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Lecture – 14 Recovery of Metals from Electronic Waste (Contd.)

So, welcome back. So, we will get started from where we left in the previous video, if you remember we were looking at the solvent extraction. So, we were basically we are looking at this particular topic recovery of precious metal from solutions by solvent extraction.

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We looked at a different types of solvent extraction for gold.

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For the system with no ammonia, the extraction reaction is iNa++2Au⁺+jS₂O₃²⁻+OH⁻+mTBP₍₀₎ = Na_iAu₂(S₂O₃²⁻)_j(OH⁻)·mTBP₍₀₎
The addition of ammonia into thiosulfate solutions, the extraction reaction is iNa++2Au⁺+jS₂O₃²⁻+OH⁻+2NH₃+mTBP₍₀₎ = Na_iAu₂(S₂O₃²⁻)_j(OH⁻)(NH₃)₂·mTBP]₍₀₎
Where i (i = 3-5) varies with j (j = 2-3), and the TBP coefficients m in the two equations are in the ranges of 1.5-2.5 and 6-9 respectively.

We also talked about things in the presence of ammonia without ammonia if you remember we looked at those 2 big equations. And then we will continue that discussion in this particular video as well, where we will look at some of the other way of extracting these heavy metals these precious metals from the electronic waste. So, let us look at the next aspect like it is say we also use activated carbon.

So, activated carbon is has been this is you if you look at the literature, in terms of trying to extract a gold from either the ore of the goal are also from an from electronic waste. There is a people have looked at the mechanism people have looked at the kinetic and as you know the activated carbon I assumed that most of you have some sort of environmental background.

So, you will if you have taken the water class or even in some extent in the water waste water. If you have gone all the way to the tertiary treatment we do use activated carbon, activated carbon is essentially a adsorption adsorption site. So, as you can see this is a and there is a difference between adsorption and absorption.

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Adsorption is a physical phenomena, and absorption is essentially you have some sort of a physical as well as a chemical phenomena can take place over there, so adsorption since so, you have a layer. So, if you think about if you look at say this is this is a surface I have this surface and on that surface things are coming and attaching it to it. So, more is the surface area bigger the particle like a surface area smaller the particle more the surface area better is the adsorption.

So, that is why activated carbon usually has very high surface area. So, here what we are trying to try to see is that how the gold is getting into this activated carbon has been looked into by many researchers, and they look at the adoption process and when wherever we talk about absorption process we have the concept of the isotherms comes in like a freundlich isotherms or Langmuir isotherms and you have a partition coefficient. A number partition coefficient is how much would be in the solid phase versus how much would be in the liquid phase.

So, for the solid and liquid adsorption process this is the typical equation that is used. So, we can this is the typical relationship where q is the quantity of solute, adsorbed per unit weight of carbon. So, this is what is getting into the this is the solute which is getting adsorbed onto the carbon q max is the maximum sorption capacities at the saturation, C is the equilibrium concentration of the adsorbate is the what is getting adsorbed in solution and b is the adsorption equilibrium constant. So, there is that is your equilibrium

in constant. So, based on that you can write down this relationship where q which is the quantity of solute adsorbed per unit weight of carbon is equal to q max which is basically the maximum absorption capacity multiplied by your b, which is equilibrium constant C is the concent equilibrium concentration adsorbate in solution.

So, you can write down this same equation as a typical equilibrium equation that you have done in a chemical equilibrium class, and then you can rearrange that and you can get that same equation there as well. So, activated carbon is also used in terms of getting gold from solution so, we have basically trying to remember in the from the previous class what we were trying what I was trying to tell you is that.

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You start with we have this electronic waste or for that matter iron ore from the ore from the solid phase first we try to bring it to the liquid phase, and from the liquid phase again we try to bring it to the pure solid phase. So, that is the phenomena we already talked about how to get it from the solid phase, from the electronic waste or from the ore to the liquid phase.

Now we are talking about from that concentrated liquid which has gold present or this precious metal present how will recover this precious metal. So, that we were we are trying to look at. So, another expression that is used for these kind of activated carbon or the isotherms is the freundlich isotherm which is very common you may have seen it in other classes as well.

