Water and Waste Water Treatment
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Lecture -25
Nitrogen Removal- II and Phosphorus Removal- I

Hello everyone welcome back to the second session in the context of removal of nitrogen and phosphorus. In the first session or the previous session we looked at understanding nitrification and then denitrification. first you are going to change the form of nitrogen from ammonia which is reduced form of nitrogen to oxidized form NH_4^+ going to or ending up as NO_3^- but NO_3^- is soluble.

You are going to use or promote different kinds of bacteria by changing the conditions and these conditions are such that it has to be anoxic.

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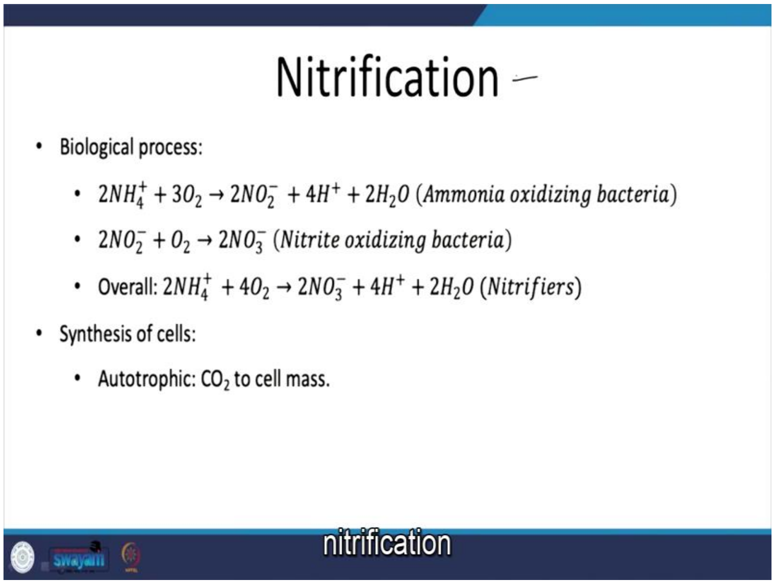

Let us look at this so we have nitrification we looked at this. So, two steps first ammonia oxidization to NO_2^-, so thus ammonia oxidizing bacteria and NO_2^- going to NO_3^+ nitrite oxidizing bacteria overall it will look like this NH_4^+ going to NO_3^- but please understand that there are series of steps. And these are autotrophic as you see for their cell mass they do not use organic source of carbon.

They do not use an organic source they use an inorganic source of carbon. So autotrophics or autotrophs. And one aspect to keep in mind is that they grow slowly. So what does that mean meaning that you have to have high cell residence times. So, that is one aspect and also their yield is less number of microorganisms or new cells produced per what we say mass off or unit mass of the substrate or food that they are consuming. I think we will come to this later so let me not digress here.

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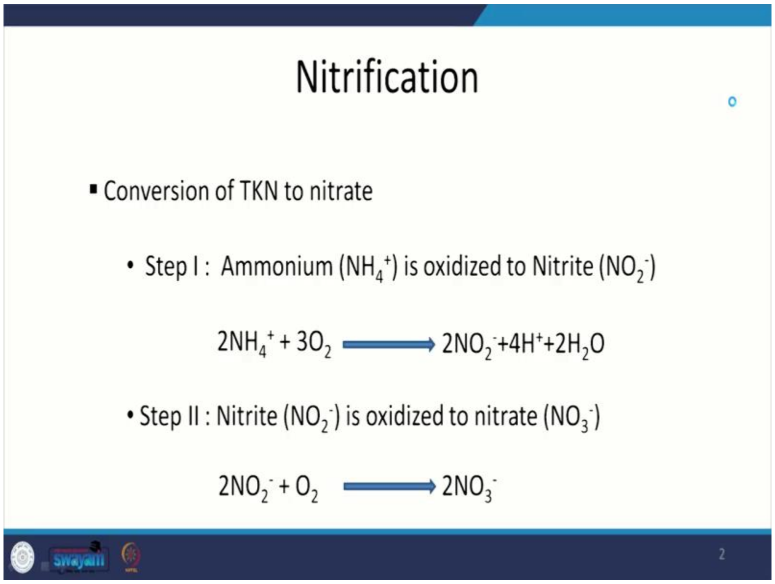

So, denitrification conversion of do we say TKN into nitrate we already summarized this in the previous slide.

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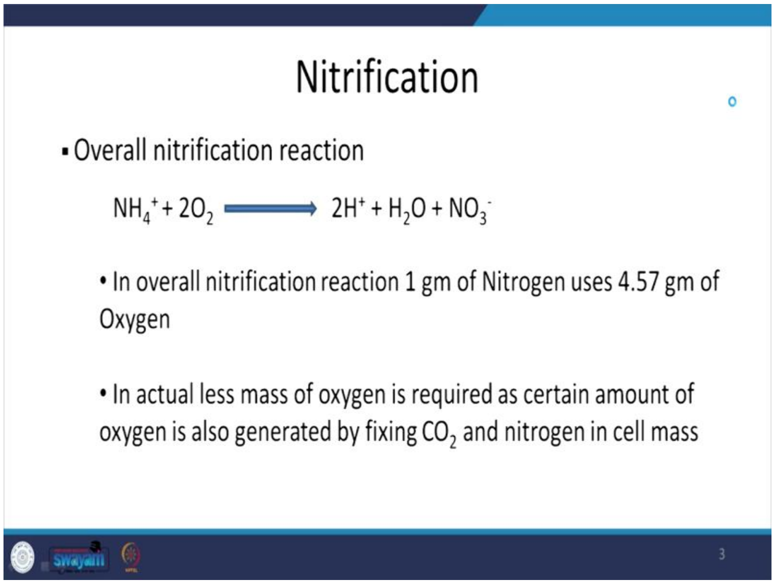

So, let us move on two steps and overall nitrification reaction years and here one aspect to note is that if you look at it from mass point of view one gram of nitrogen uses 4.5 grams of oxygen. So that is a considerable requirement. So whenever we are looking at removal of nitrogen the need for oxygen goes up a lot. Why is that because then your costs also increase but it is not as if it is 1 is to 4.7 why is that because some of the nitrogen will also be fixed in the cell mass. I think we might have the equation somewhere here.

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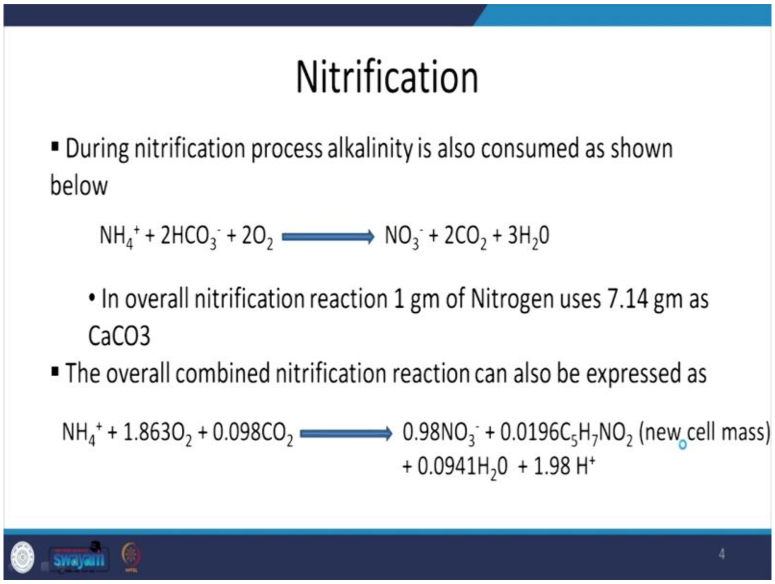

So we will come back to that particular equation. So we have it here it is NH_4^+ , 1.86 O_2 and then here you see it is NH_4^+, $2CO_2$. So you understand that some of that is going to go into new cell mass and CO_2 is being used for production of the new cells. this is the overall reaction where NH_4^+ is being degraded to nitrate and also the new cells are being produced new cells.

