

Wastewater Treatment and Recycling
Prof. Manoj Kumar Tiwari
School of Water Resources
Indian Institute of Technology, Kharagpur

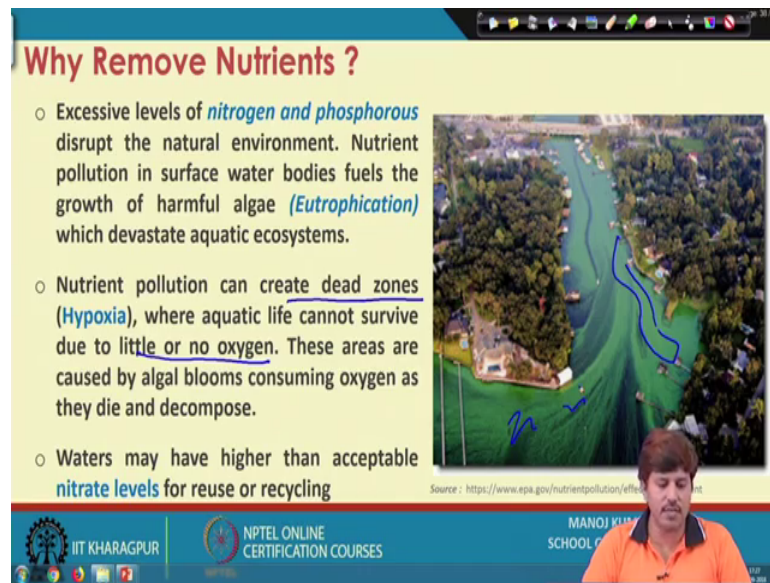
Lecture - 44
Tertiary Treatment: Nutrients Removal

Hello everyone. So, welcome to this lecture 44 of week 9. This week we have started discussing about the advanced wastewater treatment systems or which typically we call tertiary treatment systems because, they are employed usually employed after secondary treatment systems. So, we call them as a tertiary treatment systems or advanced treatment system. In earlier lecture, the first of this week we did discuss about what are the various issues with the existing conventional treatment plants which treat up to the secondary stage and what are the contaminants that are still there in the water and what kind of targets is set for the advanced treatment system. So, basically what do we need to remove as a tertiary treatment.

So, one of the thing was nutrient which is typically not removed that well in a conventional treatment systems which usually leads more than like particularly for the domestic sewage. It usually leaves more than 20 milligram per liter of TKN and more than say 1 milligram per litre of phosphorus. So, in order to remove the nutrients, we have to if particularly depending on the criteria as we discussed that for waters which is might be going to use for agricultural purpose.

We may not need to bother that much about the nutrient removal, but particularly the one which is going to be disposed in say some water body. The nutrient pollution could be of point of concern or could be a point of botheration from that perspective. So, one of the things that is deal in the tertiary treatment systems or advanced treatment systems is the nutrient removal which we are going to discuss in this lecture.

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Why Remove Nutrients ?

- Excessive levels of *nitrogen and phosphorous* disrupt the natural environment. Nutrient pollution in surface water bodies fuels the growth of harmful algae (*Eutrophication*) which devastate aquatic ecosystems.
- Nutrient pollution can create dead zones (Hypoxia), where aquatic life cannot survive due to little or no oxygen. These areas are caused by algal blooms consuming oxygen as they die and decompose.
- Waters may have higher than acceptable **nitrate levels** for reuse or recycling

Source : <https://www.epa.gov/nutrientpollution/effects>

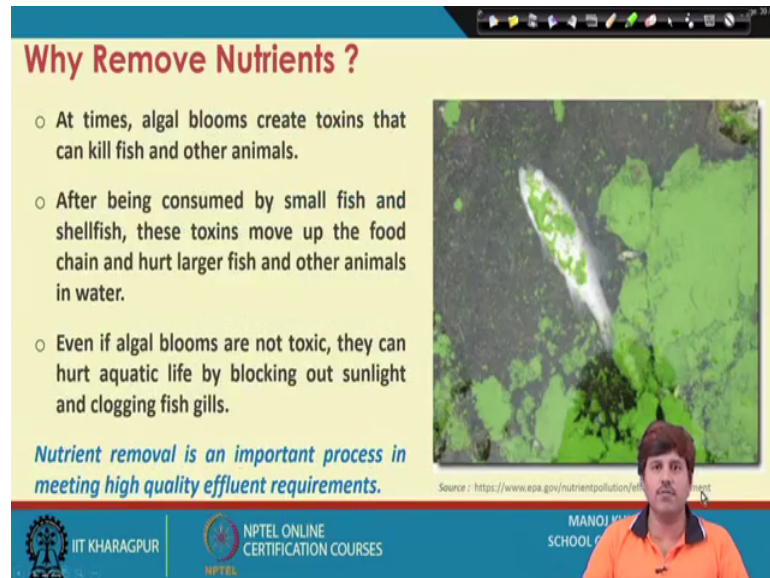
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So, excessive nutrients like nitrogen and phosphorus normally that is what we refer as nutrients. So, these disrupt the natural environment ok. The pollution in the surface water bodies kind of fuels the growth of harmful algae which is typically known as algal bloom or the more common word eutrophication ok. And this eutrophication have the ability of completely devastating the aquatic ecosystem. It is pretty common, I am sure majority of you must have seen some water body which is completely covered by the green top. So, that is actually a eutrophic water body and that is what is called eutrophication. So, this eutrophication is caused by the nutrients and when kind of nutrient pollutions are there, it may create the dead zones which is also called hypoxia. So, this is where aquatic life cannot survive and they become dead and this primarily happens because very little or no oxygen.

So, when this eutrophication happens, the kind of oxygen will be consumed by these algae and furthermore the rate of oxygen transfer also decreased because oxygen transferred to this air water interface and since that water top of the water is covered by this algae by this kind of green material. So, the rate at which oxygen transfer to the water body to the kind of lowers portion of the water body also does not also gets quite slow. And as a result not enough oxygen goes to the water and whatsoever is the available is consumed by the algae. So, that is why the we get very little do or almost no oxygen in the water which is covered by the green top. So, that can create the dead zone which is called hypoxia and the aquatic life cannot survive there ok.

Water may have higher than acceptable kind of nitrate levels also. So, if somebody is let us say, willing to use this water for some purpose. So, the level of nitrate could be higher in these things. Typically 10 milligram per liter is permitted, but it could be much higher than that which can basically restrict the uses of this for substantial purposes and particularly with for the domestic application or drinking water purposes.

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Why Remove Nutrients ?

- At times, algal blooms create toxins that can kill fish and other animals.
- After being consumed by small fish and shellfish, these toxins move up the food chain and hurt larger fish and other animals in water.
- Even if algal blooms are not toxic, they can hurt aquatic life by blocking out sunlight and clogging fish gills.

Nutrient removal is an important process in meeting high quality effluent requirements.