Where you have q is expressed as K times C to the power of n where your K is or K and n are the freundlich constants and C is the con concentration, and q is a C is there like a maximum concentration and q is a concentration at 1 look at a particular, when you are looking at how this is the maximum like based on maximum shops, and capacity and the q is the subset capacity at particular property for that particular like material.

So, K and n will be freundlich constant for based on the activated carbon. So, freundlich type multi component isotherm was developed by this another thin things are developed so, again what I am you do not have to kind of memorize or these things what we are trying to say over here is there are a lot of work going on in terms of a looking at the recovery of gold from electronic waste, and to bring to bring the pure gold. It is still lot a work mostly in the lab scale some pilot scale full scale plant of recovery of gold there are some in Japan some in Europe, but we do not we do not have any as far as I know in in India where we have this process the entire process, and that is where lot of research is needed in the country.

So, those of you who are looking at electronic waste as potential carrier for your masters or PHD project masters or PHD thesis these things and you are interested in chemistry. You have to be interested in chemistry and then you can pursue these kind of topics ion exchange.

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Ion Exchange Commercial IEX resins employing small quaternary ammonium moieties (strong base resins) have been successful in recovering gold from thiosulfate liquors. Thomas et al.2001 observed almost full recovery of gold and silver using strong base resins. Aqua regia leaching can be used (Sheng and Etsell, 2007) for recovery of gold from computer chips due to its flexibility, ease and low capital requirement

So, all these are nothing new like adsorption activated carbon, ion exchange even the previous leaching, thiosulfate leaching, cyanide leaching, all these have been used in different fields. So, we are trying to just apply that knowledge with electronic waste recovery of precious metals from electronic waste. So, in terms of the ion exchange commercial resins are used as small like a along employee small quaternary ammonium like a it is called ammonium moieties it is strong base raising, and that is have been found that once you have this thiosulfate leaching remember we have we talked about the thiosulfate leaching, now the thiosulfate has gold there.

So, we can use this raisin to recover the gold from this thiosulfate liquor. So, this but this particular research they observed an almost full recovery of gold and silver using a strong base raising. So, they could recover gold and silver from their aqua regia leaching was can be used as well, and where aqua regia is used aqua regia is used in mostly in the informal sector, when they try to do this gold recovery they use lot of aqua regia. And that is used in the becoming of gold from computer chips due to it is flexibility is a and low capital requirement. So, that also has been found has been limited it has been reported in the literature. So, these are some of the ways in which you can extract gold from the liquid phase.



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So, and for just to have a process how this process would look like if you want to recover metals from PCBs, now what is PCB this PCB is not that polycyclic biphenyl that mostly

pc mostly the PCBs that we hear and talk about in the environmental field here, this PCB is the printed circuit board. So, when we say PCB actually we are looking at the printed circuit board here not that PCB that you see in your most of the environmental book in terms of polycyclic like biphenyl.

So, a PCB scrap which is the printed circuit board which is there from can be from computers 1 can be from any sources like more any electronics, wherever you have some sort of electronics it will have a printed circuit board even your cell phone you open you will find a circuit board. So, it is there is a circuit board.

So, how will you how we potentially go in terms of recovery of metals, first thing we try to do this reading. Again why we do this reading say I keep on telling you may be many times I have said they even in this 4 week class so, far that everything that you look at try to understand why, why it is being done why it is reading because it is reading if; that means, extra energy source is not it you are applying at 1 point we are talking about environmental management environmental protection.

So, if setting is not if we have to understand why this reading is required, because reading means you have we have setting up a separate unit straighter has to be straight up it will it is we are talking about printed circuit board so, they are not easy to thread. So, it will be it will require certain energy to do that and the energy means environmental footprint. So, we have to understand why the shredding is required I think by this time I should you take a you should be able to tell me why it is done it is essentially what we are trying to do by shredding varying reducing the particle where we are reducing the particle size increasing the surface area is not it.

So, we are making it a small particle we are making it a not should not call it particle like a small pieces a small pieces of printed wire board and a small pieces means more the surface area more the surface area means better the reaction and that is why you are trying to do the shredding. So, after shredding 1 you can do the leaching now what the what we are trying to what essentially we are trying to do the in leaching, we have these heavy metals, that heavy metals present in the solid form here it is in the solid form, is not it is in the solid form.