So that is one reason why we talked about this though theoretically it might seem like one gram of nitrogen consumes 4.7 grams of nitrogen, actual requirement might be slightly less. And as thus I guess if when you say you are going to consume carbon dioxide it is not carbon dioxide or you have to I guess produce carbon dioxide too. So HCO_3^- will be consumed in this process this carbon dioxide will be released.

So why is that necessary because it will lead to decrease in the alkalinity which will give me an idea about the acid neutralizing capacity of water. these waters now you can either the ph will be affected or whenever you add an acid they cannot stop the decrease in pH but we are not going to digress there but that is one aspect to keep in mind because you see that during what we say nitrification process alkalinity will be consumed.

the overall reaction turns out to be something like this you have both the nitrification $2NO_3^-$ and new cells let us move on

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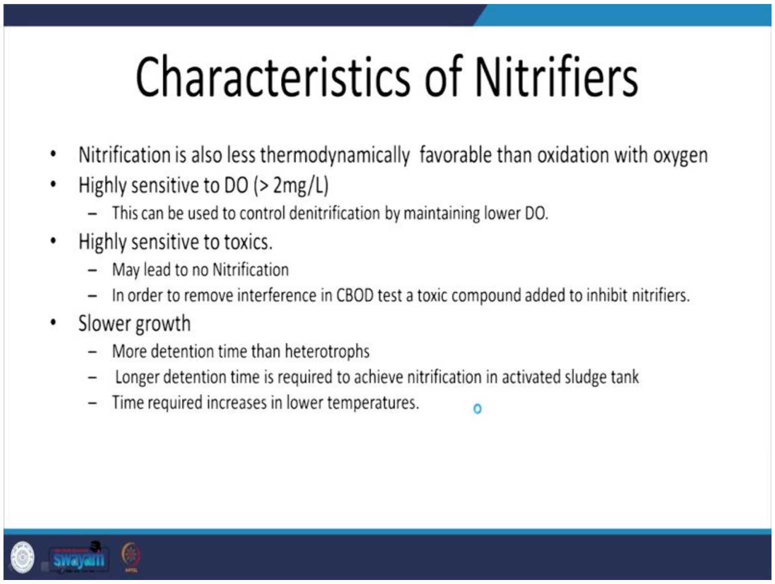

So, characteristics of nitrifiers: Nitrification is thermodynamically less favourable than oxidation with oxygen. For example if you have if you look at the energy and I think we looked at this let me explain it in a better manner. We looked at the COD test I think here we had time and here we had the COD or such. And I think we saw some graph like this and then we see that when there is no more carbonaceous what do we see oxygen demand then you have the nitrogenous oxygen demand coming up.

Why is it that bacteria do not use nitrogen when there is carbon present or organic carbon present because in those conditions a different kind of bacteria which gain more energy from the degradation of organic carbon in the presence of oxygen that gives out more energy and those microbes thrive. So that is the reason why typically they grow later that is one of the reasons and that is what we are trying to say nitrification is also less thermodynamically favourable than oxidation with oxygen. I guess it is not greatly written or poorly framed sentence here but you understand the issue.

And they are sensitive to DO so the DO is typically relatively higher this is one way to control denitrification or nitrification by maintaining a lower DO. So if you do not want to have nitrification and thirst later denitrification what is one way so you can maintain relatively low DO without being too close to zero. And at this relatively low levels you can still have aeration occurring but nitrification will not occur.

And another aspect is toxins we discussed this. So I will skip through this. toxics toxins they affect the ammonia oxidizing bacteria or nitrite oxidizing bacteria greatly then they can affect the other heterotrophs or the heterotrophs out there. So that is one aspect that is highly sensitive to toxics. And as we mentioned earlier slower growth so they require a higher retention time than the heterotrophs.

So, longer retention time is thus required to achieve nitrification in activated sludge tank. And time required increases in lower temperatures because the kinetics is the case. So you need to look at θ_C. So that is something to keep in mind on θ and θ_C.

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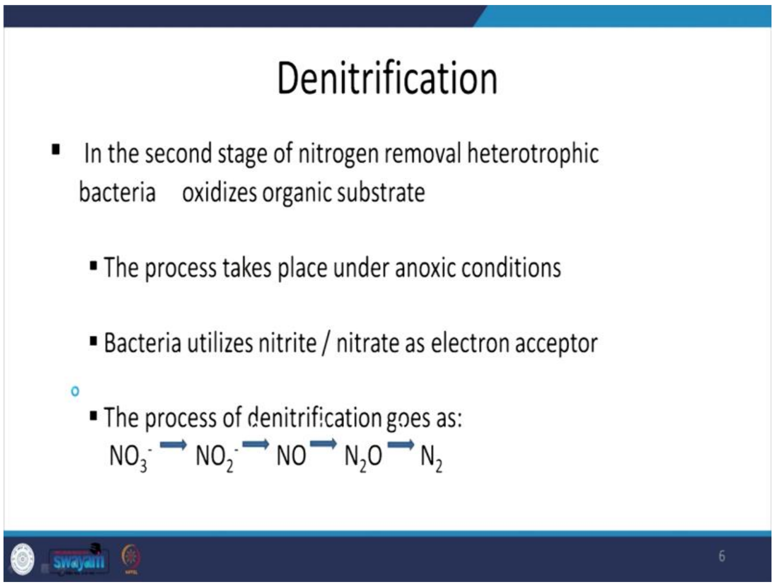

So, denitrification, so in the second stage of nitrogen removal heterotrophic bacteria why heterotrophs because they need a source of organic carbon. But unlike earlier what is the electron accepted here it is not oxygen but it is NO_3^- that was produced from nitrification. So electron acceptor is not oxygen so it is not aerobic process but it is an anoxic process yes so that is what you have and that leads to formation of N_2 so under anoxic conditions.

So this is what you have NO_3^- , NO_2^- for reduction and finally you end up with N_2. denitrifies, so that is something to keep in mind if there is oxygen you will see that.