Source : <https://www.epa.gov/nutrientpollution/effluent-requirements>

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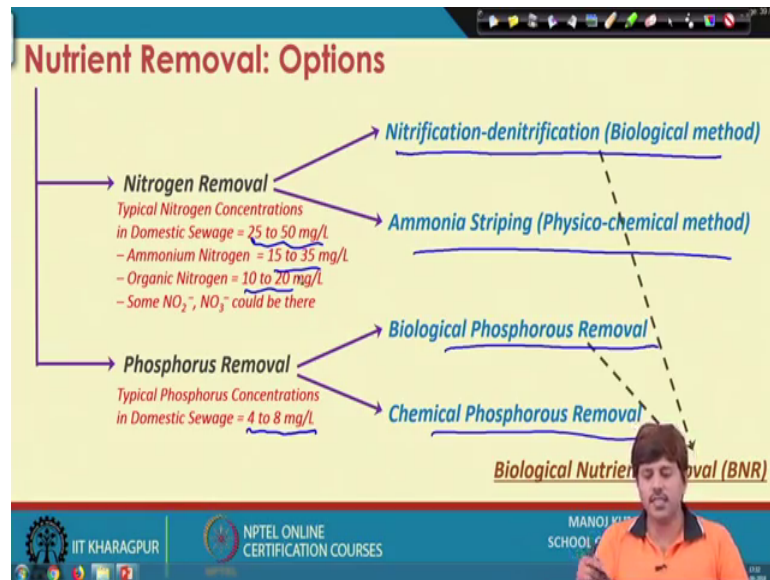
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Apart from this algal bloom can create kind of toxins which can kill the fish and other animals in the water. So, do depletion or do decreases one aspect, but it can actually lead to add some toxicants as well ok. So, if these toxicants are consumed by the small fish, they will become dead then through this food chain like these are consumed by the bigger fishes and then kind of other animals in the water. And from there it can actually lead to even the human food chain. So, even if algal blooms are kind of not toxic, they can hurt the aquatic light by blocking out the sunlight, clogging the fish gill. So, there are variety of these issues and eutrophication is one of the most short after environmental problem across the globe across the world. And the primary reason for eutrophication is the nutrient which is usually disposed of either through agricultural runoff to the natural water bodies.

Agricultural runoff is one of the major sources of the nutrient because lot of fertilizers are used in the agricultural activity nitrogen and phosphorous compounds are there in the soil. And whenever there is any rainfall happens through this agricultural runoff; these

leads to the nearby water bodies and make them eutrophic whereas, the discharge from the like sewage is also one of the point of concerns for the eutrophication point of view. So, nutrient removal that way is an important process in meeting high quality effluent requirement particularly if it is being targeted for discharge.

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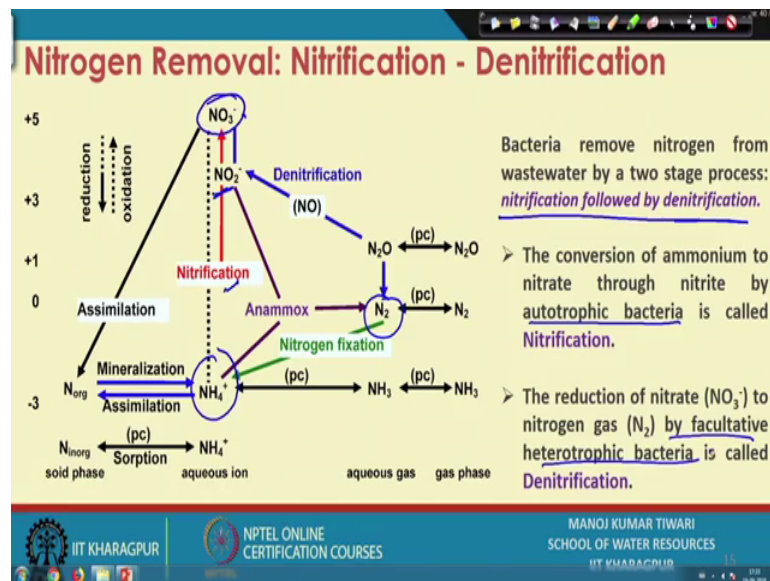
So, how do we remove nutrients? Nutrients basically we will talk about the removal of nitrogen and phosphorous throughout this lecture and then removal of nitrogen and phosphorus both can be achieved through chemical or physicochemical means as well as through biological means ok. It is nitrogen removal; if we see there are the one of the most common processes is nitrification denitrification which is biological method for nitrogen removal. There is an a box which is also kind of is being more popular these days. Then there is ammonia stripping which is physicochemical method apart from that there are a couple of other methods which are there, but very rarely used like the break point chlorination we are adding. The chlorine actually kind of first converts ammonia to the various chloramines, monochloramine, di chloramine, trichloramine and then it can eventually break that chloramine as well to release the nitrogen.

So, that is one way then of course, there are because nitrates or ammonia are in the form of ions. So, ion exchange kind of systems can be used which we will discuss later in this week, but not from the nutrient removal prospective. Because it is very rarely used for nutrient removal and of course, the membrane processes can remove various dissolved

ion. So, including nitrate nitrite or ammonia those kind of things can also be removed by those, but there are high end treatment processes and generally not deployed for removal of the nutrients or nitrogen that way.

Then for phosphorous removal we have biological phosphorus removal and chemical phosphorous removal methods which will be discussing. Typical phosphorus concentration in domestic sewage what we get is 4 to 8 milligram per liter whereas, the nitrogen concentration total nitrogen concentration is 25 to 50 out of which 15 to 35 remains as ammonia and 10 to 20 as organic nitrogen. Organic nitrogen also can be kind of through hydrolysis can be solubilized in the form of ammonia. So, the major target for the removal nitrogen removal is the removal of ammonia ok. That is the one thing in which like nitrogen usually remains dissolved in the state of ammonia until unless it actually is oxidized that way ok. Some nitrite and nitrate could also be there. So, these are the kind of things that we will be discussing.

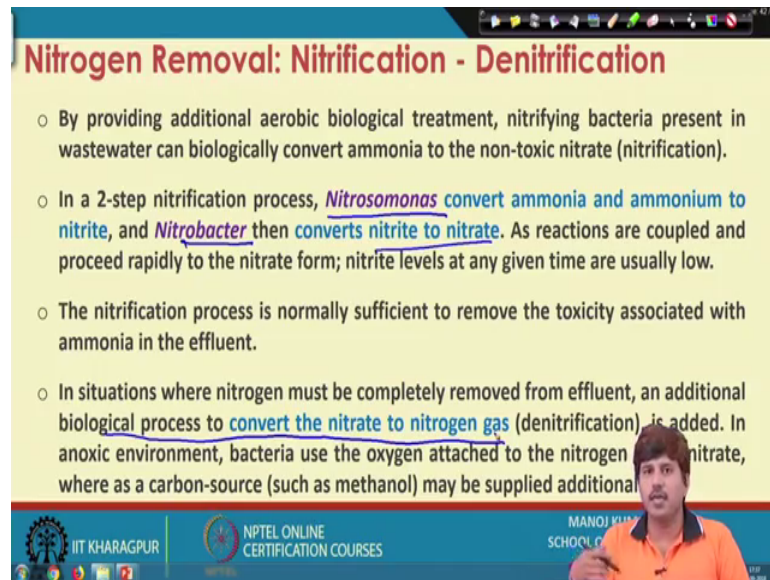
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Then if we see so, the nitrogen removal particularly the nitrification or denitrification process is essentially a biological process. So, the bacteria removes nitrogen from the wastewater in this two stage process which is nitrification first and that is followed by the denitrification ok. The conversion of ammonia to nitrate through this intermediate nitrite is called nitrification whereas, then reduction of this nitrate again through this nitrite eventually to the level of gas phase or nitrogen gas is called denitrification.

