Physico-Chemical Processes for Wastewater Treatment
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Lecture 49
AOP: Electrochemical Wastewater Treatment – I

Good day everyone and welcome to these lectures on Physico-Chemical Processes for Wastewater Treatment. So, in the last few lectures we are studying advanced oxidation processes. And we have already studied regarding photocatalysis, fenton method and ozone treatment. So, we will go further and understand another technique of AOP which is called as electrochemical wastewater treatment.

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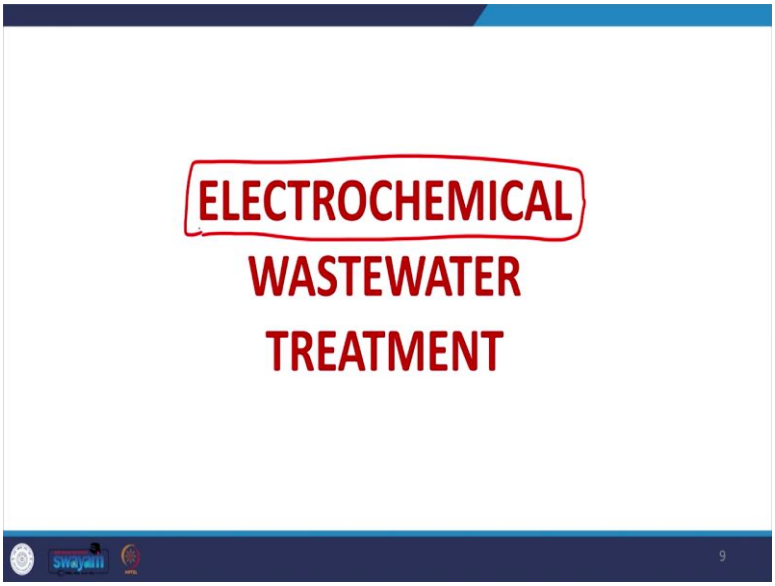

So, this electrochemical technique is getting developed and it has lots of potential of uses for wastewater treatment, in particular for those wastewater which cannot be treated by traditional means. And so, this technique can be used in many peculiar industries for wastewater treatment.

So, we will try to understand that, what is electrochemical technique? How it works? Within electrochemical technique there are three different possibilities which are there. So, we will understand this electrochemical technique more in detail as compared to other techniques that we have studied till now.

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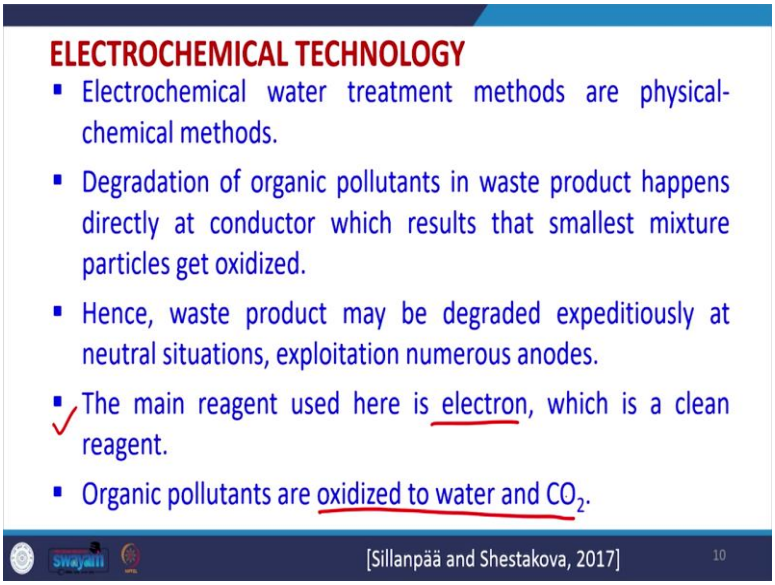

So, we will continue further. So, this electrochemical technology we will classify into physical electrochemical method. And in this case, the degradation of organic pollutants in the wastewater happens directly at the conductor, which results in smallest mixture particles getting oxidized. So, actually we use a lot of electrodes and the degradation of organic pollutants may happen directly on the electrode or they may be reduced on cathode. Also, these electrodes generate lot of hydroxyl radical or reactive oxygen species and that degrade the product.

So, we have all the direct oxidation, indirect oxidation, indirect other techniques, coagulation etc, also possible. So we will try to understand this technique in detail. The main region which is used here is electron which is transferred through the outer line and so, we have a circuit which is there. So, electron is supplied via electrode into the water and this reagent actually helps in the overall treatment of the wastewater. Organic pollutants which are present in the water are oxidized into water and CO2.

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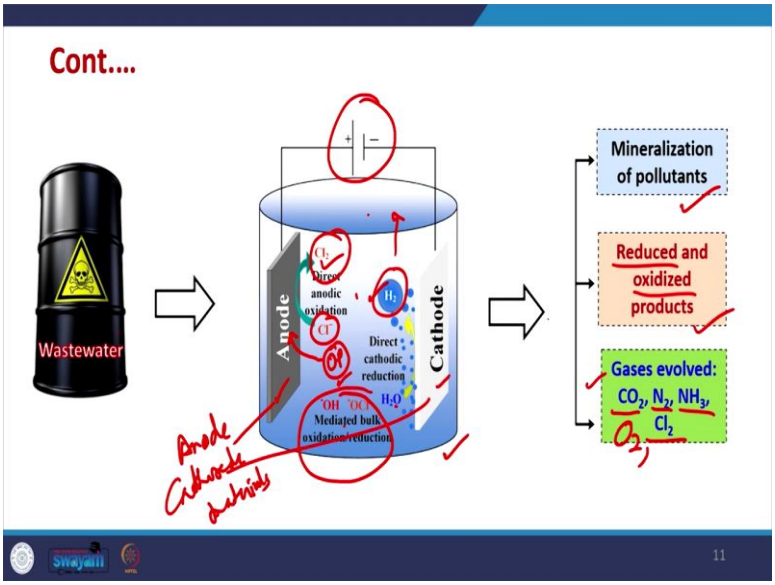

So, all the AOP techniques work on the same manner. So, here some diagram is given. So, what we do is that, we have some reactor in which anode and cathode are there. Now, these anode materials, what are the different anode materials, cathode materials that we will understand later, that what are these materials, how to choose them. So, this is there because a lot of ideas required for them.

