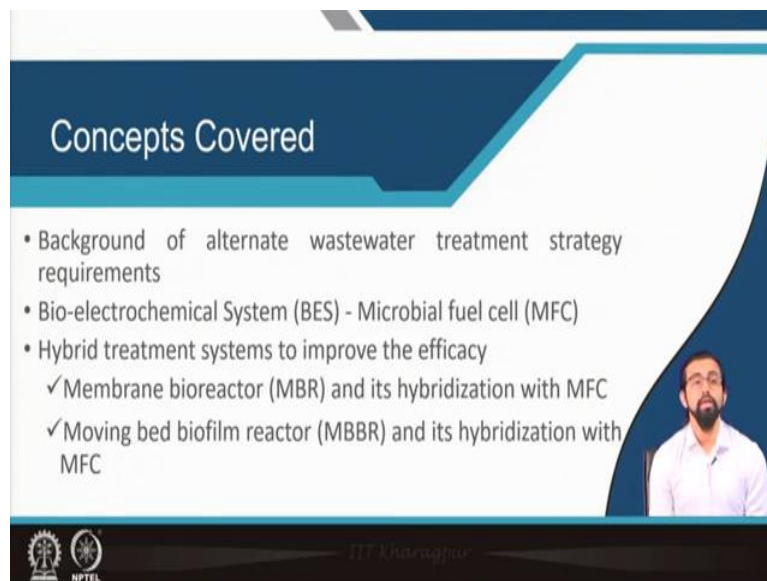


Advanced Aquaculture Technology
Professor Gaurav Dhar Bhowmick
Department of Agriculture and Food Engineering
Indian Institute of Technology, Kharagpur
Lecture 38
Bio-electrochemical system based water treatment

Hello everyone welcome to the third lecture of module 8 of advanced aquaculture technology; my name is Professor Gaurav Dhar Bhowmick, I am from the department of agriculture and food engineering of IIT Kharagpur.

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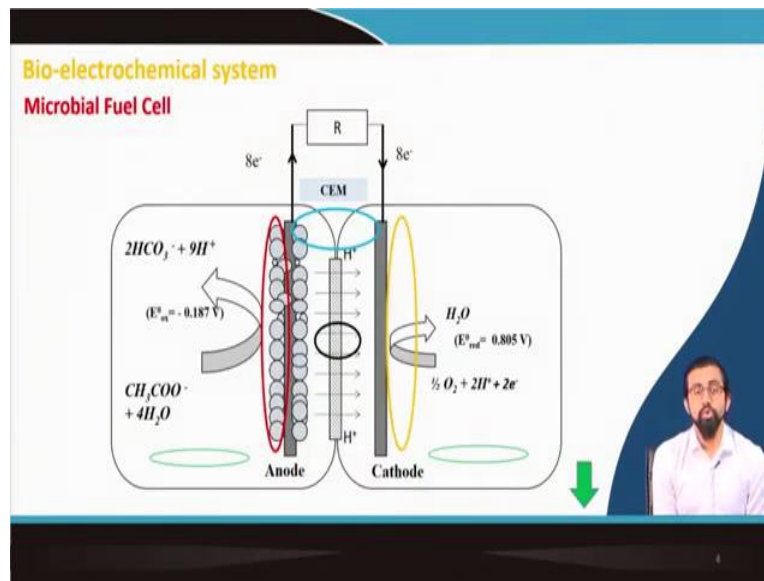
The slide is titled "Concepts Covered" and lists the following topics:

- Background of alternate wastewater treatment strategy requirements
- Bio-electrochemical System (BES) - Microbial fuel cell (MFC)
- Hybrid treatment systems to improve the efficacy
 - ✓ Membrane bioreactor (MBR) and its hybridization with MFC
 - ✓ Moving bed biofilm reactor (MBBR) and its hybridization with MFC

A small video inset in the bottom right corner shows Professor Gaurav Dhar Bhowmick speaking. The slide also features the IIT Kharagpur logo and the NPTEL logo at the bottom left.

In this lecture material I will be covering you the background of alternate wastewater treatment strategy requirement and we will be discussing about the bio-electrochemical systems, microbial fuel cells to be precise in this lecture, and in the follow up lecture we will be discussing about couple of more bio-electrochemical systems, hybrid treatment systems, which will be which normally we use to improve the efficacy. So here I will be discussing some advanced hybrid treatment technology like membrane bioreactor and its hybridization with microbial fuel cells, moving bed biofilm reactor and its hybridization with microbial fuel cells.