Nitrification is kind of achieved by the autotrophic group of bacteria whereas, denitrification is by the facultative heterotrophic bacteria ok. And since this is the oxidation process usually; so, this happens in the presence of oxygen whereas, the denitrification is takes place under anoxic conditions usually in the absence of oxygen.

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Nitrogen Removal: Nitrification - Denitrification

- By providing additional aerobic biological treatment, nitrifying bacteria present in wastewater can biologically convert ammonia to the non-toxic nitrate (nitrification).
- In a 2-step nitrification process, *Nitrosomonas* convert ammonia and ammonium to nitrite, and *Nitrobacter* then converts nitrite to nitrate. As reactions are coupled and proceed rapidly to the nitrate form; nitrite levels at any given time are usually low.
- The nitrification process is normally sufficient to remove the toxicity associated with ammonia in the effluent.
- In situations where nitrogen must be completely removed from effluent, an additional biological process to convert the nitrate to nitrogen gas (denitrification) is added. In anoxic environment, bacteria use the oxygen attached to the nitrogen nitrate, where as a carbon-source (such as methanol) may be supplied additional

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So, by providing additional aerobic biological treatment these nitrifying bacteria which are mostly present in the water anyway can biologically convert ammonia to the non toxic nitrate which is the process is called nitrification right. So,; however, this needs larger residence time ok. So, we need to give larger retention time, if we want to achieve the nitrification process because generally the nitrifiers are slow grower. So, they grow slow and they act upon slow. So, in the conventional treatment system, the residence time that we provide is not good enough for nitrogen. So, there is not much of nitrogen removal takes place and only it is the CBOD or the carbonaceous BOD which eventually gets removed in the conventional activated sludge process or those conventional aerobic treatment systems.

So, if we intend to basically remove the nitrogen or particularly the ammonia. So, what we can do? We can go for a two step nitrification process which is kind of which therefore, like which works with a nitrosomonas bacteria that converts ammonia or ammonium into the nitrate and then there is a nitrobacter that converts nitrate to nitrite. So, these reactions is coupled and kind of proceeds rapidly to their form of nitrate. So,

that is why the nitrite level at any time because as soon as the nitrosomonas convert ammonia or ammonium into nitrite the nitrobacter immediately converts that nitrite to nitrate.

So, that is why the level of nitrite it is always very low in the system which is good also because that is a toxic species whereas, nitrate is far less toxic the nitrification process is normally sufficient to remove the toxicity associated with the ammonia in the effluent. And so, for several purposes where we are just bothered about the toxicity we may not even need to go for any additional step; just nitrification is good enough because ammonia has been converted to nitrate and then we release it off or we reuse it as a nutrient because nitrate fertilizers or those kind of thing.

However in cases where we need to remove the nitrogen completely from the system, we must go for an additional biological process which converts nitrate to nitrogen gas or is basically referred as denitrification ok. And this is done in an anoxic environment and bacteria are used basically the oxygen which is attached because it is an anoxic environment. There is an anaerobic environment there is no oxygen present in the system. So, bacteria use the oxygen attached to the nitrogen in the form of nitrate and this nitrate becomes the terminal electron acceptor in this case and in the presence of a carbon source they kind of in the process of degradation of carbon source, they consume that they in order to get that oxygen separate out from the nitrogen they release the nitrogen gas and assimilate or consume the oxygen present in the nitrate.

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Nitrogen Removal: Nitrification - Denitrification

Nitrification:

$$2\text{NH}_4^+\text{-N} + 3\text{O}_2 \xrightarrow{\text{Nitrosomonas}} 2\text{NO}_2^- + 2\text{H}_2\text{O} + 4\text{H}^+$$

$$2\text{NO}_2^- + \text{O}_2 \xrightarrow{\text{Nitrobacter}} 2\text{NO}_3^-\text{-N}$$

$$\text{NH}_4^+\text{-N} + 2\text{O}_2 \xrightarrow{\text{Nitrifier}} \text{NO}_3^-\text{-N} + 2\text{H}^+ + \text{H}_2\text{O}$$

Denitrification:

$$\text{NO}_3^-\text{-N} + \text{carbon source} + \text{facultative bacteria} = \text{N}_2 + \text{CO}_2 + \text{H}_2\text{O} + \text{OH}^- + \text{new bacterial cells}$$

Wastewater:

$$\text{C}_{10}\text{H}_{16}\text{O}_3\text{N} + 10\text{NO}_3^- + 5\text{N}_2 \rightarrow 10\text{CO}_2 + 3\text{H}_2\text{O} + \text{NH}_3 + 10\text{OH}^-$$



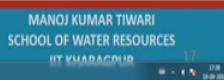
Methanol:

$$5\text{CH}_3\text{OH} + 6\text{NO}_3^- \rightarrow 3\text{N}_2 + 5\text{CO}_2 + 7\text{H}_2\text{O} + 6\text{OH}^-$$

Acetate:

$$5\text{CH}_3\text{COOH} + 8\text{NO}_3^- \rightarrow 4\text{N}_2 + 10\text{CO}_2 + 6\text{H}_2\text{O} + 8\text{OH}^-$$

Source: Water Environment Federation: Operation of Municipal Wastewater Treatment Plants: MoP No. 11, Sixth Edition, Biological Nutrient Removal Processes, Chapter (McGraw-Hill Professional, 2008), Access Engineering

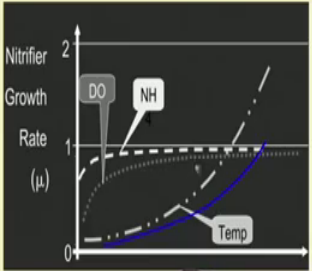
So, the reaction is like this. We have nitrification like the ammonia gets in the will react with the oxygen, will form nitrite then this will further react with the oxygen; we will form the nitrate nitrogen. So, overall reaction the ammonia can be converted to the ammonia nitrogen can be converted to nitrate nitrogen. This dash n simply reflects that this is represented as nitrogen we can remove that also. So, your reaction will still be same way when if we remove the n less whereas, denitrification process is again this nitrate nitrogen in the presence of carbon source and facultative bacteria it converts to the nitrogen and form some new bacterial cells.

So, if we consider the typical like we need a carbon source for this denitrification process. So, if we consider the typical carbon source available in the wastewater in the form of say C 10 O 3 N. So, then this is the reaction where this nitrate reacts with this and eventually converts the nitrogen converts it to nitrogen methanol can be another carbon source or acetate can be another carbon source. So, any carbon source that way will be kind of able to through denitrifiers will be able to use that and convert the nitrate into the nitrogen.