Now, we have anode and cathode, now, on this anode, there may be possibility that suppose any organic pollutant I am writing this as OP, organic pollutant is there. So, this may go into on to the surface of anode and get oxidized. So, we have direct anodic oxidation which is happening.

Similarly, if this is possible to reduce it, it is possible it may go on the cathode and it may get reduced also. So, this is possible, now, these anode cathode in combination produce lot of bulk reactive oxidation species. So, they also oxidize this organic pollutant present in the water. So, this is called indirect oxidation. Also, depending upon the pH and other conditions if chlorine ion is present in the water it will produce chlorine and depending upon PH, this may produce hypochlorite and other things. So, that hypochlorite will further degrade the pollutant, so this is another mechanism.

And similarly, water will get also converted into H2. So, that water H2 may go out, now these gases which are getting generated, they may take some of the pollutant to the top of the surface. So, any of the possibilities are there, there are many possibilities in electrochemical wastewater treatment.

So, wastewater treatment goes into this, any other things may happen, mineralization of pollutant is possible, the pollutants may be reduced or oxidized any of these things may happen, we may have gases which may get evolved like CO2, N2, NH3, Cl2, O2, all these gases may evolve out of the water. So, all these possibilities are there.

Certainly, how to choose the electrode material? How they are connected? Because only two electrodes will not be there, a number of electrodes will be there, how to convert this technology into continuous mode? So, all these things are highly great to learn all these things in detail.

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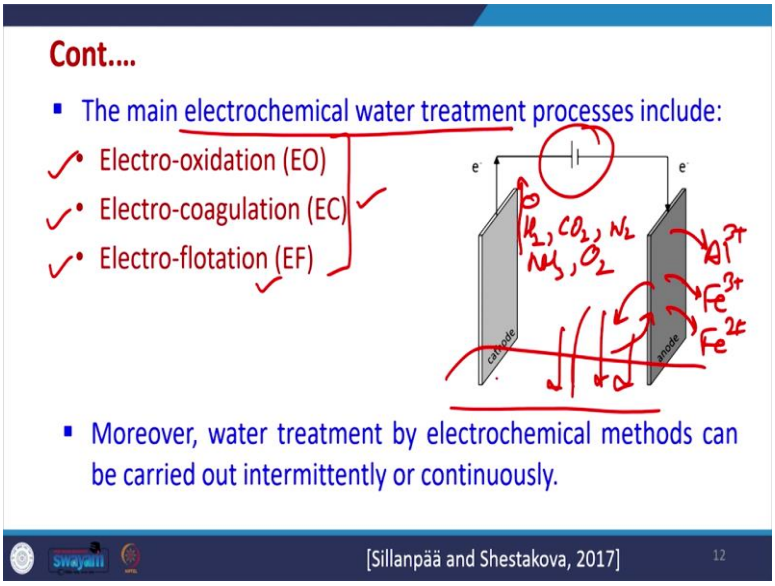

Now, the main electrochemical wastewater treatment process, it includes three processes. So, there are three different possibilities, one is called electro-oxidation and another is called electro-coagulation and third one is called electro-flotation. So, electrochemical in general will mean any of these or combination of these.

So, we will try to learn each of the techniques in detail, in the electro-coagulation there is a difference, I will just explain very quickly. In the electro-oxidation we have already studied, this cathode or anode they are stable, so, pollutant, organic pollutant get oxidized on the surface of the electrodes or via the reactive oxygen species which are generated in the bulk.

In the electrocoagulation actually what happens? This anode is made of either aluminum or iron. So, depending upon the what type of material it is there, so, it will slowly leach into the water. So, that means, in a way we are adding coagulants into the water slowly and slowly depending upon the voltage which is there.

So, this Al 3 plus which is coming out or Fe 3 plus or Fe 2 plus depending upon the anode which is getting used, this will go into the water and then coagulation of organic compounds in the water will happen, but we will generate lots of sludge. So, this will go, everything will go into the sludge and that sludge has to be treated further. So, electro-coagulation is also possible.

Similarly, we have learned that lot of gas formation takes place. So, we have H2, we have CO2, we have N2, we have ammonia which is possible, then we have O2. So, all these gases when they are generated and any of the organic compound is which may go up if density is not good enough to settle down, so under that condition these gases will take any of the pollutant onto the top of the water. So, that is called electro-flotation and that will happen more if suppose grease is present, oil and grease are present in the water. So, we will be having lots of froth formation. So, these techniques can be used.

While electro-flotation to remove oil and grease out of the water also, so this is there. So, we will try to learn all these aspects more in detail, each of the technique will be discussed more in detail in electrochemical treatment. Now, there are different arrangement of electrodes which are possible.