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So to start with we will discuss first about the microbial fuel cell, it is a one type of bioelectrochemical systems in any bioelectrochemical systems we use some electrodes and some membrane material and some biofilm. So this bio electrochemical in this bioelectrochemical systems we have a biopart of living microbiota which are helpful for harnessing energy from the wastewater then there will be electrode where the movement of electricity will be taking place and we will make a proper circle by means of different change in structural design and all Okay.

So, the first one that I will be discussing among all these systems is microbial fuel cell. It is a very interesting technology I am very much interested to showcase you discuss about this with you in this lecture material, so first of all if you see this structure it has an anodic chamber and the cathodic chamber Okay . In the anodic chamber what is happening here suppose this is the acetate feed.

Suppose in general we are providing them with the wastewater, it has its own nutrients, there will be biofilm normally the attached biofilm over the surface of the anode which will consume this feed, this nutrient from the wastewater and after consuming it will excrete or you know as a product there will be a couple of gases or there will be couple of by-products and there will be a couple of ionic byproducts as well.

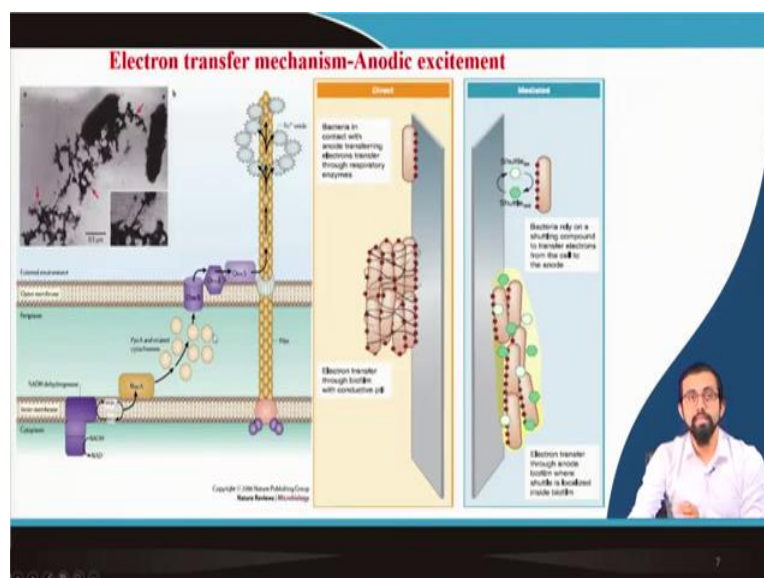
This ionic by products mainly H plus they create the protonic substances and there will be the excess of electrons. This excess of electrons it will get attached to the anodic surface and from anode it will go through the load or resistance towards the cathodic side Okay. So this excess electron how it will attach to the surface of the anode I will discuss with you in couple

of slides. So first you try to understand the whole process then we will go in details, once it comes in contact with the cathode here normally any terminal electron acceptor in general in this particular case I have given the example of oxygen; oxygen is acting as a terminal electron acceptor. It will consume the electron which is coming from the anodic chamber to the cathode chamber, it will react with this electron and the protons which are coming through the proton exchange membranes to the cathodic chamber and it will form the H₂O Okay.

So by this way it will make a complete cycle and because of that the electricity will be the generated, can be harvested here from that load; load is nothing but it is a resistance it is simply like the electron; electron normally flows through any electrical appliances, how we can harvest it we provide it with some resistance and in the resistance this electrical energy will be converted to some other form of energy, by this way we can utilize that energy for our daily purposes or for any other sensory applications and all Okay.


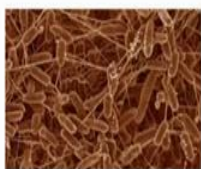
However, remember the electricity that that I am talking about in this case it is very minimum, there are certain advancement happening in this sector there are lot of researchers working on it. I will be discussing with you in details like how that is possible to stack this kind of cell and produce more electricity out of it Okay. So this is how the electricity is getting generated while the treatment of wastewater is getting placed in the anodic chamber so, do you realize what we are doing, we are treating the wastewater plus where we are generating the electricity out of it Okay. Now, let me to be more precise to go for more details I will click on what is happening in the anodic biofilm.


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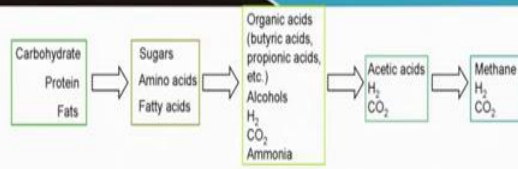


ISSUE: HOW TO STICK BACTERIA TO AN ANODE?

- Bacteria form a community on an anode called **BIOFILM**.
- Biofilm produces a matrix that sticks to the anode.
- **Sticky matrix** consists of extracellular proteins, sugars, and bacterial cells.
- Tiny **conductive nanowires** that may help facilitate electron conduction.





