**Water and Waste Water Treatment**
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**Lecture -24**
**Nitrogen Removal- I**

Hello everyone welcome back to the latest lecture session. We have been discussing aspects related to activated sludge process where we were looking at removal of the soluble and biodegradable COD or soluble organic matter which is biodegradable. In that context in the last couple of sessions we looked at design and then looked at a variation of the activated sludge process which is now being widely adapted in India which was or is the sequential batch reactor.

In sequence you have batch reactors being used more or less it is not more or less it is in the same tank. So first filling in and then aeration and then you stop the aeration let the microorganism settle down and then you have decantation settling and then you have the decantation. So we discussed that so today we will look at a very minor design problem just so that we understand the variables that we have looked at over the few or past few sessions. And then we will move on to looking at nitrogen and phosphorus removal. So let us move on and see where we are

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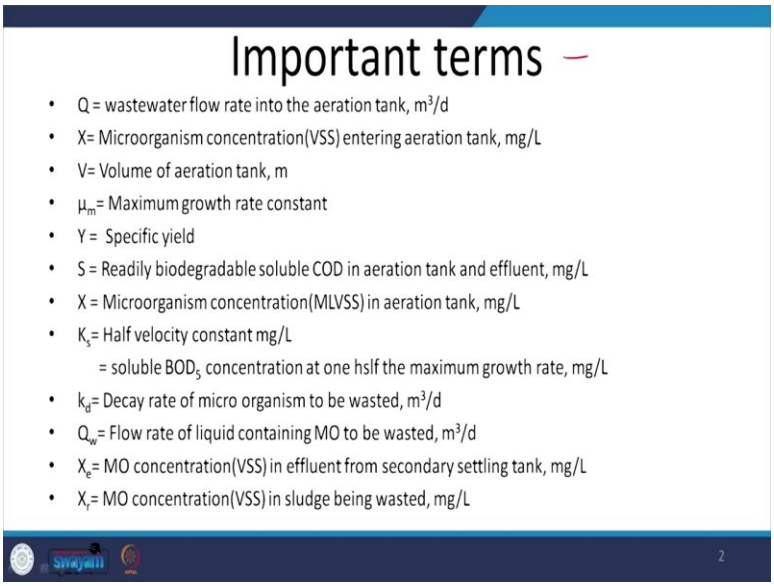

So terms we looked at this and we would also have added some more terms. So Q will give me an idea about how much or the rate at which the water is flowing into the tank volume per time. So volume per time Q flow rate. X as mentioned here it will give me an idea about the microorganism concentration in the relevant tank. So MLSS, MLVSS that is how we typically measure that.

So volume of the aeration tank typically we are looking at design of the aeration tank because that is where we are assuming with good reason that the relevant reactions happen meaning the oxidation of the organics. So growth rate constant for example when calculating or trying to calculate various variables and also trying to understand how fast the microbes grow. You need a rate constant which might be similar to draw an analogy.

We have A goes to products and k is the rate constant rate of this chemical reaction is k times concentration of A. So here I am concerned about how microbes are growing rate of growth of microbes will be depend upon mu times the concentration of the microbes.

$r_g = \mu X$

So;

$$\mu = \mu_M \frac{S}{K_S + S}$$

S is the substrate or r waste which is the food for the microbes and $K_S$ is the half velocity constant where and it is equal to the soluble BOD concentration at one half the maximum growth rate.

So this will be

$\frac{\mu_{max}}{2} = K_S$

that is what we it means and rate of growth of microbes that we just looked at. Specific yield or yield we know that the microbes are going to grow our cell synthesis is going to take place based upon the transformation of the organics. Not all the organics are going to be oxidized considerable fraction of the organics are going to be used by the microbes for production of new cells.

So how much new cells will be produced or mass produced mass of the cells produced per mass of the substrate that is been consumed. So, that is going to be equal to one not one part meat less than one . And the readily biodegradable and soluble COD which is our waste which we are trying to remove this is what we are trying to remove or degrade in our particular system that is the whole point of the design. And X we did look at it so $K_S$ we just looked at it.

$K_d$ for example we know that the rate of rate of growth of microbes we just looked at that. So rate of decay either due to death or due to predation or such you are going to have decay. So that is going to be depend upon its own rate constant $K_d$ decay rate for microorganisms

$r_d = K_d X$

to be wasted flow rate of the liquid containing the microorganisms to be wasted we looked at this from the secondary settling tank after the microbes settle down.

The sludge most of it will be recycled typically and some of it will have to be wasted otherwise and that will the flow rate of this Q flow rate of this wasted sludge is $Q_W$. $X_e$ is the concentration of the microbes in the effluent which is typically less that is what we want. $X_r$ is the concentration of the microbes in the recycle or in the wasted sludge. So that is something to keep in mind so let us try to look at the question and understand the different variables.

