

Advanced Aquaculture Technology
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Lecture 39

Bio-Electrochemical System-based Wastewater Treatment (Contd.)

Hello everyone, welcome to the fourth lecture of module-8, bio-electrochemical system based (aqua) wastewater system wastewater treatment for aquaculture, aquaculture sector in general. My name is Professor Gourav Dhar Bhowmick; I am from the department of agricultural and food engineering, department of IIT Kharagpur.

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Concepts Covered

- Introduction to Constructed Wetlands
- Constructed Wetlands – Microbial fuel cell
- Different other forms of Bio-electrochemical systems (BES)
 - Microbial Electrolysis Cell (MEC)
 - Microbial Electrosynthesis (MES)

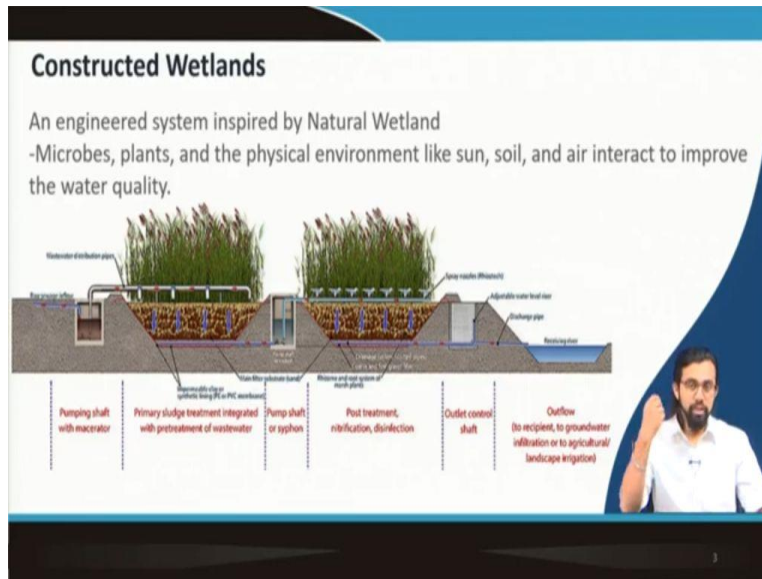
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The concepts that will be covered in this lecture material are the introduction to the constructed wetland, constructed wetland microbial fuel cell technologies, different other forms of bio-electrochemical systems like microbial electrolysis cell, microbial electrosynthesis cell. If you remember in the last lecture, we discussed about the microbial fuel cell; in general, we discussed how the microbial fuel cell can change the wastewater treatment region. Because, it will not only change, it will not only treat the wastewater aquaculture wastewater, but also it has the capacity to even you know generate electricity out of it, which is completely a bio-electricity.

That can be utilized in in as a you know for any low energy up taking devices to charge as well. So, here I will mainly be focusing on the constructed wetland, microbial fuel cell, and different other forms of BES. In the follow-up lecture also, I will continue with this lecture and continue

with this bio-electrochemical systems, where I will discuss about microbial desalination cell, sediment, microbial fuel cell et-cetera et-cetera. I hope you will be benefited with these new technologies that I am discussing here, which can be used in aquaculture sector as well.

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Constructed wetlands, you know it is an engineered system inspired by the natural wetland. It has microbes, plants and physical environment like sun, soil, and air interaction is help is utilized to improve the water quality. So, it is like mimicking the natural wetland ecosystem; and we call we call that is why we call them constructed wetland. You understand why it is named constructed wetland? So, this constructed wetland what we are doing? We are pumping the wastewater. We are pumping the wastewater to suppose a particular type of species, and a particular type of wetland in a wetland with the crops.

This crops what they are doing? They will consume the waste material; I mean the pollutant present in the waste; I mean like the wastewater, they will consume it for their you know to convert it to the biomass, because they are beneficial to them. Suppose in your wastewater, you have nitrogen or a high amount of nitrate; the nitrate can be beneficial for the crop for those wetland plant. So, they will consume them and they will make them in their biomass; they will convert it to the bio into their biomass like you know. Because of this changes, what is happening? The water pollutant level goes down; it is as simple as that.

So, then the water which is coming out of this wetland is kind of pollutant free. The removal efficiency can vary. But, the remove the most of the cases, the organic or nitrogenous or say like any other pollutant level is witnessed by different investigators to be drastically lowered than its source like you know; then it is a point of application. In this particular picture, if you see in this figure in this system, they have like you know two phase wetland systems. In the one phase, they treat it; they are collecting in a particular storm. Then, again they pump it, they treat it and they collect it in a particular pump; and then they receiving water body is there like you know , which the first stage first wetland is kind of (consi) you know.

It acts like primary sludge treatment in a unit, integrated with the free treatment of the wastewater. The next one is the kind of a post treatment, nitrification, and the disinfection unit. Then, outlet shaft, and then the outflow, where the recipient or say like surface water body, or groundwater, also infiltration to the agricultural landscape irrigation systems. So, in general, how it looks like, you I think you have understood; it is very simple. But, it is very effective wastewater treatment system. And it is used for in different sectors, in if if you remember we will discuss, we discussed about the wastewater aquaculture; I will discuss more about in details in later lectures, like what is what was wastewater feed aquaculture.