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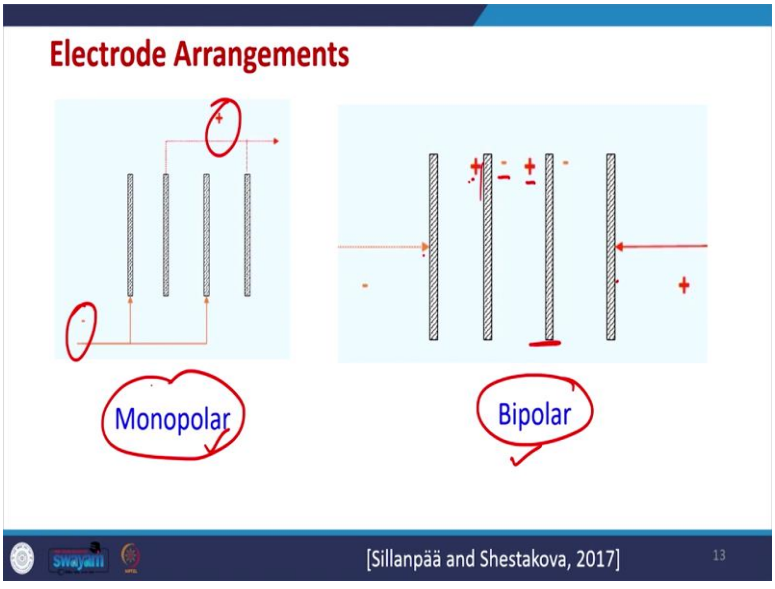

One is called monopolar another is called bipolar. So, suppose we have four electrodes, so, we can connect two of them to the this negative and two of them to be positive. So, this is possibility. There is another possibility that we connect only two of them. So, here this electrode is behaving negative with respect to this, and this electrode is this surface is

behaving positive with respect to this. Now, since this is positive so here, we have negative and positive, so, this is bipolar configuration, this is monopolar configuration.

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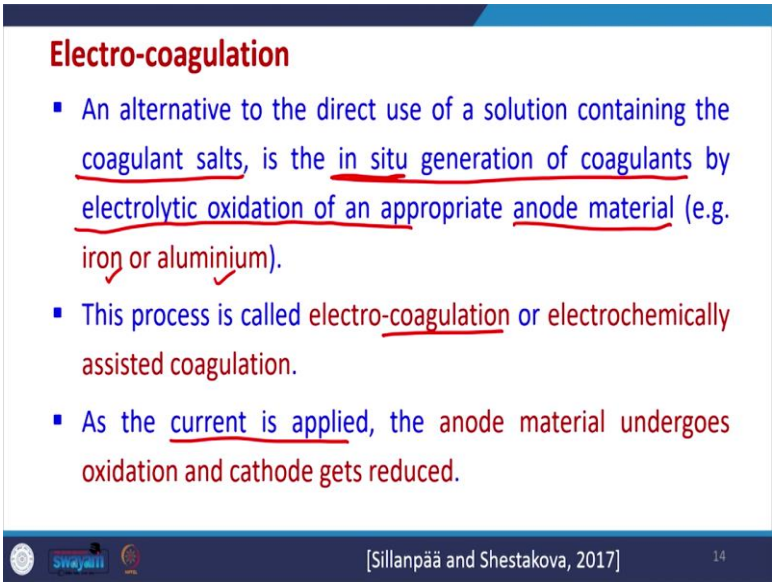

Now, we will start with one of the first technique, which is well reported. So, electro-coagulation. So, electro-coagulation there is a difference with respect to traditional coagulants. In the traditional coagulants, what we do is that, we use the coagulant salts and we add them into the solution directly. So, here in the electro-coagulation we in situ generate these coagulants by electrolytic oxidation of anode material, that anode material may be iron or aluminum.

So, depending upon the type of electrode material we use pH and also the voltage which is there, we generate in situ this electrode material, because from the anode, iron and aluminum is slowly and slowly leach. So, and once it goes into the solution, so, the coagulation will work. So, it is this mechanism it is called as electro-coagulation, because we are generating the coagulant in situ from the anode, because of its leaching with appropriate use of voltage and PH, so, this is there, as the current is applied the anode material undergoes oxidation and cathode gets reduce, so, this is there.

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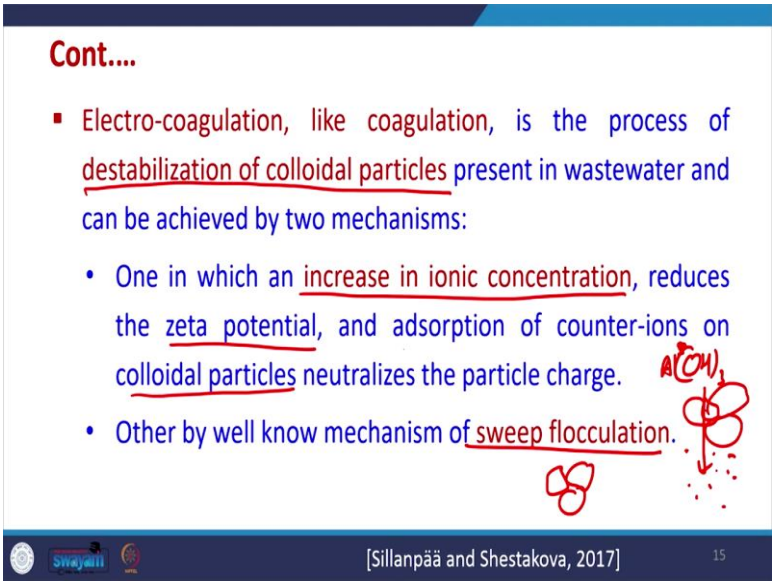

So, let us see. Electrocoagulation like coagulation is in the process of, as in the coagulation what we do is that, we destabilize the colloidal particles present in the water. So, this we have studied in detail during coagulation and flocculation section, that the colloidal particles which are not able to settle down if you can destabilize then, so, many colloidal particles first they will destabilize, so, their charge will get reduced.

So, if we are providing enough mixing, so, different colloidal particles may come together and they may form flocks and these flocks may settle down then, so, this is what is done. So, using the coagulants in situ coagulants, which are generated the colloidal particles are destabilized in the water.

Now, what are the mechanisms? One of them is that, the increase in the ionic concentration of other group will reduce zeta potential and adsorption of counter ions on the colloidal particle neutralize the particle charge. So, this is what happens, because we are continuously generating Fe 2 plus or Al 3 plus or Fe 3 plus, depending upon the type of electrode. Other well known mechanism is, sweep flocculation because, if the pH condition is high and we have Al aluminum which is getting generated, so, we will be having Al OH 3, now, this will be having a bigger size.