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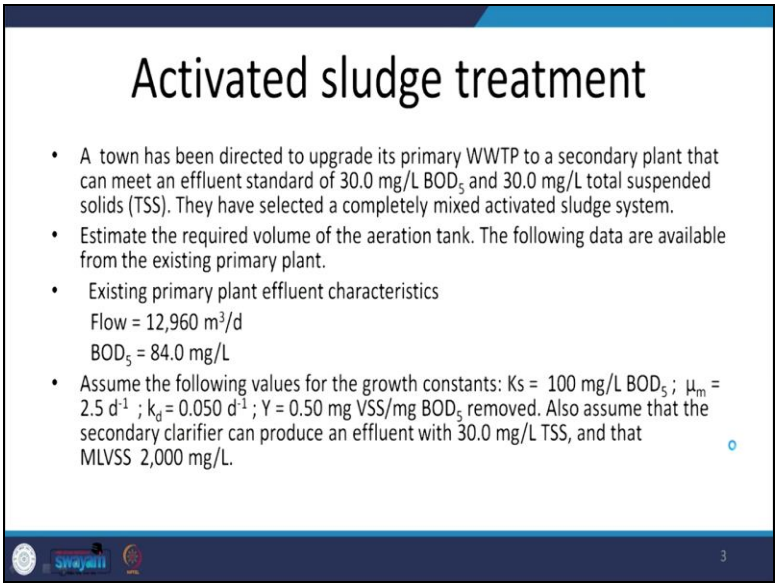


A town this is from Mackenzie or Davis, a town has been directed to upgrade its primary wastewater treatment plant. So earlier it was only primary meaning they were looking at

mostly suspended solids grit removal and so forth and then suspended solids removal and along with suspended solids some BOD around 30% BOD would have been removed and now they want to build a secondary plant.

Secondary plant we are trying to remove most of the soluble or what is that COD or the soluble organics that can meet an effluent standard of 30 milligram per liter of $BOD_5$ and 30 milligram per liter of total suspense solids. So the way I wanted to do this I did not want to look at this hopefully that was taken into account.

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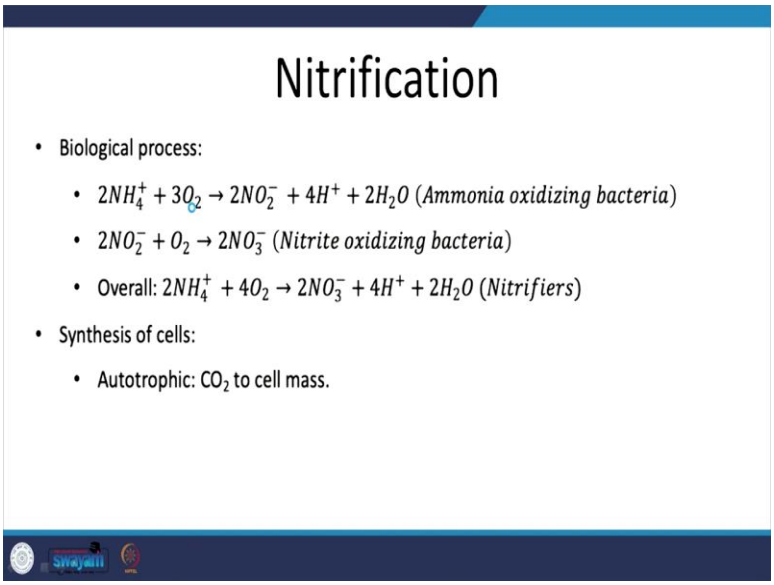


So I see this so assume that for this particular part the effluent concentration of $BOD_5$ that is required is not 30 or such but that it is 10 milligram per liter that is the one that is relevant in the Indian context in the recent years since the recent or couple of years and this is in 2020 this year is 2020. So I wanted to use 10 milligram per liters as the effluent BOD concentration. So that is what I want $S_{effluent}$ or S has to be 10 milligram per liter.

And completely mixed actuated sludge system fine what are we requiring or what do we need I need to know the volume of the aeration tank and for that I have some data. So primary from the primary plant this is the flow rate. So this is my Q and this is the BOD coming into the secondary

tank. This is my $S_0$ or the one that is present initially assume the following values for the growth characteristics.

So I know this half velocity constant $K_S$ is there and $\mu_{Max}$ we already looked at it so maximum growth rate constant that is also there 2.5 days. So how do we get this typically from what we say laboratory test $K_{decay}$ is there the yield coefficient is there milligrams of volatile suspended solids which give us an idea about the microbes per milligram of $BOD_5$ which is consumed that is the yield.

So, mass of the microorganisms being produced; per mass of the organic meter being consumed by the microbes. Assume that the secondary clarifier can produce an effluent with this we will not look at or consider for now. And that the MLVSS mixed liquor volatile suspended solids is 2000 milligram per liter.