So, there we we use these kinds of systems. So, this not only in aquaculture what is the additional thing with this? This instead of this only wetland, we can introduce in between we can introduce the pond as well. In between, in in between if we introduce a pond; that pond can also be used to reduce the load of the wastewater. What type of wastewater I am discussing here? Say like municipality wastewater okay. In case of municipality wastewater and all, there is less chance of having heavy metals; and I mean nowadays it is, but earlier it was not. There is a more of a it is mainly constitutes of the greywater, which does have the organic substances mainly, majorly; and some other surfactants and all.

These organic substances and all that can be reduced, that can be utilized by the wetland, by those wastewater fed aquaculture. And then they reduce the pollutant load of the water; and then that water can be easily supplied to the receiving water bodies, anyway. So that is a different discussion; so in general, that is how the constructed wetland works.


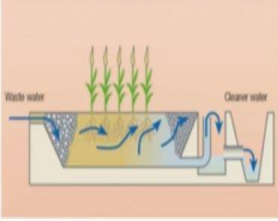
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Why Constructed Wetlands (CWs)

- No electricity
- No chemical
- No sludge problem
- No machine
- Low-cost construction with local material
- Very low operation and maintenance costs
- Suitable for variable flows and remote locations
- Really Green! Like a garden

But there are some limitations

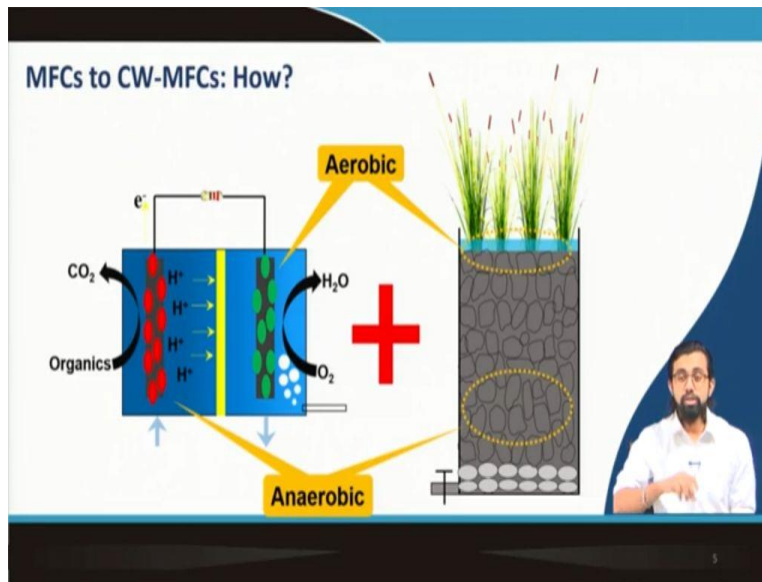
- Need Large land area
- Relatively slow process
- Moderate Treatment Performance



So, what is the why constructed wetland, why we should go ahead? Why, what is the benefit of this kind of technology? First, no electricity, no chemical is required, no sludge problem, no missionaries involved, very low-cost construction with the local material; this like you know inbound natural material, very low operation and the maintenance cost. It is it is suitable for variable flow, shock flow like in a very remote location; and it is really green and like gardening okay. What are the limitations? It needs some large land area, and relatively slow process, and moderate treatment performance is witnessed.

Other than this three, in most of the cases this constructed wetland has very high acceptance range in wastewater treatment regimes.

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Now, so what is my constructed wetland microbial fuel cell? Microbial fuel cell, we discussed in last presentation last lecture right, it is very important; try to understand, you try to remember. In microbial fuel cell we have anaerobic chamber, which is anodic chamber; aerobic chamber, which is the cathodic chamber. What is happening in the anodic anaerobic chamber? The anaerobes, exoelectrogens, a specific type of microorganisms, which can grow there in the over the anodic surface.

They consume the pollutant from the wastewater and they convert it to different different ions like electrons and protons say. These electrons are moving through the external circuit; and the protons are moving through the proton exchange membrane; and it will come to the cathodic chamber. Once it will come to the cathodic chamber, it will react with the terminal electron acceptor. What is the terminal acceptor? very famously used Oxygen. Oxygen is, it is very much available in the nature, in atmosphere.

That oxygen is supplying this oxygen; react with this electrons and the protons, which is coming from the other way, and then it will form H_2O . By this way, one cycle is cycle is finished; and because cycle is there, and because of this cycle, what has happened? We can get the electric response from this kind of fuel cells microbial. That is why it is called microbial fuel cell. The same if you just simply rotate it, and if you see constructed wetland is something like that only;

because, after a certain height, the mostly they are in constructed wetland, the anaerobic situation is prevailed.

