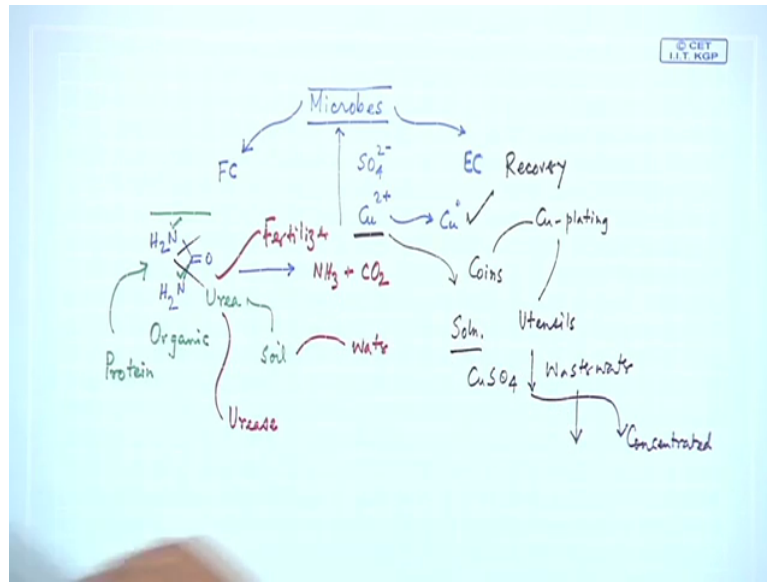


**Course on Analytical Chemistry**  
**Professor Debashis Ray**  
**Department of Chemistry**  
**Indian Institute of Technology Kharagpur**  
**Module 12**  
**Lecture No 59**  
**Applications (Contd.)**

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Welcome to this class again where we are talking about the different types of microbes if we are getting those microbes and those microbes can be utilised for 2 different types of things means one is your fuel cell and another is your electrochemical cell, so these 2 things how we can develop and also sometimes we just try to co-relate this also uhh that for something because nowadays modern industrial people, they are trying to get the help of the different microbes because these microbes can be oxidising or can sometimes be reducing in some anaerobic uhh environment in absence of oxygen that they can tackle the simple sulphate ions that means the sulphate reducing bacteria *Desulfovibrio gigas* uhh it is a very big name.

So sulphate reducing bacteria and if we consider that some reducing environment can be created by the microbes is a sulphate reducing bacteria as well as the metal ion reducing bacteria or the electrochemical part also because we know that electrons can be transferred to this copper Centre to get the corresponding metallic copper in terms of its corresponding metallurgy, so how we can co-relate this things because you talking about the electron transfer.

Now we move to the bio electrochemistry then we bring microbes and now we see something which is related to metallurgical problem also where you see how things are getting more and more complex because if you have some good idea about this analytical science that you can tackle some good metallurgical problems also there is not that it is directly related to chemistry or anything but it is only the electron transfer or the electrochemistry what we are talking about.

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In MFC and MEC microorganisms, typically bacteria --- break down organic materials, as found in wastewater, at the anode under anaerobic conditions

During this break down, the bacteria release electrons, protons and carbon dioxide into solution.

Anode collects the electrons --- travel to the cathode via an external circuit

The protons travel through the solution in the cell to the cathode. Formed carbon dioxide can be captured and reused.

So metallurgical things how we and attach with the microbes and how this microbes will be useful for giving you the corresponding 2 types of cells. So we have MFC and MEC in our hand, so these 2 taking the help of the different microorganism, typically they are bacteria microbes so very small bacteria that is why they are microbes, so they basically require for breakdown of materials we know that all these microbes and all these things are available in the soil, in the planned in the other in our body also, that if you have a very simple molecule like  $\text{NH}_2\text{CO}\text{NH}_2$  we all know and by definition what we are taking in this example is that is a typical organic molecule or a organic material because, so organic material or molecule.

It can be present anywhere because we are discarding this from our body also from our urine, we discard this so how we get it because we are getting this, we are producing this for the degradation of the protein molecules because we all know that the proteins has nitrogen the might bond so is another one also your also you have  $\text{CO}\text{NH}_2$  function but we really discharge it uhh we get from this because it is not a good one for our health.