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Nitrogen Removal: Nitrification - Denitrification

- Effective nitrification depends on sufficient oxygen and alkalinity (to maintain pH). Nitrifiers typically require 4.57 mg of oxygen and 7.14 mg of alkalinity (as calcium carbonate) for each 1.0 mg of nitrate-nitrogen formed. They yield about 0.06 to 0.20 mg of VSS for each 1.0 mg of nitrate-nitrogen formed.
- Nitrification typically requires a long retention time, a low F/M ratio, and a high mean cell residence time (MCRT). Rate of nitrification is also affected by temperature and pH.



The graph plots Nitrifier Growth Rate (μ) on the y-axis (0 to 2) against three variables on the x-axis: DO, NH, and Temp. The DO curve is a solid line that rises and plateaus. The NH curve is a dashed line that rises and plateaus. The Temp curve is a solid line that rises exponentially. A small inset image of a man in an orange shirt is visible in the bottom right corner of the slide.

Source: Water Environment Federation, Municipal Wastewater Treatment Plants: MoP No. 11, Sixth Edition, Nutrient Removal Processes, Chapter (McGraw-Hill Professional, Process Engineering)

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The effective nitrification depends on kind of sufficient oxygen and alkalinity that should be present in the system ok. So, typically this nitrifier requires 4.57 milligram of oxygen and 7.14 milligram of alkalinity as a calcium carbonate for each milligram of nitrate nitrogen formed. And they you usually yield from 0.06 to 0.2 milligram per liter of biomass or VSS for each one milligram of nitrate nitrogen which is being formed in the process of nitrification.

So, this typically requires a long residence time a low food to microorganism ratio and high mean cell residence time that way the rate of nitrification can be kind of optimized by controlling these factors and it eventually depends on the temperature and pH as well. So, like you can see here that as temperature increases the rate increases pH again for like optimum. We need a kind of optimum pH for this thing as well and do maintenance is also necessary for the achieving good growth rate of nitrifiers.

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Nitrogen Removal: Nitrification - Denitrification

- Nitrifying organisms are present in almost all aerobic process sludge but they are less in number. Under favourable conditions (BOD_5 to TKN > 5), carbon oxidation and nitrification may occur in a single reactor (*Single Stage: combined carbon oxidation and nitrification*), which could be accomplished in both suspended and attached growth process such as trickling filter, ASP, RBC, SBR, etc.
- Nitrification could be achieved in separate reactor as well (*Separate Stage or Two Stage: separate stage carbon oxidation and nitrification*), which are similar in design to the activated-sludge process for suspended growth nitrification processes. Attached-growth processes such as trickling filter process, rotating biological contactor and packed-bed reactor could also be used for separate-stage nitrification.
- Separate-stage nitrification is usually practiced when BOD_5 to TKN < 3

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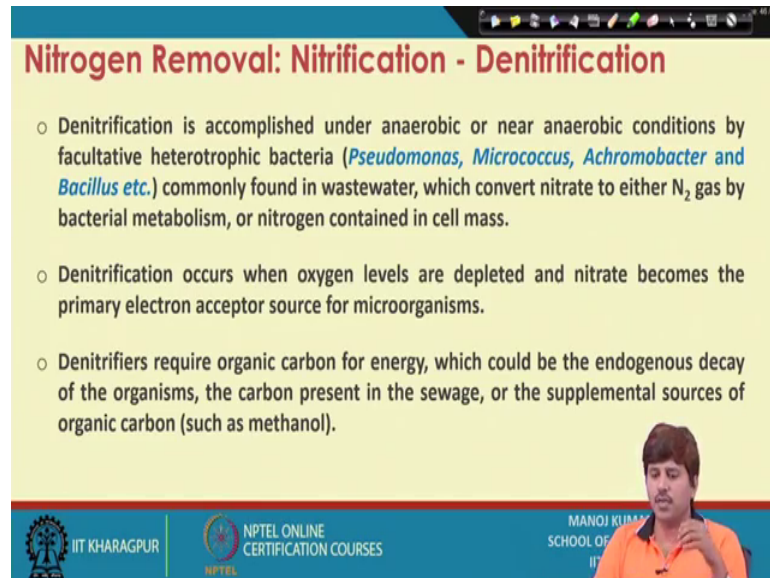
These nitrifying organisms are present in almost all aerobic processes and that way like under favorable conditions when there is usually the BOD 5 to TKN ratio is greater than 5 we can do this in that your typical activated sludge process itself. So, this carbon oxidation and nitrification we can actually do in a single reactor although we need to give larger retention time there ok. So, that is called single stage or combined carbon oxidation and nitrification or combined CBOD and NBOD removal because we are removing carbonaceous BOD and nitrogen oxygen demand also together.

So, since this is done in a single stage. So, we call this a single stage process or combined oxidation and nitrification process which can be accomplished in both suspended as well as attached growth systems like activated sludge process rotating biological contactor sequencing batch reactor all those things the nitrification could also be achieved in a separate reactor which is called separate stage or two stage process. So, like we have a thing stage process we can have go for a two stage process where the carbon oxidation and nitrification takes place in a separate stages and in a separate reactors ok.

So, this typically for suspended growth systems it is the even the nitrification design is similar to the design of activated sludge process where is an attached growth system like trickling filter rotating biological contractor or packed bed reactor could also be used for

the separate stage nitrification. The separate stage nitrification is usually practiced when we have BOD five to TKN ratio usually less than 3 ok.

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Nitrogen Removal: Nitrification - Denitrification

- Denitrification is accomplished under anaerobic or near anaerobic conditions by facultative heterotrophic bacteria (*Pseudomonas*, *Micrococcus*, *Achromobacter* and *Bacillus* etc.) commonly found in wastewater, which convert nitrate to either N_2 gas by bacterial metabolism, or nitrogen contained in cell mass.
- Denitrification occurs when oxygen levels are depleted and nitrate becomes the primary electron acceptor source for microorganisms.
- Denitrifiers require organic carbon for energy, which could be the endogenous decay of the organisms, the carbon present in the sewage, or the supplemental sources of organic carbon (such as methanol).

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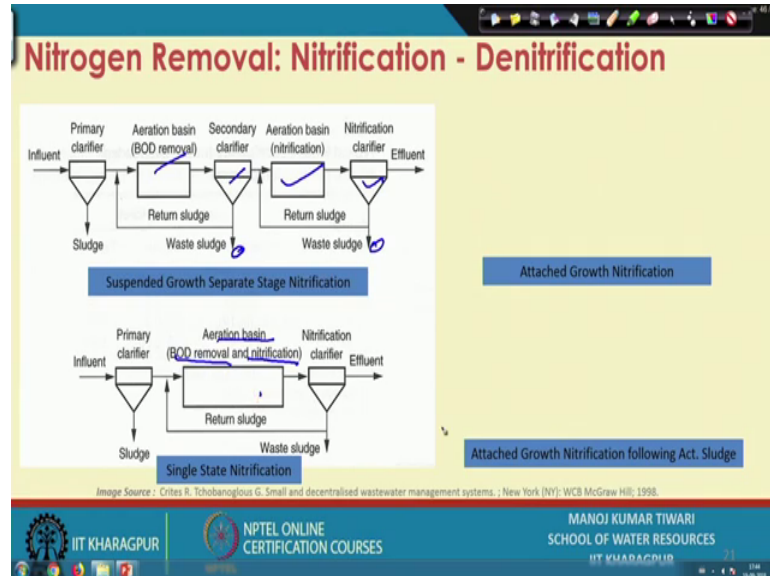
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Now so, once this nitrification is done the denitrification is accomplished under anaerobic or near anaerobic conditions where the facultative heterotrophic bacteria like pseudomonas micrococcus or achromobacter. So, all these bacillus these species eventually, they are available in the waste water typically they are present in the waste water. So, these convert nitrate to either nitrogen gas by the bacterial metabolism or assimilate nitrogen into their cell mass. So, that is how the nitrogen is removed the dissolve nitrate is removed from the system. This denitrification occurs when the oxygen levels are depleted and the nitrogen or the nitrate which is their becomes the primary electron acceptor ok. So, if there is oxygen. So, in the process that actually accepts electron, but in the absence of oxygen nitrate nitrate becomes electron acceptor and that way it is reduced further by accepting electrons.