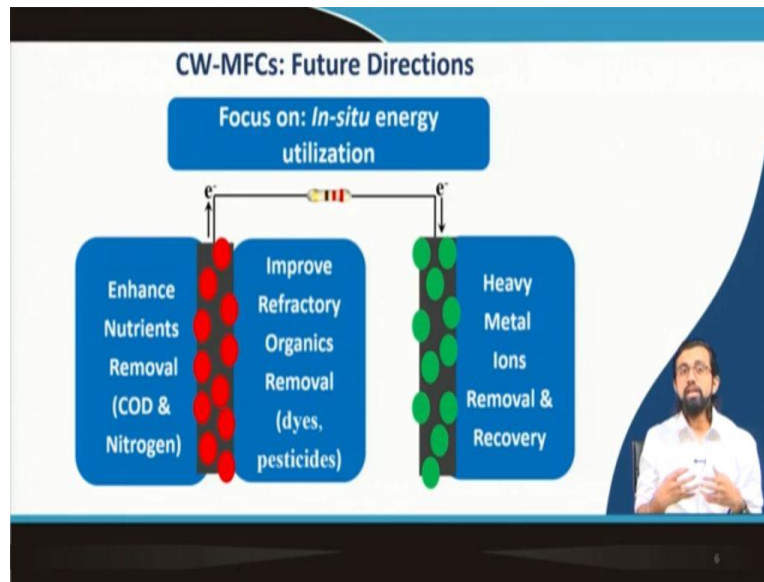
And and in the top, it is like mainly the water it has this water, available water; and it has mainly in contact with the atmosphere, that place is aerobic in nature. Why not we use it as a constructed as a constructed wetland microbial fuel cell? That is what is being done. In that is why what is the future direction of this kind of constructed wetland microbial fuel cell? So, what it what is done if I if I give you again in a very brief way. Anode is placed in the bottom, in a far like you know or like a little bit far from the surface; and the cathode is placed on the on the surface of this constructed wetland.

And then it is connected through external wire; we do not need any membrane or nothing. You will see the, you can see the changes in the electricity; because I mean it is change in the potential You can see the potential difference is there, if you put the multimeter. And that if you can harvest and it is a more like a school project we used to do. You have a pot like a big pot. In this big pot, you have your the normal soil, you use you have your crop in this pot. You keep on adding a water and nutrient solution time to time for your crop to grow. So, what you do in the pot? In the bottom you place.

And the extreme bottom you place one graphite plate, or say carbon plate, or carbon rod. And there at the top, you plate one carbon rod. You connect them with the titanium wire or say a copper wire; and in the middle, you put the resistance say 100 ohm, 200 ohm resistance. Time to time after certain days, you will see that there is a changes in the electric port and the changes in the (potential); you can you can witness the potential difference. That means the electricity is getting like you know generated there. If you put a small LED bulb there, you will see the LED bulb will lead. So, you can try it, you can try; this is like school days experiment that we used to do; so it is more like that.

So, if you, the why it is happening? Because of the anaerobicity. There because of the the in the plate, there is some exoelectrogens they keep on growing. And because of the water which we are supplying along with the nutrient that will help to grow them very nicely in the bottom; and they will it is like it will replicate replicating the microbial fuel cell in general.

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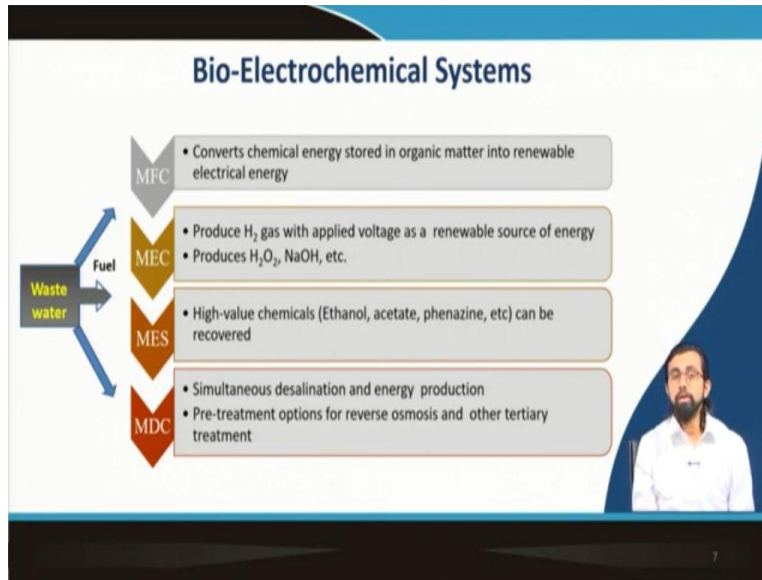


This, what is the future options for this kind of constructed wetland microbial fuel cell? It can be used to enhance the nutrient removal chemical oxygen demand, plus nitrogen removal, organic (refran) refractory organics removal, refractory organics. What do I mean by the refractory organics? What is degradable? You know biodegradable and degradable, biodegradable organics. What is refractory organics? Refractory organics you know in a in a gross way, you can you can just; you should understand that refractory is maybe we can call them hardly biodegradable component.

