Biological Process Design for Wastewater Treatment
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Lecture: 07
Wastewater Characterization - IV

Welcome back everyone in this NPTEL Online Certification Course on Biological Process Design for Wastewater Treatment. So, today again we will continue with the wastewater characterization aspects. In the last few lectures we studied regarding the chemical oxygen demand and biological or biochemical oxygen demand. So, today we will be learning the difference between the biological oxygen demand and the chemical oxygen demand.

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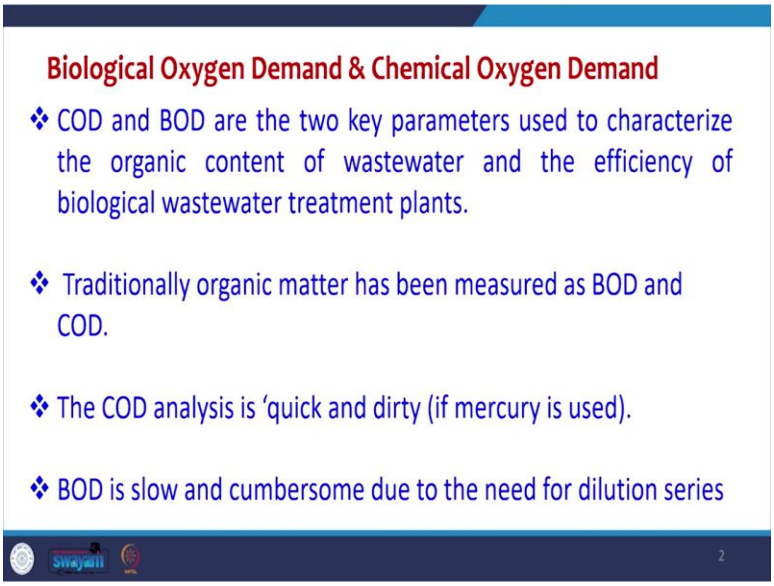

And will further study few more parameters which are related to oxygen demand or amount of carbonaceous carbon present in the water sample. So, COD and the BOD are two most important key parameters which are used to characterize the organic content of the wastewater. And they are determined before the treatment and after the treatment so to determine the efficacy of biological wastewater treatment plants.

Traditionally, the organic matter is measured via both BOD and COD. The COD analysis is quick and it required some harsh chemicals. So, in a way it is dirty and if in particular Mercury is used. BOD is slow and cumbersome and requires lots of dilution. And many times the test fails after 3 days or 5 days at whatever temperature because of some oxygen going into the water sample or because of non-presence of microorganism or because we have assumed a certain dilution and which dilutions are not working.

So, BOD test has lot of issues and the BOD test may fail after 3 days or 5 days. So, in a way, all our efforts for analyzing BOD go wrong. Now, what is the difference between the BOD and COD?

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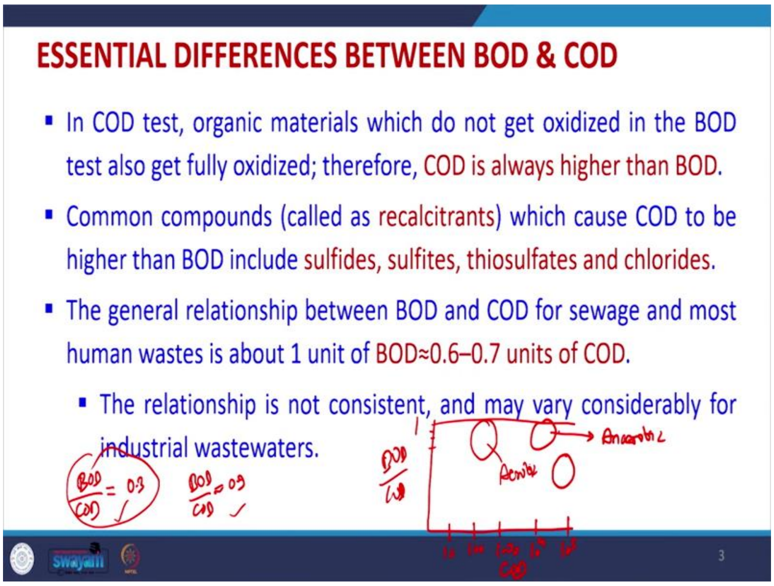

In COD test what we do is that organic materials which do not get oxidized in the BOD test, they are also fully oxidized because we are using highly oxidizing chemical for oxidizing the organic matter. Thus, all the organic matter gets oxidized, which does not get oxidized in the BOD test also so COD is always generally higher than the BOD value.

Common compounds which are recalcitrant, recalcitrant means that which do not get biodegraded by the microorganisms present in the water. They are recalcitrant, they cannot be they resist degradation. These recalcitrants cause COD to be higher than BOD, and these recalcitrants includes sulfides, sulfites, thiosulfate, chlorides, et cetera.

In the general relationship between BOD and COD for sewage and most human waste is about one unit of BOD is equal to 0.6 or 0.7 units of COD, the relationship is not constant and may vary considerably with industrial wastewater sample. Now, determining the value of BOD COD is very very important.

So, thus if the BOD to COD value suppose this is equal to 0.3 that means, the amount of biodegradable organic matter is very less in the water sample and it is not good to go for the biological treatment. We will require other types of chemical and physicochemical treatment for removal of the oxygen demand out of this water. And this the BOD this low value represents that this particular wastewater contains lot of recalcitrant.