Now, in the leaching process what we are trying to do we are trying to get this solid into the liquid form. So, we are trying to dissolve we are trying to dissolve this heavy metals, in acid that is why you see that amenity in their leeching acid or some sort of or sometimes even base is used any solution. Now what kind of leaching solution will be used, in general if you look at the electronic recovery what kind of any leaching solution, which has the potential of bringing the required metal the targeted metal the targeted metal from the solid phase to the liquid phase, whichever whether it is an acid or a base does not matter whichever serves the purpose of bringing, these heavy metals from the solid phase to the liquid phase that is kind of the leaching fluid will be used.

So, here 1 to 6 molar HNO 3, 1 to 6 molar HNO 3 is used to get the things in solution some of them will come in solution some of them may precipitate depending on the solubility product, remember you all have done that KSP when I IAP ion activity product is greater than KSP that when IAP a ion activity product is greater than KSP things will precipitate that says in it we all learned about it in our high school chemistry. So, this is concept is actually used a lot in into environmental remediation environmental like a this kind of exercise, chemistry chemical industry.

So, this concept of solubility product is it is very basic concept which we use a lot in terms of our like a in terms of our application in different industrial process. So, here you will have tin precipitation as metastannic acid. So, tin will precipitate out so, when if the tin is precipitating out. So, we can take it out in the solid phase now you filter after filtration let us clean this that it becomes clear.

So, you have the tin precipitation, after that you do the filtration after filtration now what we have, we have the tin is gone most of it there may be some is still left, but the tin is gone then we have the other there could be other metals present a little bit of tin and other things could be present as well. So, you dissolve in 1.5 molar HCl dissolution is 1.5 molar you could have some electrode the electrode deposition in tin, and neutralization by sodium hydroxide that will have electro deposition of copper and lead. So, you can recover copper and lead that way, then you can use H 2 O regeneration for reuse so, you try to reuse it back HCl. So, some with HNO 3 some with HCl again then we can recover ICl recovery for H 2 Sn O 3 solution. So, we get back over there.

So, this whole that is how the process is done here the target has been tin copper and lead, but interface the target has been something else the type of solution may have changed. The type of solution that is needed and the ph conditions, basically we are

playing with the chemistry of that heavy metal. If you have we are essentially playing with the chemistry of that heavy metal and trying to separate them out, there is also a concept called sequential extraction, now what does that mean sequential means in sequence is not it.

So, do not again do not try to memorize try to understand sequential will be what in sequence. So, in sequence means you will try first 1 metal, once that has been recovered then you go to another metal. So, that way that is the sequence you are following a particular sequence at a extracting 1 metal at a time or 1 element at a time depending on what you are looking at. So, that is what those are the concept used in terms of recovery of metals from electronic waste, and here we are looking at an example of printed circuit board then us so, that is you. So, far we have looked at several methods in terms of mostly based on chemistry.

Now we will be looking at some methods where we are chemistries. So, it is a bore as a biochemical method, now what we mean by biochemical and the biology is actual also playing a major role here, because if you think about the mother nature, then a lot of microbes a lot of bio actually it is a any anything or happening in the nature it can be biology we could be there, chemistry could be there, geology could be there, a lot of other things could be there many times we call it take a biogeochemistry as well because all these factors are there.

So, and if you have a taken any solid waste class we talked about in the landfill or anaerobic digestion or as simple as BOD test BOD test is a biochemical test is not it because of bacterias are there which is doing your most of the oxidation and the oxygen is consumed because of that and but there could be some chemical reactions happening as well based on what kind of contaminants are present there might be some reactions going on, but when we say COD which is a chemical oxygen demand, which is essentially we are trying to make it chemistry test like it is a chemistry test very quickly there it is done.

So, now, we look at some of these bio metallurgical process, where we have we are making use of these biological methods, biological methods in terms of metallurgical process means what mostly it will be leading to this extraction may extraction of metals, whole this metallurgical engineering is based on trying to get. So, mining people mines the gets the raw material, then our metallurgy people gets those from the raw material to it is more usable form, then the mechanical and other people will try to have those use those material like, aluminum sheets copper sheets which the metal and then also civil electrical, and all we will use all those material, and then now even computer science hardware engineer.