Hydrolysis
Acidogenesis
Acetogenesis
Methanogenesis


Anode reaction

Electrogenesis:
 $\text{CH}_3\text{COO} + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 7\text{H}^+ + 8\text{e}^-$

Methanogenesis:
 Acetoclastic
 $\text{CH}_3\text{COO} + \text{H}^+ \rightarrow \text{CH}_4 + \text{CO}_2 \quad \Delta G = (-36 \text{ kJ/mol})$
 Hydrogenotrophic Methanogenesis
 $4\text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta G = (-131 \text{ kJ/mol})$

Methanogenesis suppression techniques

- Hexadecatrienoic acid from marine algae *Chaetoceros*
- Lauric acid
- 2-bromoethanesulfonate (concentration of 0.1–0.27 mM)
- Heat treatment
- Ultra-sonication treatment



In the anodic biofilm, see this is the electron transfer mechanism that is happening because of the respiration process that is happening inside this specific type of microorganisms which we call electroactive microorganisms or electrogens, so what they do they utilize the food or nutrient and they excel they let excess electrons and all.

This excess electrons and excess ions what happens to this excess protons and electrons, see there is nothing called this excess electron access proton, if we talk about the Rutherford model, if we talk about the like it is the electron cloud model it will be completely different just to just I am saying in is a gross perspective Okay. Do not take my word in like you know in certain way that so electrons are moving it is like a one electron is coming from here it does not go do like this it is a portion of charge which is moving, anyway I am not going into deep physics discussion.

So here what we are doing this excess charge is getting accumulated to its locomotive organ what is the locomotive organ in case of this bacteria or biofilm this flagella they are their locomotive organ and you know this is a very standard scientific fact that most of the cases the accumulation of charge happens when the area is minimum that is why we keep this arrow like structure in the high rise buildings, so if the lightning effect it will capture the electricity and it will directly grounded to the deep earthen body so that it will go to the earth directly Okay.

Why this is sharp, this things are there because that is the standard tendency electricity is normally getting accumulated to the sharp objects first Okay, I am not going into details again to the scientific discussion you know it better you have already passed the class 12, we know already this basic scientific details.

From there the electrons how to collect that electrons which is in this locomotive organs, how to do that, we have this anodic surface, see this second picture direct transfer in the anodic surface when it is getting attached because of the phillion it will get attached to the anode and by means of that then electron can be easily transferred to the anode.

Sometimes it may create some like conductive proper network of electrode, network of a biofilm and this network of biofilm through their network they can easily network of this locomotive organs they can supply the electrons to the anodic surface. We can use the external mediators, suppose we have some type of the some the of the microorganisms which are not in attached to the anode but in suspended form inside the anodic reactor Okay, so from that anodic reactor to collect these electrons there is some type of mediator or chemical substances, we normally sometimes additionally supply. Those chemicals or the mediator that we call this mediator what they do they collect the charge from the electron from the microorganisms and they supply to the anode surface.

The same way it can be transferred through the quorum sensing mechanism, nowadays people are working on quorum sensing, how they can treat they can like kind of trick the microorganisms that, so there if you come here you will get a food you do it like they will ask other microorganisms to come here and put it is like they are treating their communication network and will ask them to provide the charge the excess charge which will be provided to the anodic surface. So this is how the things are going on this bacteria which can form a community of the anode it is called the biofilm right, you see this they are making a community of microorganisms this is how the biofilm looks like Okay.

From there the biotin produces a matrix that sticks to the anode; this sticky matrix consists of extracellular protein, sugar and the bacterial cells. Tiny conductive nanowires that may help in facilitate the electron conduction are utilized in this type of electron transfer processes and all Okay. So again what will be the next, let us discuss about how it happens like how this anodic reaction is taking place. In anodic reaction in general before going to the anodic reaction I want you guys to understand some basic information about how different nutrients are being consumed in this microorganism and all Okay. Say we have carbohydrate, protein and fat when the hydrolysis takes place by hydrolytic microorganisms they convert it to sugar, amino acids and fatty acids respectively.

Then the acidogenesis takes place where these sugars, amino acid and fatty acids convert into different organic acids like butyric acid, propanoic acid, alcohol, H_2 , carbon dioxide and ammonia. Then acetogenesis takes place where all these products will be converted into acetic acid, H_2 and carbon dioxide; then there comes the methanogenesis where the methanogenic microorganisms mainly it is a type of archaea, so they act on this raw materials and they converted to the methane, H_2 and carbon dioxide.