In the second case, it is possible that the BOD upon COD value is of the order of 0.9 that means the amount of recalcitrants present in the wastewater sample are very less and we should go for biological treatment of wastewater. Now, there are some we can for different types of wastewater samples, we can easily determine the type of wastewater sample et cetera using some graph.

So, like if we plot the logarithmic scale and then there will be different types of wastewater which will be having the BOD-COD ratio in different ranges and the overall COD value also may be higher like if we plot in the logarithmic scale 10, 100, 1000 then maybe 10 raise to 4, 10 raise to 5, suppose this is the COD value, and this is the BOD to COD ratio.

So, the wastewater ranges for municipal wastewater suppose this is the value one. So, for municipal wastewater, the values may lie here between 100 to 1000 but the BOD-COD ratio will be higher in this range 0.6, 0.7, 0.8 whereas, for some wastewater samples, the values the BOD-COD ratio may be lower, but the overall COD ratio is very high. So, this is possible.

If the same water sample has good BOD to COD ratio, but the COD value is high still we can go for biological treatment under that condition for this wastewater sample will go for it will be preferable to go for anaerobic treatment of wastewater so that all the carbonaceous content can be converted into some gases like methane et cetera.

And we can get fuel out of that. So, this is possible so we will go for anaerobic whereas here we can go for aerobic treatment. So, there are different strategies, depending upon the BOD to COD ratio, and what is the overall value of COD and BOD.

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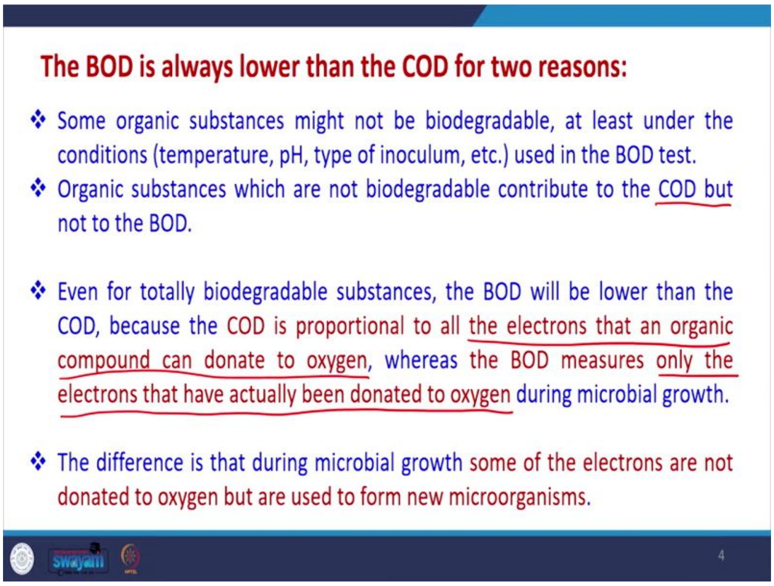

Now, when further the BOD is always lower than the COD for two reasons, some organic substances might not be biodegradable, at least under the conditions of temperature pH type of inoculum et cetera using the BOD test. So, organic substances which are not biodegradable, they contribute to COD, but not to the BOD.

So, that is why the COD value is higher. Also even if the all the carbon is biodegradable, the BOD value will be lower than the COD because COD is proportional to all the electrons that an organic compound can donate to the oxygen. Whereas the BOD majors only the electrons that have actually been donated to oxygen during microbial growth.

And the difference is that during microbial growth, some of the electrons are not donated to oxygen, but are used to form new microorganisms, because new microorganisms are getting formed they are not going to oxygen. So, actual oxygen demand is not only towards conversion to CO_2, it is towards conversion to microorganism.

So, that is why BOD value for the case where substance totally contains biodegradable substances also will be lower than the COD value. So, these are the two basic reasons because of which the BOD is always lower than the COD or vice versa, we can say the COD value is higher than the BOD value.

Now, we will take one problem which is not directly related to here, but it will give some idea that how that convergence happened with respect to various things. So, let us take this example.

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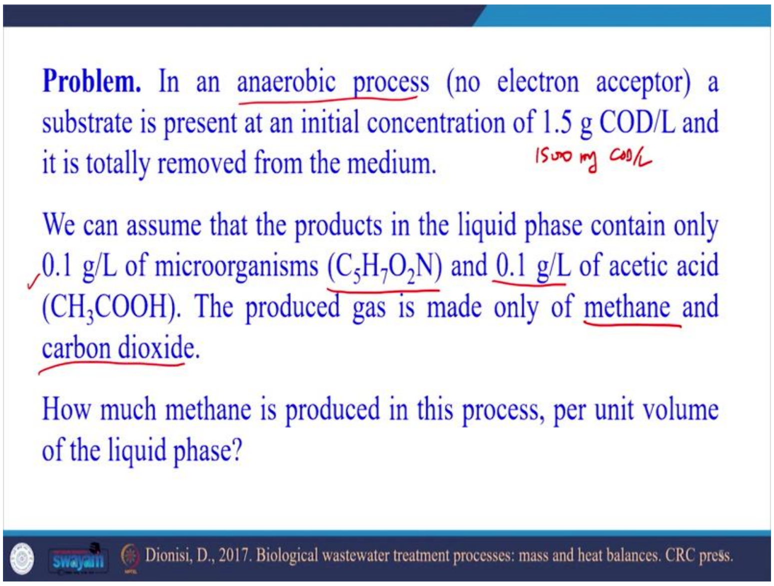

The question given here is that in an anaerobic process, new electron acceptor, so since there is an aerobic, there is no oxygen. A substrate is present at an initial concentration of 1.5 grams COD per liter. So, the wastewater contains 1.5 grams COD or we can say 1,500 milligram COD per liter.