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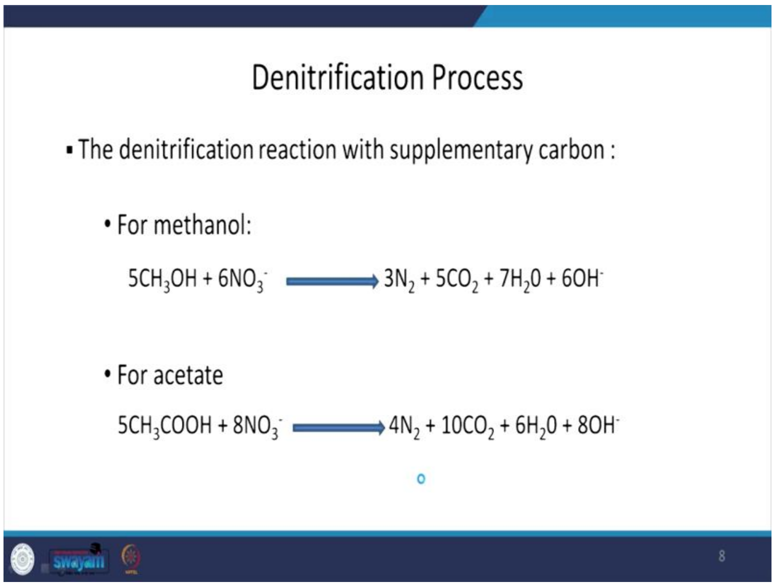

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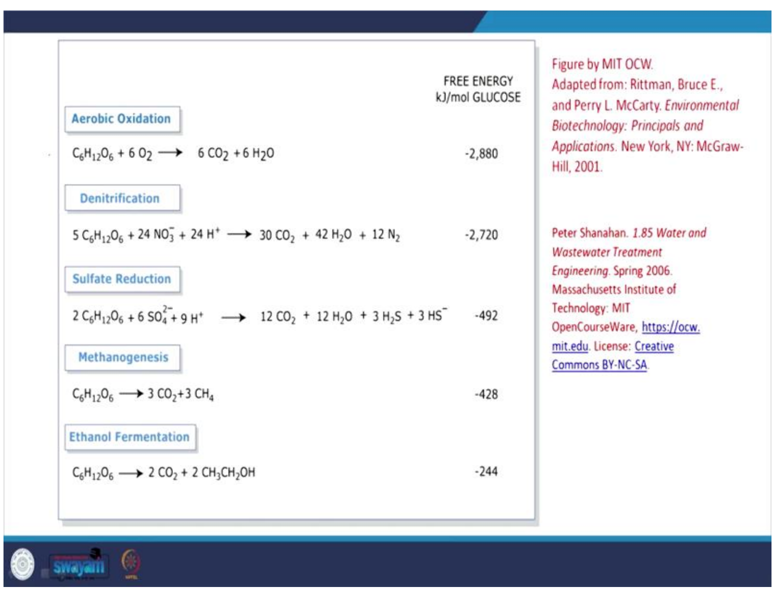

I think we have the relevant table that I want here. So this is the case that we will compare glucose the amount of energy released and for denitrification the amount of energy released. So, as you see not a great plot of energy but some energy or relatively more energy is released. When we have oxidation of the organics by oxidation oxygen so you should not have oxygen.

Because if oxygen is present the kind of microbes that thrive will be different and you will not have this reaction taking place if you do not have this reaction NO_3^-, $2N_2$ will not happen so thus you have to prevent oxygen from being present so that is something I wanted to mention. So if organic matter is present fine that will be used organic matter can be the waste water itself or the waste in the wastewater itself that can be used. But depending on how you are configuring the system if you do not have organic carbon where is the electron donor?

There is no electron donor so in that case you add carbon or source of organic carbon so methanol or a state is added sometimes.

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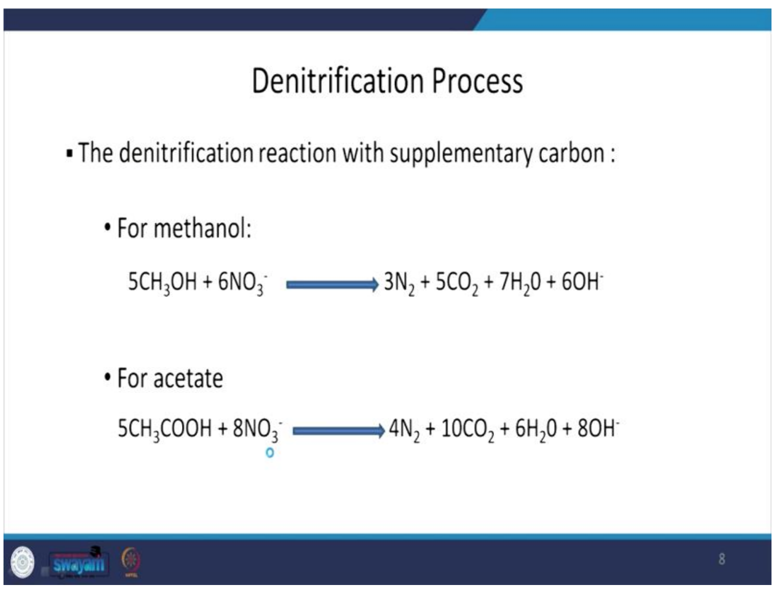

And I guess here is the relevant redox reaction CH_3OH and CH_3COOH carbon is being oxidized and nitrate is being reduced. Electrons transfer so that is something that you can see when are you going to add methanol when you do not have enough carbon for driving this particular reaction. And we already looked at this so I will skip this aspect.

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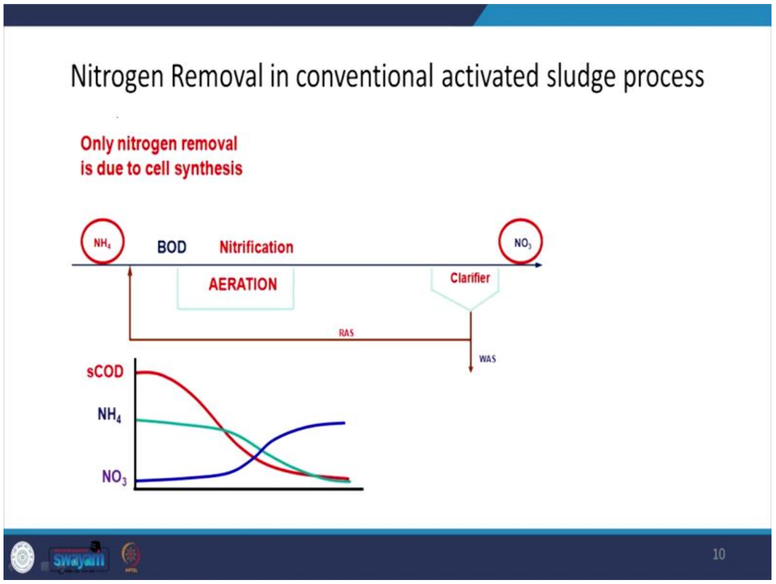

Let us just look at one system. In a conventional asp let us understand nitrogen removal assuming that the θ_C and θ such that are long enough such that you have nitrification taking place. We know that there are slow growers so they need more time. So θ_C is more. NH_4^+ and BOD are coming into the effluent here and here assuming that we spend or let the bacteria spend enough time such that nitrifiers are also what you see in the picture.

You are going to have some nitrification and then BOD removal. So that is what you see soluble carbonaceous oxygen demand it is decreasing that is something that you would expect. So NH_4^+ is also decreasing assuming that we maintain the conditions and NO_3^- is increasing. And then what is happening though we will end up discharging NO_3^- into the effluent. But we know that NO_3^- is not something we want to or should discharge into the wastewater there are standards primary reason being NO_3^- is toxic to us too to humans.