So there are several things also because when this is there this is Urea, so this urea when it is present in soil also, so we will take this so soil definitely when it is present in soil it can be present in your water or wastewater. So when urea is present in there and we know that urea is a good fertilizer also, so all these things are very closely related it is not that we are directly memorizing something and we try to solve this problem because the nature of this problems and the applications are complex.

So if we talk in terms of this urea as the fertilizer because this thing as well as the nitrogen demand of the plants should be satisfied by the addition of this fertilizers, so you have to have some breakdown of this urea, so the enzymes which is responsible for breaking this urea is urease, so what we get at there are some saying that microbes, this bacteria and all these things and break this organic molecule and we all know that this can be broken into your ammonia plus your carbon dioxide.

So ammonia and carbon dioxide breaking into ammonia and carbon dioxide because we cannot fix very easily from the environmental or the nitrogen or the  $N_2$  die nitrogen what is present in air or the atmosphere, so there is some mechanism that means during lightning process we know some amount of nitrogen can be fixed as the ammonia, so the source of hydrogen is also required to get the required amount of uhh required amount of ammonium salts.

Compared to ammonium salts, ammonium nitrate is a good fertilizer. This one is basically going for if you have urease in soil or any other area, so this urease can be responsible for your breakdown of this molecule such that you can have a slow release of ammonia it is not that whenever you get these things, so that is basically lost the entire thing cannot be consumed by the planned material.

So is a slow release process so enzymes and all bacteria and the microbes will be available to breakdown any organic matter, so this organic material can be your urea simply and something what is we are discarding in some wastewater (6:29) effluent which is coming from some industry or our household use and all these things as your kitchen waste, your bathroom water and all these things, so breakdown is responsible for breaking down this wastewater.

So microbes if available can breakdown this organic molecule like the very simple urea molecule at the anode under anaerobic condition, so that we are talking about that it can be

broken down into anode and in absence of oxygen that means in anaerobic condition, so what basically it does at we can have, so when you have this breakdown, so we are going for the microbes will break, breakdown means in terms of a chemist.

What we can understand what you should also understand is that how you cut certain good bonds like the corresponding breaking of these bonds was how you get uhh the corresponding uhh molecules from this urea if you break this then only you can have the separate part otherwise you have the carbon nitrogen bond you have to break this carbon nitrogen bond also.

So bond breaking process in this way so during this breakdown have to break this uhh molecules so is we are moving basically towards the opposite direction, so bacteria releases trace, so this bacteria under anaerobic condition uhh bacteria give rise to some electrons, some protons and carbon dioxide into the solution.

So these are very complex reactions what bacteria does but if we have to have some idea that we can track, we can locate the amount of electrons what is being produced, the protons what is being produced because we know that this microbes, these bacteria are one type of bacteria are also known as hydrogenises, so like urease the hydrogenises can consume proton and can also give rise to you the elimination of hydrogen gases.

So during removal of this electrons, protons and carbon dioxide from the solution what we get the anode collects those electrons, so when anode collects those electrons what we get there is that after collection that means you know that when it connects those electrons, it travels to the cathode via an external circuit.

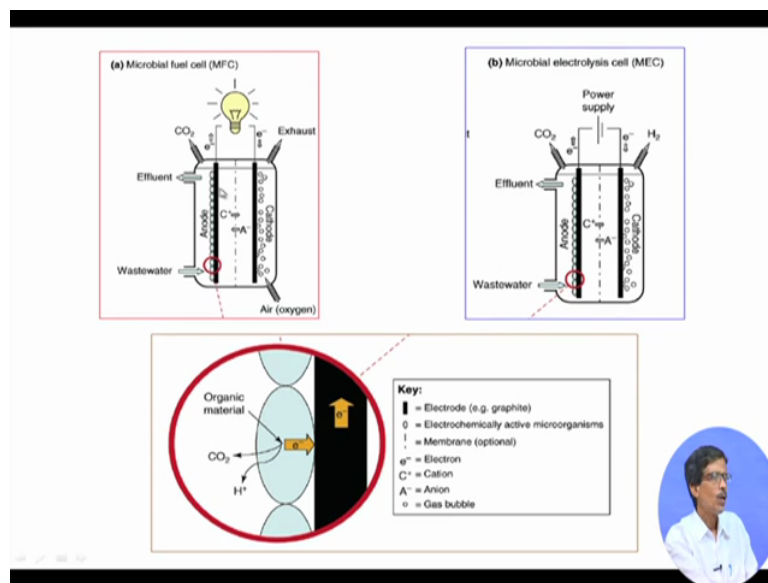
So if it collects electrons on the bacteria and those electrons if you can push to cathode via an external circuit, what it happened at the same time that within the solution it is from the external circuit because we are talking about now the current the electricity in the external circuit. But the other one means the microbes as we have defined that it can go to the opposite directions that electrons and protons are there uhh bacteria is also producing the within the cell solution the protons travelled through solution in the cell to that cathode.