So, this is good amount of COD and it is has to be totally removed from the medium. We can assume that during the anaerobic treatment, the products in the liquid phase contain only 0.1 gram per liter of microorganism and this microorganism can be represented by this formula. So, this formula is given which actually represents the microorganism.

Now, another acetic acid is also present which represents 0.1 gram per liter again, and then after everything is converted into gas, and which contains methane as well as carbon dioxide. So, the produced gas is made up of only methane and carbon dioxide. So, it is desired to know how much methane will be produced in the process per unit volume of the liquid phase?

So, we have to determine the tentative value of methane which will get produced. So, if we know this this problem gives idea that beforehand that if we know the COD, if you know the, what is the final concentration which is present in the liquid sample of some of the organic acids or alcohols et cetera and microorganisms, then we can tentatively calculate the methane produced. So, let us tentatively find out how we can calculate further.

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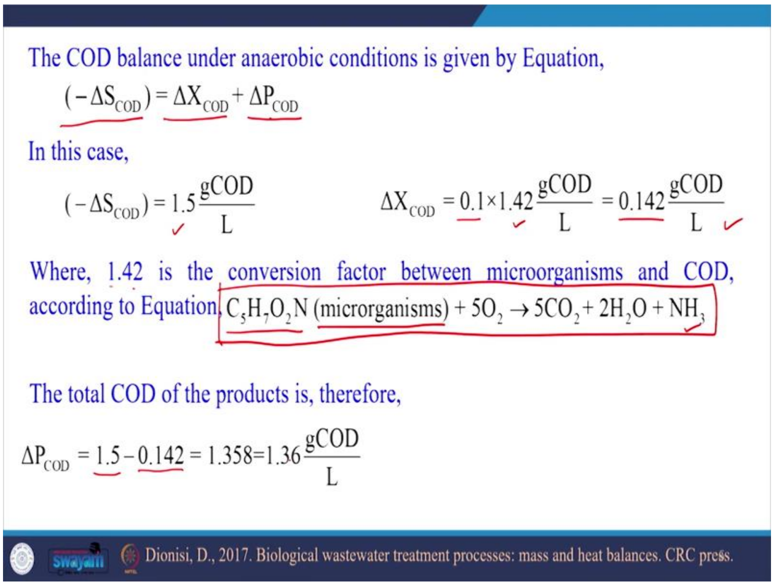

The COD balance under anaerobic conditions is given by Equation,

$$(-\Delta S_{COD}) = \Delta X_{COD} + \Delta P_{COD}$$

$$(-\Delta S_{COD}) = 1.5\frac{gCOD}{L}$$

$$\Delta X_{COD} = 0.1 \times 1.42\frac{gCOD}{L} = 0.142\frac{gCOD}{L}$$

$$C_5H_7O_2N \text{ (microrganisms)} + 5O_2 \rightarrow 5CO_2 + 2H_2O + NH_3$$

$$\Delta P_{COD} = 1.5 - 0.142 = 1.358 = 1.36\frac{gCOD}{L}$$

The COD balance under anaerobic condition is given by this equation, the decrease in the COD value is equal to the one which is used for biomass formation and another for product formation. Now, the drop in COD is 1.5 gram per COD per liter. So, this is already given that we have to decrease this to zero. So, this drop is 1.5. Now, the COD which will go to the increase in concentration of biomass is given like this.

So, here it is given that we had to find out the conversion factor if the concentration values are given. Now, for the microorganisms, it is given that the formula is represented by this. So, what we do is that we try to find out an equation balancing like this, where the nitrogen is converted into ammonia and then the carbon is converted into CO_2, hydrogen is converted to H_2O and we balance this equation.

And if you balance this equation, we can find out then 1.42 is the conversion factor between the microorganism and COD and this is a conversion factor and since 0.1 is the concentration so we can easily find out that out of the total COD, the COD which has been converted into biomass is 0.142.

Now, the total COD of the product is therefore, we can for product we can find out by subtraction so subtraction 1.5 minus 0.142 we have 1.358 we can assume this to be 1.36 grams COD per liter. So, the product which is going into the product the COD is 1.36 grams COD per liter out of 1.5.