So how do we change it so here the key is to understand that this NO_3^- is formed when you have oxygen. And NO_3^- is removed to nitrogen when you have no oxygen. So that is the key so you will have anoxic conditions and aerobic conditions.

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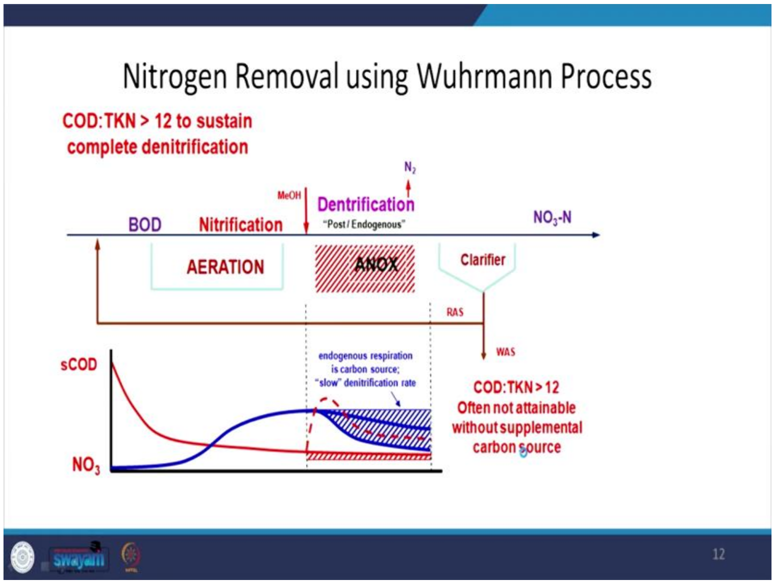

So nitrogen removal let us look at one other aspect here. So here you have aeration so during this process. Let us understand how the system is going the same case as earlier the first part is the same case as earlier during aeration BOD removal takes place. So that is what you see this BOD is being removed the BOD or COD soluble COD is being removed. So that is happening during aeration and assuming that we maintain the θ_C such that nitrification also takes place you are going to see formation of NO_3^-.

So NO_3^- is formed. So here at after aeration there are two cases. If there is not enough organic matter because I now have NO_3^- I want that to go to NO_2 but I do not have an electron donor so I need to have some organic compound. So, that this is what can maybe take place. So if the organic compound is not already present in the water I have to add it so as mentioned we are going to add methanol.

So that is what you see so that is why while the organic COD or COD is decreasing until now after addition of methanol you see that it increases. And then the methanol is being degraded by this particular reaction and simultaneously NO_3^- is being reduced to N_2. So this is the path. So this is the path for NO_3^-. But if I do not add methanol what is going to happen? There will still be some BOD or COD in this treated wastewater.

So that can act as the source of my organic carbon for this reaction but typically in my treated wastewater the organic carbon will be relatively less. And thus this rate of this reaction will be relatively slow and if there is no methanol or additional organic carbon present so you are going to have a slower removal of nitrate or even a more or less slower and finally lower removal of nitrate.

So that is what you see here in this anoxic tank nitrogen is the end product that is what you see. So typically what is it that we have some additional information COD to TKN if it is greater than 12 then it can lead to or you can sustain the system to lead to denitrification. So that is one aspect to keep in mind. But in general for wastewaters without adding a carbon source looks like you cannot achieve that level of denitrification or complete denitrification. So that is something to keep in mind so I guess work man process yes let us move on.

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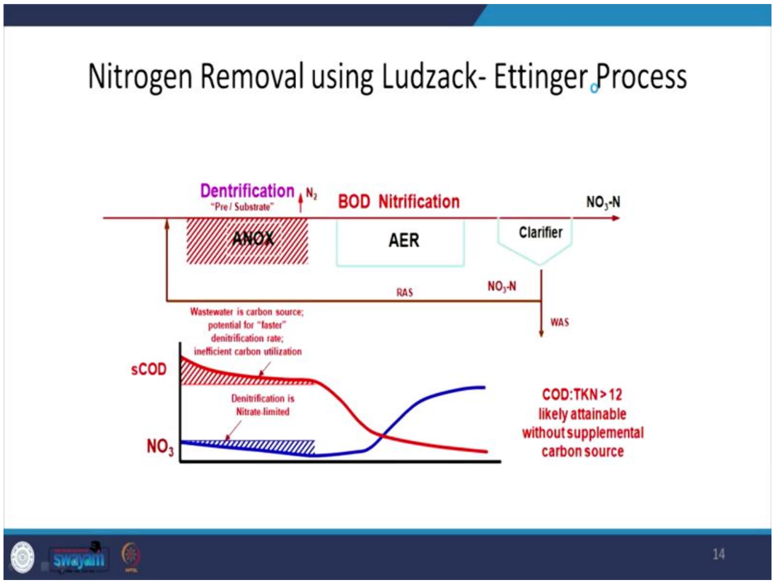

Nitrogen removal so what else do we have different kinds of for configurations. So Lutzec Ettinger process so what do we have? Here please note that the anoxic tank is present before the aeration tank. But then how is it that I am going to what do you say have nitrate here. For example in the anoxic tank that NO_3^- goes to N_2 but it needs some organic carbon. Fine organic carbon is coming from my influent wastewater organic carbon my waste is the organic carbon.

I want this reaction to take place fine but where is the nitrate coming from? So, that is why you see that this nitrate will be recycled from here, if not from here it will be recycled from here. Or probably even here that is also fine. Because you do not want it to leave a lot from here so depending on that you can recycle from here or here. So you are going to recycle this so here what is going to happen you have recycled that is bringing in nitrate from the treated wastewater.

So you have nitrate here you have the organic compound here and then this anoxic process goes forward or denitrification goes forward and N_2 is degraded. So what is it that we see wastewater is the carbon source as I mentioned and because there is considerable carbon or organic carbon because wastewater is infinite wastewater has higher carbon so potential is faster or the kinetics will be faster with respect to the denitrification rate.

But inefficient carbon I understand what I should have done a minor aspect so let us consider this case. The case where we are only looking at nitrate coming in from this particular aspect or here. And note that some nitrate will leave the system from here so what is happening though so looks like there might not be enough nitrate here. So that is one aspect to consider so the removal is based on nitrate limited.

Inefficient carbon utilization so the aeration tank the soluble COD is decreasing and in the aeration tank now you have oxygen and the organic ammonia and NH_4^+ is being degraded to NO_3^- and from here this NO_3^- is being recycled to come back out here. So you have the removal off or pre-anarch I guess so that is something to keep in mind let us move on.