These denitrifiers require organic carbon for energy as we were just seeing that it we can actually, it can use the organic carbon present in the wastewater itself. So, if nothing is present the endogenous decay of the organisms could itself provide source of organic carbon. However, for faster rate it is preferred that there should be some carbon source present in the seepage in the waste water. So, if the carbon source is present in the wastewater it is fine, if not a supplemental source organic carbon like methanol or

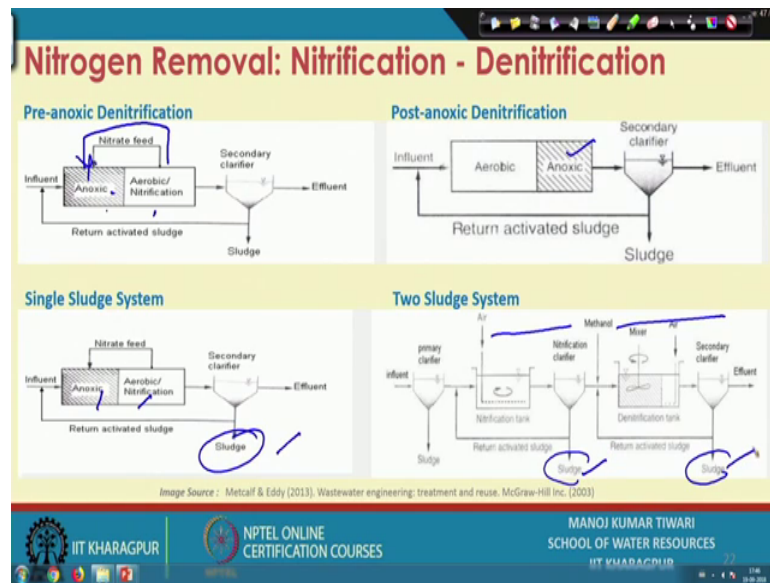
acetate those kind of things can be supplemented for the process for the organic carbon requirements of these anaerobes.

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So, these are couple of this thing. So, we can have suspended growth, separate stage nitrification process where this is kind of a separate stage nitrification process. So, we see that sludge is coming first it is going to the radiation level for BOD removal secondary clarifier is happening and then there is another aeration basin for nitrification and then there is clarifier for nitrate. So, we are actually getting two stages of sludge production as well. This is a typical suspended growth system; we can have single stage nitrification as well. So, we get rid off the other part and the BOD removal and nitrification is done in a single aeration basin. Only thing is the residence time has to be given little longer here ok.

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So, there are a couple of pictures which has not come somehow, but you will get that in the materials when it is uploaded anyway. There could be various different configurations like pre anoxic denitrification. So, in this one what is done that we for denitrification purpose, we put an oxygen before the nitrification. So, whatsoever is there it is converted first; then it is again converted to nitrate and then nitrate feed is recycled back to the aerobic system. So, that nitrogen is removed. So, that is when we add prior hand, we can have kind of post anoxic system as well.

So, where the anoxic zone is kept after aerobic; so, there is no need of returning nitro nitrate feed over here. Similarly we can have single stage system or two stage sludge production system as just we were seeing. So, we can have like nitrification in a separate this thing and denitrification in a separate system ok. So, that is two stage sludge systems and here since denitrification and nitrification are taking place in this thing and then, it is going to secondary clarifier. So, sludge which is generated contains both kind of sludge whereas, here these nitrifiers and denitrifiers sludge is kind of separate. So, we have that way two stage denitrification can also have.

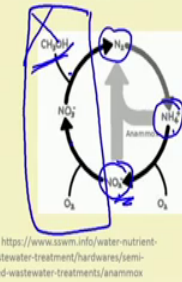
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Nitrogen Removal: Anammox Process

Anaerobic Ammonium Oxidation (Anammox), discovered in the early nineties achieves bacterial transformation of ammonium (NH_4^+) and nitrite (NO_2^-) directly into nitrogen gas (N_2) and water, instead of passing through a two-stage process of aerobic nitrification and anaerobic denitrification. The reaction is carried out by Anammox bacteria (*Candidatus Brocadia anammoxidans*) belonging to the group of planctomycete.

The Anammox reaction can be represented as: $\text{NH}_4^+ + \text{NO}_2^- = \text{N}_2 + 2\text{H}_2\text{O}$

Advantages	Disadvantages
<ul style="list-style-type: none">• Oxygen addition can be reduced (results in energy and cost savings)• Anammox bacteria do not require organic carbon (e.g. methanol) as they do in nitrification• Production of excess sludge is reduced• Reduces CO₂ emissions	<ul style="list-style-type: none">• Not a lot of knowledge available (skilled operation and maintenance required)• High construction costs if the Anammox process replaces the conventional nitrification/denitrification in treatment plants



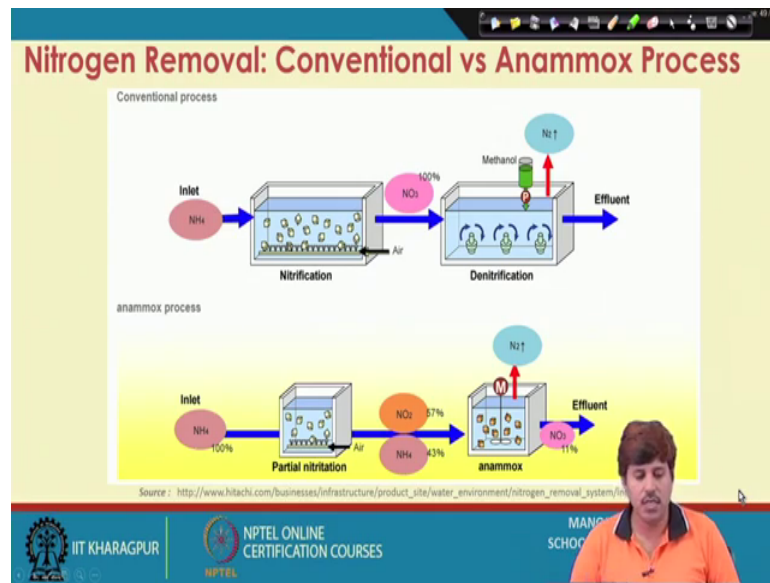
Source: <http://www.sswim.info/water-nutrient-cycle/wastewater-treatment/hardwares/semi-centralised-wastewater-treatment/anammox>

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There is another biological nitrogen removal process which is Anammox which is kind of a newer term or newer technology. So, this is Anammox is essentially anaerobic ammonium oxidation which we typically call as Anammox ok. So, this is discovered in early nineties and it what it does. So, instead of going for the complete process of nitrification and denitrification, it converts the ammonium and nitrite through this partial nitrification into the nitrogen directly. So, we get rid off the conversion into the nitrate and then denitrification of nitrate with the source of acetate. All these things are actually get we get away with this. So, just ammonium and nitrite ion are converted to nitrate, it actually the Anammox bacteria which is kind of *Candidatus Brocadia anammoxidans*.