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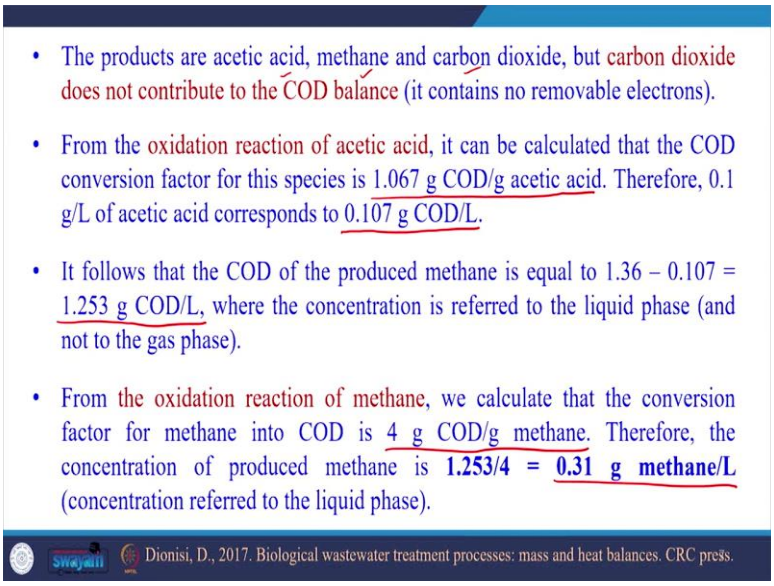

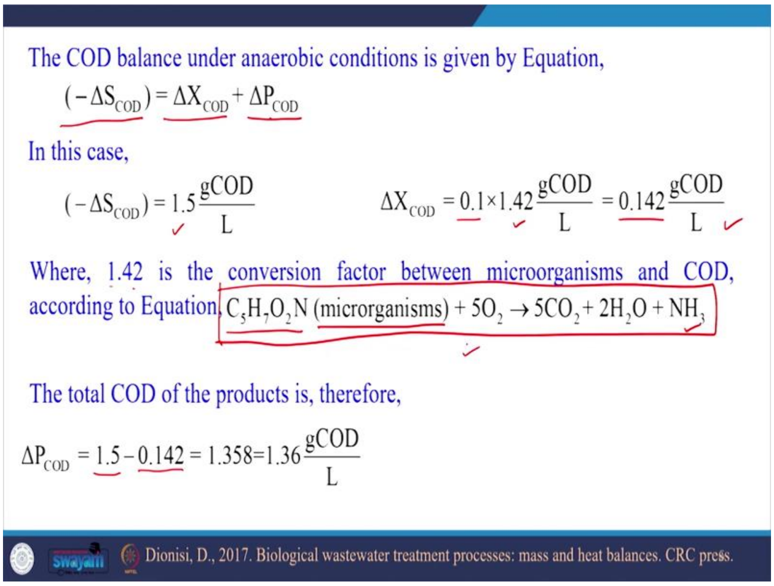

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$$\Delta P_{COD} = 1.5 - 0.142 = 1.358 = 1.36\frac{gCOD}{L}$$

Now, the product itself contains few things, the products are acetic acid, then methane and carbon dioxide. Carbon dioxide does not contribute to the COD balance so we can neglect it. Now, the remaining two are acetic acid and methane. So, again the for the oxidation reaction of acetic acid, we can like previously we can write an oxidation reaction of acetic acid also. And if we calculate from that, we will be finding that the conversion factor the COD conversion factor for the acetic acid is 1.067 grams COD per gram acetic acid.

So, therefore, 0.1 gram per liter of acetic acid actually represents 0.107 gram of COD per liter. So, it follows that the thing which is going into methane actually in the product is 1.36 which was on the total product minus 1.067. So, this will be minus 0.107. So, this gives 1.253 gram COD per liter for methane. So, this is the methane actually represents this much amount of COD which is getting produced.

Now, for methane also we can write equation and the conversion factor for methane into COD is 4 grams COD per gram methane. So, that means, if you divide this value by 4 we can get the amount of methane per liter which is produced. So, it is 0.31 gram of methane gets produced per liter of the wastewater sample out of which the wastewater itself contains 1.5 grams COD per liter.

So, the wastewater which contains 1.5 grams COD produce 0.31 gram of methane. So, and we can convert into more we can convert this into volume also depending upon the temperature and pressure. So, this way we can calculate. So, from tentative equations and some convergence we can determine the theoretical amount of methane which can get produce. Certainly it may vary little here and there.

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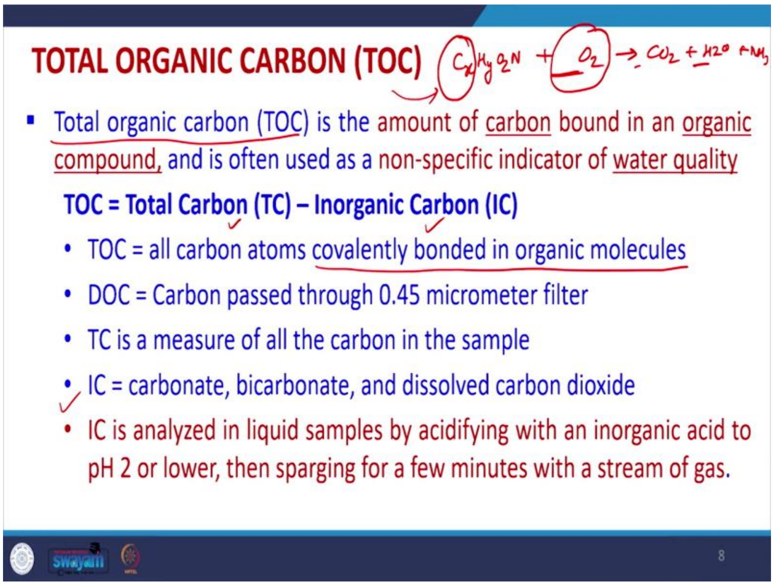

Now, there is another parameter that we should be study and that is nowadays used very commonly for determining the wastewater characteristics and this is called Total Organic Carbon and it is the amount of carbon bound in an organic compound. So, what is TOC? So, any compound $C_xH_yO_zN$ suppose, is also there.