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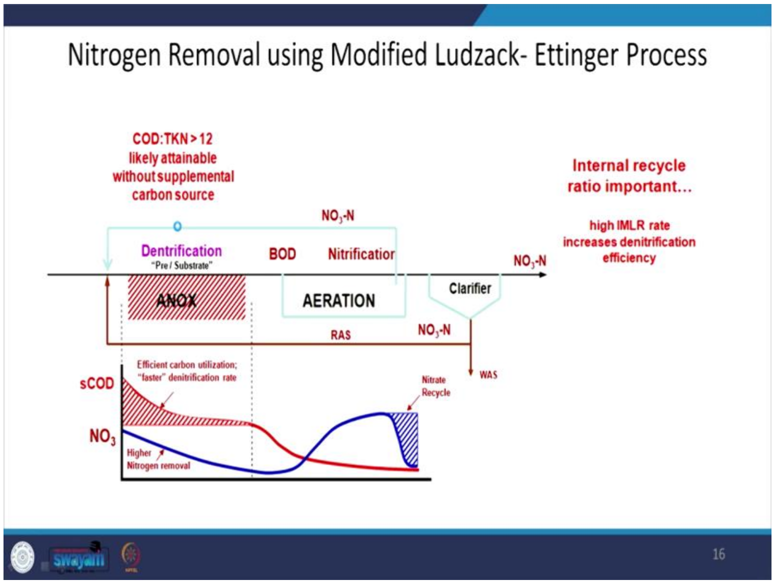

So another adaptation based on what I just mentioned earlier. So we are internally recycling it here there are two cases or aspects that I want to mention earlier if you remember I was keeping ead and saying that you can recycle from here but this case let us just consider that we are recycling only the sludge which has nitrate. Two reasons to recycle want to bring nitrate out here and also to bring out the microorganisms but nitrate is leaving the system so thus we have another way you have what we say nitrate being recycled from the aeration tank internal recycle.

So internal recycle this ratio is what we say pretty important. So what do we have now, we have higher nitrate concentration coming into the picture because you can recycle or control this rate. And at this particular point now you have both high organic compound and concentration and also relatively high or enough nitrate concentration. So this reaction is pretty much fast compared to the previous process and you will have N_2 and CO_2.

you need to balance this reaction. So, let us just understand the system here and here we are recycling it for the sake of the microbes and any nitrate present here will also come in here. But overall if you look at it the much lower nitrate concentrations will be achieved here so that is something to keep in mind compared to this processes. So here we have high COD and high enough nitrate and efficient utilization in both context.

So you have both the organic carbon decreasing and also nitrate being denitrified at this case. And here at this stage in the aeration process your organic compounds are further decreasing while the ammoniacal nitrogen and the organic nearly bound ammonia is being oxidized to nitrate at this point we are having the internet will recycle. So this goes back here and we are now going to have enough nitrates there.

That is why this is what we say concentration is coming back down why is that because nitrite recycle internal because of the nitrate recycle. You can compare that with this particular system do that is something to keep in mind. Let us move on.

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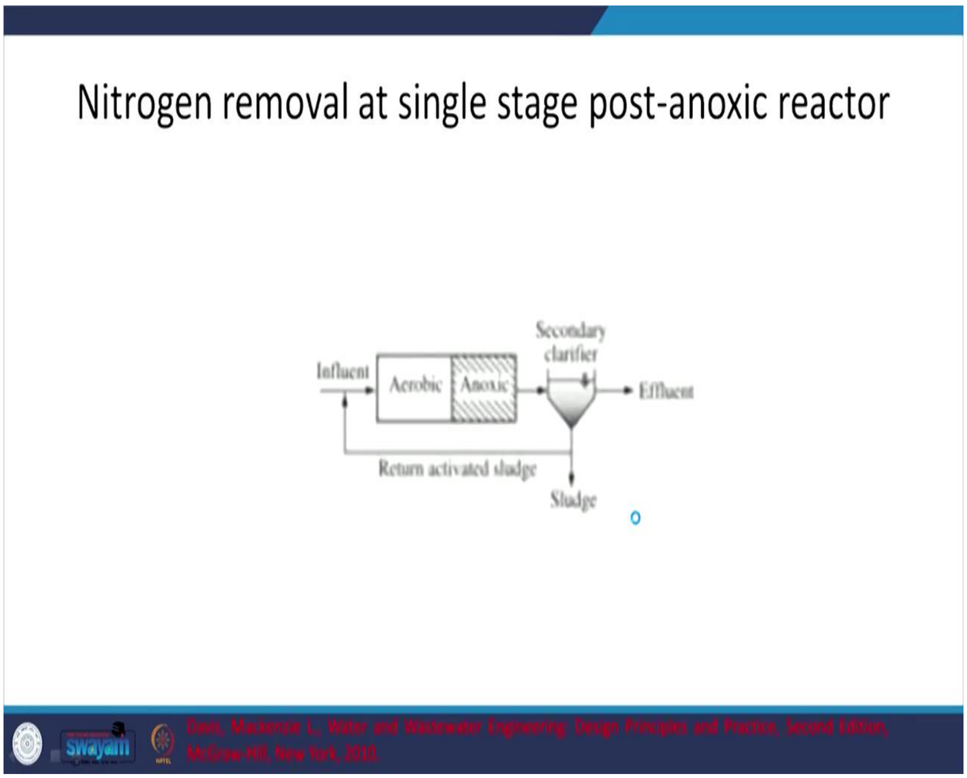

I guess we have different such processes or aspects.

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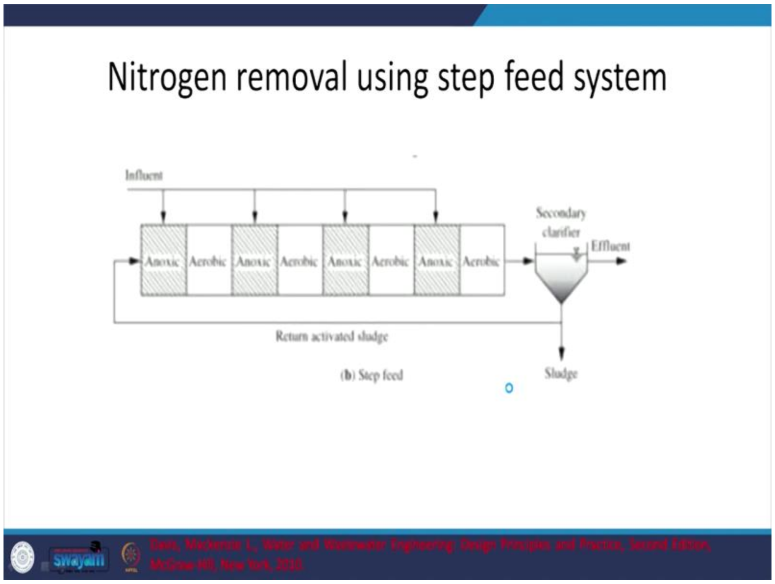

But we already looked at that. So another case is when you have anoxic aerobic anoxic aerobic series and influent is given out into the anoxic tanks to provide for your organic compound. In anoxic tank what do you need you need nitrate and that is coming in from the recycle and you need organic compound that is coming in from the infrared. in series so this is called step feed.