Hardly biodegradable component because there is now science has progressed in, up to very highest in a very high speed; and it has reached to that stage that there is nothing called non-biodegradable. Now, everything is biodegrade, everything is biodegradable; we have even found some type of fungi which can even consume the plastic. So nothing is non-biodegradable; so, there is biodegradable, there are hardly biodegradable. So, refractory compounds are some they are like this. They have this benzene rings and all; because of that, it is very hard for them to, hard for the biological compound to degrade them like dyes, pesticides and all.

Even this kind of waste constructed wetland microbial fuel cell can be used to reduce, to remove these kinds of pollutants as well, which has which is refractory in nature. It can be used for heavy metal removal and heavy metal iron recovery and removal; And this is these are all the users.

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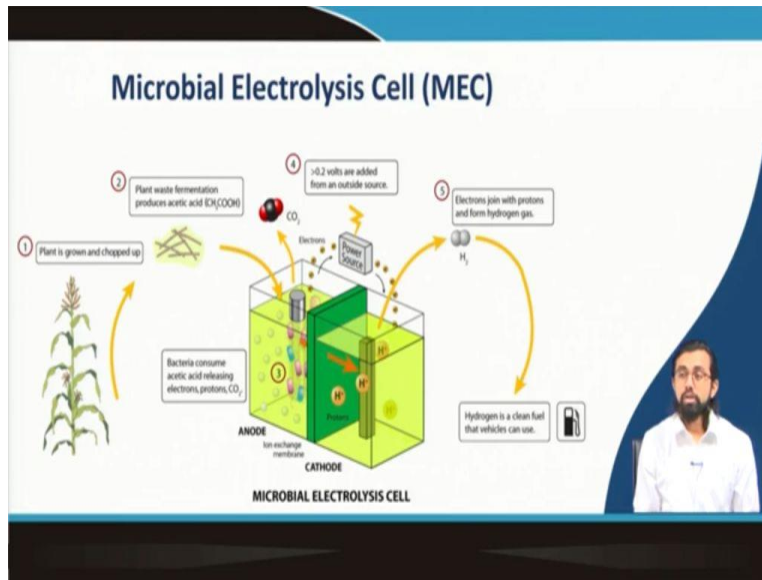
What are the other type of bio-electrochemical systems? We discussed already discussed about the microbial fuel cell, which converts the chemical energy stored in organic matter into renewable electricity, electrical energy. Now, we will discuss about the MEC and MES in this lecture; and the coming lecture I will discuss about the MDC. What is MEC? Microbial Electrolysis Cell. What is what is it saying? It is saying that it can produce hydrogen gas with the applied voltage as a renewable source of energy; and it can produce the H₂O to NaOH et-cetera.

I will discuss about in coming slide. What is MES? Microbial Electrosynthesis Cell; it has a high value. You can you can recover high value chemical like ethanol, acetate, phenazine et-cetera from out of nowhere. I would say out of nowhere, because all maybe you can use the flue gases. Like You can simply use the carbon dioxide; what is flue gases right? In the industrial gas, industrial release of gas which we can call is flue gases. That flue gases if you supply it here, it does contain huge amount of carbon dioxide. That carbon dioxide can be captured and utilized to recover high value chemicals using this microbial electrosynthesis cell.

Is not it amazing, is not it something is very interesting? I will discuss about it in detail how it works. And another one is Microbial Desalination Cell MDC. In a desalination from the name itself you can understand what is what it does? It desalinate the saline water. So, simultaneous desalination energy production is possible from microbial desalination cell Okay. And it can be used as a pre-treatment option for reverse osmosis and other tertiary treatment. I will discuss

about it in next lecture. So, today I will mainly be focusing in the coming couple of slides MEC and MES.

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To start with the microbial electrolysis cell, if you remember as I discussed, it is a it is also bio-electrochemical system. It does also have anode and cathode and all these things okay. In the anode what is happening? You have some inoculums, you have some you are providing some inoculums; you are providing some say plant waste or a normal waste and all. In that from that waste and all, and it is connected to a power source. In that power source, you have to provide more than 0.2 volt of potential difference like voltage.