So, because it is having a bigger size, when it settles down any smaller organic compounds which are there in its vicinity, they get trapped inside this flock, so, that because of that, the sweep coagulation or sweep flocculation may happen, so, this is there.

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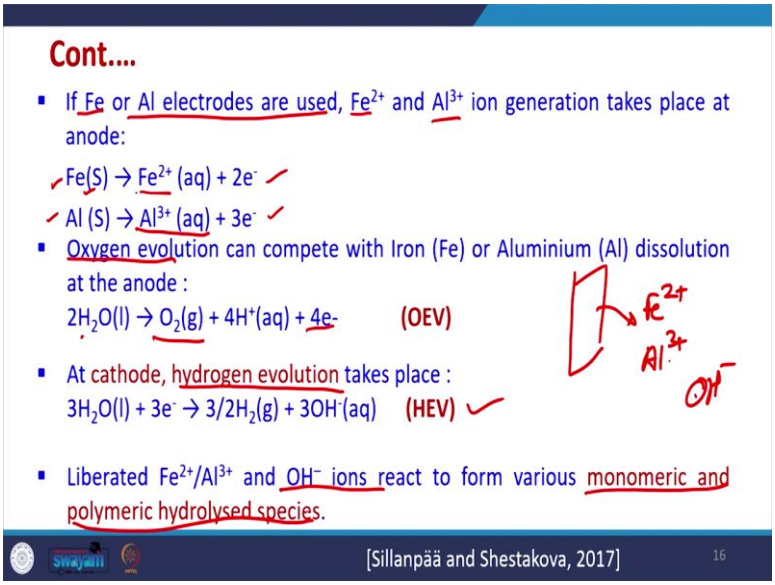

Now, let us understand further, if suppose iron or aluminum electrodes are used. So, we may generate Fe 2 plus or Al 3 plus ion generation via this mechanism. So, if we have iron, iron in solid form will get converted into Fe 2 plus with release of two electrons, similarly, aluminum will get converted into Al 3 plus with the release of three electron.

Now, some other evolution, high oxygen evolution and hydrogen evolution reaction will also take place whenever voltage is applied. So, depending upon these will compete with iron and aluminum dissolution reaction at the anode and the reaction is like water getting converted into O2 4H plus and 4 minus electron minus. Similarly, at cathode hydrogen evolution reaction may take place via this particular reaction.

Now, what will happen this Fe 2 plus and Al 3 plus ion so, they are getting released out of the anode. So, suppose this is the anode and from here either depending upon the iron or aluminum, so, these will come out. So, if they are coming out and already different OH ions present in the water, because depending on the pH conditions, so they may react with this and the reaction may form different types of monomeric or polymeric hydrolyzed species depending upon pH.

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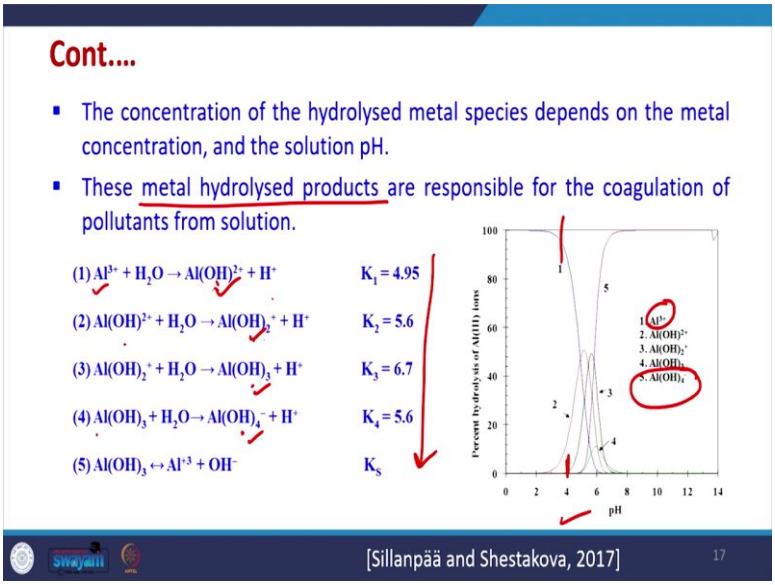

So, this also we have understood earlier, that if the depending upon the pH if suppose pH is less so, the metal hydrolyzed products which are responsible for coagulation of pollutant from solution so, any of these may be possibility is there. So, how they are formed? It is seen here, that if Al 3 plus is there it will combine with water to form Al OH2 plus this may combine with water to form Al OH2 only single this is monomeric, then Al OH3 then Al OH4 minus and these are its K1 values or PK values we can calculate and from this we can draw this graph.

So, we can see up to 4 pH the majority of Al if aluminum is getting released, it will remain as such Al 3 plus, beyond certain pH value, it will be Al OH4 minus. So, this is a graph assuming that other types of anions cations are not present. So, this will not be graph exactly in the water because other cations, ions are not, are also present in the water but still, we can understand from it some of the basics. So, this way these ions of aluminum will be present and they will destabilize that collide present in the water.

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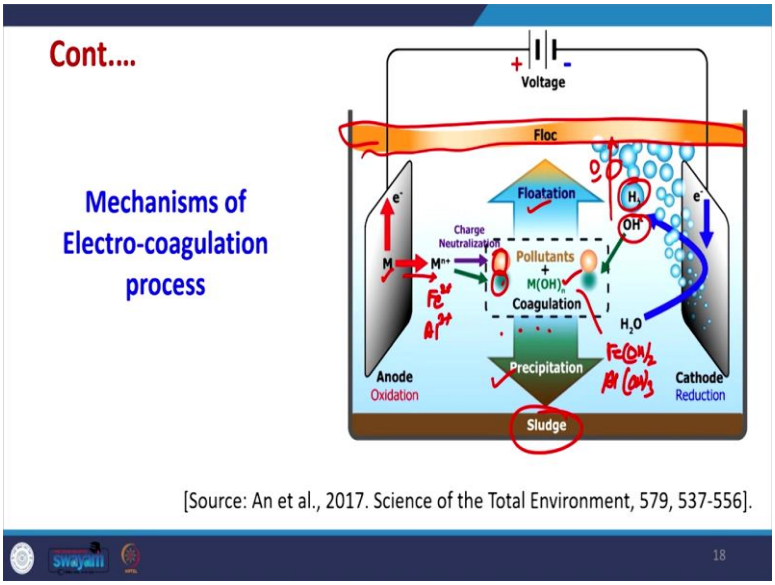

