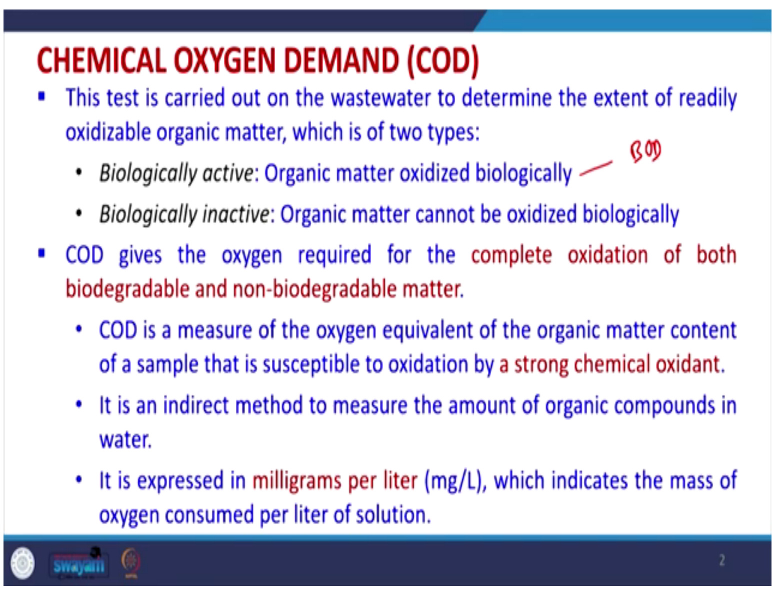
Physico-Chemical Processes for Wastewater Treatment
Professor V. C. Srivastava
Department of Chemical Engineering
Indian Institute of Technology, Roorkee
Lecture - 08
Water Quality Monitoring: Biological/Biochemical Parameters - II

Good day everyone and welcome to this course on Physico-Chemical Treatment of Wastewater and in this course, we are continuing with our lectures on water quality monitoring. In the previous lecture, we studied regarding the biological or biochemical parameters and within that we learned regarding the biochemical oxygen demand, which is like BOD.

And in BOD actually, we estimate the amount of oxygen demand that will be incurred when any water containing organic material is discharged to an aquatic body or it is being just being left for natural degradation to occur. So, we want to determine the oxygen demand which will be there because of the micro-organisms which are present in the water. But, it is possible that the organics present in the water they may not be easily degradable, they are called as recalcitrant organic matter and they cannot be oxidised biologically.

(Refer Slide Time: 01:33)

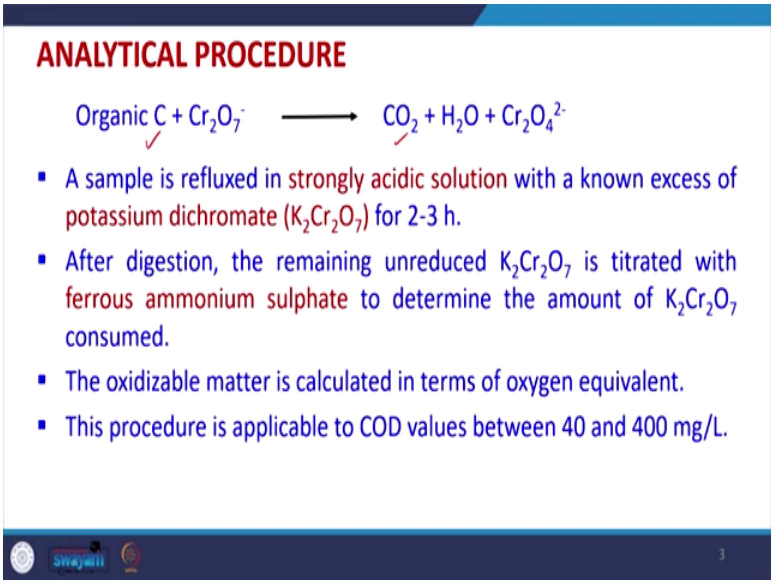


So, in organic matter which is present in the any water or wastewater may be biologically active and biologically inactive. So, biologically active means the organic matter which can be oxidised biologically and this can be determined using BOD estimation method. But, there may be a biologically inactive organic matter and which will not be oxidised by biological means, it will but it will take lots of time for degradation to occur much much slower than the usual scenario.

So, in this case, another test is used which is called as chemical oxygen demand. So, we need to report the chemical oxygen demand to find out the what will be the total oxygen requirement for complete oxidation of both biodegradable and non-biodegradable organic matter present in the water.