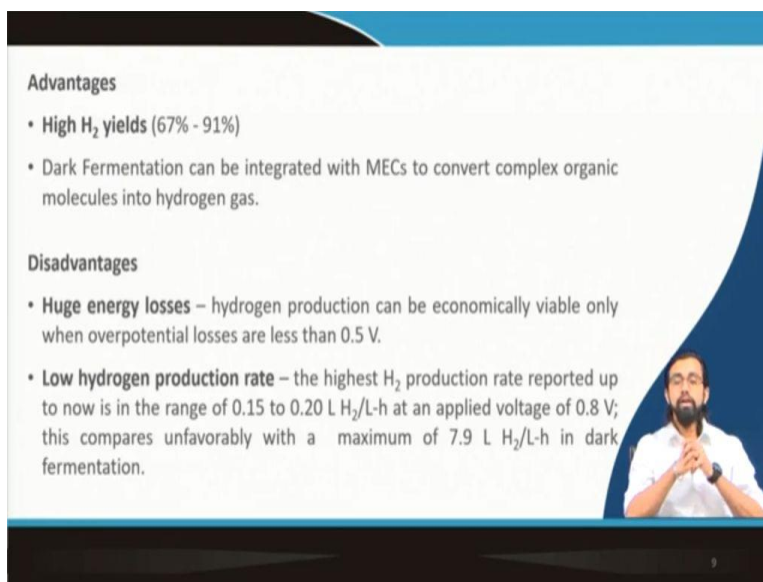
Once you are applying this from this outside source of this particular amount of power, like this point more than 0.2 volt of potential difference to anode and cathode. What will happen? In the cathode, in the anode there is this exoelectrogens will be developed; they will consume the acetate and all. They will consume this acetic acid and they will release the electrons, protons, and carbon dioxide. And this protons, which will come through the proton exchange membrane towards the cathodic side, and the electrons which are being supplied from the power source; there is no (external) external terminal electron acceptor here. What is happening?

The electron and this proton is they combined in the surface of the cathode and they form H_2 ; pure H_2 , which is used as a clean fuel that vehicles can be used. So, microbial electrolysis cell is used to generate hydrogen pure hydrogen okay. So, this is this is not up to the you know, you

cannot say like it is not as good as hydrogen fuel cells and all; but, it does also people are also working on it. And there is a high chance it will also surplus with this you know; it will also surplus. It is I mean like it will somehow manage its all the cons part of the disadvantages of it; and in the very near future, it will also be a very reproducible system and cutting it.

It is already cutting edge technology, a lot of industries are also working on it. They in maybe very near future, you will see it in a home to home bases like this kind of microbial electrolysis cell generate the hydrogen; which will be used for you know has a very high calorific value that can be used for as an alternative to the all the non-renewable fuel sources and all okay; the fossil fuels and all.

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Advantages

- High H₂ yields (67% - 91%)
- Dark Fermentation can be integrated with MECs to convert complex organic molecules into hydrogen gas.

Disadvantages

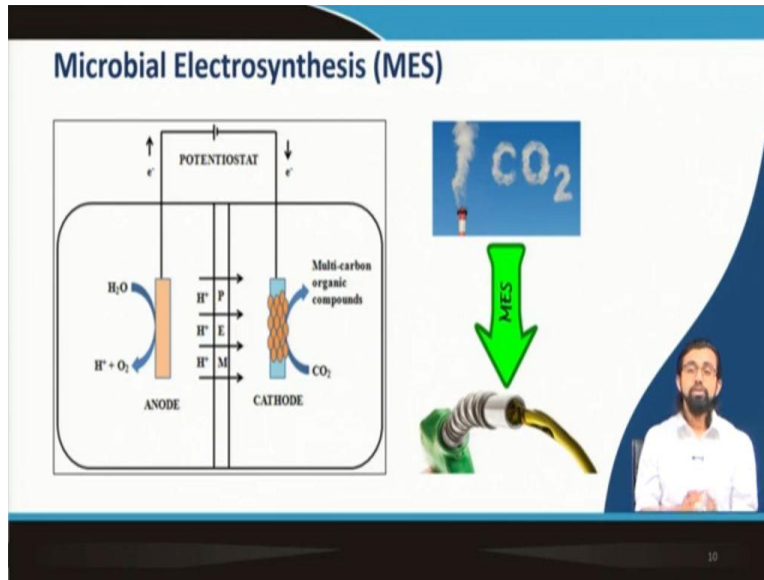
- **Huge energy losses** – hydrogen production can be economically viable only when overpotential losses are less than 0.5 V.
- **Low hydrogen production rate** – the highest H₂ production rate reported up to now is in the range of 0.15 to 0.20 L H₂/L-h at an applied voltage of 0.8 V; this compares unfavorably with a maximum of 7.9 L H₂/L-h in dark fermentation.

So, what are the advantages of it? It has a very high hydrogen yield capacity almost 67 to 91 percentage. Dark fermentation can be integrated with MECs to convert any complex organic molecule into hydrogen gas. What is the disadvantage? A huge energy loss; hydrogen production can be economically viable only when over potential losses are less than point 5 volt. And low hydrogen production rate like you know; in general, that is what I was talking that time. In general, the highest hydrogen production rate reported up to now is in the range of point 15 to point 2 liter of hydrogen per liter per hour, of at an applied voltage of point 8 volts.