This methanogenesis is a electron scavenging reaction we do not want the methanogenesis to happen in our system in general Okay in in anodic chamber. What we need, we need up to acetogenesis, this is a very gross technology I am talking about now it is even scientist I find that even methanogenesis also can be helpful we can somehow reverse engineer this, we can retrofit in the system I am not going into the very basics, very much advanced details just remember that acetogenesis, methodologies we try to avoid.

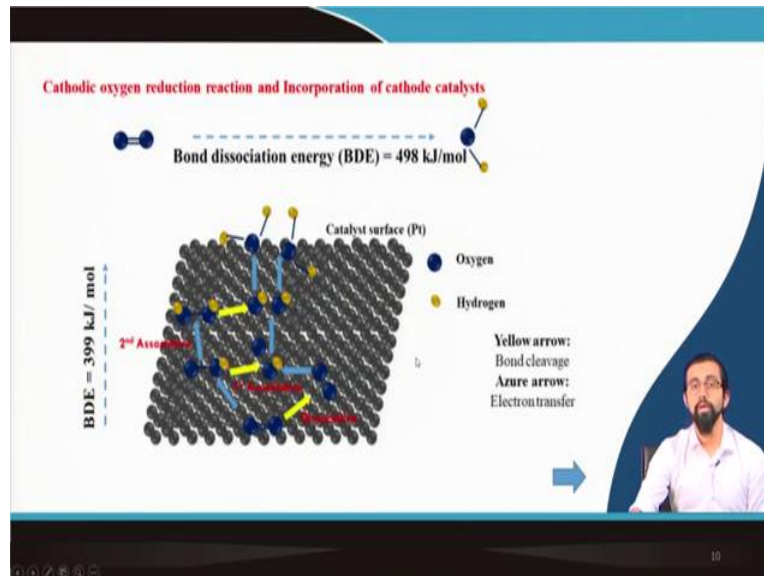
For that there are different methanogenesis suppression techniques are available, we can supply some additional amount, some type of plant extracts, we can supply some kind of acidic products, we can do the heat treatment, so how it is done in the anodic chamber in order to start the reactor how to start the reactor?

Before supplying the wastewater there needs to be some inoculums, what is inoculum it is a bacterial mass or the microbial mass. Where I have to collect it, we have to collect it from say existing aerobic treatment unit or existing anaerobic treatment units Okay. Existing anaerobic treatment units you go you take some sludge from there because you know they are the ready-made sludge the elements that mix the microorganisms are still alive there you collect them and proper transporting mechanism you have to utilize and then you pour it in your microbial full cell in the anodic chamber of microbial fuel cell.

Make sure it is completely closed, the lid is closed so that there will be no oxygen availability inside the anodic chamber. Then you supply drop wise or somehow you can make some arrangement so to supply the sludge or the anaerobic microorganism or the inoculum into your system in an anodic chamber. Then with time when you supply it with the enough amount of wastewater with time the biofilm will develop Okay. Before supplying this inoculum to your chamber we go for methanogen suppression technique, so that there will be no methanogens present in your system, Methanogens are what, this is specific type of archea this specific type of microorganisms they use is methanogenous phenomena.

How to get rid of them, as I said that different marine algae Chaeto and all marine algae Chaeroceros, we use lauric acid, we use heat treatment, ultrasonication treatment, so by using all this treatment we try to get rid of the methanogen population in your inoculums then you supply it to your anodic chamber Okay. Now your anodic chamber has the exact amount of electrogen that you need you know the procedure how it is to be collected or how it is to be get attached to the anodic biofilm in the anode.

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Proton transfer mechanisms

❖ Bound water facilitates proton transfer in **Grotthuss mechanism**.

❖ Whereas **free water** does it in **Vehicle mechanism**.

Now let us see what is happening in the cathode, in the cathode when the oxygen is acting as a terminal electron acceptor. So oxygen it acts with the electrons and protons coming from the anodic chamber and they form H₂O Okay. So normally we try to form it in the catalyst on the cathode surface but it is very sluggish in nature, this oxygen reduction reaction is very sluggish in nature that's why when it needs to be provided with some catalyst.

What catalyst we do say platinum; platinum is a very standard catalyst. Catalyst will accelerate this process because if the acceleration of this process is happening what will happen because of the accelerated process of the oxygen reduction reaction the whole cycle will be faster in nature right?. There is a scarcity of electron in the cathodic side from the anodic side more amounts of electrons will try to pull it up Okay.

Just think it as a complete cycle, the more you suck from one side though the cycle will be more interesting and faster and then the electricity though more treatment efficacy can be increased right?. So that is how it works and if you see in case of oxygen all this bond dissociation energy that is like 498 kilojoule per mole, that is normally the that has to be overcome and that can be done with this different type of catalyst material.