So, it is like what we do is that we use a strong chemical oxygen and that oxidizes everything which is present in the water sample and that way we determine the oxygen equivalent of the organic matter which is present in the sample. So, it is like indirect method of measuring the amount of organic compounds in the water and generally it is expressed in milligrams per litre, where milligram is actually the mass of oxygen consumed. So, milligram per litre is mass of oxygen consumed per litre of the solution.

(Refer Slide Time: 03:31)



So, and in actual what we do is that, we reflects the sample water sample with a strong acidic solution and with known excess of potassium dichromate for two, three hours. So, under that condition all the organic matter gets converted into CO2 and similarly, H will get converted into H2O.

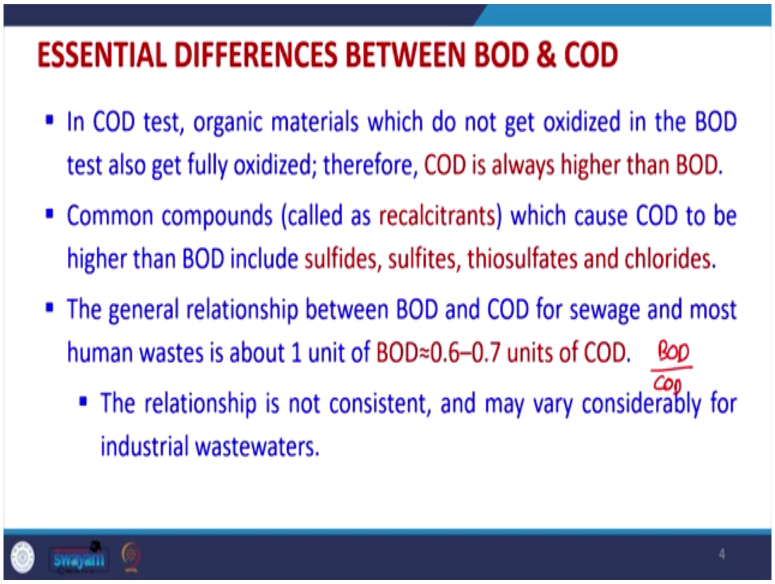
So, this way after doing this, the remaining unreduced potential dichromate is titrated with ferrous ammonium sulphate and this way we determine that how much potassium dichromate has been used and by doing so, we back calculate and determine that what amount of oxygen equivalent demand was there.

So, this method is used very commonly and this is it like titration method and we can determine. There have been a reflex is still done, but now instruments have been there and also colorimetric titration method has been developed using the pro similar to UV visible spectrophotometer. So, we can determine the final amounts very quickly and through that we can determine the COD values. So, this is there.

So, in COD test the organic materials, which do not get oxidised in the BOD test also get fully oxidised. So, that means, COD measures oxidizable, easily oxidizable and recalcitrant materials both. So, COD value is always higher than BOD, this is for sure and if it is not. Therefore, any sample then we should cross check it, or both the test should be done again.

Now, some common compounds, which are called as recalcitrant, they are not easily biodegradable and they may be like sulphides, sulphides thiosulfate, chloride et cetera. So, if they are present in any sample or highly aromatic organic compounds, they may also not get easily biodegraded. So, they will not be estimated by the BOD, so, their oxygen demand will not be estimated during the BOD test.

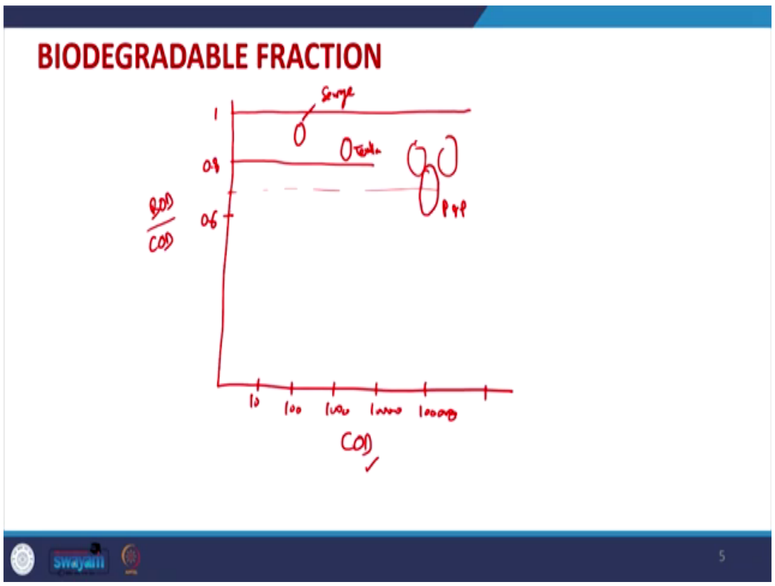
(Refer Slide Time: 06:03)



So, there is some general relationships can be developed for determining the relationship between BOD and COD. For sewage and most human waste which are there, the values lie between 0.6 to 0.7 per unit of COD, the BOD value is like that, but this relationship may vary differently for different types of organic material and amount of total organic material present in those and it is more common for industrial wastewater.