So, we are actually in depth it we if there is no mining good mining engineers, no good metallurgy engineers, we cannot really do much because we will not have the material. Even if you want to make a chip there are these days there are so, much fascination about all these electronics data analytics, and financial engineering financial risk management whatever, but for anything to be built we need material, we need energy and for that well we have to really be very thankful to our mining people and metallurgy people, because they make things happened for us they prepare the raw material for us which we can use in different applications and material science and other people. So, what I am saying mining and the material way I am talking about all people who are involved in those particular area. So, let us look at the bio metallurgical process. So, in terms of to what is that it is a biochemical process.

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• One of the most promising technologies.

Its involved in the treatment of metals it has been using for last 2 3 more than 2 decades actually people are working on growing investigation for the last 20 years it also there is another side of application as a environmental engineer, we also talk about bio

remediation of we try to do bio remediation which is again we are trying to extract metal this when we try to do the bio remediation, what we are trying to do we are trying to get the metals especially in when we talk about this fight or remediation for example, that is also 1 kind of our mining only you are trying to mine, you are trying to get this raw I can arsenic or whatever cadmium or what whatever the contaminant from the soil which is a contaminated soil to the biomass. So, that is again 1 sort of reaction taking place there.

So, it is a material ones mineral industry there is great interest because it is a it is an for it is a new technology and it is a comparatively green technology. So, one of the most promising technologies, that bio metallurgical process people are the people want to use it to find out.

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At present mostly research and development is in process we can for nickel, cobalt, zinc, gold, silver and for all these we use microbes again anything bio you use microbes is not it by microbes are used. So, microbes are employed for a structural function and catalytic functions. So, we are using microbes, and they are both type different types of microbes are there you do not have to worry about the type of the microbe you just try to understand the concept, and do not as a engineer we do not have to remember the microbes name.

And the type of microbes whenever will be designing this bio metallurgical process, will get people involved from the biology side who can help us with that so, but we need to as

a engineer we need to understand like how this process will work the process is more important

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And the details of the process in terms of the more is specific anything biology, we can have the biologists help us with that. So, bio metallurgy you can have bio leaching and bios option, now what is bio leaching and bios option leaching we already talked about sorption we already talked about. So, we have just added a term bio there is small be a like a 3 letter word bio there so, what is bios leaching means leaching with the help of biological organisms.

So, you are trying to have things what is leaching, leaching is things moving from solid phase to the liquid phase. So, here hardly we have use the chemicals now here we use the microorganisms to do that work for you. Similarly we can have the bios option it can be on the biofilm it can be certain like if things can sharp on to the biological kind of surfaces we can say and we will talk about that in a little bit in more detail, and we make things happen that way.

So, bio leaching it is successfully applied in many in recovery of metals from metallic sulfides people have used it for metallic sulfides, which are the major bearing minerals for many base and precious metal. So, sulfides why sulfides have you ever thought that I have just made a made a statement here, that metallic sulfides are major bearing minerals for many base and precious metals.

Why sulfides are major bearing mineral for many sulfide many stuff why. So, why anything else why sulfide, because sulfide you typically if you remember from your KSP solubility product sulfide has pretty low solubility product in most of the cases. So, for most of the metals. So, that is makes it easy to be precipitated out. So, over in the nature we have most of these minerals, most of these ores, like a where things are in sulfide form copper or lead or arsenic they are always in our char and they are in the form of sulfide, because the solubility product is pretty low things do they precipitate and it comes into the solid form.

So, bio that is the bio leaching part where we try to recover metal from sulfides biosorption process is essentially a physical chemical interaction where between the charged surface and on charged surface of microorganisms. So, it is a charged surface of the groups of microorganisms, and the ions in solution and which livings as well as the data organisms is used. So, you will have that is the process of biosorption and we will talk about these 2s in little bit detail

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So, in classification of bio leaching you can have direct indirect. Now direct leaching where you are using like a like a biological organism they are helping. So, when how they how they will help in the leaching, they will break down those whatever is the big molecule present in which our targeted heavy metals is present they will break it down,

in some like a reaction and as a part of breaking down the iron the metal will get free and it will come into the solution.

So, that is what essentially it is going to happen indirect leaching like sometimes using the thiosulfate pathway, polysulfide pathway things do get form. So, not directly it is going there if it is becoming from the sulfide it is becoming sulfate. So, that is and from the sulfate you can recover those heavy metals, or from poly sulfide you can recover those heavy metals. So, that is the indirect so, but things are will ultimately will come to the solution.