So, this is how it works. So, some mechanism is given here of electro-coagulation we can see, so, we have metal coming out in the form of Mn plus so, it may be called as Fe 2 plus or Al 3 plus, now, this will neutralize these colloidal particles, so, this is possible one possibility is this. Second possibility is that, they may react with OH minus ion to form M OH n so, that may be, we can call it Fe OH 2 or Al OH 3 so, this is possibility. So, this way they may settle down and in between any pollutant are there so, that will also precipitate

So, we have sludge which is getting formed also these gases are getting generated H2 similarly O2 gas or any other. So, any of organic compounds are present that will go to the top, so we have flog forth formation or floc here you can see here, so, this is a for both precipitation flotation is possible in the electro-coagulation process.

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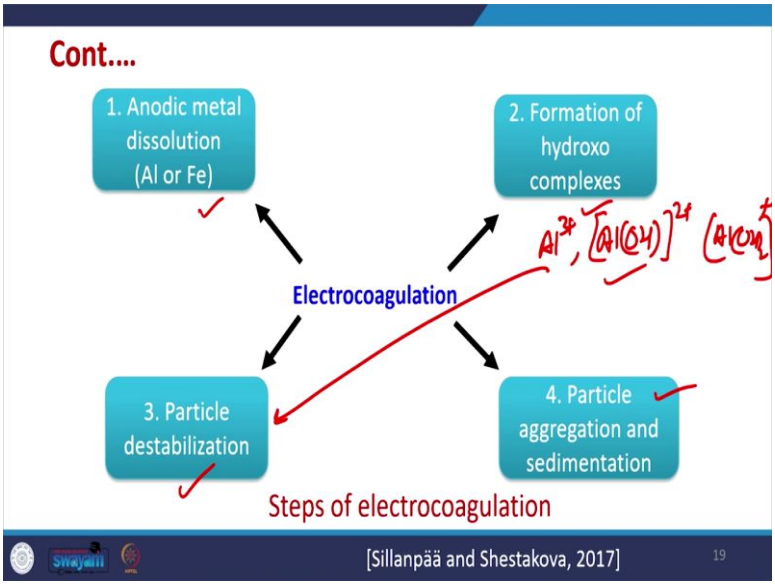

Now, electro-coagulation, so, we have a anodic metal dissolution, this is one thing which is happening, also formation of hydroxo complexes. So, we have already told that we have possibility of Al 3 plus Al OH overall if we call it 2 plus the similarly Al OH 2 overall it will be only plus. So, all these complexes are possible.

Similarly, these Al 3 plus this will destabilize the particle and also once destabilization occurs, there is a possibility of aggregation and settling down, so, these are the different steps which are there in the electro-coagulation, these are the different types of electro-coagulation unit we can see here.

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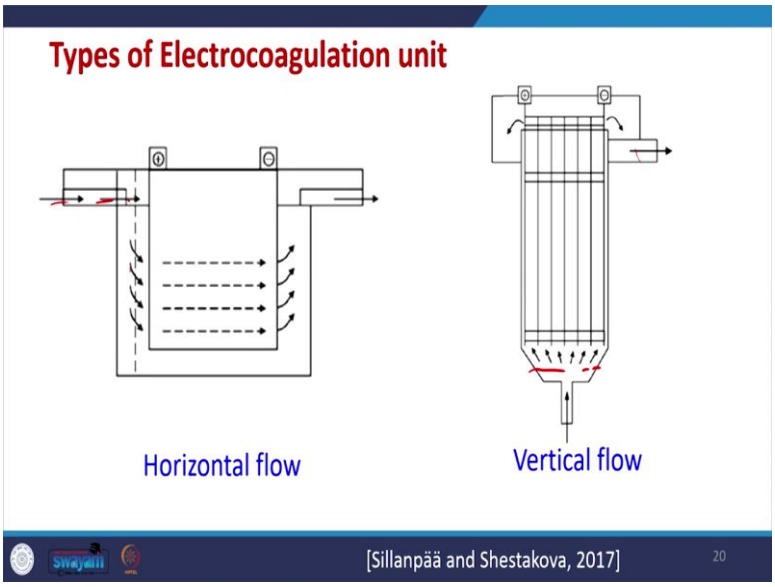

So, this is how the flow is happening, so we have different types of configurations which is possible, this is vertical flow, this is horizontal flow, here, these electrodes we can see here, they are connected differently either in monopolar mode or bipolar mode and the water is going up and after treatment it is settling down, the sludge will settle down here, there are different possibilities of electro-coagulation being used for wastewater treatment.

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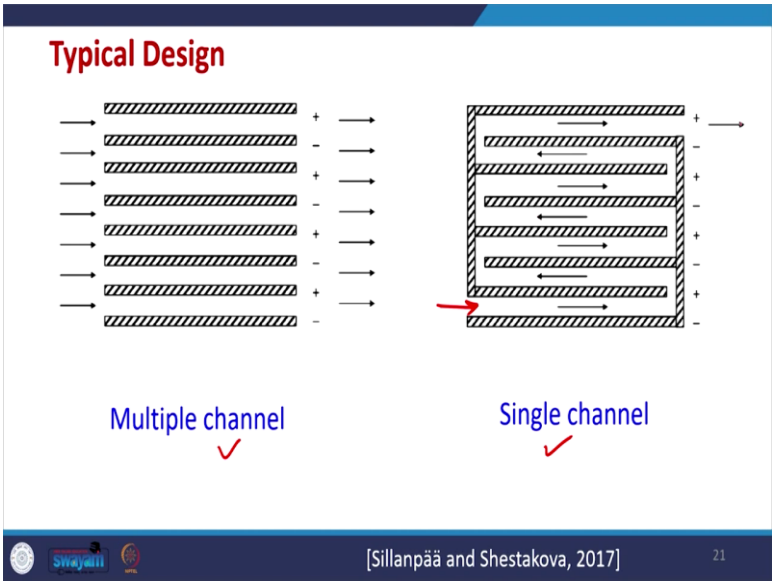

The typical design we can see here, this is positive this is negative, the water is flowing like this, then there is another possibility this is a multi-channel, there is a single channel possibility that water is going from here, it is going like this and the treatment happens once it passes through. So, all these typical design units are there. And these design units are not only for electro-coagulation this is true for electro-oxidation as well. So, we will continue further and learn little bit about the principles, though I have already understood.