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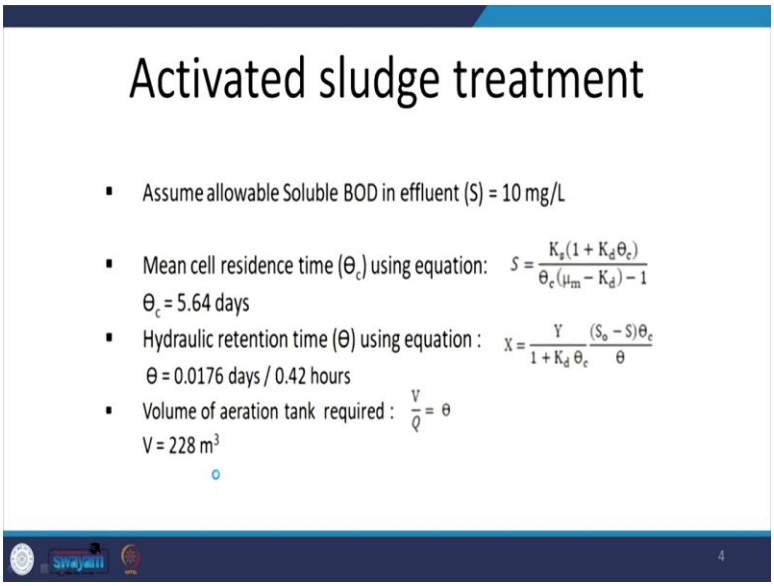


So let us look at the relevant approach. So at the end of the day I need to be able to calculate volume. Volume is ɵ times Q. So in that question I should have also asked to calculate ɵC. So in this question I want to calculate $ɵ_C$ and volume. Volume for that I need ɵ - hydraulic retention time this gives me an idea about how much time the water molecule is spending in the system.

This will give me an idea about or this is the cell residence time or solids retention time SRT and this is the HRT. Note the difference please this will give me an idea about how much time the microbes are spending in the system. Volume of the tank will be the hydraulic retention time ɵ into Q so for that theta I need to calculate that so we can calculate that. So to be able to calculate theta we have this particular equation derived from the mass balance. If you remember we looked at the three major equations one was based on the mass balance on the microbes around the total system.

Those were the aspects that were considered and then for the same system we also looked at mass balance on the substrate yes and then we looked at rate of growth or our net of the microbes is equal to rate of growth minus rate of decay r net. And we can also understand the rate of substrate utilization in terms of Y and rate of growth of the microbes. So these were the so one two and three these were the equations we played around with we know that rate of growth is equal to μX.

And we play run around with them and we got these particular equations. So how do I get theta from this I can equation I can get theta as we know X is depend upon both ɵ and $ɵ_C$ so in this equation I have all the other variables if you see but I do not have $ɵ_C$. So I need to calculate $ɵ_C$. So for that I have another equation that is out here. So we can look at that.

So as we know substrate in the effluent there is a function of $ɵ_C$ and we already have this, this as I said for discharging to Ganga we know in India it is 10 milligram per liter that is why I am using this and this equation is a function of $ɵ_C$. And if you see $K_S$ we have that $k_d$ this is not a capital k this is small d $ɵ_C$ we are going to calculate $ɵ_C$ we are going to calculate $\mu_{Max}$ we have that $k_d$ decay constant we have that.

And IS is 10 milligram per liter, so from this I can calculate $ɵ_C$. And I know that x there is an equation where X is a function of theta and $ɵ_C$ so since I already have $ɵ_C$ and I have X and $ɵ_C$. So I can calculate theta X is there MLVSS or MLSS. So yield is given $k_d$ is given $ɵ_C$ we just calculated $S_0$ is what 84 milligrams per liter what is coming into the system that is 84.

This is with respect to substrate $S_0$, $S_{effluent}$ is10 mg/L we have this $\theta_C$ we calculated above. From this equation I can calculate theta once I calculate theta I can substitute here and get the volume of my tank. That is the approach. In general if other variables are given you will play around with it but sometimes depending upon the level of difficulty at least from a theoretical point of view we can change the assumptions.

And assume different or give you different conditions so that is the reason why we looked at the mass balance. In general if I just give the equations you will not be able to deal with either the theoretical questions or understand how the system depends on different variables or is interlinked between different variables and the practical scenario too. From both the aspects we needed to look at mass balance. So that is the reason we looked at it so let us move on.

