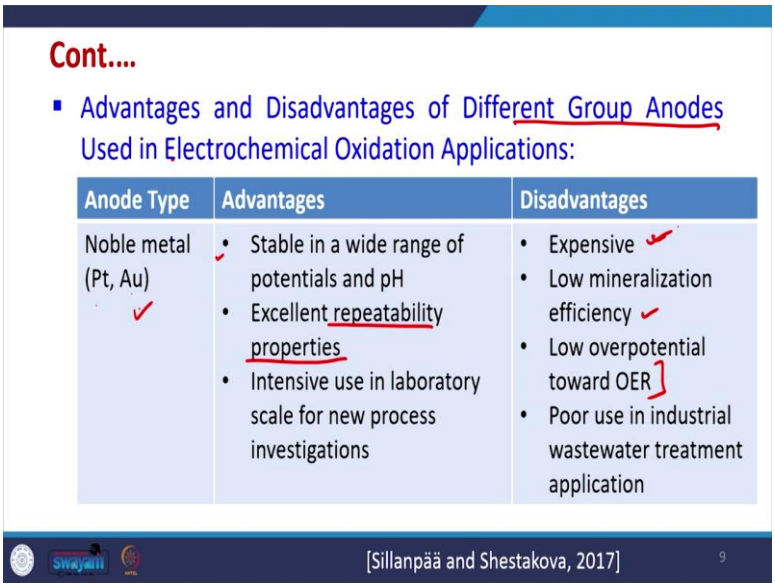

Now, advantages and disadvantages of different group anodes, so, different anodes are listed here used in the electrochemical oxidation application. So, some advantages and disadvantages have been clubbed together here. So, depending upon anode type whether platinum or Au is there. So, advantages is that they are stable in wide range of potential and pH, they have excellent repeatability properties, so, they will work, which save efficiency for longer duration, but the efficiencies are not very high one thing, but they still work very well.

They can be intensively used in the laboratory scale for new process investigations, already there are very large number of studies reported on this. The disadvantages are that they are certainly expensive, they have low mineralization efficiencies as compared to other and other anodes which are reported, low over potential towards oxygen evolution reaction, so this is there. Poor use in the industrial wastewater treatment because of expensive nature certainly, so this is there.

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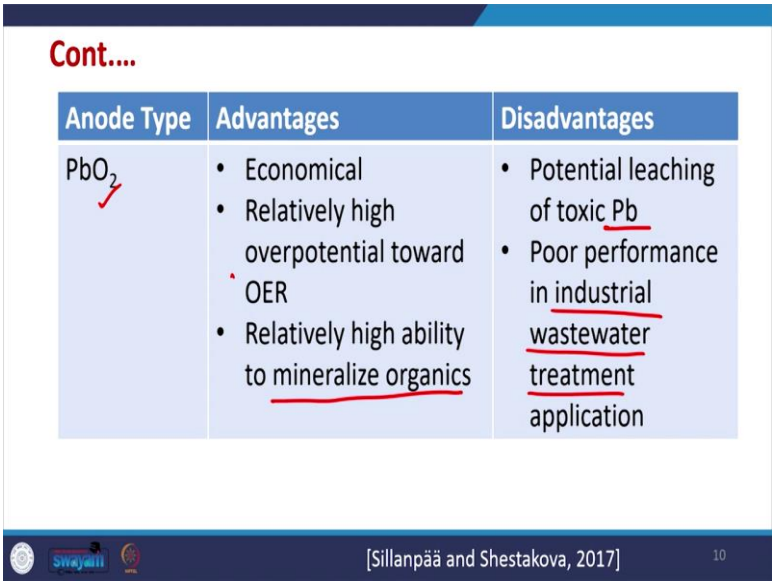

Then we have lead oxide, it is economical, relatively high over potential towards oxygen evolution reaction and relatively high ability to mineralize organics, so they have better ability as compared to platinum or other, but the problem is that the this lead may leach into the system if the lead gets leached into the system then the water we have secondary pollution which is happening. So, this is the problem. For actual industrial wastewater treatment, the performance has not been that good with respect to simulated water, so this is there.

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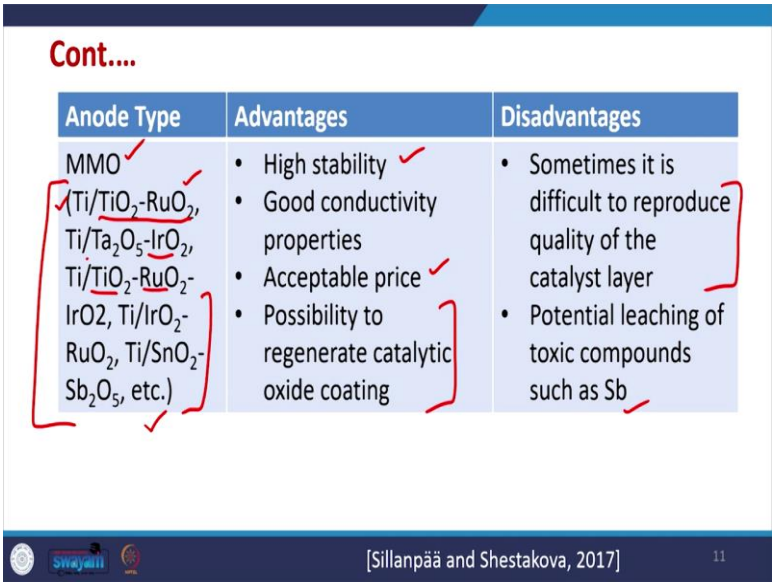