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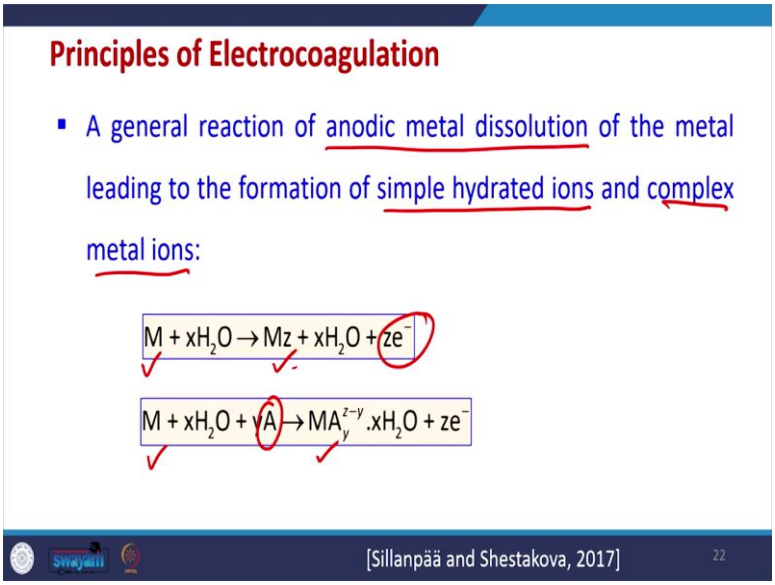

A general reaction of anodic metal dissolution of the metal leading to the formation of simple hydrated ions and complex metal ions is shown here. So, M is getting removed. So, we have M which is coming out and we have electron which is getting generated. Now, similarly metal can form this type of complex also, depending upon whether something is available in the water or not. So, these complexes are also possible.

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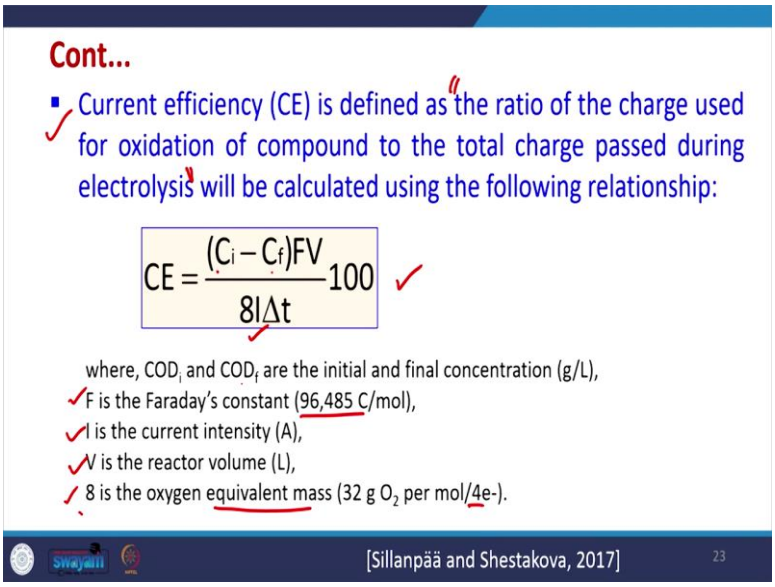

Current efficiency (CE) is defined as:

$$CE = \frac{(C_i - C_f)FV}{8I\Delta t}100$$

where, COD_i and COD_f are the initial and final concentration (g/L),

F is the Faraday's constant (96,485 C/mol),

I is the current intensity (A),

V is the reactor volume (L),

8 is the oxygen equivalent mass (32 g O_2 per mol/4e-).

Then, there are some other terms which are very common in electro-coagulation electro-oxidation et cetera, and one of the term is called as current efficiency. So, it is defined as the ratio of charge used for oxidation of compound or for release of metals to the total charge passed during the electrolysis. So, this is calculated using this formula and were the Ci and Cf may be the initial COD final COD are concentrations initial concentration, final concentration etc, F is the Faraday's constant which is well known 96,485 coulomb per mole.

Then, here I the current density, current intensity, V is the reactor volume, 8 is the oxygen equivalent mass for oxygen, so, it is 32 gram per oxygen per mole divided by 4, so, that is 8. So, we can calculate the current efficiency to know at what efficiency the system is performing better.