If we write the oxygen balance like this. So, we represent a CO_2 plus H_2O plus ammonia like this and we balance and wrote the values here every place. So, this is the, suppose after balance whatever is the venue. So, in the BOD and COD we are concentrating on the amount of oxygen which is getting consumed whereas, in the COD we are concentrating on the amount of total organic carbon which is present in the wastewater sample.

So, TOC actually concentrate on this value. So, in place of oxygen we are measuring C_x, a carbon value and so TOC is the amount of carbon bound in an organic compound. It is used as a nonspecific indicator of water quality. So, TOC actually is determined via determining the total carbon in the wastewater sample and subtracting the inorganic carbon.

So, thus we can find out the Total Organic Carbon. TOC all carbon atoms which are covalently bonded in an organic molecule they represent the TOC and then there is a DOC value also which is called as the carbon which passes through 0.45 micrometer filter. TC measures the all the carbon in the sample. IC represents the carbonate, bicarbonate, dissolved carbon dioxide. So, inorganic carbon maybe any of these.

An inorganic carbon is analyzed by as defined within inorganic acid to pH 2 or lower and then sparging for a few minutes with the stream of gas and then we determine the inorganic carbon so thus we can find out that TOC. So, TOC can be found out using instruments which are available nowadays, through which we measure the Total Organic Carbon.

They essentially measure the total carbon and as well as the inorganic carbon and by different they give that TOC.

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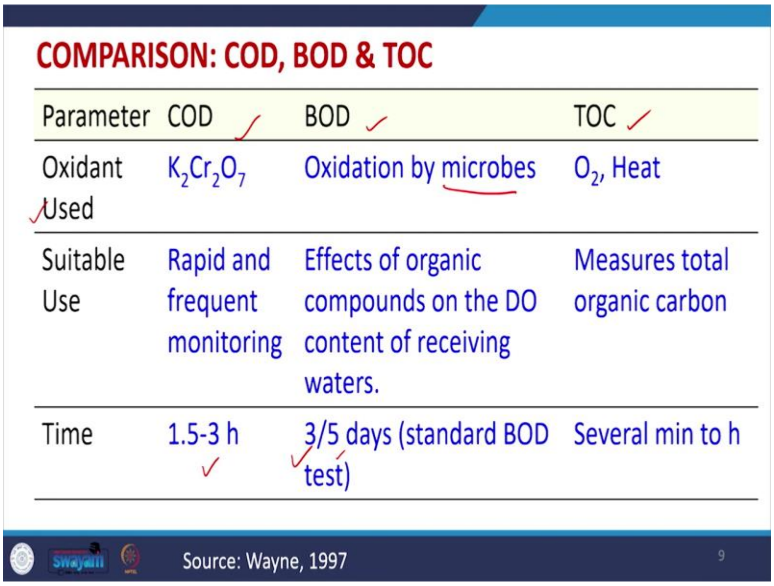

COMPARISON: COD, BOD & TOC

Parameter	COD	BOD	TOC
Oxidant Used	$K_2Cr_2O_7$	Oxidation by microbes	O_2, Heat
Suitable Use	Rapid and frequent monitoring	Effects of organic compounds on the DO content of receiving waters.	Measures total organic carbon
Time	1.5-3 h	3/5 days (standard BOD test)	Several min to h

Source: Wayne, 1997

Now, what is the difference between COD, BOD and TOC? We have learned 3 parameters till now, COD value, BOD value and TOC value. So, when to use which one and what are the different pros and cons of all? Now, in terms of oxidants use, well, in the COD we use highly oxidizable material which is potassium dichromate. Whereas in the oxidation in the BOD is carried out by microorganisms.

In the TOC analyzer, we use oxygen or heat for oxidation. Now, COD is very rapid, and it is frequently used. And the time taken for this is around 1.5 to 3 hours. In the BOD takes a standard BOD test, it requires 3 days or 5 days and effects of organic compounds on the DO content on the receiving water is measured and thus we determine the BOD value. In the TOC takes hardly several minutes only up to maximum 1 hour to measure the Total Organic Carbon. So, and here we use instruments are finding that TOC value.

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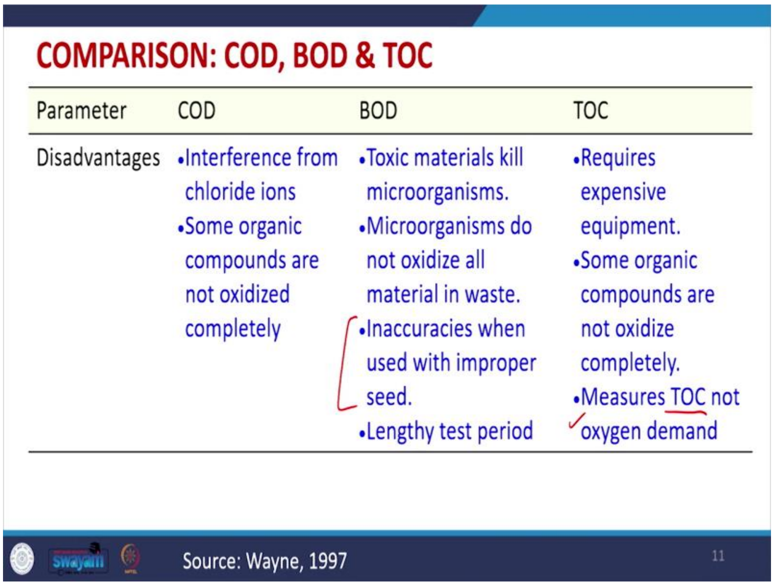