Now, there are mixed metal oxides, lot of mixed metal oxides have been reported and hear the most of the research is being done towards application of electro oxidation techniques at the actual industrial wastewater treatment or otherwise. So, there are different mixed metal

oxide electrodes are possible, these are like titanium, ruthenium, tantalum, iridium, then again titanium, ruthenium, iridium. So, that we can see here tin the tin oxide. So, there are different combinations. So, base metal could be titanium on which different these oxides have been coated, so we see that titanium is a base metal for large number of such mixed metal oxide.

Similarly, some people have reported zinc also, but titania is one of the most common base metal for these mixed metal oxide, they have very high stability, good conductivity properties and they are generally available at acceptable price. So, they have a lot of potential for scale up to the industrial scale. They have the possibility to generate the catalytic oxide coating we can once the coating is like it has been removed after treatment of large amount of water. So, we can again record the electrode and reuse it.

Sometimes the disadvantages is that, sometimes it is difficult to reproduce the quality of catalyst layer after once it is used up, so, this is one there. This potential leaching of some compounds such as Sb, so, that is possible. So, that will depend upon the type of coating that we are using. So, certainly it will depend upon that, so these are there.

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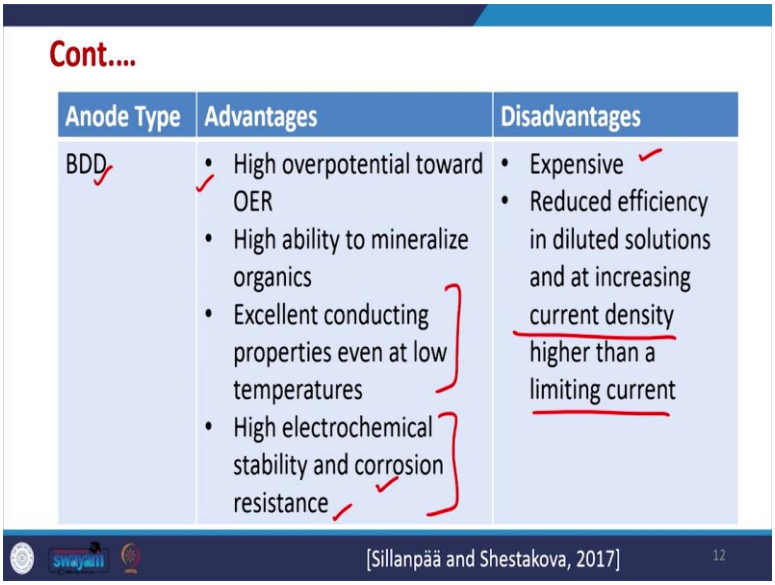

Then we have boron-doped diamond electrodes which have been reported in large number of studies. So, they have the advantage of high overpotential towards oxygen evolution reaction, high ability to mineralize large number of organic compounds, excellent conductive, excellent conducting properties at low temperatures as well and high electrochemical and stability as well as chemical stability. So, they are corrosion resistance as well.

And these boron-doped diamond electrodes are expensive though, so, this is only the drawback, major drawback with respect to use of these electrode materials and they their efficiency gets reduced in dilute solutions and at increased current density higher than the limiting current.

So, beyond the limiting current, they certainly they have reduced efficiency. So, these are the various advantages and disadvantages of using a dimensionally stable anodes for electro-oxidation.

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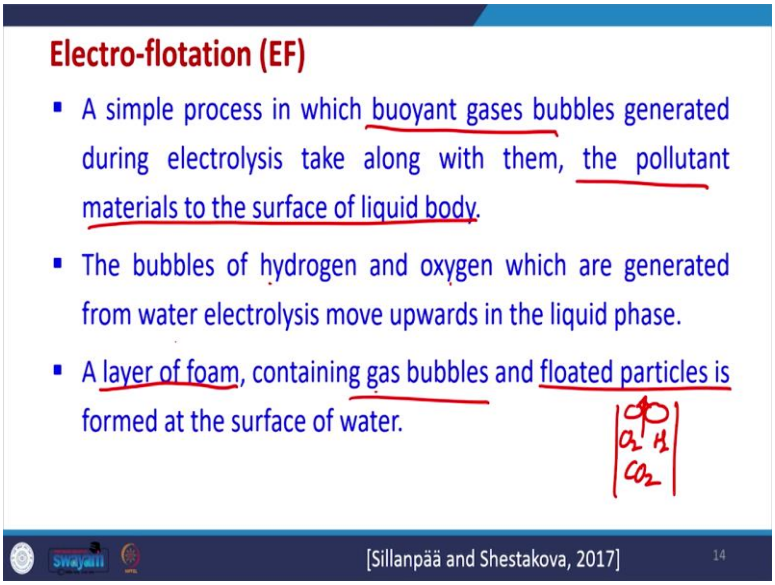