So platinum is used as a catalyst but it is very costly, so people are now trying to find out, try to do research on different other type of catalyst, cathode catalysts or oxygen reduction reaction catalyst to replace the platinum and to work as well as and even better than platinum with a very cheaper way. Then there comes the proton transfer mechanism that also I want you to know that how oxygen need electron and proton, so that means protons are also coming from the anodic chamber. How it is coming, in general the protons are coming through the proton exchange membrane, so this proton exchange membrane, we have two

mechanisms that we normally think is their standard Grotthuss mechanism and Vehicle mechanism. In case of Grotthuss mechanism what is happening, you see this picture in the left top most figure they are just giving charge, this proton to one ion to another. Simply think about a water molecule complete chain of water molecule is there in your proton exchange membrane.

This water what they are doing they are H_2O , right once they get in touch with one H plus and it will become hydronium, H_3 plus O , so once they becomes hydronium ion what it will do it will supply to the neighboring molecule, neighboring H_2O . So it is like one from hydronium to another H_2 it will become hydronium it will become H_2 , so this way the H plus ion will migrated from the anodic chamber to the cathodic chamber, this is called the Grotthuss mechanism.

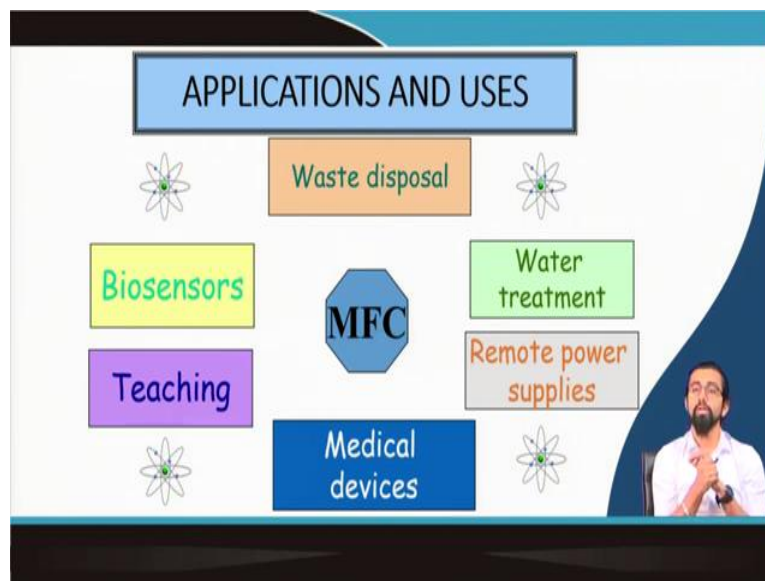
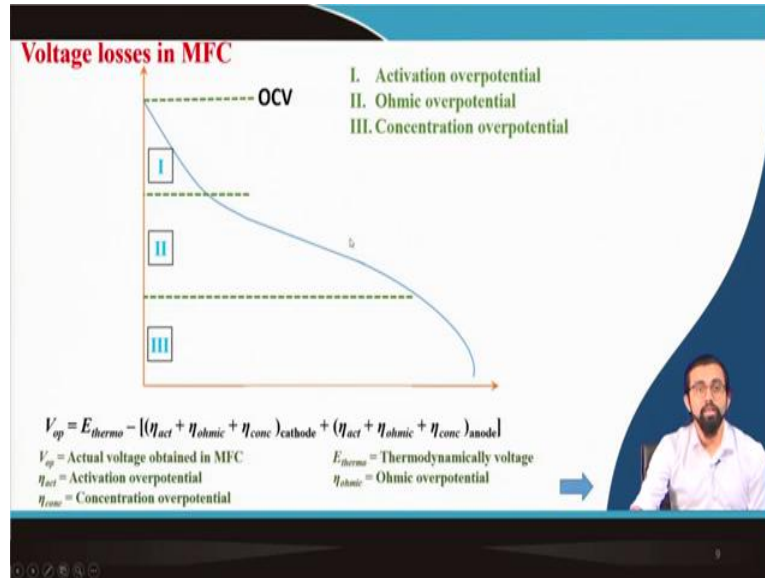
It is not as simple as I mentioned Okay, there are a lot of other functionalities going on, a lot of other factors are in in this picture but just to give you a broad idea about how it works Okay this is called Grotthuss mechanism jumping way. Then there comes the Vehicle mechanism; when one water molecule will collect how to say this proton from anodic chamber and it will take it from the anodic chamber to the cathode chamber by itself, so in that case it will be called vehicular mechanism Okay.