COMPARISON: COD, BOD & TOC

Parameter	COD	BOD	TOC
Disadvantages	•Interference from chloride ions •Some organic compounds are not oxidized completely	•Toxic materials kill microorganisms. •Microorganisms do not oxidize all material in waste. •Inaccuracies when used with improper seed. •Lengthy test period	•Requires expensive equipment. •Some organic compounds are not oxidize completely. •Measures TOC not oxygen demand

Source: Wayne, 1997

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Now the advantages of COD is that it correlates with the BOD on the waste with constant composition. So, we can easily find out once we can find out the COD, we can find out the BOD. Toxic materials do not affect the oxidants because we are using a strong oxidizing agent, the analysis time is also short.

In the BOD, it is mostly when we have determined the BOD, it closely models the natural environment when actually we are using a proper seed water. And it actually measures the actual oxygen demand that will incur in the natural environment. Then the TOC correlates with BOD on waste with constant competition, but not with the COD that much, because the oxidation reactions are different. The analysis time is certainly very short.

So, in a way TOC is a good, analysis is very quick. The disadvantage with respect to COD is that there is a lot of interference from chloride ions and some organic compounds are not oxidized completely if they are very high recalcitrant, it is possible. In the BOD test if highly toxic compounds are present, they will kill the microorganisms.

So, microorganisms will be killed and the BOD test will fail. Microorganisms do not oxidize all the material in the waste also it is possible that waste will contain some recalcitrants and that will not be oxidized, it is in if we use improper seed that the seeded dilution water does not contain microorganism. So, the test will may fail, then it is lengthy because it takes lot of 3 days or 5 days. So, it may fail after that. Again we have to repeat the same test.

TOC the major disadvantage that we require expensive equipment for measuring TOC. So, it is costlier, some organic compounds are not oxidized completely here again. It measures COD, it does not measure the oxygen demand. So, TOC essentially measures the TOC, we can tentatively have an idea regarding the oxygen demand one TOC is measured but it is not a direct representation.

These are the advantages and disadvantages of measuring COD, BOD or TOC.

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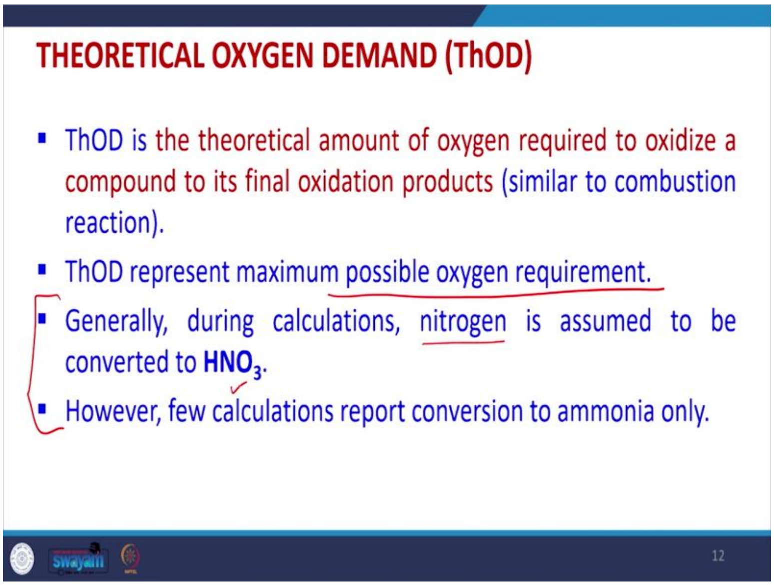

Now, there is another parameter which is called theoretical oxygen demand. So, sometimes we use these parameters ThOD for determining the theoretical oxygen demand and this particular parameter can be used to calibrate the instruments also to check whether we are determining our values correctly or not.

So, ThOD is very important. So, ThOD is the theoretical amount of oxygen which is required to oxidize a compound to its final oxidation products similar to combustion reaction. So, what we do is that we write a combustion reaction and we try to find out that ThOD value. Now ThOD value always represents the maximum possible oxygen requirement. So, it will give the, whatever is the maximum possible oxygen requirement.

Now, there are certain things that we have to consider generally during calculations the nitrogen is assumed to be converted into HNO_3 whereas, in COD it gets converted into ammonia. So, there are some confusions that in few places the nitrogen is assumed to be converted into nitric acid whereas, other places it is converted to ammonia only. So, this is the difference. Let us try to differentiate between all the.