Now, we will go further and understand the electro-flotation process, which is also possible using the electrochemical a treatment technology. So, within this the third aspect is electro-flotation.

Now, a simple process in which buoyant gases, gases bubbles, which are generated during the electrolysis, they take along with them the pollutant material to the surface of the liquid body. So, we know that the in the electrode these gases are getting generated. So, we have H2 we have O2 we have CO2, which is getting generated because of mineralization of pollutant. So, these gases will take all the pollutant to the top, in particular, if it is not settling down very quickly and it is larger in size.

So, the bubbles of hydrogen and oxygen which are generated from water electrolysis move upwards in the liquid phase, a layer of foam containing the gas bubbles and floated particle is formed at the surface of the water, so, this may happen. And in particular, it will depend upon the type of compound which are present in the water, whether it is oil, whether it is grease or

it may take up a suspended materials also and similarly, it may take along with the oil and grease surfacting materials also, so depending upon what type of materials are present in the water this flotation may work.

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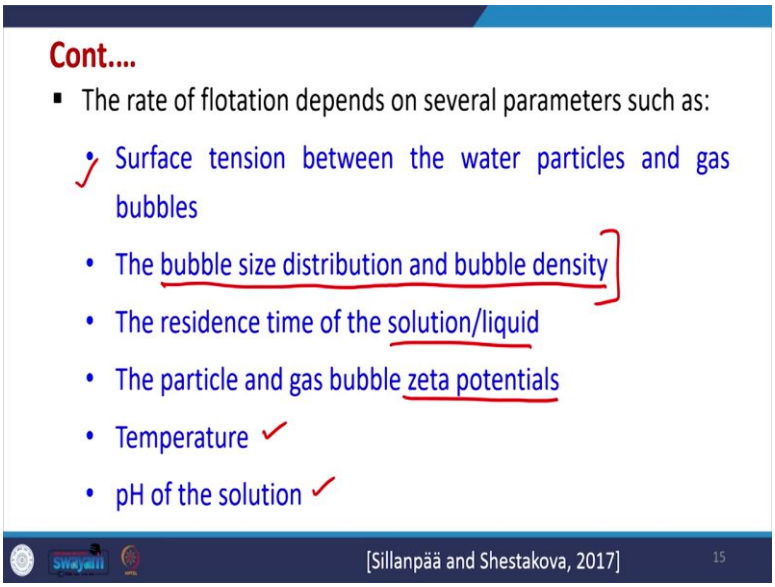

Now, the rate of flotation depends upon several parameters. So, these parameters are like surface tension between the water particle and the gas bubble, this is very, very important that what is the surface tension between the water particles and the gas bubbles? So, depending upon that, these gas bubbles will go up. What is the bubble size distribution and the bubble density? So, that means, how many number of bubbles are getting formed and what are their size distribution what type of bubble?

So, whether it is that bubble is broken down before actually it reaches the surface or not? So, all these, depending upon these things this is a very, very important parameter. The residence time of the solution at the liquid. So, this is that whether we are using continuous, if we are using continuous system what is the residence time of the solution in the system?

The particle and gas bubbles zeta potential. So, depending upon the zeta potential of the particle as well as the gas bubble their interaction will happen. So, these zeta potential become very important parameter for interaction of these gas bubbles and the particle and depending upon that, the particles will be taken to the top.

Now, the temperature and pH of the solution are other important parameters. Because they determine a number of things, like what is the rate of moving up of the bubbles through the water? What is the amount of formation of bubbles depend upon the pH because it in turn is

dependent upon the how much amount of H2 or O2 evolution is taking place, the pH is very important parameter, so, this is there.