So anode is taking the electrons and in the cell the corresponding protons is moving to the cathode and form carbon dioxide it can be captured and reuse, so you can form the corresponding carbon dioxide also and if we can reduce by these 2 things and the protons and

electron can be combined together and if can go for the typical reduction of this proton what will you get? You will get hydrogen.

That means hydrogen is can be your fuel for your fuel cell and you can produce a large amount of hydrogen, like that the bacteria is producing, the metal enzymes are producing because metal ions are there in those hydrogenises, so hydrogenises like hydrogenises you can produce hydrogen from there.

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So one such schematic very basic drawing for the cell what does it mean by saying it as a microbial fuel cell or MFC? So you have the enclosed chamber and we all know now the like your living cell, it is the electrochemical cell either you can have the electrolysis or you can have the fuel generation, so the waste water a bottom basically you are injecting the waste water and thinking that in the waste water you have that dissolved organic matter which can be degraded or which can be broken down.

So is moving there and this red circle part is our interest is the anode, from the electrode surface what is happening? What are those of circles half bubbles type of thing and these are full bubbles. So in cathode you have this the air is there and you have the oxygen basically bubbling over there and you have the exhaust, the exhaust is taking out the other part and close to the anode can take carbon monoxide as the same time your electrons moving anode to the cathode through a bulb or any meter where you can measure the corresponding generated electricity or the current.

But the other one we have 2 apply some external power supply is that we can go for electrolysis, so during this process you get the corresponding electrolysis cell and the microbes are there, the microbial are there for generating that particular electrolysis for going for that electrolysis, so wastewater is coming inside and these 2 parts basically the red circle part for the microbial fuel cell and the red circle part for the electrolysis cell construction wise both of them are same because the around anode and around cathode you see this bubbles and all these things are there but here in one case we have as the hydrogen is coming out so the if you go for the electrolysis cell, your product will be the hydrogen gas but when you go for the microbial cell we are looking for the generation of the amount of electricity what we can have.

So during this process your microbial fuel cell will give you the current or the electricity and your exhaust is your some other thing apart from your carbon dioxide, so when you elaborate this part that means the dotted lines is reaching here and this dotted lines are reaching here, so elaboration so you get this so you expose it out for this particular red circle and this red circle part.

So this black part, this black part is your electrodes and in this case the cathode and anode both can be your graphite electrodes, the carbon rod. Simple carbon rod as we know and we use the battery cells for your torchlight, these are typical graphite rods, so this graphite rods in both these 2 cases that it can be your anode or it can be your cathode also. Then here basically your organic material is coming which is a very small one so this wastewater and this organic matter is basically not degraded and is electron is dumping on the anode material and electron is moving because anode is your good conductor which can carry the electron out to this wires and go to this bulb.

So what is basically happening or your fuel cell is this part so you have the electrochemically active microorganism, electrochemically microbes all these half circles all these because it is when it is attaching forming a film on the electrode, the microfilm basically when you see in a bigger size, you see that some part is already attached to the electrodes surface, so basically the biofilm the formation of the microbes biofilm on the electrodes surface is also important.

So the formation of those microbes biofilm on the electrodes surface is there and then this is the passage of the electron and what you can have in the electrolytic cell, we have the solution you generate some amount of cation and some amount of anion, so cation will move

to the cathode as electron is moving from anode through this electrical circuit to the cathode, so your anion is also moving to your anode.

So this fuel cell your cathode is uhh cation is moving to the cathode and anion is moving to the anode since there is a fuel cell which is reverse in the direction for your electrolysis cell where electrolysis cell they form these things is the anion and the cation will also move the cathode and anode respectively but the transfer of those electrons in the power supply what we are giving to generate the hydrogen from the corresponding reduction that means the hydrogen ions is the corresponding thing that it generate those gas bubbles close to this cathode.

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Copper recovery can be combined with electricity production in a **Microbial Fuel Cell**

A metallurgical MFC is an attractive alternative for recovery of copper from copper containing waste streams.