So there also this ion exchange takes place but not how to say in general these ions will be migrated through definite molecules only Okay. In case of bound water you know what is bound, water what is free water. If you add some water in say like if you have a glass beaker you have some soil in it, you add some water and from the bottom you make a hole when you add some water from above what will happen because of the gravitational force most of the water will go through it. Right?

After you say put like after 10 ml of water almost 9 ml of water will go through hole as free water that is called the free water. That means the water is free in nature that is moving through the gravitational force or some other external physical sources means of forces right. Then what will happen to the rest of the 1 ml, it actually gets attached to the surface of the soil particles, so that is what we call the bound water. See these bound waters are very hard to well it depends there are other type of water also but bond water in general they are the one who are responsible for Grotthuss mechanism. They will collect the electrons protons from one side and then they will supply to the other, so bond waters are normally fascinated the

proton transfer Grotthuss mechanism and free water does it for the vehicle mechanism Okay.
So that is how the protons are being connected to the cathodic chamber.

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NEGATIVE SIDE OF THE PICTURE

- Scale up is still a big challenge,
- High cost of cation exchange membranes,
- Potential for biofouling,
- High internal resistance to power generation limits the practical applications of MFC.

(A small video inset in the bottom right corner shows a man with a beard and glasses speaking.)

Now what is happening when we talk about the voltage losses, voltage losses is like how this matter is coming into the play, this is a term called very important term we call it over potential losses. In general theoretically speaking suppose for a particular amount of wastewater which has a particular amount of nutrient it may give you say 1.1 or 1.2 volt of potential difference has to be there Okay.

However, this voltage cannot be attained by your microbial fuel cells because of different kind of losses, different type of resistances or over potential losses we call it Okay. There are activation laws, there are atomic over potential loss, there are concentration over potential loss, so because of different losses in cathodic chamber, in anodic chamber, in the electrode, in the conducting wire and all also at the load or the resistances.

So because of that this different kind of losses are happening Okay I am not going into details of it I am just giving you this idea that why we cannot achieve the desired level of potential difference that we are expecting theoretically in case of microbial fuel cell, these are the losses that because of this only.

So we already know how it works in general Okay, so let us think about what are the applications and uses of it Okay, we use this for waste disposal, we use MFC for water treatment, for powering the remote power supplies where human being cannot go and there is of no possibility of wiring system connection or wire, you just simply design a microbial full cell, which will keep on giving you enough energy for running that particular appliances.

Same for medical devices, nowadays people are researching on medical devices where this microbial fuel cell is powered by human sweat, human urine and all these things and because

of that the treatment of that the treatment of this sweat and urine that is used as a you know supply of it is like a fuel for microbial fuel cell, it is like just like we use petrol diesel this human sweats and the urine that these are used as a fuel human excreta is used as a fuel and it is called bioelectric toilet also that is being developed in India also in different places in the world also people are working on it right now.

So in this microbial full cell this is used as a feed and then this organisms this microorganism they conduct the electricity and this electricity is sufficient enough if you device it correctly sufficient enough to run the remote power supplies, different biosensors, for medical devices and chips and all to implant inside our body and all, also for teaching a new thing in our research purpose for sure.


What are the negative side of the picture, scale up is still a big challenge Okay; if it is not by this time you might have seen like microbial fuel cell everywhere like you just have wastewater you treat it and that is it you treat the wastewater plus you will have a electricity out of it, but scaling up is a big challenge, field scale applications are still under research and there are a lot of physical applications still going on and people are doing it successfully but still it is considered as cutting-edge technology with a low TRL level. To be in order to reach high TRL, TRL technology readiness level and all ,so if it is needs to be high enough for mass applications some still some research has to be done and it has to be well added to the bio demand Okay.

High cost of cation exchange membrane or the proton exchange membranes, potential of biofouling is there so you have to repetitively clean the electrodes, high internal resistance to power generation limits is the practical application of MFC. All these factors are actually still limiting the practical applications but research are going on there are plenty of research, plenty of papers and patents are available, people are working on commercial level practices also now for different like you know low energy uptake in devices and all so there definitely will be a good part of it we will see in near future.

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Some more cons...

- Existing high-cost cathode catalyst material for MFC application needs to be replaced with novel low-cost alternatives.
- Existing proton exchange membranes used in MFC are mechanically weak and need to be improved drastically in order to apply for the field-scale application.
- Integrating bio-electrochemical systems like MFC with MBR could be a game-changer for treating medium-strength wastewater like fish processing wastewater.