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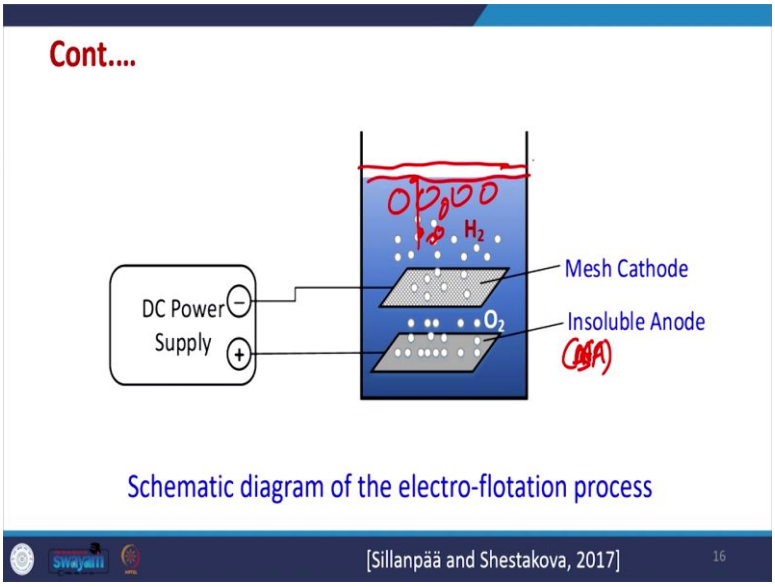

So, we have electrodes, we can see, the mesh electrodes, insoluble electrodes. So, that means these are DSAs. So, if DSA is dimensionally stable anodes. So, from here the O2 or H2 evolution is taking place and these bubbles when going up, they will interact bigger particles or other organic compounds and they will react with these bubbles and they will be taken and we have a foam layer which will be formed at the surface, so, this is there.

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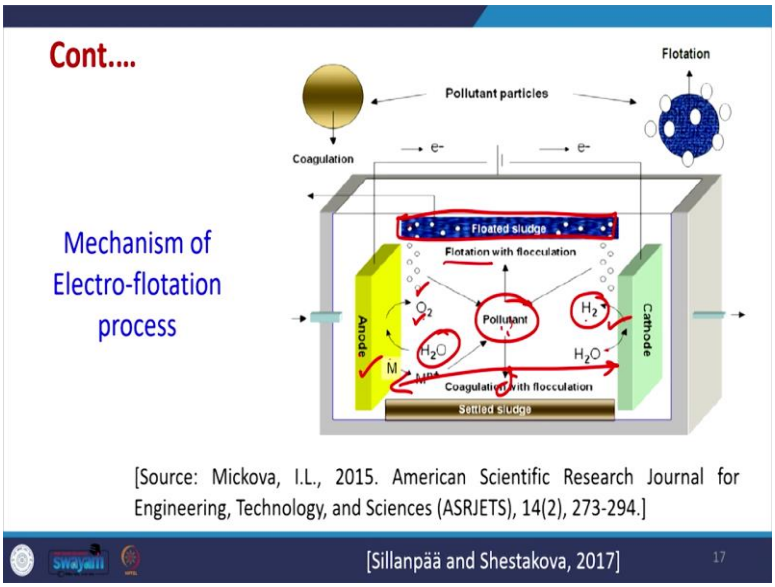

So, this is what is shown here we have from H2O depending upon this metal, it may be a stable unstable type of sacrificial anode or stable anode. So, H2O is getting converted into oxygen. So, we have oxygen evolution taking place at anode, we have hydrogen evolution which is taking place at the cathode depending upon the gap which is there in between. So, this gap is much lower as compared to what is being shown here in this figure.

So, these H2 and O2, these gas bubbles while moving up, they will interact with the pollutants and these pollutants get floated, like flotation will happen. So, there flocculation may happen and once they may get floated also along with these gas bubbles, so, we have floated sludge which is getting formed on the surface of the water and this may be skimmed off to remove these compounds from the water. So, this is how it works.

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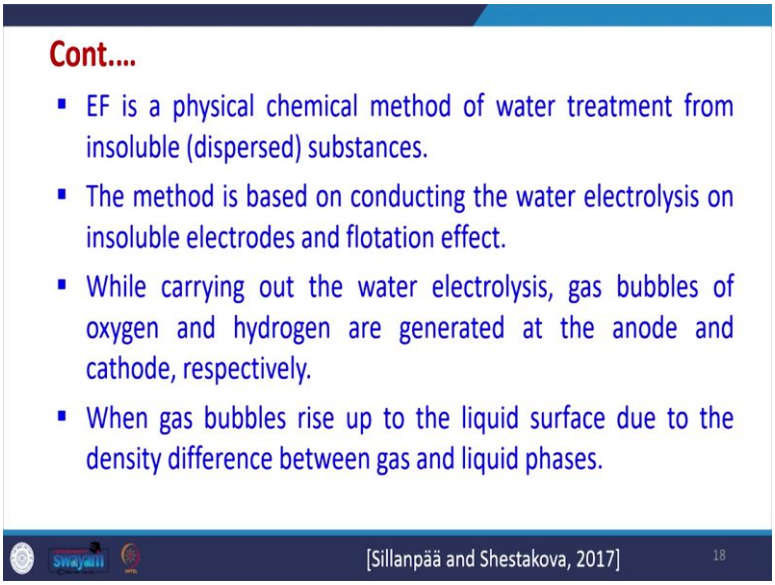

So, electro-flotation is a physical, physico-chemical method of water treatment from insoluble dispersed substances, the method is based upon conducting the water electrolysis on insoluble electrode I am then using the flotation effect, while carrying out the electrolysis, that gas bubbles of oxygen and hydrogen are generated at anode and cathode respectively. When gas bubbles rise up to the liquid surface due to the density difference between the gas and liquid, they entrapped a lot of organic compounds.