Metal is recovered in its metallic form at the cathode -- energy for reduction can be obtained from oxidation of organic materials at the anode with the possibility of generating electricity

Pure copper crystals were formed on the cathode, and no CuO or Cu<sub>2</sub>O was detected

The cathodic recovery of copper compared to the produced electricity was 84% (anaerobic) and 43% (aerobic)

6

So in one case your gas is carbon dioxide and in another case your gas is hydrogen. So the basic formation of all these and the basic generation of all these things can give rise to other things that you are talking about, how we can see in terms of its corresponding recovery of this copper from a copper containing solution because this copper containing solution you can have because you can know that that our all these uhh banks and all these they are producing or making coins for us and we require a copper solution for good copper plating.

So we are not going for gold plating and all these because the plating of gold is very few but the copper plating is there for coin, copper plating for utensils and several many things also because for decoration purpose and all these things some material can be plated by copper, so the solution what you are taking for that purpose is your copper containing solutions say copper sulphate solution.

So when you take this copper sulphate solution you go for electrolysis and its concentration of this copper sulphate in the (())(17:01) or the solution is decreasing with time. So at one point of time we just basically discard this it will be your effluent or a wastewater and we dump it on river, we dump it on lake or we dump it on seawater. So if we get that particular one and this wastewater is available and this wastewater if we can use for your copper recovery that means if possible because the waste water should be pre-concentration step it should cover that means it should be concentrated, so at high concentration it will again be useful for deposition of copper by electrolysis.

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So this copper recovery process what we are seeing here is that through some electrolysis process but it can be now combine with electricity production that means we have something and good idea, some imagination because you have the knowledge, you have the intuition and imagination also such that even have something and when you do all these things for several years we were pretty experienced to develop new thing or other microbes to be used for development of microbial fuel cell for metal extraction.

So is a copper recovery, so metallurgies or the people who are engaged in going for this recovery of metal ion from ore for other solutions even for the electroplating solution what we can use for electroplating of some coins, some ornaments or some materials. So a metallurgical microbial fuel cell, the same MFC we are in about but we are now tagged with it is as a metallurgical MFC.



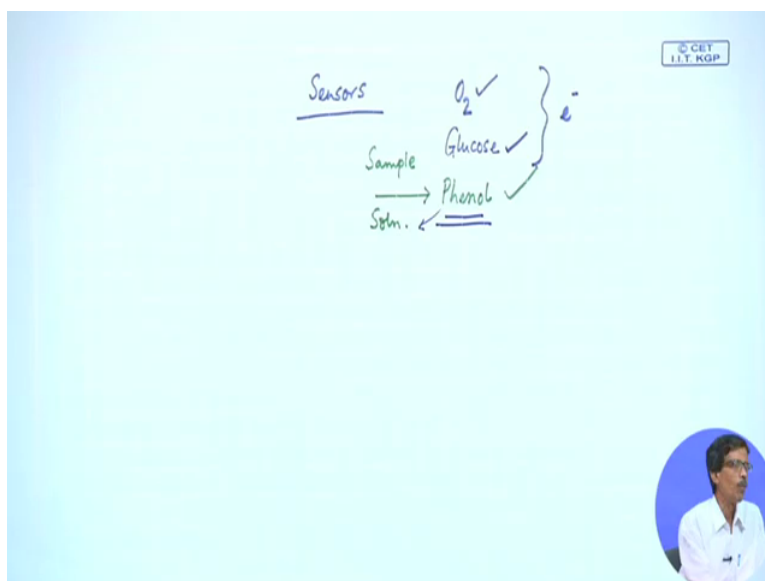
So metallurgical MFC is an attractive alternative for recovery of copper from copper containing waste stream whatever we are talking about so far, the waste water molecules uhh waste water system or the waste streams, basically we are throwing it out contaminating our environment, contaminating our water, water reservoir everything because copper at a particular concentration is harmful or our body also at lower concentration level is useful for our body provided you have good assimilation and is such that you are assimilate that copper for our body such that we can synthesise good copper protein or copper enzymes or copper-based methyl enzymes what you require for our body also.