So, the BOD to COD ratio gives an idea whether the whether our water sample is easily biodegradable or not. So, through that we can have an idea we can select whether we are going for biological treatment or other treatment, physico chemical, thermal treatment et cetera. So, this is this gives a lot of idea. So, how do we understand?

(Refer Slide Time: 06:49)



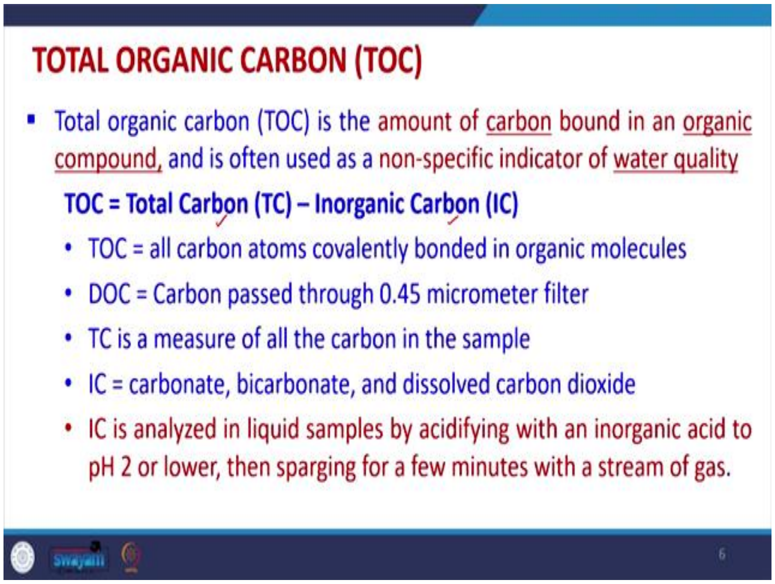
So, if we take example for some of the wastewaters and we plot graph like this. So, in this case, like if we plot the COD values here and the BOD to COD values here. So, ultimate value will be like 1 and here the COD value we may assume like 10, 100 on the logarithmic scale, so 1000 and maybe 1000, 10,000 100000.

So, through this we can plot like this. So, for these cases are maybe 1000000. So, for sewage the values may like be here. So, that means, they have very low value of COD and the organic fraction is very high because they are reaching the value of 1. So, it may be like here we can take this to be 0.8, 0.6. So, these type of graphs give an idea like for sewage this will be here.

Now, if you take the extreme case like pulp and paper and distillery wastewaters are they have lot of high oxygen demand. So, if for pulp and paper if we take. So, it may be laying somewhere here, because the oxygen demand will be in the range of 100000, 80,000, 70,000 like this and but the biodegradable fraction will be only 0.7 or like this, but the value is still very high in the per-litre of water the BOD though the fraction is less, but amount of BOD demand is still high.

So, we can still go from methanation. So, this is like for pulp and paper. Similarly, we may have that similar range for distilleries maybe sometimes higher, sometimes, it may be now on this side or maybe lower. Similarly, for textile water, it will be coming down it may be a little higher. So, this way we can plot for different we can estimate and have an idea that what is the use of BOD to COD fraction as well as what is the total COD value. So, higher the COD value it is very very difficult to treat that water, but if it contains a biological faction, we can still go for some anaerobic treatment etc. so as to take out all the methane out of that wastewater et cetera. So, these graph gives lots of idea regarding the treatment methodology that we have to follow.