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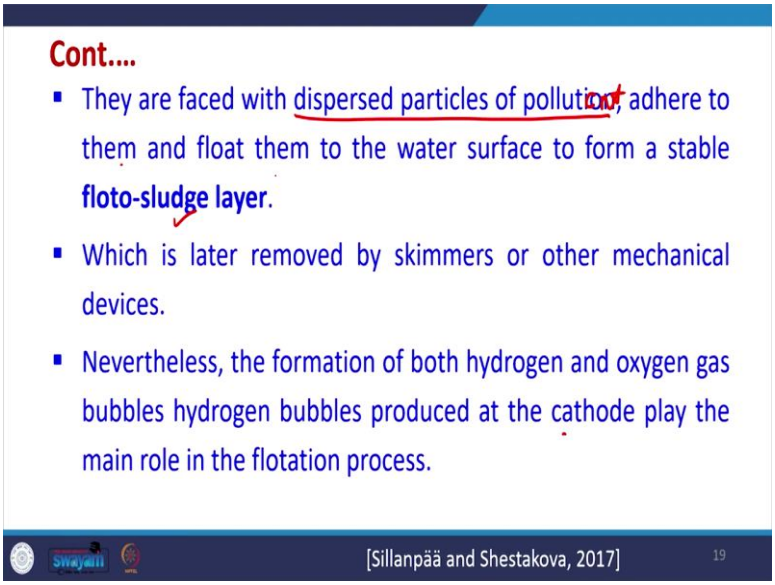

And so, they are faced with that dispersed particles of the pollutants which are there, so, that pollutants may be there and they are adhered to them and float them to the water surface to form a stable floto-sludge layer in a way this may be called which is later on skimmed and by various means, may be mechanical devices to remove them from the top of the surface. So, the formation of both hydrogen and oxygen gas bubbles produce at the cathode or anode, they play the main role in the flotation process.

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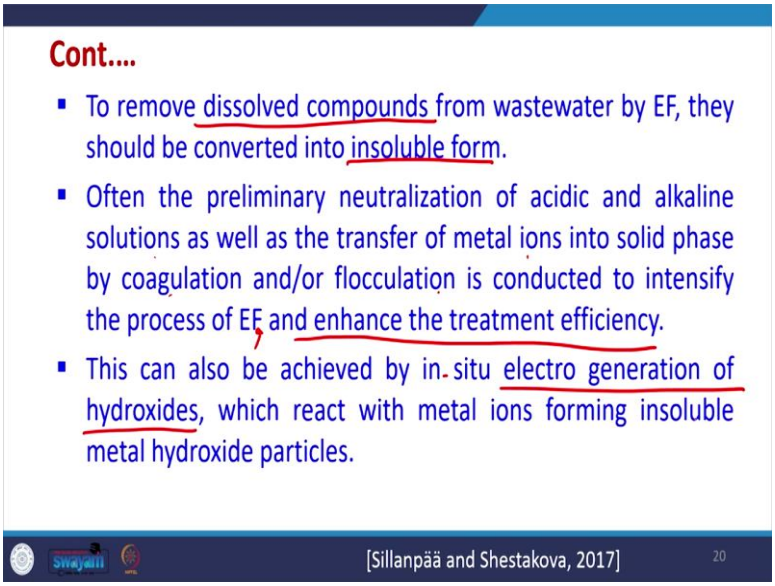

To remove dissolved compound from wastewater by electro flotation they should be converted into insoluble form. So, any dissolved compounds which may be present in the water, if you want to float them, they should be converted into insoluble form. Often this can

be done by neutralization of acid and alkaline solutions as well as the transfer of metal ions into the solid phase by coagulation and or flocculation.

So, during electro-coagulation also electro-flotation may work along with them. So, and it actually enhances the overall treatment efficiency if both are working together, this can also be achieved by in situ electro generation of hydroxide which react with metal ions forming insoluble metal hydroxide particles, so, that is there.