So is a typical metal is exactly metal not the metal ion so exact metal as the metal 0 state is recovered from its metallic form at the cathode, so energy for that particular reduction and we all attain from oxidation of organic materials, so if your organic material is there and microbes are available to oxidise it to break down those organic materials, so at anode it is happening just now what we have seen that for anode on the anode surface if you have the biofuel, so there is a possibility of generating electricity side-by-side when you recover copper for copper reduction from the metallic state as the copper ions will be reduced.

So pure copper crystals or the metallic copper uhh the copper depositions can take place on the cathode we can get now because the cathode is responsible for giving you the electron for the reduction and interestingly here in this particular case also because it has the good selectivity because we know that deposition of copper oxide as a material or deposition of cuprous oxide as material can also take place side-by-side but in this particular process no cupric oxide or cuprous oxide has been seen has been observed to be deposited on the electrodes material.

So the cathode recovery of copper you can consider that cathode is utilised for the reduction of copper from the copper solution, so the cathode recovery of copper compared to the produced electricity was of different percentages because the copper is being recovered as that deposition of copper from the copper ion to copper 0 and at the same time you can have the electricity what you can generate, so in an anaerobic condition is higher but in aerobic condition there is less it is 43 percent compared to 84 percent. So side-by-side if we move that, that means you have the microbes, the microbial things and how we move something because already we are now experienced enough to handle all these things, should say all these things.

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So quickly we can see how we use the sensor for good purpose because the development of sensor is not only the sensing but you can have something the detection also some good molecules, some value-added molecules. So already we have seen that how we can handle or we can detect the O<sub>2</sub>, how we can detect glucose so one such good molecule of our interest is now the phenol. So we should know where from you get the phenol because the sample what you will be handling of our interest for sensing phenol in that particular solution.

So it can be a solution or it can be a solid material also because the phenol is the constitute material for so many things. So those things one after another we will see such that you can have good idea that all those materials, you can degrade those materials for getting phenol in solution. So you have to bring that phenol in the solution such that you have a good sensing mechanism definitely it can be electrode-base but what are the other things the enzymes and other materials what you can use to sense that particular phenol in the solution, okay.

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**Phenolic Biosensors**

Interests in the development of -- simple, sensitive and accurate analytical procedures for the measurement of phenolic compounds in environmental protection, drinking water production, medicine, biotechnology and food quality control.

Phenolic compounds are very common substances in nature -- formed, in part, as a result of biodegradation of natural compounds like humic acids, tannins and lignins.

Phenol and related compounds are used in the large-scale manufacture of resins, plastics, pesticides, explosives, detergents and pharmaceutical products.

Variety of phenolic compounds are also generated in industrial processes, such as paper bleaching, coal mining, oil refinery and production of dyes, and appear as industrial pollutants in the environment.

So the development of phenol sensors how we can go so we should have the interest first that we should have some good idea some interest and knowledge also the required amount of knowledge we should have for a simple sensitive and accurate analytical procedure because the sensing mechanism is a typical analytical procedure, so it talks about the analytical science once for the measurements of bearing ranges of phenolic compounds where from, the phenolic compounds in environmental protection.

So if you have a EPA in environmental protection energy in abroad we know that different countries have environmental protection agencies, they have the strict regulation for the level of phenol in water, level of phenol in soil, so they also know that during the drinking water production that if you are handling or if you are purifying some phenol contaminated water, your drinking water might have some amount of very low level of concentration of phenol in it.

Then during the medicine we all know that the some transformation of the phenolic compound like making aspirin, we start from the phenol or the substituted phenol molecules but if the conversion is not 100 percent, if we are not able to go for complete conversion of phenol based molecules to medicine, you have some impurities remaining with that medicine, so we should know the level of those impurities in those medicines.

Then the different biotechnology, the biotechnology farm and Agro farms, the agricultural chemistry related farms and the agriculturalists also and the food quality control will also will be interested to know because the phenol is there in the food material but to a certain extent

to a certain concentration but once you monitor everything in terms of the concentration it is the analytical chemist job to strictly control that concentration and he should know the concentration and monitor that means the quality control you can have and that quality control, the quality assurance could be there such that your concentration level of those phenol which can be toxic should be in the permissible concentration range.

So they are also very common in nature because we are getting from the naturally occurring compounds, as we are talking about the bio bio biomaterial, so your bio food, bio fruits and all these biomaterials so but most of these things we are getting from the nature and a natural product have so many components which are not properly analysed for everything but the purity of the synthetic molecule or the synthetic material is more compared to your natural thing.