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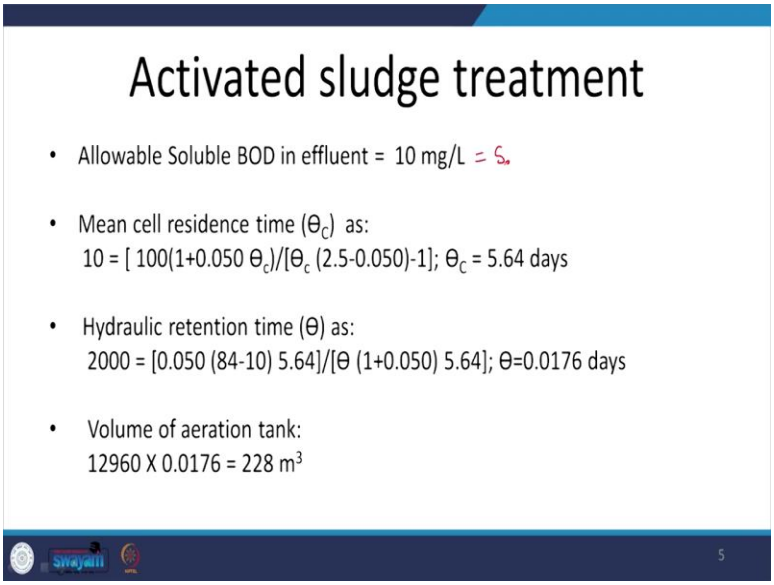


So what do we have I as I mentioned in this question I wanted $S_{effluent}$ or S to be 10 mg/L this is the acceptable $BOD_5$ in the effluent. So $\theta_C$ as I mentioned we can get this from this equation so this is S, and what are the different variables $K_s$ and so forth. And from that we get a cell residence time the microbes are staying in the system for a time of 5.6 days as you see it is considerable time from that we are substituting into the equation for X which is a function of theta and $\theta_C$ to calculate $\theta$.

And X is nothing but and that MLVSS is 2000 milligram per liter that is equal to X that is what we are assuming to be X and so from here we calculated theta. So one aspect to note is this is an r or less than an r is it? It is less than an r but it will typically not be so low. But it is not unreasonable either. So you see it is just more than or about half an hour but you can look at how much time the microbes are spending in the system consider and compare that with the time that the water molecule or the organics are spending in the system.

Why is this feasible because in our system which is like if this was the case both $\theta_C$ and theta will be would have been equal but because we want lesser volumes and good level of removal while ensuring that the volume of the tank is less what are we doing? We are capturing the sludge or the microbes and then we are putting that back in. Because of this recycle $\theta_C$ is far greater than $\theta$.

So that is what you see out here. And then volume of the aeration tank theta into theta is equal to V/Q and we now can get the relevant volume which is 228 $m^3$. So that is good enough there so let us move on to the next major aspect.

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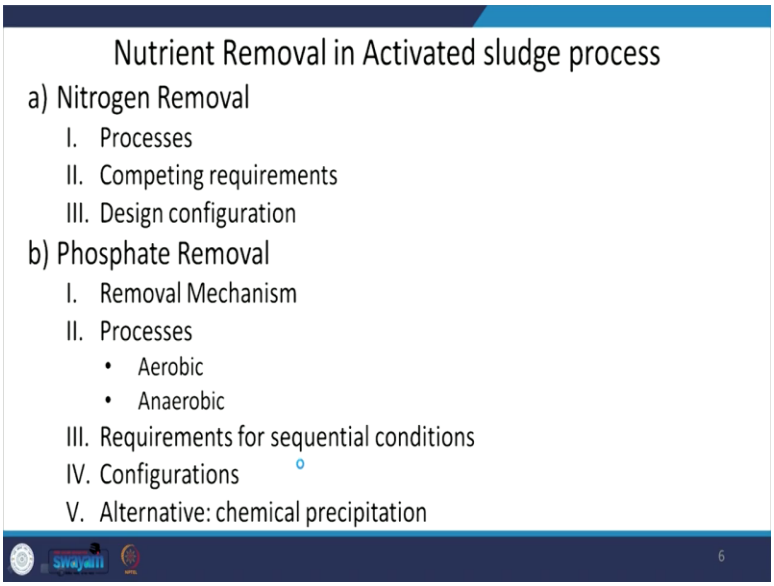


Until now what I have we removed let us just take a quick recap. So primary treatment first we want to lift the water from one head to the other. So that is one thing and what else do I want to remove I want to remove particles that can mess up my machinery I will have different types of

screens yes and then I will remove the heavier particles grit which is relatively inert. And this is during our headworks or preliminary treatment.

And then in primary I will this is optional when wastewater treatment plant depends upon your own priorities because here if you remove it you will have a lot of sludge which you need to deal with. So that is up to the relevant plant designer or such primary treatment. What am I trying to remove here primarily those compounds that are suspended in the water or wastewater but which are heavier enough to be removed reasonably or within a reasonable amount of time.