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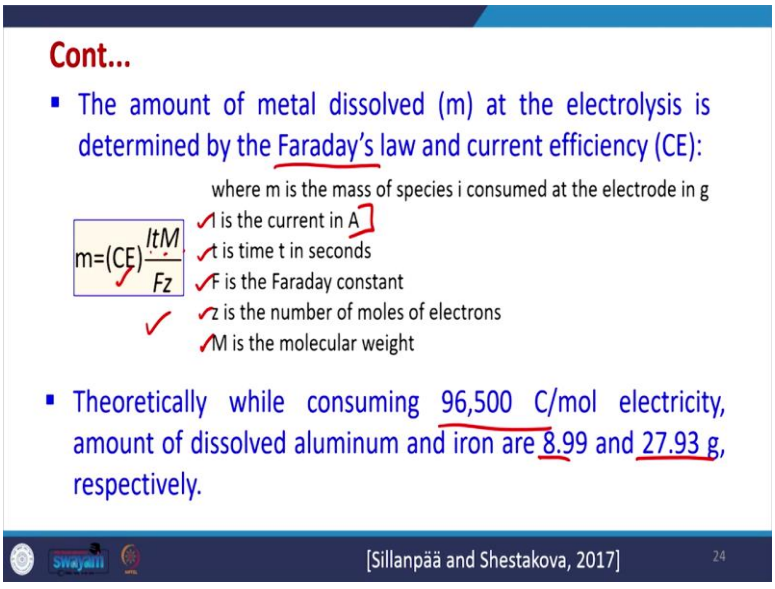

The amount of metal dissolved (m) at the electrolysis is determined by the Faraday's law and current efficiency (CE):

$$m=(CE)\frac{ItM}{Fz}$$

where m is the mass of species i consumed at the electrode in g

I is the current in A

t is time t in seconds

F is the Faraday constant

z is the number of moles of electrons

M is the molecular weight

Similarly, we should know the amount of metal dissolved at the electrolysis, so, this can be determined by Faraday's law and current efficiency. So, this is the relationship, CE is the current efficiency and ItM Fz, so, I is the current, t is the time, F is the Faraday's constant, z is the number of moles of electrons, it will depend whether we are using aluminum or iron and M is the molecular weight.

So, theoretically while consuming this much coulomb per mole electricity amount of aluminum dissolved or iron dissolved should be this, but it may be different and while manipulating this we can slowly release the coagulant as per our desirability, so, this type of calculation can be done for the electro-coagulation system also.

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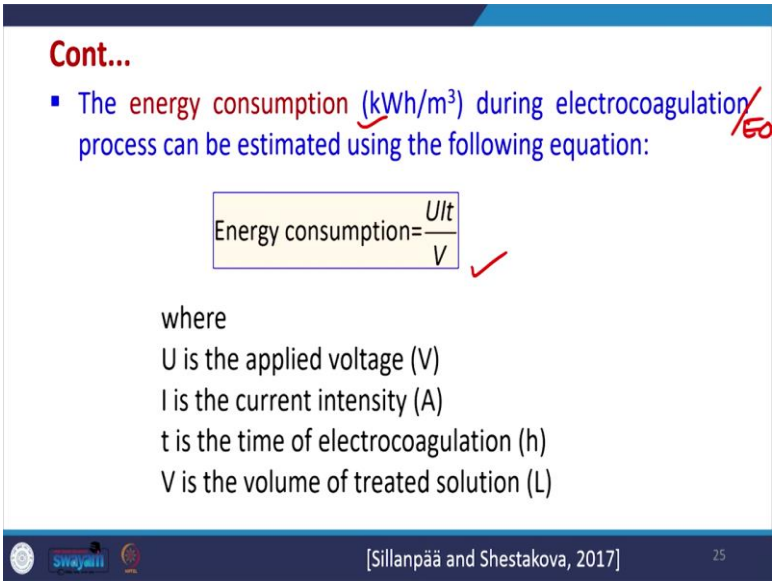

The energy consumption (kWh/m^3) during electrocoagulation process can be estimated using the following equation:

$$\text{Energy consumption} = \frac{UIt}{V}$$

where

U is the applied voltage (V)

I is the current intensity (A)

t is the time of electrocoagulation (h)

V is the volume of treated solution (L)

Similarly, we should find out the energy consumption during treatment. So, this is always found out that, what is the kilowatt hour of energy consumed for the overall unit per meter cube during electro-coagulation. We can do it for electro-oxidation also and this can be performed calculated via this particular equation. So, we can calculate the energy consumptions also. So, we perform all these calculations.

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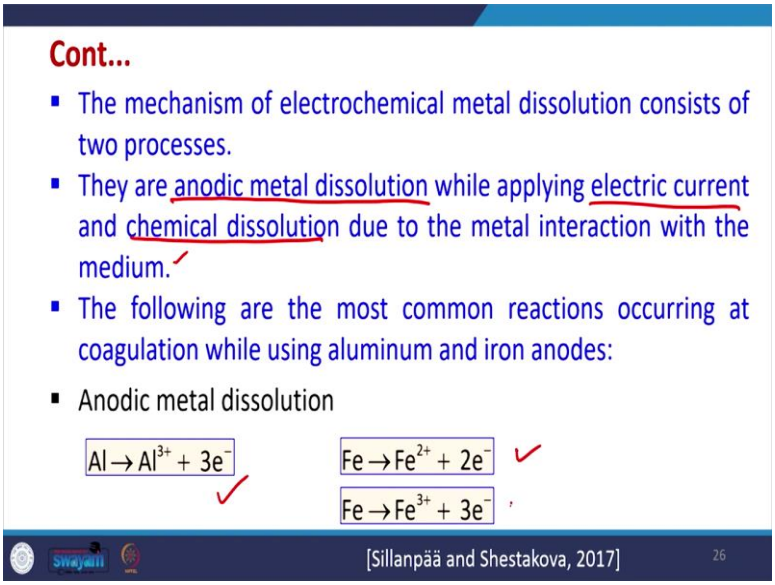

The mechanism of electrochemical metal dissolution consists of two processes. So, they are anodic metal dissolution, while applying electric current and chemical dissolution also due to the metal interaction with the medium. So, depending upon the pH, there will be chemical dissolution also, and also what type of species are present in the water and there will always be anodic metal dissolution because of electric current. The following are the most common reactions occurring in the coagulation. So, already we have known these things, so, this is there.