So that is why we are though we are taking half and half-based materials but the corresponding concentration of the other part of those half because we know that some active ingredient is there, so this active ingredient like your neem leaf we all know, so the molecule we all know that is the something (C<sub>26</sub>H<sub>35</sub>N) that means the uhh nitrogen based molecules, nitrogen based heterocyclic is there.

So nitrogen based heterocyclic molecule is present on this neem leaf but the other material we do not know, so in the nature so they basically form in part as a result of those biodegradation of natural compounds like humic acid, tannins and lignins. So phenolic compounds will be very common when we handle those natural products they will be present in humic acid, tannins and the lignins, so we should know very quickly how the phenol and related compounds can be used for large-scale manufacture of other very value-added compounds as well.

So we can have the synthesis of resins, the phenol we all know the phenol formaldehyde resin we all know the bakelite we all know. So for making resins also that we are handling some bio or agri-based compound or molecules from naturally occurring thing but making plastics, pesticides also what they are we have seen during our electrochemical reduction or cycling voltammetry like polydol what we told the parathion we have talked the pesticides is the nitrophenol part is there so one of them is the phenol part.

So if the degradation can take place the nitrophenol can come out from those pesticides then making explosives also, then detergent also and the pharmaceutical compound, so all these

areas all these industries will be dependent on the analytical science to monitor their level of those phenol only. So phenol is a very simple very useful molecule from our school days we are learning but the presence of those phenol say to 5 to 10 compounds or useful compounds is the point of interest of our knowledge.

So varieties of phenolic compounds are also generated by different industrial activities when you go for some reactions in industry some industrial processes, so we get those phenolic compounds such as in paper bleaching industry when you go for paper bleaching we also produced some phenol because we are talking in terms of lignins, tannins and all these things, if we try to break them phenols are coming.

So then in coal mining, in oil refinery production of dyes also and appear as industrial pollutant in the environment, so phenol appear as a good industrial pollutants, good amount not good for us, so is a good amount of phenol is coming from so many activities and which are contaminating our environment which are contaminating our water and all this.

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Many phenolic compounds occur in food products, especially those of plant origin, e.g. olive oil, wine, herbs and spices, coffee, various fruits and vegetables, and also milk and dairy products.

Phenol Oxidation by Water-Producing Oxidases and Oxygenases

Tyrosinase is a copper-containing monophenol monooxygenase

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So what we find then that many phenolic compounds also occur in food products also because we deliberately knowingly uhh we add something to improve the food quality, to improve its fragrance and all other thing especially those phenolic compounds are coming from plant origin when we handle olive oil, we handle wine, we handle herbs that is why we are talking about some herbal medicines also, then spices, coffee various fruits, vegetables and also milk and dairy products.

So those things can be contaminated very nicely from activity what we can have that the milk can be contaminated, the daily products can also be contaminated by this phenolic compound, then the wine, than the herbs. So the origin of all these phenolic compounds can be there and how we handle those molecules that is the point of concern for everybody to us also how we can oxidise those phenol.

The idea is that, the way we are talking about the corresponding handling of the O<sub>2</sub> molecule, so O<sub>2</sub> molecule was there in our hand, so these O<sub>2</sub> molecules is also with us then glucose is also there, so in both these 2 cases we have seen that either the electron reduction or the electron oxidation, one electron or 2 electrons is there for your handling O<sub>2</sub> and glucose, so phenol can be there so we can have some biological molecules available which can go for 2 types of reaction one we consider as oxidase reaction and another is the oxygenases.

So these things are there that oxidases are there that were you go for direct insertion of oxygen atom in the molecule and oxygenases are based on oxygen can be utilised for electron transfer reactions. So phenol oxidases will be there and those phenol oxidases will be in our hand for our production of water, so the electron transfer reaction based on phenol can go to water production as we have seen earlier that you have the corresponding O<sub>2</sub> and that O<sub>2</sub> can be converted to your water producing molecules, so we can have one example just now we will continue it to our next class from this point that copper containing monophenol monooxygenase that means it can go for one insertion of oxygen.

It is showing some oxygenase reactions, so insertion of this oxygen on the phenol unit or it can go for electron transfer reaction which is copper based, that copper is going for your electron transfer reactions these are the tyrosinase. So how tyrosinase or any other copper containing enzymes can be useful to detect a level of phenol in any unknown solution that is of our interest to know develop the phenol based sensors, okay. Thank you very much