So mostly suspended matter and some BOD also I think we mentioned around 30%. And then in the secondary treatment system what are we trying we are trying to remove all the other BOD and any or some of the suspended solids that is what we looked at until now. But with increasing urbanization and then greater pressure on the water resources and the water system is not able to recoup itself what do we need to look at we also need to look at removal of these nitrogen and phosphorus nutrients.

We looked at I think examples some eye catching examples from china . So we will look at how to remove these nutrients which are nitrogen and phosphorus. Nitrogen removal we will look at the processes and what are the requirements and then from the requirements we can look at the design configuration. this is relatively straight forward , in the removal of organic matter or body what is the principle.

The microbes need energy and also they want to synthesize new cells. They are going to degrade these organic matters by using an electron acceptor what is the electron acceptor that is the oxygen you are pumping out. The principle is more or less the same in nitrogen removal so that is easy. In phosphate removal it is a bit trickier. We will look at that. There is a particular removal mechanism we will understand the mechanism and we will see why we need to have both anaerobic and then aerobic or alternating conditions of anaerobic and aerobic we will look at why.

And in that context we'll require look at the requirement for the sequential conditions. Maybe look at a couple of configurations if you want to achieve phosphorus removal how do you need to look at the plant or redesign the plant. We will just look at that briefly and if I am not able to achieve that I can remove phosphorus by chemical precipitation. So we will briefly look as look at that aspect. in this session we will be mostly looking at this aspect. And in the next session we will be covering phosphorous removal. Let us move on.

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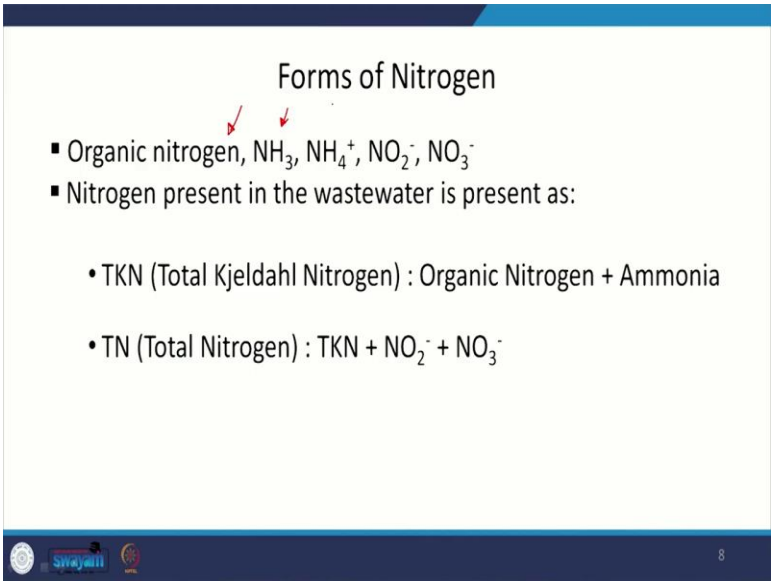


So first nitrogen removal what are the forms of nitrogen we already discussed this in one of the earlier sessions but a quick recap. So we have organically bound nitrogen. Nitrogen that is bound to organic compounds $NH_3$ and $NH_4^+$ ,they are in equilibrium typically based on the $H^+$ or pH of the solution and you will have an equilibrium dissociation constant. that is acid base environmental chemistry you can look that up.

And then depending on the level of oxidation you can have nitrite : $NO_2^-$ or nitrate: $NO_3^-$. So these are the forms we are concerned with typically we measure them as TKN nitrogen. So that will give me an idea about both the organic nitrogen organically bound nitrogen and ammonia. Why am I concerned typically about this because this is the nitrogen content that can consume oxygen that is why I am concerned about TKN and in general organic nitrogen is relatively easily degradable into ammonia.

And total nitrogen as the name indicates it is TKN plus the oxidized forms of nitrogen which are number two minus and no three minus as you can see this is a reduced form $NH_4^+$ or $NH_3$ and $NO_2$ and then well $NO_3^-$. As you can see oxygen here relatively more oxidized form reduce forms of nitrogen and after being oxidized in the presence of oxygen by different microbes they will be transformed into or oxidized into nitrates and nitrites.