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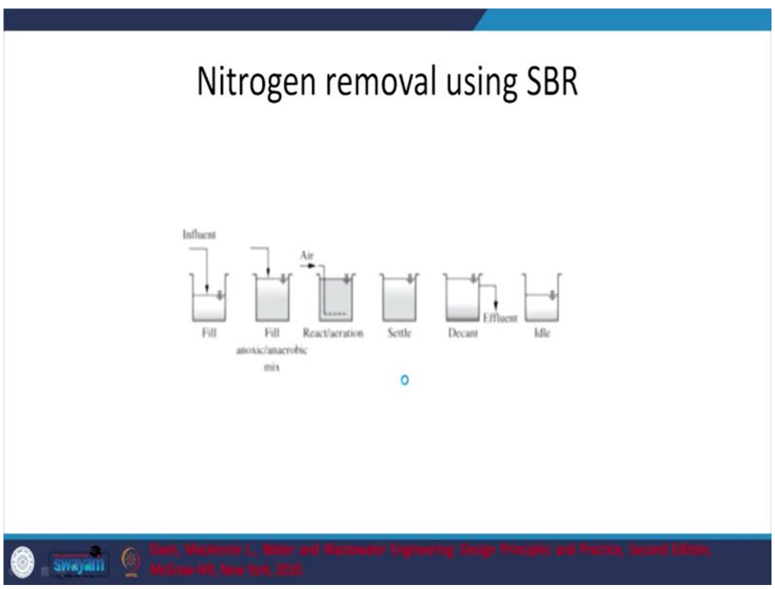

And in SBR sequential batch reactor based on how you are filling it and how you are providing aid after filling it you can have alternate anoxic and aerobic conditions. So depending on how often or how frequently or with respect to time how you are providing oxygen within the same tank you can have your anoxic and aerobic conditions let us move on.

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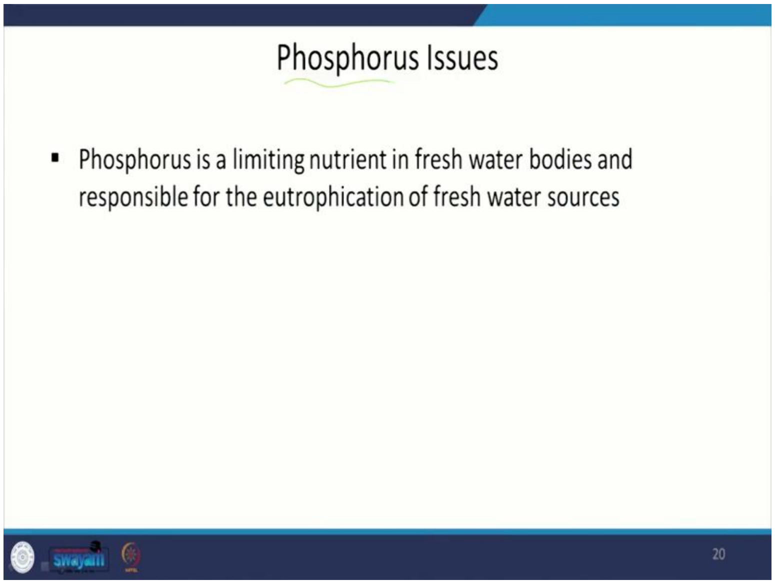

So next aspect is removal of phosphorus as I mentioned phosphorus is typically the limiting nutrient and we will move on without spending too much time there.

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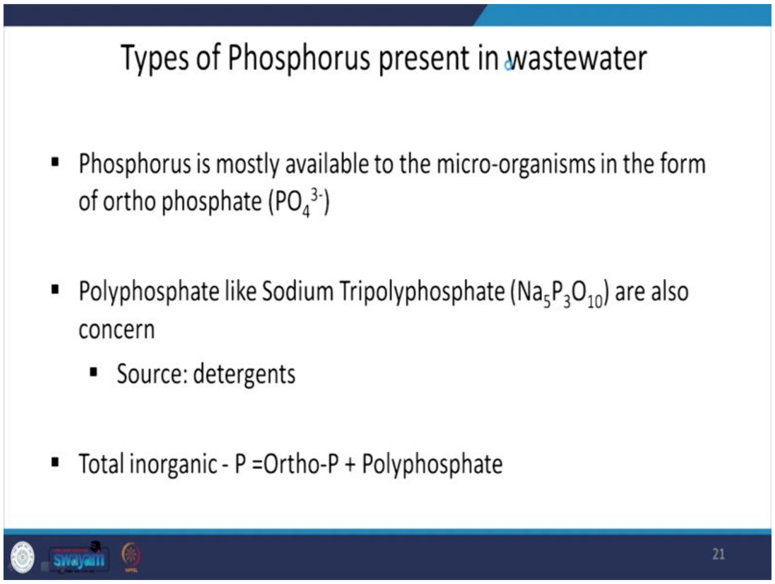

Unlike the case of nitrogen the phosphorus that is organically bound it is relatively difficult to be degraded by the microbes because it seems like this will take time to be what do we, say become soluble. So to go to PO 4 3 minus are the ortho phosphates and these are the phosphates are the form which are more easily taken up by the microorganisms. So typically are the phosphates relatively easily taken up.

And we are typically also concerned at least in India because at least in India we are concerned about polyphosphates like sodium tri polyphosphates, sodium tri-polyphosphate. Why is that because we use a lot of detergents and I think people might have seen the case of Bangalore where phosphorus was released in the case of or in the form of or due to excessive usage of detergents but polyphosphates too difficult to be absorbed by the microbes.

So thus there are concerns so try to avoid detergents that have a lot of phosphorus. So, total inorganic phosphorus is orthophosphates plus the polyphosphates. But in general only the ortho phosphates are taken up by the relevant microbes relatively easily

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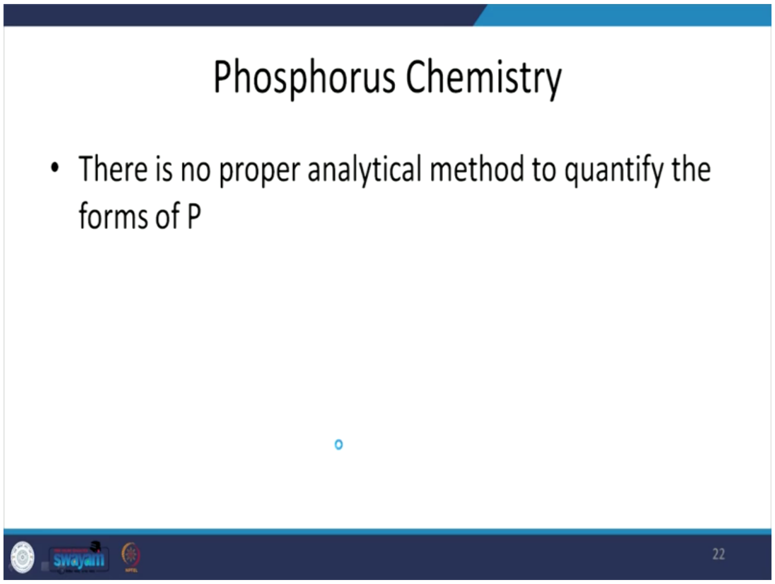

So one aspect here is that there is still considerable uncertainty to look at to identify the forms of P that are readily accepted by or assimilated by the microbes but in general orthophosphorus.