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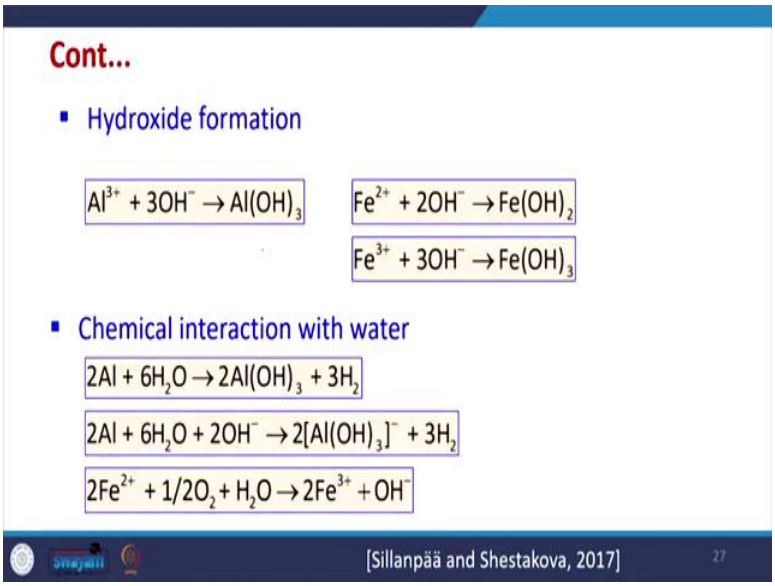

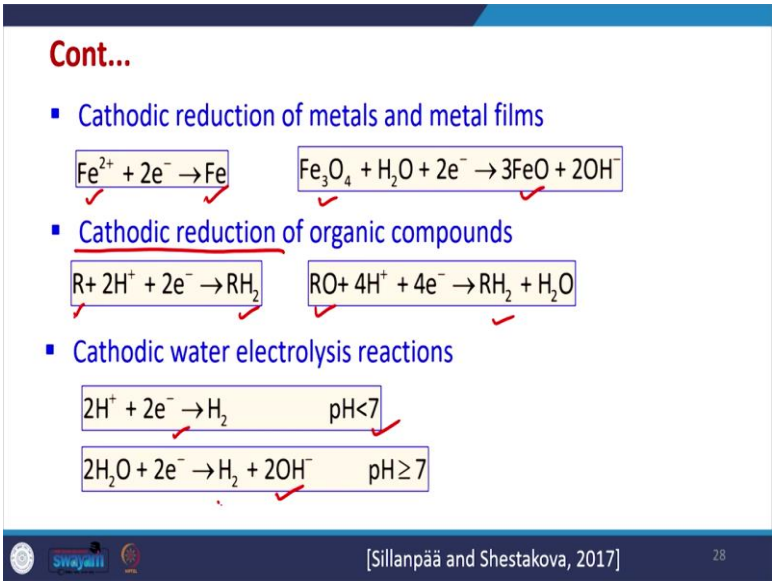

And hydroxide formation will take place we have already studied, then chemical interaction with water is possible this also we have understood and then cathodic reduction is also possible of metal and metal fields. So, we can see at the Fe 2 plus ions may get reduce on the cathode.

Similarly, here also we can see Fe 3 O4 also getting reduced into FeO, there is a possibility of cathodic reduction of organic compounds also. So, all these organic compound is getting reduced into this, so, depending upon that what type of organic compound? What is the pH? How much electricity we are applying or voltage which is there?

So, depending upon that these cathodic reduction reactions are possible during electro-coagulation, during electro-oxidation in any of the electrochemical technique. Then cathodic water electrolysis reaction is also possible depending upon pH. So, if pH is less this reaction will be dominate, if pH is more this reaction will be dominating. So, this is how the H2 generation reaction is happening.

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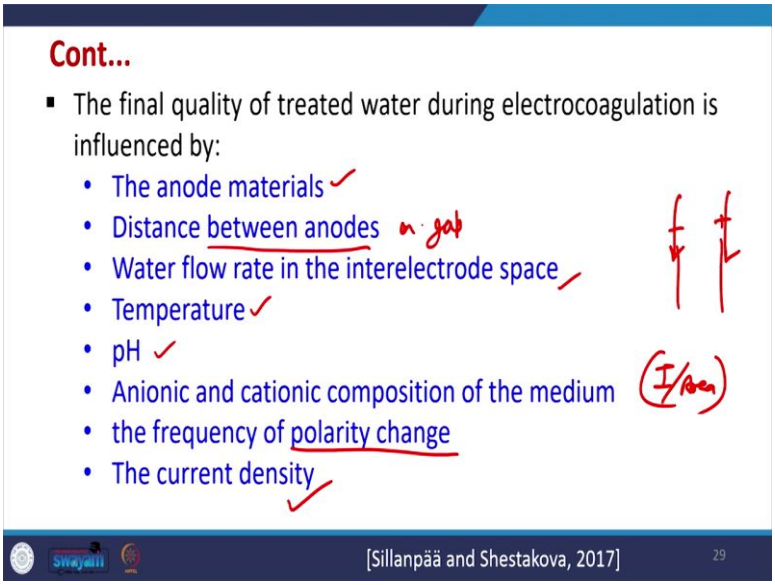

The final quality of treated water during electro-coagulation will be determined upon the type of anode material we are using, whether it is iron or aluminum or any other, what is the distance between the anode? This is called as or it is called as gap between the electrode that gap is very important because it will tell, what is the resistance, how much is the flow of ions inside the water. Then water flow rate in the interelectrode space what is the flow rate. So, we should have enough time so, that treatment may happen.

Depending upon the temperature pH and anionic and cationic composition of the water itself also because these electrodes they get passivated with time. So, many times what we do is that this negative and positive electrodes they are reversed. So, this is called polarity change. So, what is the frequency of polarity change?

And the most important thing what is the current density? What is the voltage which is applied and depending upon the voltage what is the current flowing through this electrode? So, that is very important. So, current density is basically current divided by the area of the electrode, so, this is there.

So, current density is important parameter and it is used in the scale up of these systems from the lab scale to the large scale. So, with this we will end today's lecture. Thank you very much. We will continue with the electro-oxidation and electro-flotation in the next lecture. Thank you.