So, that actually is used here and this reaction is something like this. So, ammonia will react with the nitrite and form nitrogen and H₂O. This process has several distinct advantages ok. The oxygen addition can be reduced because we are not going for complete nitrification, we are just going for partial nitrification. Then these bacteria do not require organic carbon source like methanol and those kind of thing, we are not going for denitrification anyway. So, production of sludge is also reduced because larger aeration larger biomass and the reduction of CO₂ is also kind of is there; CO₂ emission is decrease. So, these are the advantages whereas, it is a process under development. So, there is kind of lot of research still needed and there is a high construction cost of these processes. So, these are kind of the demerits of this.

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Now if we compare it with conventional processes when conventional processes we have ammonia coming through a nitrification basin and then converting into the nitrate which is going to the denitrification releasing nitrogen and effluent. And in the process it needs a methanol or some organic carbon source.

Whereas in Anammox process, it is just partial nitrification and then the remaining ammonia and nitrate reacts and kind of forms into that way and little nitrate which goes into the effluent. So, that way is the Anammox process is used

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Nitrogen Removal: Conventional vs Anammox Process

	Conventional process (Nitrification-Denitrification)	anammox process
Reactor principle		
Reactor volume	Large	Small
O ₂ supply	Large	Small
Chemical dosing (for denitrification)	Need	No Need
Sludge production	Large	Small
Optimum temp	Normal (10-37°C)	High (25-37°C)

Source: http://www.hitachi.com/businesses/infrastructure/product_site/water_environment/nitrogen_removal_system/

If we compare the your typical these steps are gone here as you can see here in Anammox process. The reactor volume makes become small the oxygen requirement become small we do not need any further chemical dosing like is methanol or those kind of thing sludge production is small and kind of optimum temperature this works at 25 to 37 degree Celsius.

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Nitrogen Removal: Air (or Ammonia) Stripping

Under properly controlled conditions, air stripping can remove ammonia nitrogen from wastewater by converting it to ammonia (NH_3) which exists predominantly in the unionized, gaseous form at high pH levels.

The gaseous phase NH_3 and aqueous phase NH_4^+ exist together in equilibrium, controlled by the pH and the temperature. $\text{NH}_4^+ + \text{OH}^- = \text{NH}_3 + 2\text{H}_2\text{O}$

Dissolved ammonium is converted to gaseous phase and then dispersed in air, thus allowing transfer of the ammonia from wastewater to the air. The pH must be greater than 11 for complete conversion to NH_3 .

Image Source : http://files.dep.state.pa.us/operator/Certification/TrainingModules/wwOIL/water_wb.pdf

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So, temperature control is essential, it cannot work in very cold climate that way. There is air or ammonia stripping which is another method for removal of the nitrogen. So, the ammonia stripping is again physicochemical process not a biological process that way. So, what happens that because there are kind of ammonia present in the system and ammonia is ammonium ion particularly in such a species that they remain ammonia gaseous ammonia and aqueous phase ammonium ion remains together in a equilibrium and their equilibrium is controlled by the pH and temperature. So, depending on the pH, what pH is and what is the kind of temperature as we see the different temperatures; we can see what fraction of ammonia or what fraction of ammonium ion will be there in the water.

So, just by controlling the pH particularly, if we move the pH towards alkaline zone say around 12 or 11 if we if you may be able to make pH around 11 or 12. So, we see that the maximum portion will be actually in the form of ammonia gas and not in the ammonium ion. So, ammonium ion is something which is dissolved in the water, but if it is

converted to the ammonium ammonia gas which predominantly exist like kind of an ionized gaseous form. So, that can be kind of then released back ok. So, these can be made to escape to the atmosphere; if we go for a air stripping process.

So, the idea here is that dissolved ammonium is converted to the gaseous phase and then, dispersed in the air. This allows kind of transfer of the ammonia from wastewater to the air and pH must be greater than 11 for complete conversion of ammonia. So, around greater than 11 pH, we see at around 20 degree Celsius, we have here 98, 99 percent of 98 to 99 percent of actually the total nitrogen remaining in the form of ammonia and not the ammonium ion.

Ammonium ion is soluble in water that will remain in the water, but if it is converted to ammonia gas. So, this gas can be basically then stripped off which is done in the ammonia stripping process.

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Nitrogen Removal: Air (or Ammonia) Stripping

- Typically lime is the most common means for raising the pH.
- Enough lime must be added to precipitate the alkalinity and to add the excess OH⁻ ions for pH adjustment.
- The air to wastewater ratio ranging from 2000 to 6000 m³ of air/m³ of wastewater is used for design.
- Tower depths are generally less than 7.5 m, and hydraulic loading vary from 40 to 46 L/min.m² of tower.
- Ammonia Stripping works well for 10-100 mg/L ammonia and is less expensive than nitrification-denitrification, but it does not work very efficiently in cold weather.

The diagram shows a vertical stripping tower. At the top, 'Air out' is indicated. Below it is a 'Demister' section. 'Contaminated water in' enters from the left and passes through a 'Water distributor'. The main body of the tower is filled with 'Packing'. A 'Water redistributor' is located in the lower part of the tower. 'Air in' enters from the bottom left. 'Water out' exits from the bottom right.

Image Source : https://en.wikipedia.org/wiki/Air_stripping

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So, typically kind of lime is the most common means for raising the pH lime is added. So, that pH is raised. There is enough lime must be added to precipitate the alkalinity and to kind of increase the OH ion for the pH adjustment. The air to water ratio ranges from 2000 to 6000 meter cube of air per meter cube of wastewater which is typically used in the design and this works well for 100 to so, 10 to 100 milligram per liter range.

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Nitrogen Removal: Air (or Ammonia) Stripping

Image Source: http://en.citizendium.org/wiki/air_stripping

Image Source: <http://www.tecnium.es/en/lixivate-stripping/lixivate-stripping>

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There are different kind of strippers which can be used; there are packed bed strippers when there is a packing of this thing. So, we kind of flow liquid from the top and air from the bottom. So, they as they pass the they interact with each other, air gets out liquid gets collected in the bottom or we can have a sieve tray. So, where there are trays again liquid moves in. So, liquid actually falls from these trays to each other and then there is a air which actually kind of through these pores and bubbles moves up.