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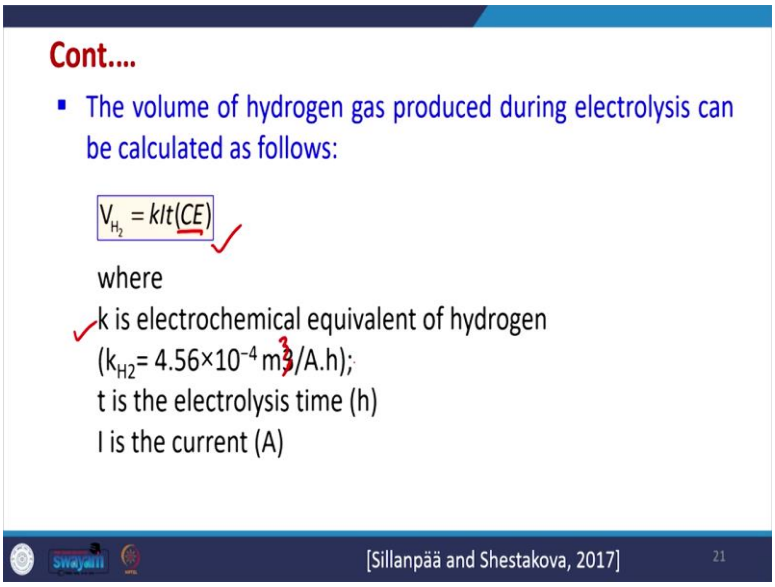

The volume of hydrogen gas produced during electrolysis can be calculated as follows:

$$V_{H_2} = kIt(CE)$$

where

k is electrochemical equivalent of hydrogen

(k_{H2}= 4.56×10^{-4} m3/A.h);

t is the electrolysis time (h)

I is the current (A)

Now, we can also perform some calculations, that how much volume of hydrogen gas is getting produced during electrolysis? So, that can be calculated using this particular equation,

where C is the current efficiency that we, this formula was given earlier as well. So, k is the electrochemical equivalent of hydrogen so, this is given here, this is 4.56 10 raise to minus 4 meter cube per ampere hour, t is the electrolysis time and I is the current.

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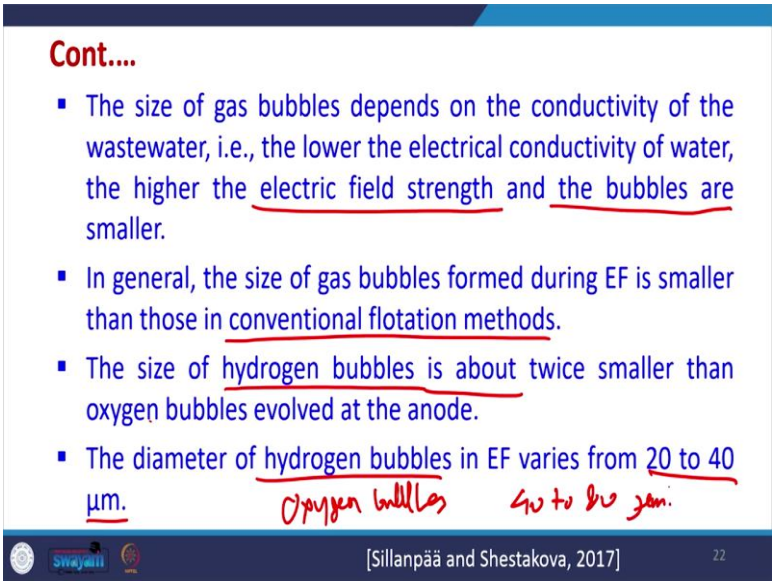

The size of gas bubbles that depend it depends upon the conductivity of the wastewater. So, what is the size and how much amount of gas bubble formation is taking place? So, this is important. So, the size will depend upon the conductivity of the waste water, the lower the electrical conductivity of the water, higher is the electric field distance and that bubbles formed are smaller in size. In general the size of gas bubbles formed during the electro-flotation is smaller than those in the conventional flotation method. So, here the size of bubbles is much smaller.

The size of hydrogen bubble in general is around twice that size of the oxygen bubbles evolved as the anode and the diameter of hydrogen bubbles itself may vary from 20 to 40 micrometer. So, it is a, so, does the oxygen bubbles will be ties up that it may be a little bit more than this.

So, hydrogen bubbles are smaller oxygen bubbles are much larger as compared to hydrogen bubbles. So, and hydrogen bubbles themselves are in the range of 20 to 40 micrometer. So, thus the oxygen bubble may range from 40 to 80 micrometer So, this may be the size range. So, it may vary certainly depending upon the conditions.

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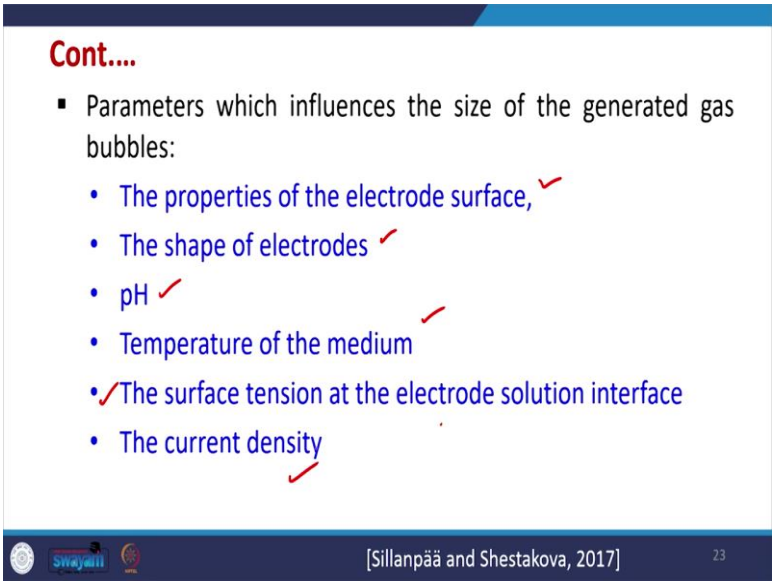