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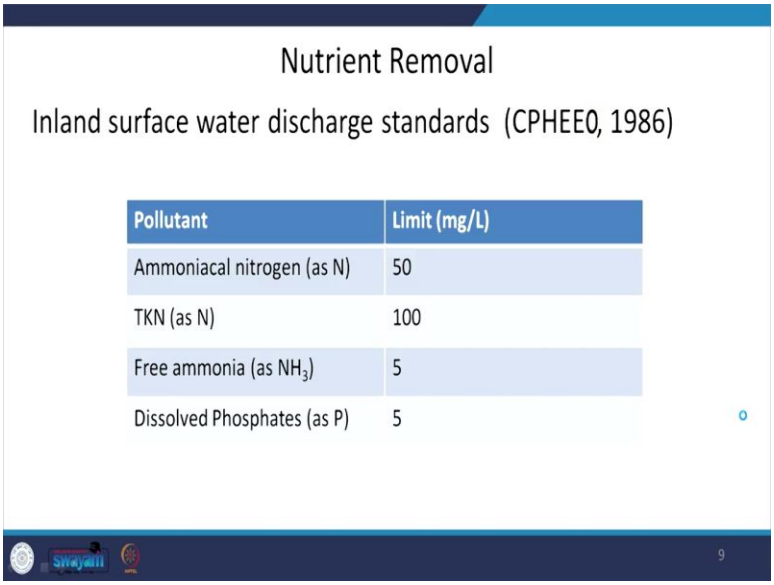


So nutrient from the CPHEO manual and if you are discharging water or treated waste water into inland surface water so people have been revising it. So ammonical nitrogen as N expressed as N this is not $NH_4^+$ itself but as N and then TKN expressed in the units as N. So you have the different standards for free ammonia but typically we have decreased these values. And dissolved phosphates value is much lower. , why is that because typically in surface waters this is the limiting nutrient. Let us move on.

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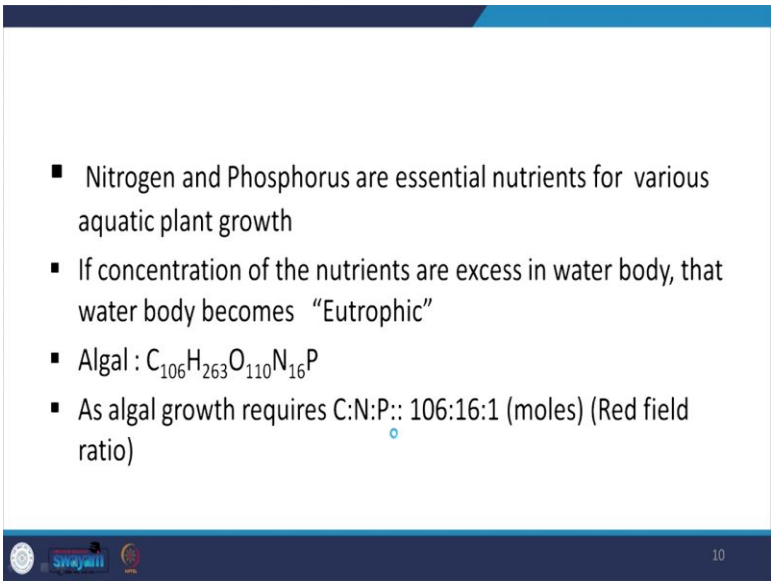


And why am I concerned with removing nitrogen and phosphorus. So we looked at algal bloom when you have the essential nutrients which are nitrogen and phosphorus you can have what we see explosive growth of algae. And later when the algae die they are a source of organic content for the microbes. Microbes consume the algae in the presence of oxygen or what we say by consuming oxygen and thus you are going to have depletion of oxygen and relevant septic conditions.

Other than that this algal bloom will also interfere with the aquatic life beneath it the penetration of light will be affected. So you are going to have considerable issues some kinds of algae are toxic to us yes and what else . Those are the major aspects I would have covered most of the aspects earlier too. And so nitrogen with respect to nitrogen $NO_3^-$ is not what we say something that we would want to prefer to be in our drinking water.

It is a regulated compound $NO_3^-$ so that is one more reason to remove these nutrients. For example we talked about algae and eutrophication and in that context we talked about algae. So typical formula to represent algae is C H O N P and these are the ratios of the relevant what do we see elements here. And as you see the ratio of carbon, nitrogen, phosphorus is 106 to 16 is to 1 molar ratio 106, 16 is to 1.

So this is also the red field ratio if you see that this will give me an idea about which one is the limiting nutrient or if I know the ratio now of a particular lake and I see carbon nitrogen and phosphorus. And I can calculate and see which one is the one that is the missing link. So typically a lot of carbon will be present so carbon is not the limiting factor usually we are dealing with lack of nitrogen or phosphorus.

But in inland surface water bodies typically phosphorus is the limiting nutrient. So you can look at this ratio of nitrogen phosphorus or carbon to nitrogen phosphorus and understand which is the limiting nutrient.