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Membrane Bioreactor (MBR)

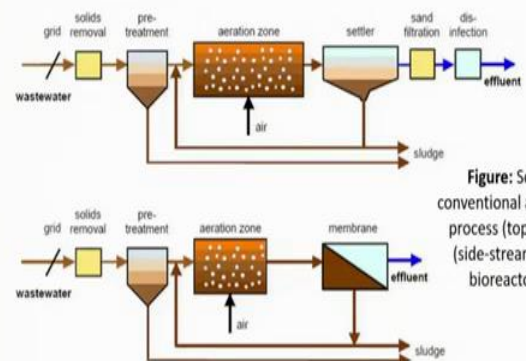

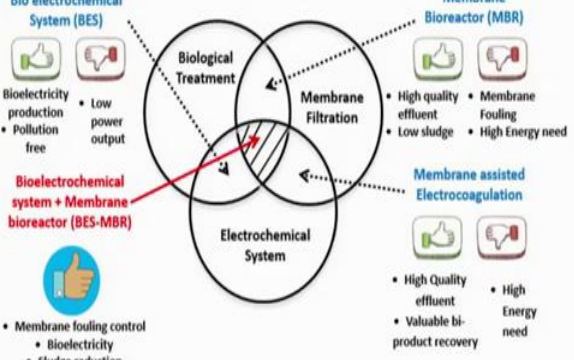


Figure: Schematic of conventional activated sludge process (top) and external (side-stream) membrane bioreactor (bottom)



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Why to combine MFC-MBR ?



Bio electrochemical System (BES)

- Bioelectricity production
- Pollution free
- Low power output

Membrane Bioreactor (MBR)

- High quality effluent
- Low sludge
- Membrane Fouling
- High Energy need


Membrane assisted Electrocoagulation

- High Quality effluent
- Valuable bi-product recovery
- High Energy need

Bioelectrochemical system + Membrane bioreactor (BES-MBR)

- Membrane fouling control
- Bioelectricity
- Sludge reduction

Figure: Venn diagram showing how hybrid MFC-MBR system interconnected with biological, membrane filtration and electrochemical systems and their pros and cons.



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Some more cons like some more negative part the disadvantage existing high cost cathode catalyst material for MFC application needs to be replaced with the novel low cost alternatives, researchers are going on on this field and I want you guys to why I am more focusing on providing some disadvantages also so that you will come up as a scientist or researcher in near future and you will come up with this idea how to go ahead with the further research and make it possible for physical application or real life applications. Existing proton exchange membranes used in MFC are mechanically also weak, so we have to find out some mechanically strong proton exchange membrane.

Integrating the bioelectro chemical systems like MFC with MBR therefore can be a game changer for medium strength wastewater like fish processing wastewater and all. That is what we re going to discuss in in a couple of slides later that why integration is important in these bio-electrochemical systems. Before discussing about the integration, this is the membrane bioreactor if you see it also this is also aerobic, in general MBR is aerobic treatment process but anaerobic MBR is also available.

When we talk about the standard aerobic treatment processes like say activated sludge process we discussed in last lecture right?, in activated sludge process we have solid removal, we have this aeration basin and then there is settler. Before that we have this primary sedimentation, primary treatment units then sand filtration and disinfection all this tertiary unit is also required.

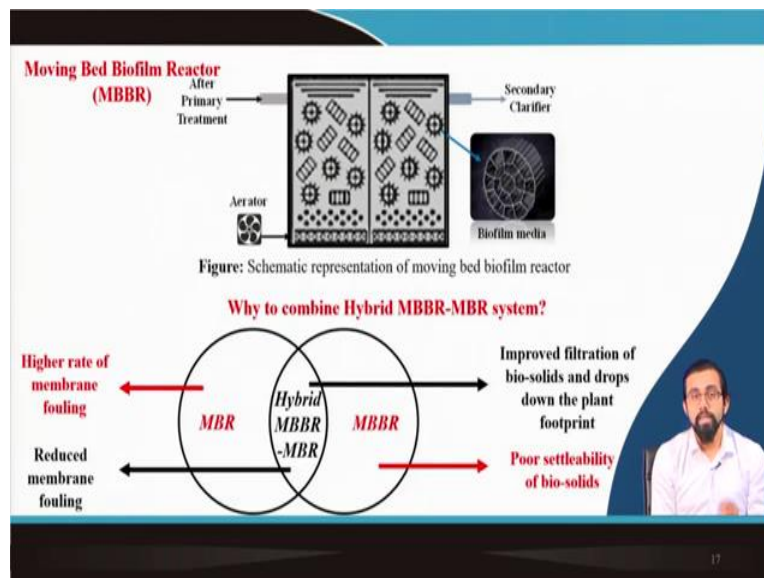
In case of MBR you are doing all the secondary and tertiary treatment in a single module it is possible, how it is done? Instead of aeration, after aeration you can simply put it through the membrane, ultra filtration membrane, micro filtration movement or nano filtration membrane or you can simply put it inside the aeration basin also and then you apply the negative pressure and suction pressure because of suction because the water will go through this filter material and because of this filtering membrane they can filter out all the unwanted materials and the water which will be coming out of the system is free of all the pollutants and all. So it is doable and it is not only doable but it is practiced all over the world it is very famous it is a very standard technology.