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• # \$ • 4 🖽 **/** / # • • • 🖬 \$ **Bioleaching** (Direct) □ An example of mechanism of bacteria by Metal-Sulphide action. □ In direct action mechanism, microorganisms will directly oxidize minerals and solubilize metals $MS + H_2SO_4 + 0.5O_2 \rightarrow MSO_4 + S^0 + H_2O$ S^0 +1.5 O_2 + $H_2O \rightarrow H_2SO_4$

So, in the metal sulphide action if you look at the bio leaching direct where you have microorganisms; directly oxidized minerals and solubilize metals. So, you have this metal sulphide. So, H 2 O in the presence of H 2 SO 4 from oxygen it will make metal sulfate which is sulfate means it will come in solution. So, it will solubilize the metal, and then sulfur will come out and the sulfur can again can be used to get H 2 SO 4 and that the reaction can go back. So, we can use more as to a support. So, here it is a bacterial mediated reaction. So, it is a bacteria which is doing the job. So, it is a bacteria medicated mediated reaction. So, bacteria is doing the work for us and things are getting into the sulfide phase and which is the soluble phase.

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In direct method what you will do it. So, again you have your metal sulphide so, in the case of I feel like a ferric ion is the oxidizing agent. So, you have metal sulphide with the ferric ion. So, this will act this will take a electron and becomes Fe 2, and in that process the sulphur, so here we have this will be an electron acceptor.

So, electron will get released. So, 1 electron will come from actually here. So, your M 2 plus and S, they are this will get sulphur this bond will get broken down by the iron reducing bacteria, which will work actually for you and get M 2 plus. And now this Fe 2 plus you can either oxidize it back or make Fe 3, and then Fe 3 can be used back into the reaction. So, here your iron reducing bacteria many times you hear the term IRBs, IRBs are used to they are reducing iron 3 to iron 2, and in that process when the iron 3 accepts a electron.

So, electron has to be come from somewhere. So, electron will come in the process of when ms will broke down. And then M 2 plus and then 2 sulfur it is a negatively charged. So, at the negative charge of that particular thing has to come out in terms of electron and that electron will be taken up by iron to make iron to go from iron 3 to iron 2. Now iron 2 can be oxidized back to iron 3 and can we use back over here. So, that is the cycle can continue. So, middle sulphide here are leached via 2 different reactions we can have by a thiosulfate or polysulfide. So, those reactions are used as a intermediary reaction basically.

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Thiosulfate leaching is also done again you can you can have a thiosulfate mechanism where iron through a so, FeS 2 where this will go to iron from iron 3 it will go to iron 2, in between they will have a thiosulfate being formed and from thiosulfate then again iron 3 will it will go 2 iron 2 plus iron 2 plus is soluble iron 3 plus is non soluble. So, it is a based on that you can get this iron out from this particular reaction. So, it is a you can make more and more iron 2 is in solution and you can from hen you can recover iron 2 and make those iron products.

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So, polysulfide again the other ways of doing it do not worry too much about the mechanism. So, there are different ways of doing that. So, we are polysulfide mechanism allows for a dissolution of iron 3 into by proton.

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So, in both leaching bacteria consists of regeneration of iron 3 and so, bacteria is making a use of in terms of iron 3 ions by iron introducing bacteria is working here, as said of will like iron 2 oxidizer. So, controls the redox these at iron 3 iron 2 ratio is important. So, my main drivers are iron oxidizing microorganisms. So, there are iron reducing bacteria there are iron oxidizing bacteria as well. (Refer Slide Time: 26:25)

Bioleaching of Metals from E-Waste Dust collected from shredding processes of electronic scrap was used in the investigation (Brandl et al., 2001). The leaching experiments was performed by using a mixed culture of *Thiobacillus ferrooxidans* and *T. thiooxidans*.

Two steps process are introduced to reduce the toxic effects on microorganism.

So, we can this iron oxidizing bacteria can be used for that particular, and let us see what happened here just a see yeah so, we were yes. So, iron oxidizing microorganisms are either in the mesophilic or the thermophilic range that can be used for that. So, from E waste there has been some a study being done, say dust we are collected from the shredding processes of E scrap the leaching experiment was performed using the bacteria, do not worry too much about the type of bacteria. Because it is basically it is an bacteria which an oxidize iron and so, the 2 step are involved and reduce the toxic effects.