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Phosphorous Removal

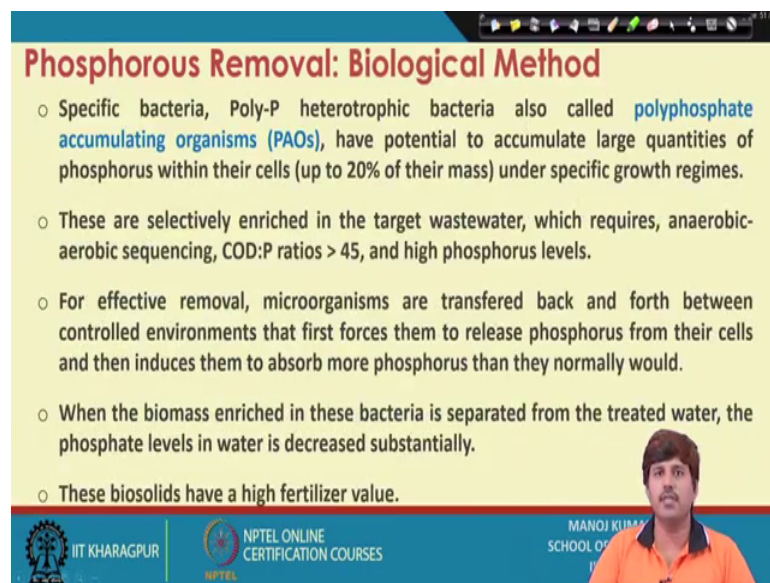
- Normally secondary treatment can only remove 1-2 mg/l of phosphorus, so a large excess of phosphorus remained in outlet from secondary units.
- Generally it appears as orthophosphate, polyphosphate and organically bound phosphorus.
- Phosphate removal is currently achieved largely by chemical precipitation as it is reliable in performance and easy to operate, but is expensive and causes an increase of sludge volume by up to 40%.
- An alternative is the biological phosphate removal (BPR), which is accomplished by sequencing and producing the appropriate environmental condition in the reactors.

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So, that kind of aerator is there. This is how typically stripping system looks like. Another nutrient that is there in the water is phosphorous which kind of normally secondary treatment can remove 1 to 2 milligram of phosphorous. So, a large excess of phosphorous still remains in the outlet of the secondary unit. There is kind of different forms of phosphorous. It could be in the form of orthophosphates, polyphosphates or originally bound phosphorus.

This removal of phosphorous can be achieved through chemical methods or biological methods. Chemical methods are more reliable and easy to operate that is why more popular although they are expensive and cause of kind of increased sludge volume which could increase as high as 40 percent. The alternate biological phosphorus removal methods are also there. They are kind of more environmental friendly which are achieved by kind sequencing and producing the appropriate environmental conditions in the reactor where the bacteria assimilates the phosphorous.

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Phosphorous Removal: Biological Method

- Specific bacteria, Poly-P heterotrophic bacteria also called **polyphosphate accumulating organisms (PAOs)**, have potential to accumulate large quantities of phosphorus within their cells (up to 20% of their mass) under specific growth regimes.
- These are selectively enriched in the target wastewater, which requires, anaerobic-aerobic sequencing, COD:P ratios > 45, and high phosphorus levels.
- For effective removal, microorganisms are transferred back and forth between controlled environments that first forces them to release phosphorus from their cells and then induces them to absorb more phosphorus than they normally would.
- When the biomass enriched in these bacteria is separated from the treated water, the phosphate levels in water is decreased substantially.
- These biosolids have a high fertilizer value.

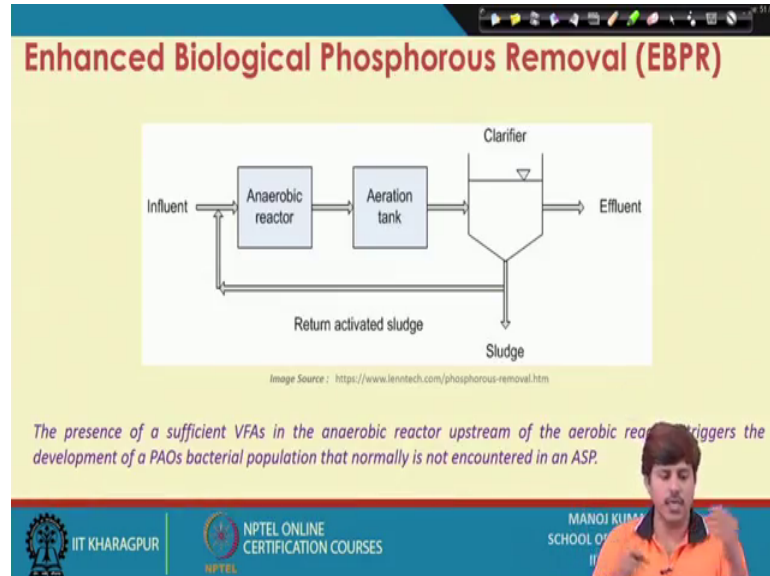
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So, from the biological methods, there are specific bacteria which is Poly-P heterotrophic bacteria ok. This is also called polyphosphate accumulating organisms or PAOs. So, they have potential to accumulate large quantities of phosphorous within their cell mass. So, in their cell structure they can accumulate as high as around 20 percent of the total mass could be actually of the phosphorus. And, but that is not in the usual case that is under specific growth regime and we have to provide that growth regime. That growth regime

is kind of ensured by a anaerobic aerobic sequencing. The co due to phosphorus ratio should be greater than 45 and there has be high phosphorous level in the system.

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So, for effective removal these microorganisms PAOs are transferred back and forth between the controlled environment that first forces them to release the phosphorus and then kind of. They first release the phosphorus from their cell and then once they again introduced in the other system, they adsorb more phosphorus that they would normally have and that is why the accumulation of phosphorus increases.

When this biomass enriched in this bacteria is separated from the treated water the phosphorus level in the water will be decreased because most of the for majority of the phosphorus has been assimilated into the cell mass ok. And the cell mass which is separated because of its high phosphorus content has a very high fertilizer value. So, these bio solids are helpful in that way as well. So, there is kind of it is as we said that it is a anaerobic aerobic sequence process. So, what happens that the there has to be presence of sufficient VFAs in the anaerobic reactor upstream and which kind of from where the flow goes to the aerobic system. So, this VFAs helps in development of these bacteria PAOs ok.

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Enhanced Biological Phosphorous Removal (EBPR)

- In the anaerobic environment, the PAOs absorb VFAs in their cells in the form of internal polymers such as polyhydroxy-butyrate (PHB). To supply the energy, the PAOs use the energy of previously stored polyphosphate, which is split into orthophosphate (PO_4^{3-}) and then released from the cell.
- In the subsequent aerobic reactor, the PHB is used by the PAO as an energy source. Part of the released energy is used to regenerate the polyphosphate released in the anaerobic reactor. In this process, phosphate is absorbed from the liquid phase by the PAOs.