So, parameters which influence the size of generated gas bubbles, so, there are similar to electro-oxidation, electrocoagulation the property of electrode surface, the shape of electrodes also is very important, whether it is meshed or not, whether it is played electrodes depending upon various shape and type.

So, it will depend upon that, then the pH temperature, surface tension is very, very important parameter first gas bubbles generation. So, the surface tension at the electrode solution interface is very important and the current density which is common for all electrochemical treatment system.

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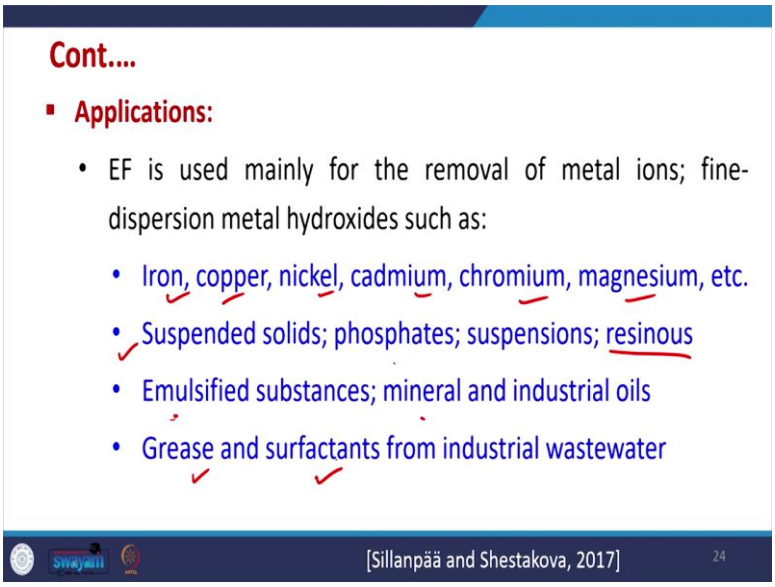

This electro-flotation system can be used for removal of metal ions, fine dispersed metal hydroxide such as iron, copper, nickel, cadmium, chromium, any of these can be removed. Similarly, it can be used for removal of suspended solids, phosphates, some suspensions and resinous also, then emulsified substances minerals, industrial oils etc, can be separated. Similarly, grease and surfactants can be removed from industrial wastewater using electro-flotation technique.

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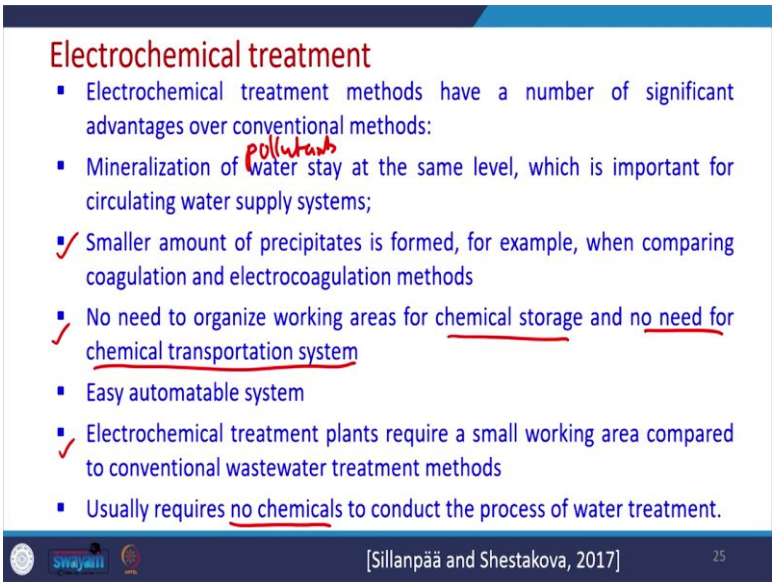

Now, after studying electro -coagulation, electro-oxidation and electro-flotation, few general slides are given for electrochemical treatment here. So, electrochemical treatment have evolved in last 10, 20 years and they have lots of significant advantages over conventional method.

So, they can perform mineralization of pollutants very quickly also depending upon the various parameters, and they can totally oxidize many of the pollutants present in the water and small if suppose electro-coagulation we are using, so, it is smaller amount of precipitates are formed when comparing the coagulation and electrocoagulation both of them together because we can here control the in situ generation of coagulants. So, that helps in reducing the amount of sludge foam as compared to traditional coagulation method.