This compares unfavorably with the maximum 7.9 liter of hydrogen per liter per hour in dark fermentation method. Anyway, if you can make proper combination of dark fermentation or

MFC MEC; and if you can improvise the electrochemistry of MEC, and we really work on it. There are a lot of people working on it, experts working on it from all over the world. So, definitely we can come out with some solutions, which will which will further increase the hydrogen yield. And in general, it will have a very high effective application in treatment of wastewater as well as electricity regeneration.

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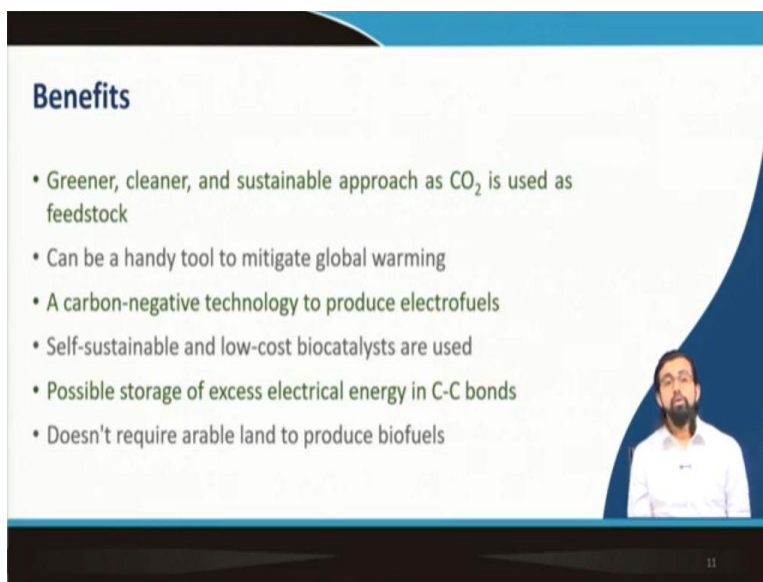
Microbial electrosynthesis cell is electrosynthesis cell and all; that is what we were discussing in last last two slides also. Remember that I told you that it is used to generate you know some very important byproduct, very valued byproduct I would say okay. How it is done? You simply have a potentiostat where you apply the external potential. In your cathode, you are supplying with the flue gases; especially you supplied with the pure carbon dioxide if you want to increase the efficiency. This carbon dioxide upon accepting the protons and accepting the electrons from the potentiostat, it will convert into much multi carbon organic compounds like ethanol, butanol et-cetera, which has a very high potential market value.

So, it is like carbon dioxide is used fast; it is used, it is considered you know, it is reducing the carbon dioxide (consump). I mean, it is reducing the carbon dioxide emission from the industry, when you it is used. And you know from in the for industrial flue gases, it can be used as a carbon dioxide utilization and in the capturing device; and this capturing. And it can also give you the byproduct which has also a very high end value and all. Nowadays, in different places in

Europe, in India also people, a lot of people are working on this technology microbial electrosynthesis cell, MES.

Just remember it; it will be a very futuristic technology that I am discussing here. It is it has the capacity to convert carbon dioxide in a valuable byproducts in biofuel; simply completely biofuel. And also the whole technology requires a very less amount of you know energy and all; rather than all the other technologies available for generating the biofuels and all okay. And it is also not only generating biofuels, but also it is reducing the carbon impact of of the system, of the of your industry, of your farm and all okay. So, this is how the microbial electrosynthesis works.

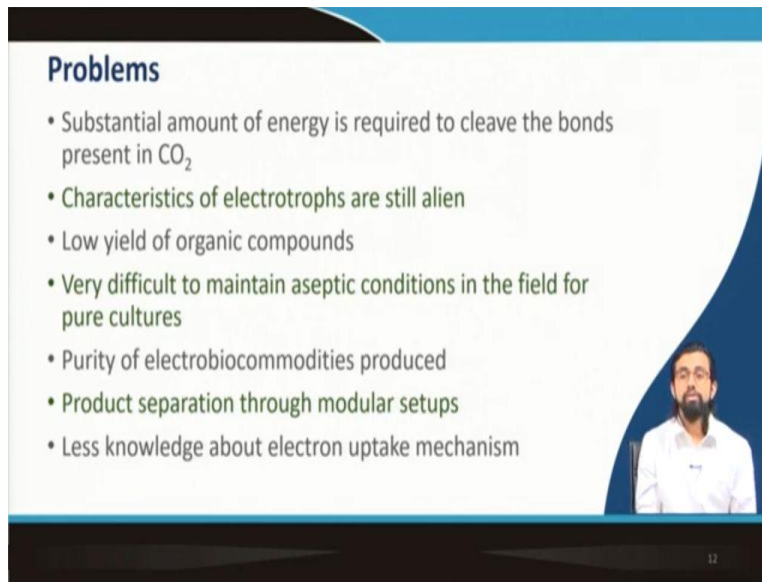
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In general, it is used for, it is a very greener, cleaner, and sustainable approach of as carbon dioxide is used as a feedstock. And this carbon dioxide can be introduced this all the industrial carbon dioxide that is being generated through the flue gas of the food processing industries and all. Or aquaculture processing industries and all that can be supplied to this kind of system, which can be a very handy tool to mitigate the global warming as well. It is a carbon negative technology to produce electrofuels or the biofuels. It is self-sustainable and very low-cost biocatalyst can be used.