However, the membrane comes with a very high energy requirement that is also that is one of the drawbacks of this system, because to run the pump it needs a huge amount of energy. So in order to minimize this energy requirement and all these things why not we go for combination of MFC-MBR systems, just to give you a thought this bio-electrochemical

systems it is good for bioelectricity production, it is a pollution free, low in low power input, lower power output rather it will provide with the power. If you see this Venn diagram this biological treatment, membrane filtration and electrochemical systems if you see the overlapping regions between biochemical, biological and electrochemical, its bioelectrochemical system overlapping between membrane filtration and biological treatment it is a membrane bioreactor. Overlapping between membrane filtration and electrochemical system is the membrane assistant in electrocoagulations.

Overlapping between three of the Venns it is considered is what we are targeting, it will give us all the prosper possible, it will give us a high quality effluent, low sludge production, valuable byproduct recovery, bioelectricity generation, pollution free, membrane falling control, sludge reduction a lot of a lot of possible advantages can be possible if we try to think about researching or try to think about you know find out some solutions which will act as a bioelectrical system plus membrane bioreactor, it is a hybrid system design of a hybrid system which will act as a wastewater treatment unit plus it will provide us some bioelectricity that will reduce or somehow try to neutralize or at least somehow like you know somehow reduce the overall energy requirement of the MBR.

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Take away message

- BES technology can replace the existing wastewater treatment technologies after overcoming some major concerns.
- The hybridization of these technologies with the MBR or MBBR can be a game-changer for application in aquacultural practices.

NPTEL

Second thing, second discussion the second type of treatment unit that I want to discuss is like moving bed biofilm reactor. What is moving bed biofilm reactor, in general it is either aerobic or anoxic depending upon our applications so mostly it is aerobic in nature mostly we use in aerobic MBBR, in case of aerobic MBBR or we provide it with the aerator you see in the picture and there is this bio media, this is plastic based biofilm medias are they are floating around because of the aerator it is floating around inside the reactor and it is a perfect ground for attached biofilm growth, because it has a very high specific surface area you see they have a very high, there are like lot of nodes a lot of protrusions and all.

So it will give high amount of specific surface area for biofilm to grow on its surface. When there is higher specific surface area; when there is a like high amount of biofilm are growing on its surface it will consume more amount of pollutants isn't it?. That is why MBBR is a very it is considered as a very standard, it is a very high-end technology, nowadays people are using in wastewater treatment, in water treatment units and also if you properly design it is possible to incorporate it with the MBR systems, moving membrane bioreactor systems.

If you add it with the membrane bioreactor systems it will give you high quality effluent Okay and we can get rid of all the problems that we are associating with other technologies Okay and if it is added with the MFC then is also for sure it is good because it will give you some additional electricity generation also.

So as a takeaway message we can say that the BES technology bioelectro chemical system can replace the existing wastewater treatment technologies after overcoming some major concerns that we have discussed, but it has some possibilities it has shown a lot of applications already all over the world. However, we will discuss more about the BES

technology more in details in coming lecture, here we already discussed only microbial fuel cell Okay. Later we will be discussing more about other applications of BES technology as well, and then we will see how we can utilize all this technology for aquaculture purpose, how we can utilize this technology for aquaculture wastewater treatment, how we can utilize it for fish processing wastewater treatment Okay.

Hybridization of these technologies with MBR or MBBR can be a game changer for application in aquaculture practices, so that is what we are going to target and we are going to this lecture material this module is I designed it in such a way so that it will make you think further it is not something that you only know some bookish knowledge or what is already there it is just to give you some idea about what is the existing research going on in all over the world in this type of field and how we can involve yourself in future to be the person who is responsible for like you know coming out with some advanced technology, which can treat the wastewater plus generate the electricity for solving different purposes Okay and also and it will reduce the global warming and it will also help in the environment in general Okay.

So that is it for the day and I will discuss more about it this different kind of bioelectrochemical systems in coming lecture. In the next lecture only and there we will discuss about how it can be utilized in aquaculture systems also Okay, thank you so much see you in the next lecture.