There is no need to organize working area for chemical storage, no need for chemical transportation system etc in the coagulation, electro-coagulation method and they are easily automatable system. Then electro chemical treatment plants require a small working areas compared to conventional wastewater treatment methods. And generally they will not require

any chemical except that if conductivity is not there, we may have to use salts from outside, so, this is there.

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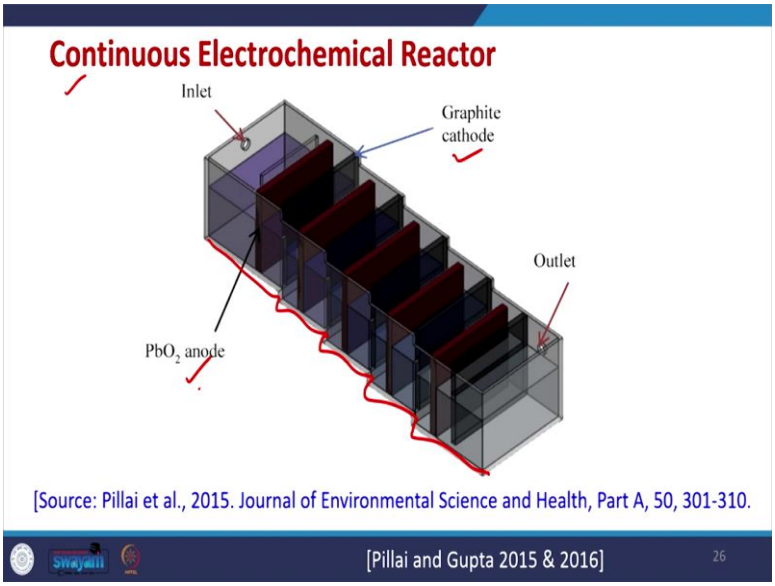

Some of the continuous electrochemical reactors are getting developed. So, this is one of the configuration which is given here with PbO2 and anode and graphite cathode, but any combination of electrodes are possible, any anode and cathode depending upon the type of water being treated the water containing which type of compound. So, depending upon all those things, we can choose any of the electrodes.

Then this is the simple water. So, we can see the water is flowing slowly and this is stepped also the natural flow of water this is one of the configuration, the different configurations are slowly and slowly getting reported in the literature and they are being used in the actual treatment of water in the industrial scale as well.

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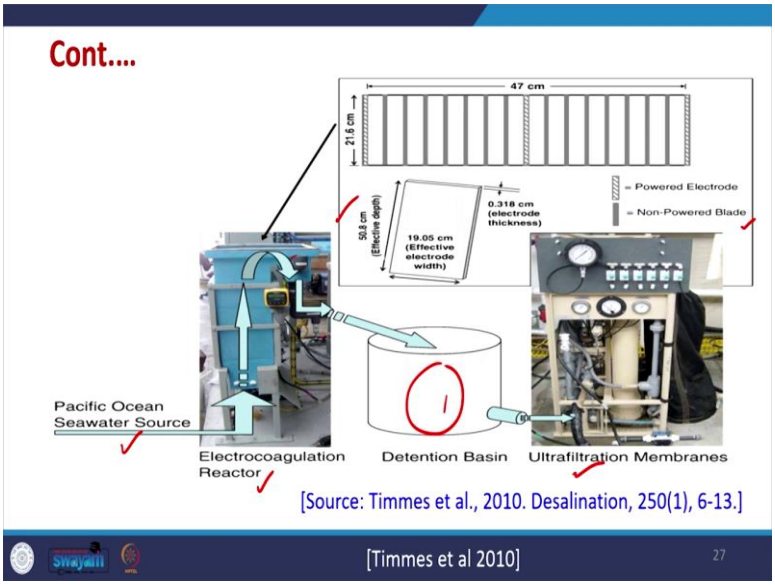

So, this is another which is reported, so, this is like Pacific Ocean sea water source, so electro-coagulation is being performed and after electro-coagulation there is some detention basin is which is there. So, the setup of electrocoagulation is given here, so, electrodes we can see a number of powered electrode and non-powered blades are there within this electrode configuration and after that this is being further treated by ultrafiltration membrane.

So, combination of electro chemical system with traditional wastewater treatment techniques is also possible or they can be used as a pretreatment step, also they can be used as one of the last step for treatment as well.

So, depending upon the water characteristic the uses of electrochemical technology is increasing and they have lots of scope and potential for further use. And any of the three techniques electro-oxidation, electro-coagulation, electro-flotation can be combined together depending upon the requirement as such for treatment of that particular wastewater.

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So, these are the some of the references which have been given here. You can go and study them. So, with this we will end this lecture on electrochemical treatment techniques. So, we will further study the AOP methods in next lecture. Thank you very much.