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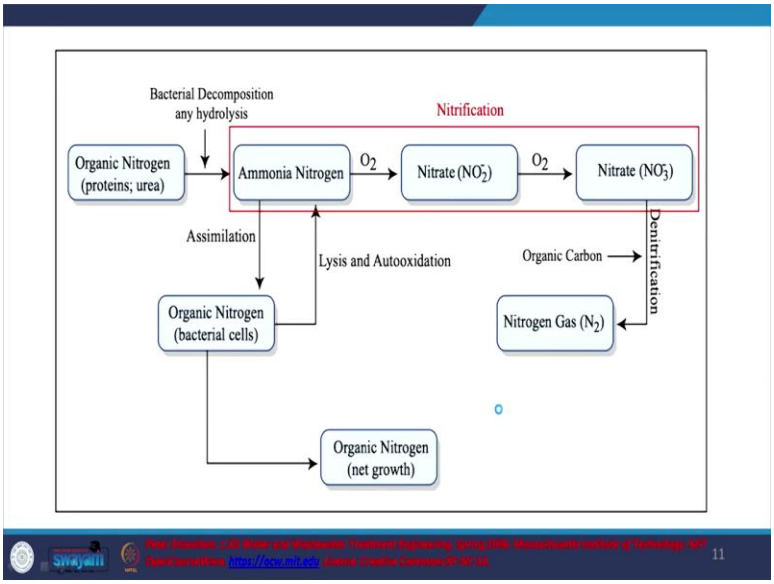


So here is a good schematic which gives us a holistic view. So I have organic nitrogen and where is it coming from proteins and in our urine you have considerable urea. So we take in proteins years we synthesize them some of it or some forms of nitrogen are going to be released amino acids . So bacterial decomposition and hydrolysis you are going to form ammonia nitrogen.

So organically bound nitrogen will be transformed into ammonia nitrogen and this is relatively fast. And some of this ammonia or the nitrogen will be used by the bacteria I think we saw that it was around 12% of the nitrogen content this we looked at when we were looking at the oxygen requirements. And we saw that or we detected this amount. And there is going to be a cycle because you are going to have lysis or death of the relevant microbes so more or less.

You have ammonia nitrogen that is in equilibrium with the organic nitrogen but the one within the cells itself. So, depending on the; kind of bacteria and the concentration of bacteria so you are going to have a balance between ammonia nitrogen available for oxidation and the nitrogen in the bacterial cells. So I have $NH_4^+$ and as you can see this is a reduced compound and in the presence of oxygen it can be oxidized by microbes to this is nitrite.

And this is nitrate $NO_2^-$ and $NO_3^-$ so it will be oxidized to $NO_2^-$ first and then to $NO_3^-$ . So here we are forming the nitrates nitrite and nitrate. So that is why this process entire process is called nitrification. But I am still ending up with nitrogen in the water these are remarkably soluble I cannot remove them by precipitation or by trying to change the phase from wastewater to the gaseous phase I cannot do that.

What do I need to do I need to transform it into a phase which will allow me to remove nitrogen from the water. So that phase is not the solid which is which we would have tried to achieve by precipitation but by changing it from the aqueous phase meaning dissolved in the water to the gaseous phase. So here the nitrate will be will undergo denitrification into nitrogen gas here.

as you see it is $NH_4^+$ is the reduced compound electron donor electron acceptor is oxygen and then you have formation of $NO_2^-$ or later $NO_3^-$. So here there is no role of organic compounds. So thus they are called I mean the kinds of microbes are autotrophs. But here what is happening here you have $NO_3^-$ and you want that to go to $NO_2$ ; oxygen state is 0 here it is what is it minus 6 from here x plus minus 6.

$x-6 = -1$

So it is + 5 from +5 it is being reduced to 0 the nitrogen oxidation state. So 3 multiply by -2 = -6; x – 6 the total oxide state is -1, so oxygen state of nitrogen in $NO_3^-$ is +5. So here it is going to end $N_2$ are being reduced to $N_2$. So it is being reduced so it needs a source of electrons or an electron donor is required. Electron donor it has to be carbon from the wastewater or any source of organic form of carbon which is relatively reduced.

This is the electron donor and this is the electron acceptor. One thing to note is that in the usual activated sludge process where we are degrading the microbes not microbes the organic content are our waste oxygen is also the electron acceptor. So that is good enough for nitrification. But for denitrification as you see $NO_3^-$ is the electron acceptor. So if oxygen is present in the system denitrification will not take place.

If you look at the derma thermodynamics microbes that use oxygen as the electron acceptor in the presence of organic content typically gain more energy. So those kinds of microbes will be prevalent especially if you have oxygen. So that is the reason why you have to prevent oxygen from being present when you undergo or try to have denitrification. So what else that is it in a nutshell what we have.