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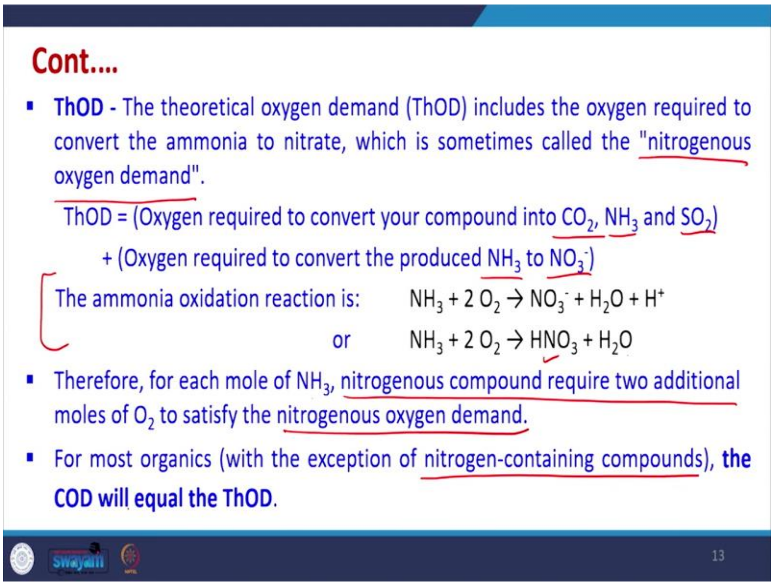

The ammonia oxidation reaction is: $NH_3 + 2\,O_2 \rightarrow NO_3^- + H_2O + H^+$

or $NH_3 + 2\,O_2 \rightarrow HNO_3 + H_2O$

The theoretical oxygen demand includes the oxygen required to convert the ammonia to nitrate also which is sometimes called as nitrogenous oxygen demand. So, ThOD measures the oxygen required to convert the compound into CO_2, ammonia and SO_2. Further oxygen required to convert the ammonia into nitrate. Now, for ammonia oxidation reactions, the reactions are written here.

So, if ammonia is oxidize into HNO_3, then this particular reaction is there. Therefore, for each mole of ammonia nitrogenous compound we required two additional moles of oxygen to satisfy the nitrogenous oxygen demand. So, depending upon that whether ammonia if suppose, nitrogen is also present in the wastewater sample or the sample that we are making by ourself by adding some amount of nitrogenous compound into the water sample, so that ThOD calculations will require the conversion fully into this HNO_3.

Now, for most organics with the exception of nitrogenous, containing compound the COD will always be equal to ThOD. So, this is good thing if we use some compound which does not contain nitrogen, which contains carbon, hydrogen and oxygen only the COD will always be equal to ThOD, if the compound contains nitrogen, then certainly there will be a difference between COD and ThOD.

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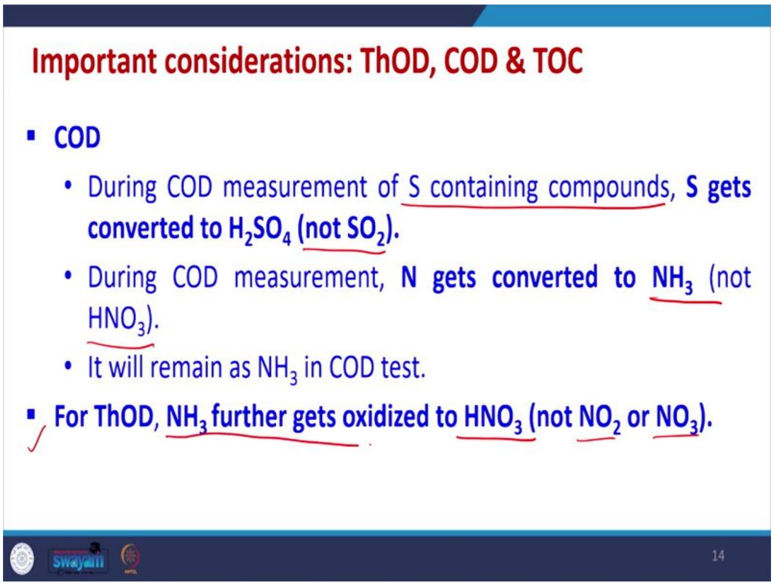

The important considerations are there that during COD measurements of S containing compound that means the compound which contains sulfur, the sulfur gets converted into H_2SO_4 not SO_2, so during COD measurements that we have to remember. During COD measurements, the N gets converted into ammonia not HNO_3 but in ThOD calculation the ammonia further gets converted into HNO_3.

So, not NO_2 or NO_3. So, remember for ThOD there is an additional step that the ammonia has to get converted into HNO_3 whereas for COD it gets only converted into NH_3 only.

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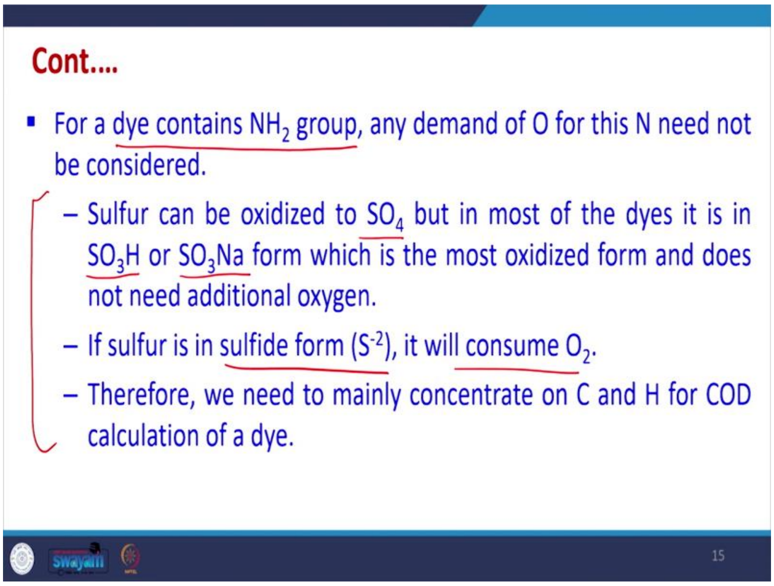