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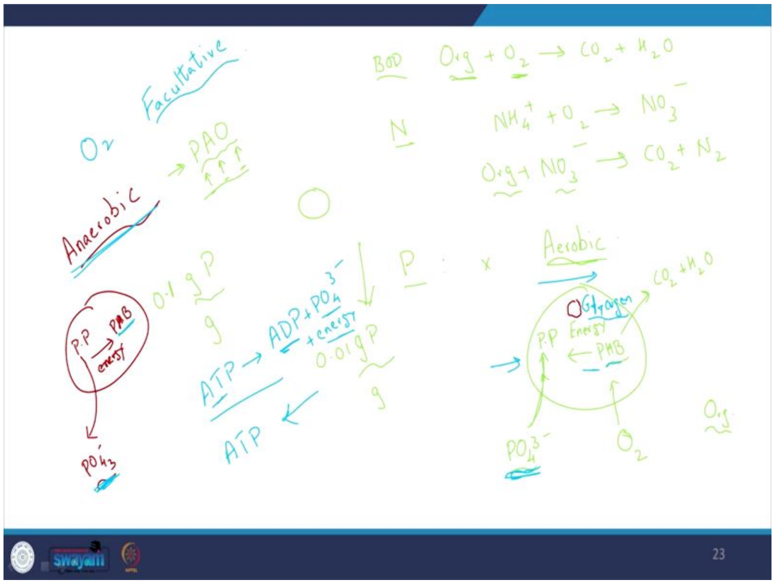

So before we go further let us just try to understand the picture. for BOD how are we doing it

$$Organic\ Compound + Oxygen\ = CO_2 + H_2O$$

Oxygen is the electron acceptor. So for BOD and I am decreasing my organic compound for nitrogen removal how am I doing it redox process. This is a redox process oxidation and reduction is occurring this is being oxidized this is being reduced. So for N_2 what are we doing initially NH_4^+, we are converting or oxidizing it to nitrates finally.

And nitrates in the presence of the organic compounds we are going to oxidize the organics. But the stem electron acceptor is nitrate and we are going to these products. so both are redox process space. But with respect to phosphorus that is not the case though. So here we are trying to let a certain kind of microbes thrive and the microbes that we are trying to propagate here are the are called phosphorus accumulating organisms.

So as the name indicates these microbes or the phosphorus accumulating microbes can accumulate phosphorus. But these are specific microbes. So thus you need to create the condition specific to these microbes to let them thrive. And in general these microbes thrive under what we say two conditions both anaerobic and aerobic. Well I should not say under two conditions under the conditions which are put forth by having alternate anaerobic and aerobic.

Why is that? In such conditions the microbes are under stress in aerobic when they have oxygen and carbon source they have access to energy. But under anaerobic conditions they do not they need to gain or still function and thrive. So they will not accumulate pardon me so these phosphorous accumulating organisms are acclimatized to these conditions. when we provide alternating conditions of stress and no stress, anaerobic and aerobic.

what are we trying to do we are trying to form these phosphorous accumulating organisms once we form them and then when we settle them out in sludge we are going to remove them. So it is not degradation it is just that we are trying to see to it that the phosphorus in the water is accumulated by these PAO or phosphorous accumulating organisms and then later you are going to remove them or separate them from the water that is the principle.

But we need to create or what do we, say provide conditions in which these PAO's thrive and stress and no stress. So first let us look at aerobic conditions what do these PAO's do under aerobic conditions? this is the relevant cell under aerobic conditions you have oxygen and you have what are called PHB's polyhydroxybutyrates. So what happens here you have this being oxidized and going to CO_2 and H_2.

These are source of you can say a carbon a type of compound that is stored internally. So here these phosphorous accumulating organisms under aerobic conditions do need or at least for this part of the process do not need an external organic compound. So what is going to happen oxygen is being used and this is going to happen and then energy is released. Here this energy is released and there are two or two ways.

So let us take the simpler way we will look at the other case later and then during this condition the energy that is given out will be used to excessively store phosphates PO_4^{3-} goes to poly phosphates this energy is used to store PO_4^{3-} in the form of polyphosphates typically looks like 0.01 gram of phosphorus per gram of cell for the usual heterotrophs.

But for phosphorus accumulating microorganisms it can be as high as 0.1 gram of phosphorus per gram of that particular microbe or cell mass. So you see it is almost 10 times higher the phosphorus is going to be stored here this is what happens in the aerobic phase. What is going to happen in the anaerobic phase. Anaerobic phase they are under stress they do not have energy or such or they need energy.

What is going to happen out here? you have these polyphosphates that were stored. During the anaerobic phase firstly these polyphosphates not firstly one of the process is that these polyphosphates in this process polyphosphates are transformed such that phosphorus or orthophosphates are given out and energy is given out energy. And here there is no oxygen though but the carbon source that was present here you can think of this.

And that is used to form these poly hydroxy butyrates. So here you need to have two conditions what is it one is anaerobic because first you want to have this formation of polyhydroxybutyrates you want to have this so you will have anaerobic conditions. First and then in the aerobic conditions what is going to happen you are going to have these poly hydroxybutyrates being degraded for either production of new cells or such.

And then in the same process you are going to have uptake of the phosphorus but one might ask that here the phosphorus is being released phosphorus is being taken up so on. One hand I am taking it up and in the other hand I am giving it out so what is the big deal it is the same but well if I look at the net more phosphorus is taken in than phosphorus that is released. Let us look at one of the aspects or one other aspects.

So some other mechanisms also say that there is a middle path or glycogen that is stored glycogen will be stored in the aerobic conditions such that it can be used during the anaerobic conditions so that energy is also given out that is an intermediary so we do not need to go into that now. So here polyphosphates we talked about adenosine triphosphate energy carriers.

So these are the reactions that can happen ADP + PO_4^{3-} + energy. This is what happens in the anaerobic phase and in the aerobic phase the opposite happens in the aerobic phase you see that PO_4^{3-} and energy from this particular reaction and ADP goes to ATP. So these act as the energy carriers in the cell that is something that they wanted to talk about or mention.

no need to complicate things so you have alternating anaerobic and aerobic conditions in anaerobic conditions you are going to have release of phosphorus and or orthophosphates. In aerobic conditions these microbes which have which are thriving here they will what we say accumulate phosphorous, why because they want to be able to use it what we say for their energy needs or part of their energy needs later, yes when they are in anaerobic condition.

So that is why you need to put them in alternating conditions of anaerobic and aerobic, anaerobic and aerobic. They are going to accumulate what we say during the aerobic phase and use part of it during the anaerobic phase that is one aspect to consider and also here you need to have anaerobic conditions. Why if there is oxygen the carbon sources are the kind of microbes that are going to be thrived are going to be different and you are not going to have phosphorus accumulating organisms.

Other than that you need to have anaerobic conditions because you want to have faculty to microbes. These are microbes that can thrive in both anaerobic and aerobic conditions and why do we need them because they can lead to or cause fermentation of the organic compounds.