Possible storage of excess electrical energy in C-C bond; and does not require arable land to produce biofuel.

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Problems

- Substantial amount of energy is required to cleave the bonds present in CO₂
- Characteristics of electrotrophy are still alien
- Low yield of organic compounds
- Very difficult to maintain aseptic conditions in the field for pure cultures
- Purity of electrobiocommodities produced
- Product separation through modular setups
- Less knowledge about electron uptake mechanism

It has a lot of benefits and; but, obviously it comes with some problems as well, some disadvantages as well. And what are the disadvantages? Substantial amount of this energy which is required to keep the bond present in the carbon dioxide; because you know carbon dioxide has to be first the bond (dissociation) dissociation energy has to be supplied; and then only it can form the other high end byproduct. The characteristics of the electro electrophy electrotrophy are still alien; means the electrotrophy that is used that is normally generated, or they form the bio fuel over the anode is still alien; and still people do not know.

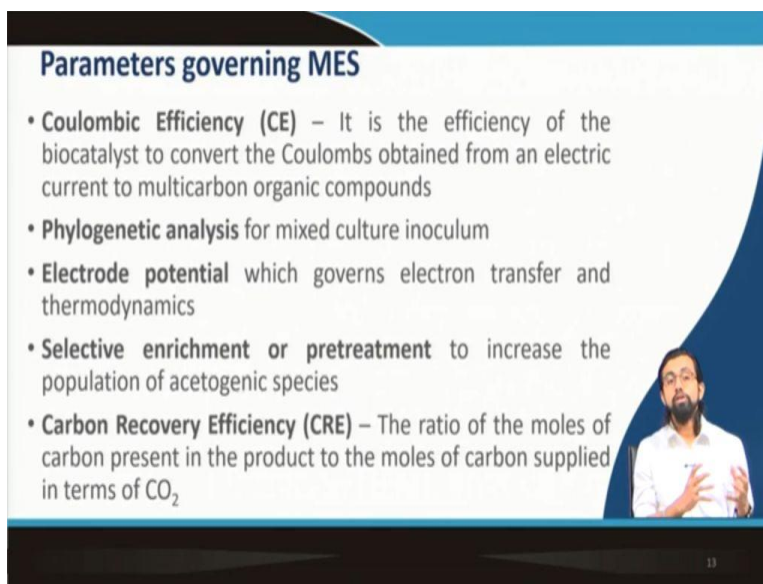
Still experts are trying to understand more and more details about it. Still, the science is, I would say the experts have already come up with some very important outcomes and important parameter identification. But, still some work to be done to be 100 percent sure about the exact characteristics and the total fallout of the events okay. The low yield of organic compound; one problem you know is this ethanol's and all, it is not you cannot do it in a industrial scale; people have started doing it. Now, a couple of industries in Europe, they have already started it; especially, in Belgium and the in Netherlands. But, the problem is like they are still; it is very, the yield is very low okay.

So, and also the purity is also very important; the purity is also, because it comes with a different production and all. So, you have to be very precise about segregation of the product of your byproduct; and also it is very difficult to maintain aseptic condition in the field in the field of you

know for pure culture. Suppose, you are providing any pure culture, but it is very difficult to that you can get rid of all the other microorganisms, or all the other pathogens and all. Because aseptic conditions, in general what is called like an aseptic means? A microbial free situation, or like harmful microbial free situation in general, we call aseptic condition.

The product separation through the molecular modular setup is very difficult; and less knowledge about the electron optic mechanism. Still, we are struggling stills, we are working in it all over the world; different lot of experts are working on it. Even in our lab in IIT Kharagpur also people are working on it; how what how this electron optic uptake mechanism is working. How deep how from this (elect) this electrophile, this exoelectrogens; the electrons are being consumed by the, like you know these electrons are being transferred to anode and all. Anodic biofilm, through anodic biofilm to the anode, it is still a matter of discussion matter of, still some activities. Experts are working all over the world to understand the mechanism in details.

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Parameters governing MES

- **Coulombic Efficiency (CE)** – It is the efficiency of the biocatalyst to convert the Coulombs obtained from an electric current to multicarbon organic compounds
- **Phylogenetic analysis** for mixed culture inoculum
- **Electrode potential** which governs electron transfer and thermodynamics
- **Selective enrichment or pretreatment** to increase the population of acetogenic species
- **Carbon Recovery Efficiency (CRE)** – The ratio of the moles of carbon present in the product to the moles of carbon supplied in terms of CO₂