For a suppose a dye containing NH_2 group now, we have a dye which contains NH_2 group and any demand of oxygen for this nitrogen if we have to calculate all these considerations have to be done, sulfur can be oxidized to SO_4 but not in most of the dyes because most of the dyes it is in SO_3H form or SO_3Na form which is the most oxidized form and does not need additional oxygen.

So, for dye containing ammonia group the sulfur will not be considered because already it is most oxidized form. If sulfur is in the sulfide form it will consume O_2, if it is in this form, SO_3H or SO_3Na form it will not consume oxygen. Therefore, we need to only concentrate on carbon and hydrogen for COD calculations of a dye. So, there are some always some exception that we should remember.

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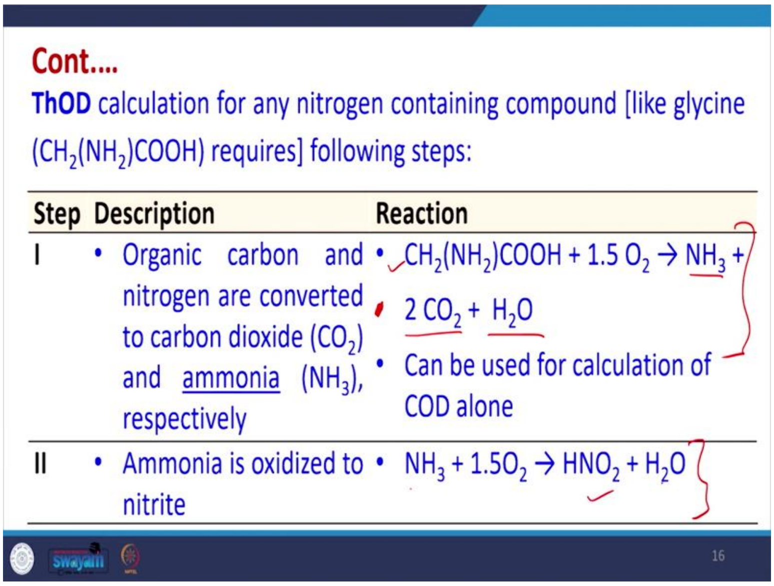

So, this is the ThOD calculation for any nitrogen containing compounds like glycine which is the formula is given requires following step. The organic carbon and nitrogen are converted to carbon dioxide ammonia respectively and then ammonia is oxidized to nitrate. So, we can see here this is the, this should not be here.

The glycine is getting converted into ammonia, CO_2 and H_2O and this step can be used for calculation of COD only. Now, when we add ammonia is further converted into HNO_2, this step is added for calculating that ThOD. So, this is there.

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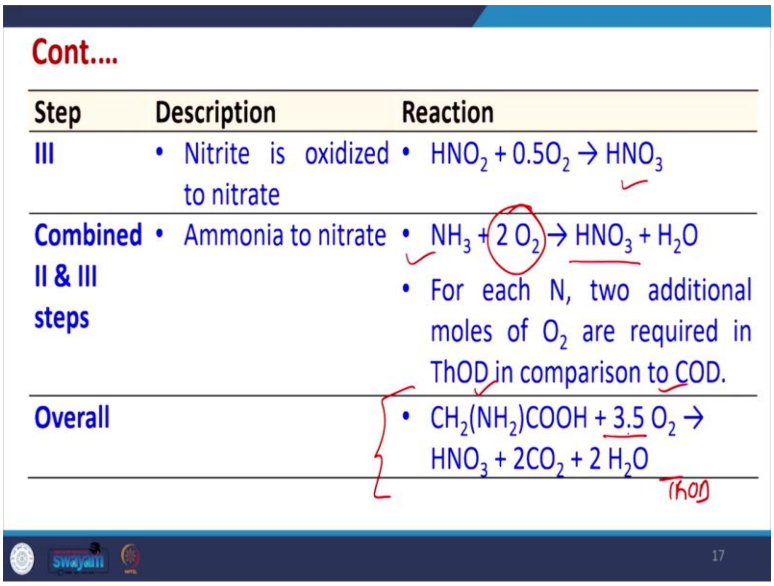

The third step nitride is oxidized to nitrate. So, this is an additional step. So, if we combine second and third the step will be ammonia is converted into HNO_3. So, we have two additional moles of oxygen which is required for each nitrogen, two additional moles of oxygen are required in ThOD in comparison to COD.

So, overall if we combine our first, second and third, this will be the reaction which will be used for ThOD, whereas, for COD only this is there. So, here we can see 1.5 oxygen, whereas here 3.5 oxygen, because two additional oxygens are required per nitrogen, molecule or element so for each and two additional. So, this is the difference.

And we will take some examples for solving a calculating COD, ThOD et cetera in the next class. So, will continue further in the next lecture. Thank you very much.