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So, first stage biomass was introduced in the absence of electronic straps. So, first we want to we want to make sure that. If you load too much what happens with the bacteria is that if they get inhibited if then it is becomes toxic it and becomes a problem. So, we want to make sure that the bacteria survives so, in that case we first make the life comfortable make them accumulated to the atmosphere.

So, biomass was produced in the absence of electronic strap first then was added in different concentration and the cultures were incubated. So, leaching result confirmed that 5 to 10 grams per liter respectively. So, we did find and this thiobacilli were able to leach more than 90 percent of the available aluminum, copper, nickel and zinc. So, they could bring based into the solution.

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Bioleaching of Metals from E-Waste	
At higher concentration, reduced.	, metal mobilization was
□ Pb and Sn were not detected in the leachate.	
It is proposed that Pb precipitated as PbSO ₄ and Sn precipitated probably as SnO.	

At higher concentration the mobilization was reduced maybe because it was becoming ah little bit of toxicity or it was getting toxic to those microorganisms lead and tin were not detected in the leachate. So, it led could not come out it was possibly led become precipitated out or then tin also got precipitated out for so, it did not come into solution at that particular PH. So, for the copper for the printed copper from the printed circuit board that also been looked into by some researchers. (Refer Slide Time: 28:15)



So, here iron sulfate formed using the bacteria Ferro oxidants, oxidizes the element copper and to from PCBs to the cupric ion. So, those are the way it has being already kind of talked about.

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Biosorbents are also being used from for a mineral like waste biomass of algae fungi bacteria. So, they are used as they are at the surface, for this option you need a surface is not it. So, acid condition you can have biosorption of precious metals from solution so, you can put it on the if things can sorp on bacteria. So, research have looked at the previous metal especially focused on gold.

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So, biomass may be used in this case as well Biosorption by Chitosan derivatives that has been used quite a bit alternative for recovery of precious metal Chitosan is a deacetylated derivatives of chitin. So, that is where second most abundant like a polymer on earth after cellulose.

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So, major advantage of using chitosan is that amino sites of chitosans are easily protonated in acid media. So, it is a protonated then the it is a charged, and then you can use that charge to get the other charge that is accentuating the electrostatic force often that is increases the sorption.

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So, freely suspended biomass has certain some disadvantage because of a small size and all that. So, in terms of the biosorption what we are trying to do we are trying to make a bacterial surface with it charge. So, that the metals that we are trying to target will get attracted to this particular charge and (Refer Time: 29:54) then we can recover we can take this biomass out, and recover heavy metals from there. So, that is the pretty much the concept behind it.

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Mechanism of Biosorption

- Biosorption of precious metals from solutions can be simplified as chemical sorption mechanisms and physical sorption mechanisms.
- Chemical sorption mechanisms include complexation, chelation, micro precipitation and microbial reduction.
- Physical sorption mechanisms generally involve electrostatic forces and ion exchange.

So, mechanism it is a as I was trying to explain you gets simplified as chemicals option mechanism, if chemicals option you have the complexation chelation micro precipitation microbial reduction physical sorption means generally electrostatic force, and ion exchange which we talked about.

So, bias option it can be chemicals option mechanism as well as physical could be combination.

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It is kind of a hybrid. So, generally biological leaching is a cost effective technique, but it does take time anything biological take times, and complete recovery by just by biological may not be enough. So, chemical leaching is comparatively rapid. So, many times you try to use it chemical leaching also has like hazardous waste problem and all that. So, many times we try to use it in combination.

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Hybrid take techniques have been proposed involving combination of chemicals, and safer chemical biological leaching and it is can enhance the efficiency as well.

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So, hybrid technology using extraction of jetting copper involving EDTA using Ferro oxidants bacterial strain of DSM so, all these as you can see several papers have been have looked into these this what this type of hybrid technology not that much popular in industry right now.

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But things have been used from there. So, let us stop some to this particular point and we will continue our discussion in the next video. Where we will stop with this hybrid technology, and then we will talk about some of the E waste issues a specifically for India and that would be the last I think the last video for this particular week. So, again thank you looking forward to your discussion on the discussion forum we will be more than happy to answer any question and Is hope you are enjoying the course.