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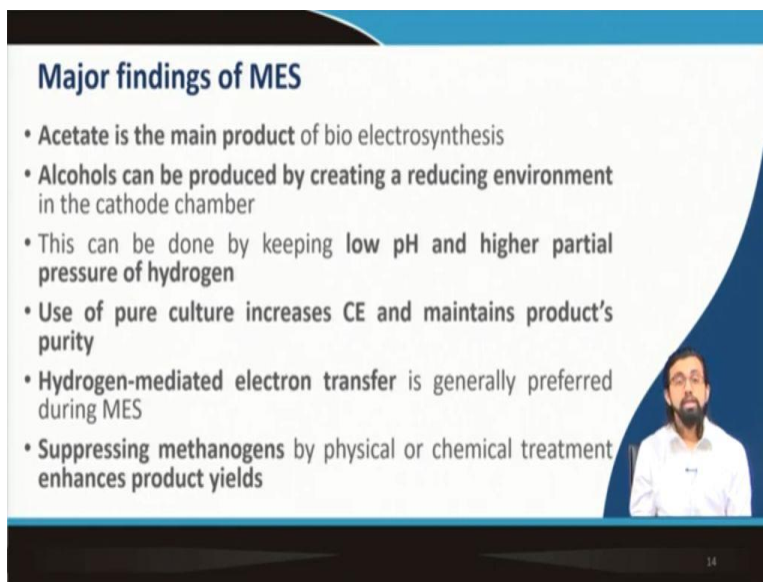
What are the parameters that govern the MES? Mainly the Coulombic efficiency, which is the efficiency of the biocatalyst to convert the Coulombs obtained from an electrical current to multicarbon organic compounds. So, it is like in a denominator, we have the Coulomb available with electric current that you supplied. And in the numerator, you have the multicarbon organic compounds. You know What is Coulomb right? It is a unit of charge. So, this Coulombs, the amount of Coulomb present in electrical energy that you supplied, and the amount of Coulomb

that is you know required to make these to prepare this multicarbon organic compounds; is this efficiency is called the Coulombic efficiency.

Phylogenetic analysis of mixed culture inoculum is very important to understand the phylogenetic classification. Means what are the microorganisms? What are the type of archaea bacteria, or the virus, or fungus; whatever it is like it is present in the culture. Electrode potential, time to time to govern the electron transfer and the thermodynamics of the whole this fuel cell. To selective enrichment or the pre-treatment, to increase the population of acetogenic species. If you remember in last lecture, I discussed how acetogenic acetogenic species can be enriched; because we do need methanogenic population to be there.

Methanogenic population what they do? They will consume and they will kind of scavenge the electrons from the system; and it will reduce the overall efficiency. Carbon recovery efficiency: the ratio of the moles of carbon present in the product to the moles of carbon supplied in terms of carbon dioxide; this is called the carbon recovery efficiency.

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Major findings of MES

- Acetate is the main product of bio electrosynthesis
- Alcohols can be produced by creating a reducing environment in the cathode chamber
- This can be done by keeping low pH and higher partial pressure of hydrogen
- Use of pure culture increases CE and maintains product's purity
- Hydrogen-mediated electron transfer is generally preferred during MES
- Suppressing methanogens by physical or chemical treatment enhances product yields

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Some of the major findings of MES are the acetate is the main product of bio electrosynthesis. Alcohols can also be produced by creating a reducing environment in the cathodic chamber. This can be done by keeping a low pH and higher partial pressure of hydrogen in the cathodic chamber. Use of pure culture increases the Coulombic efficiency; and also it maintains the products purity. Hydrogen-mediated electron transfer is generally preferred during the microbial

electrosynthesis cell. And suppressing methanogens by physical or chemical treatment is very much important you know to enhance the acetogenic microbial quantum presence; and they can enhance the overall product yield.

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Take away message

- CW-MFC has many futuristic applications including in the field of aquaculture.
- MEC produces H_2 gas with applied voltage as a renewable source of energy.
- High-value chemicals (Ethanol, acetate, phenazine, etc.) can be recovered using MES.

Dr. Chandrajit

NIPTEL

So, I hope you get to know this two very interesting technology, cutting-edge technology I would say, which are there in the field and people are working on it. It has a lot of futuristic application in aquaculture; and it will be used in very much in the aquaculture in a very recent era. And it is started you people started already using it, especially the constructed wetland microbial fuel cell; or microbial electrosynthesis, electrosynthesis cell, or microbial electrolysis cell. And for different high-value chemical production and also hydrogen gas for biofuel production as well.

I hope this lecture material helps you helps you with the understanding of the by different bio-electrochemical system in general. I hope in the coming lecture, I will be discussing more in details about different other microbial desalination cell and all. And those will also be and also sediment microbial fuel cell, which will definitely help you with more in details; like how this bio-electrochemical systems can be used as a water treatment, futuristic water treatment option for aquaculture practices okay.

I hope you understood this technology in very good manner. If you want to know more in details, you can simply google search it; and you can simply see my profile as well. There also you can see some research paper, and review paper, and the book chapter, which you can follow to get

more details about it. I hope you get to know something very informative and nice information knowledge; and I hope it is helpful to you. Thank you so much; see you in the next lecture.