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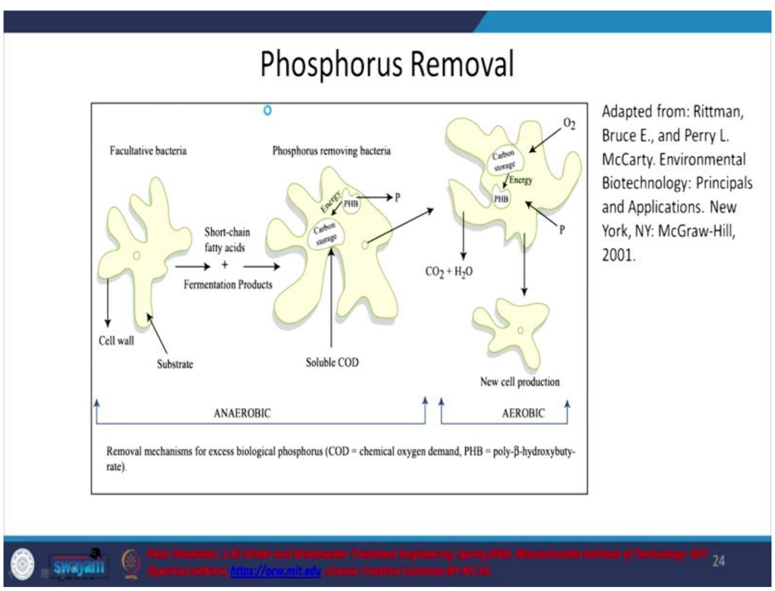

And lead to what we say formation of if I am not wrong acetic acid or acetate part formation of state when we say fermentation product we say acetate. So why do we want to prefer formation of a state because these phosphorus accumulating organisms like to use a state as there, soluble

COD. So this is another picture. So we have the relevant references given out here let us look at this for a second.

what do we have we have faculty to bacteria and this is the anaerobic condition in the anaerobic condition these facultative two bacteria wire fermentation will lead to formation of acetate. And this estate is something this that these phosphorus removing bacteria or phosphorus accumulating organisms like. So during this anaerobic phase we saw what is going to happen but here the representation is in a different form please note that though there talking about carbon storage .

But you more or less we do agree that phosphorus is being released. So these aspects you can look at it based on what I just discussed here. So that is what you have out here. So we have phosphorus being released and out here during the aerobic phase what is going to happen now this what is it now you have oxygen present. And new cells being produced and the carbon source or the PHB going to CO_2 and H_2.

but here the key aspect is phosphorus is being taken up in the aerobic phase and phosphorus is being given out in the anaerobic phase

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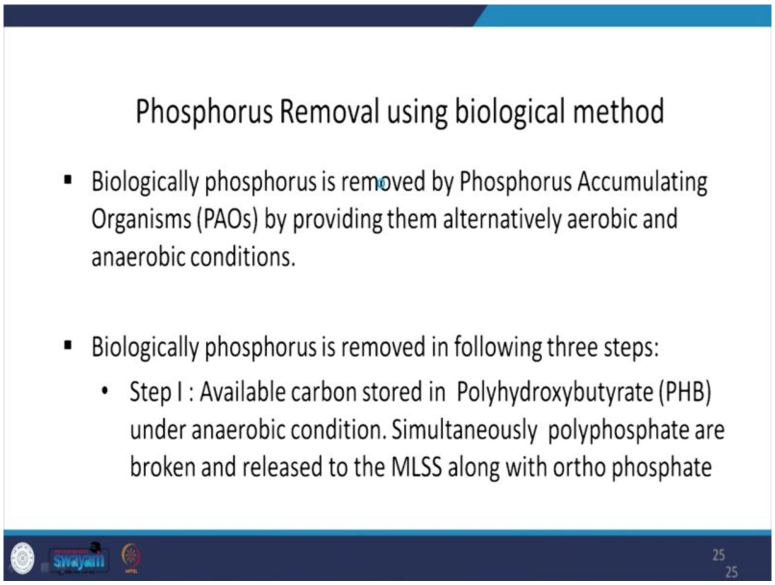

So I looked at this or mentioned this already so let us move on.

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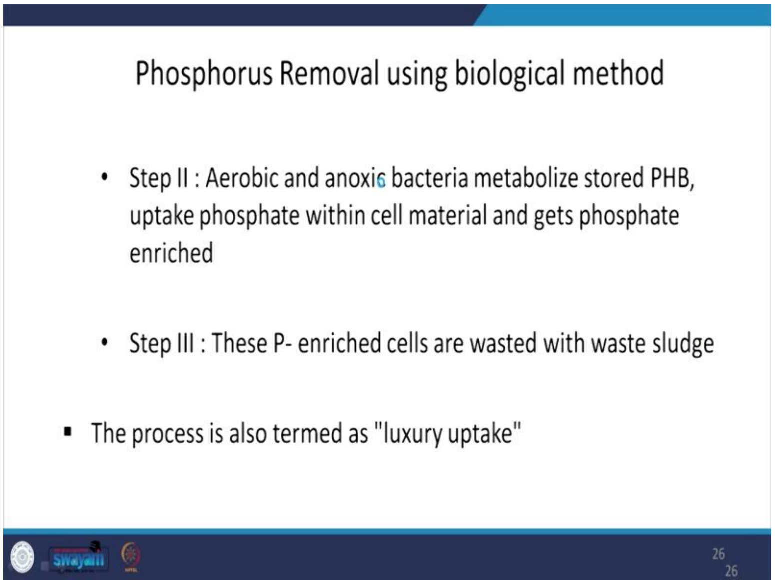

So, luxury uptake I guess luxury uptake we mentioned stress and no stress conditions they are in luxury conditions and they take up phosphorus which will be used during stress conditions. Let us let us move on.

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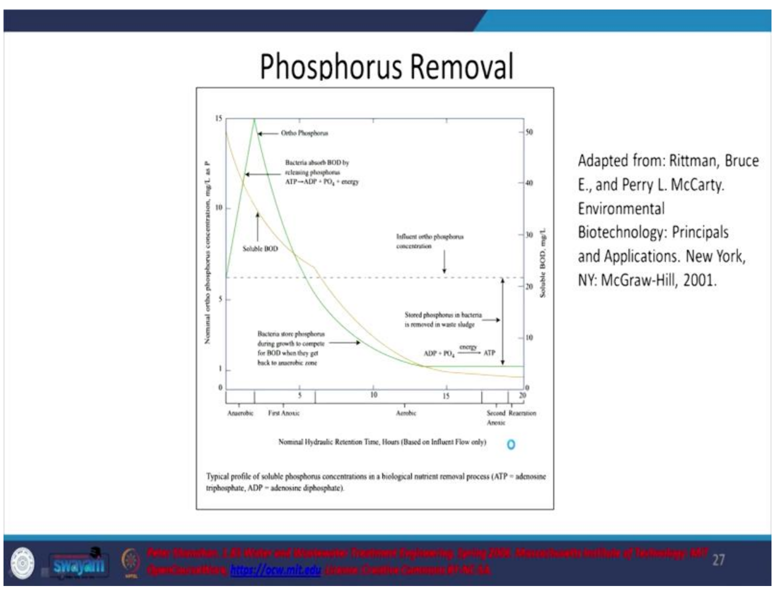

So phosphorus removal, so this is a good graph and I am out of time. So we will look at this later or in the next session. But one aspect is anaerobic conditions they release phosphorus and during aerobic conditions they are no more under stress but would like to take up phosphorus. So that it can be used for its, what we say energy needs if I may say so later under the anaerobic conditions.

So thus we are having net accumulation of phosphorus. So anaerobic and aerobic process so you have to have a recycle. But we will look at the relevant configurations in the next session and thanking you for your patience I will end today's session.