Image Source : <https://knowhowtogo.wordpress.com/2011/02/01/biological-phosphorus-removal-from-waste-water/>

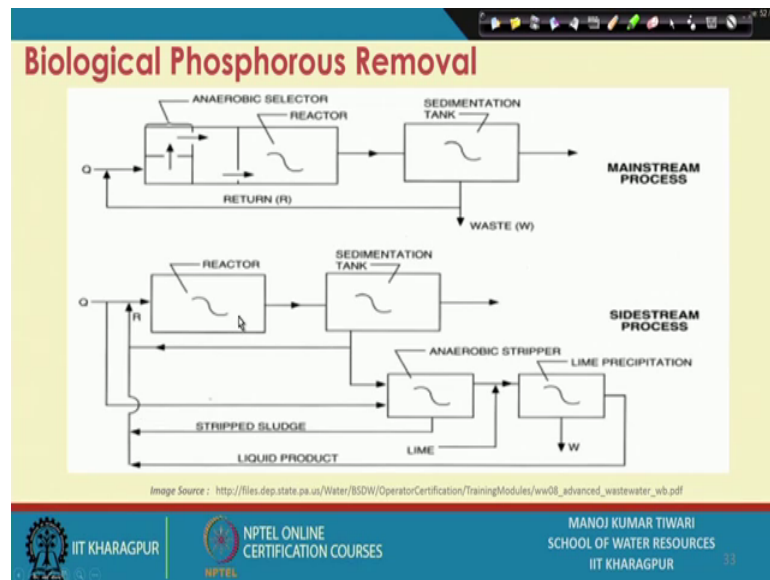
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And that because in conventional activated system they will not develop that much so, this anoxic environments helps in that development of those microorganisms. So, what happens that in the anaerobic environment; if we see in the anaerobic environment, these the PAOs adsorb these VFAs which are there in their cells and in the form of kind of internal polymer such as PHBs. So, these VFAs are adsorbed as a PHBs in their cell in the anaerobic this thing and the phosphorus that poly phosphorus that we have that is also kind of converted is used as a source of energy.

So, the ATP is generated which is used as a energy and in the process, this phosphate is released from the cell. This happens in the anaerobic environment, then when we move to the sequential aerobic system. So, in there these PHBs is which are kind of assimilated VFAs and this then this PHBs are used to form the new cell and to generate the energy to fulfill the energy requirement as well. So, through this NADH, they produce ATP and they produce new cell mass as well ok.

So, part of this release energy which is released is again utilized to regenerate the poly phosphate in the cell and in the process this phosphate which has been released in the which is there in the water gets kind of assimilated gets consumed. So, in this process phosphate is adsorbed from the liquid phase by these PAOs and that way the concentration of phosphorus decreases and it actually moves to the cell.

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So, there are kind of it there are mainstream processes where we can have anoxic reactor followed by in kind of aerobic system right away or we can have a side stream process, where this anaerobic process done is in a side stream. And, then actually it is again supplied to the conventional aerobic system that way.

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Phosphorous Removal: Chemical Method

Lime based precipitation:

Excess of lime is added to the wastewater causing phosphorus to form a precipitate with calcium hydroxide. This precipitate can be flocculated and removed from the wastewater by settling

- Calcium reacts with phosphate in the presence of hydroxyl ion (high pH) to form an insoluble precipitate, hydroxylapatite. The following equation describes the reaction that occurs:
$$10\text{Ca}^{+2} + 6\text{PO}_4^{-3} + 20\text{OH}^- \rightleftharpoons \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \downarrow$$

calcium phosphate hydroxyl ion hydroxylapatite
- The amount of lime required for treatment is generally independent of the amount of phosphorus present and depends primarily on the alkalinity of the wastewater.
- Typically, the pH of the wastewater will be raised to the range of 10 to 11 with the addition of lime to properly precipitate the phosphorus present.

Source : http://files.dep.state.pa.us/Water/BSDW/OperatorCertification/TrainingModules/ww08_advanced_wastewater_wb.pdf

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So, then there are couple of chemical approaches for phosphorus removal as well. So, the biological approach was the one that we discussed. Chemical approach it is actually a simple chemical precipitation. So, either lime based precipitation or alum based kind of

flocculation and precipitation is what is used. So, lime based precipitation there is access lime is added in the waste water and which kind of cause phosphorus to form precipitate with the calcium hydroxide.

This precipitate then can be flocculated and removed from the water by simple settling. So, what happens that calcium is there it will react with the phosphate and it will form this hydroxy lapatite which is kind of precipitate. So, this is heavier this will settle down in the system. The amount of lime required for this treatment is generally independent of the amount of phosphorus present in the system and will basically depend on the alkalinity because there has to be adequate alkalinity present in the system for this reaction to take place. Typically pH of the wastewater will be raised because we are adding lime. So, pH will be raised in the range of 10 to 11 with the addition of lime and that way the proper precipitation of phosphorous takes place which is quite a reliable method this sludge's are heavier. So, they quickly get settle out.

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Phosphorous Removal: Chemical Method

By Alum Flocculation:
When alum (aluminum sulfate) is added to wastewater, a precipitate of aluminum phosphate forms. Aluminum phosphate is not a dense precipitate and requires flocculation with a polymer, and often filtration to achieve adequate removal of the precipitate.

The following key reactions occur during alum precipitation of phosphorus from wastewater:

$$\text{Al}_2(\text{SO}_4)_3 + 2\text{PO}_4^{3-} \leftrightarrow \text{AlPO}_4 \downarrow$$

aluminum sulfate + phosphate → aluminum phosphate

$$\text{Al}_2(\text{SO}_4)_3 + 6\text{HCO}_3^- \leftrightarrow 2\text{Al}(\text{OH})_3 \downarrow + 3\text{SO}_4^{2-} + \text{CO}_2$$

aluminum sulfate + alkalinity → aluminum hydroxide + carbon dioxide

When alum is mixed with wastewater, it acts as an acid, reducing the pH of the wastewater (by reducing alkalinity). Optimum phosphorus removal is generally achieved at a pH range of approximately 6.0 to 7.0.

Source : http://files.dep.state.pa.us/Water/BSDW/OperatorCertification/TrainingModules/wwO...wastewater_wb.pdf

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Whereas alum precipitation with the alum. So, where aluminum sulfate or what typically we call as alum is added to the wastewater and here a precipitate of this aluminum phosphate forms ok. So, these alum reacts with the this thing and a precipitate of this alum phosphate forms.

This aluminum phosphate is not that a dense precipitate and that is why it needs to be basically some kind of flocculation is needed where we can add a polymer dose or

something and it can flocculate that way. So, and then we can make it settle make it precipitate or we may actually need to go for the filtration as well because of the presence of the micro flocks of aluminum phosphate in the system ok. So, when the alum is added, it acts as an acid this reduces the pH of the wastewater by reducing the alkalinity because alkalinity will also be reduced alum will react with the alkalinity and form alum minimum hydroxide which also will precipitate. So, that way excess alum is reduced, but it kind of reduces the alkalinity as well. So, optimum phosphorus removal is generally achieved at a pH range of approximately 6 to 7.

Apart from these there is kind of iron salts kind of ferric chloride or those kind of coagulant or can also be used for the removal of phosphorous ok; however, these are the more popular ones. So, that way the chemical removal of the phosphorous takes place ok. So, with this we kind of conclude this session here and in the next class, we will take up the removal of we will take up some other advanced treatment approaches or tertiary treatment approaches for the removal of the remaining contaminants.

So, thank you and see you in the next class.