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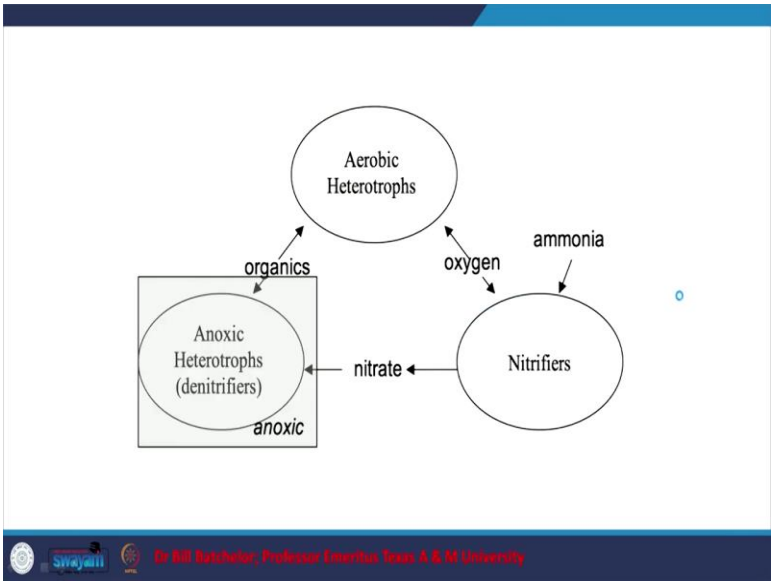


For example we know that $NH_4^+$ oxygen goes to nitrite and nitrate. So here there is no organic compound CHNO x y z and a these are the stoichiometric coefficients here. So, $NH_4^+$ plus oxygen so there is no need for an organic compound here, so these are heterotrophs we I seem to have put in a typo here because here you do not have the need for any organic source of carbon.

these are autotrophs not heterotrophs but they are aerobic because you have they need oxygen. So chemotrophs yes because they derive their energy from chemical sources but heterotrophs are when you have organic compound as the source of energy. But here it is not organic carbon so

these are aerobic autotrophs. So what do they do they either we have two kinds ammonia oxidizing bacteria or nitrate oxidizing nitrite.

So ammonia oxidizing bacteria take it to $NO_2^-$ and another kind of bacteria nitrite oxidizing they take it to $NO_3^-$. So these they take oxygen ammonia nitrofires and finally the end product is nitrate, so I am left with nitrate. So $NH_4^+$ is taken and oxygen is taken and these aerobic autotrophs degraded to are oxidized to $NO_3^-$ and $NO_3^-$ we now have anoxic conditions an oxygen there is the electron acceptor is not oxygen.

But the electron acceptor is nitrate. So these are anoxic yes because no oxygen but these are heterotrophs this is the electron acceptor but there has to be an electron donor. Electron donor has to be an organic compound because it is an organic compound it is in heterotroph and because it does not use oxygen they are anoxic. So these are called the denitrifiers, yes. So that is what we have organic compound and anoxic what is it heterotrophs they degrade it to nitrogen gas.

And nitrogen gas will leave the system and that is how as you see your nitrogen is being removed from the system. First two $NO_3^-$ and then reduce it to nitrogen gas and then it is leaving the system.

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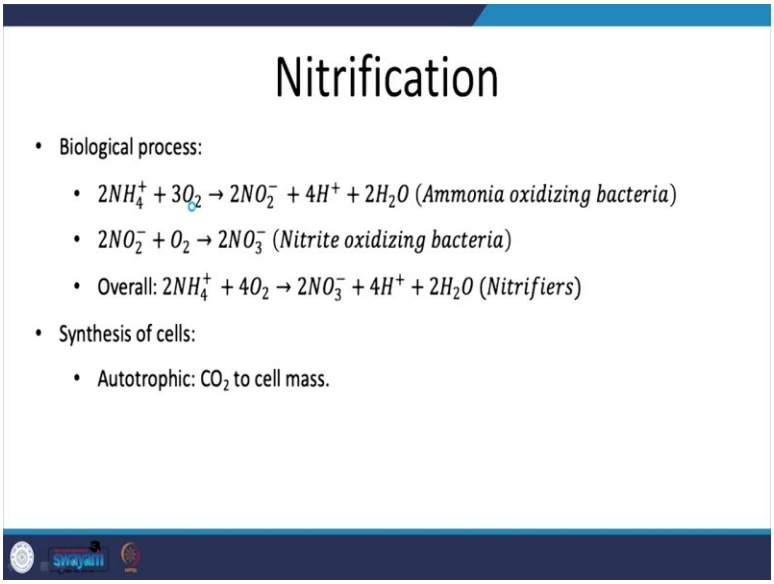

So  I am almost out of time. So let us just quickly summarize this slide and we will end for today. So biological process I think we discussed this earlier or now too ammonia oxidizing bacteria. Ammonia is being oxidized to nitrate and then this nitrite is being further oxidized to nitrate thus we have nitrite oxidizing bacteria. So, overall; though it looks like ammonia is going to nitrate.

And some these are autotrophic as I just discussed $CO_2$ goes to what we say provide cell mass it is not from so it is inorganic source it is not an organic source of carbon. So that should be enough for this session. In the next session I will continue talking about nitrification denitrification. We will look at the mechanisms and then we will move on to looking at phosphorus removal, thank you.