(Refer Slide Time: 09:33)

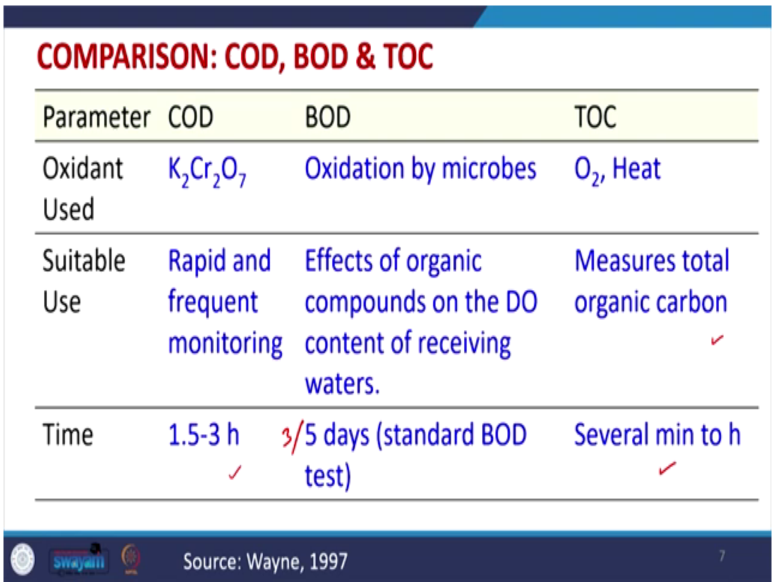


Now, there are certain other parameters which are similar to BOD and COD. One of them is called total organic carbon. So, it is like a quick method of estimating the organic content present in the water and it gives the amount of carbon bound to an organic compound and it is like used as an indicator of water quality.

So, TOC is determined as total carbon minus inorganic carbon. So, or TOC in TOC we want to estimate the all carbon atoms which are covalently bonded in the organic molecules and for determining the dissolved organic carbon, we can pass through the all the water sample through micro 0.45 micro metre filter and whatever passes through we call it dissolved organic matter and in that we can find out the all carbon in the sample which is TC and then also we can find out the carbonate, bicarbonate and dissolved carbon dioxide using which is called as inorganic carbon.

And these are estimated by acidifying the liquid samples with an or inorganic acid to lower pH and then by sparging for few minutes in a stream of gas we can determine that TOC because everything will be converted into CO2 and we can find out so, this method is used and there are TOC analysers, which can determine the TOC.

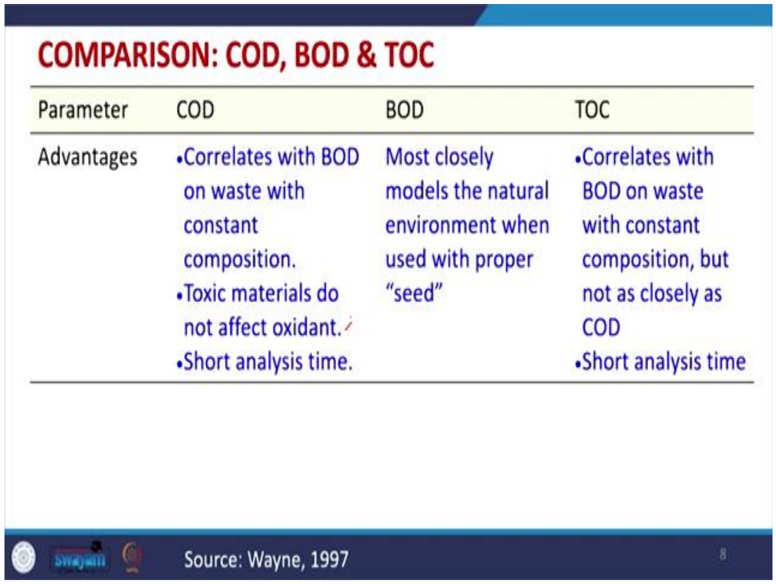
(Refer Slide Time: 11:14)



Now, we should have a comparison also of COD, BOD and TOC. So, this is done in the slides. So, COD we use the oxidants which is like potassium dichromate. In the BOD we use microbes for oxidation and then TOC we use oxygen and heat for as a oxidant. Now, out of these TOC is the fastest because it measures the total organic carbon and the time taken is also very fast from minute, only few minutes it takes to determine the TOC.

In terms of time, the COD takes 1.5 to 3 hours and the BOD test may take 3 days up to 5 days. So, it may be 3 days to 5 days, standard BOD test. Now, suitable use COD is a very good estimation technique for determining the total oxygen demand. But if you have to find out only the biodegradable fraction, we had to find out the BOD value as well.

(Refer Slide Time: 12:25)



COMPARISON: COD, BOD & TOC

Parameter	COD	BOD	TOC
Advantages	•Correlates with BOD on waste with constant composition. •Toxic materials do not affect oxidant. •Short analysis time.	Most closely models the natural environment when used with proper "seed"	•Correlates with BOD on waste with constant composition, but not as closely as COD •Short analysis time

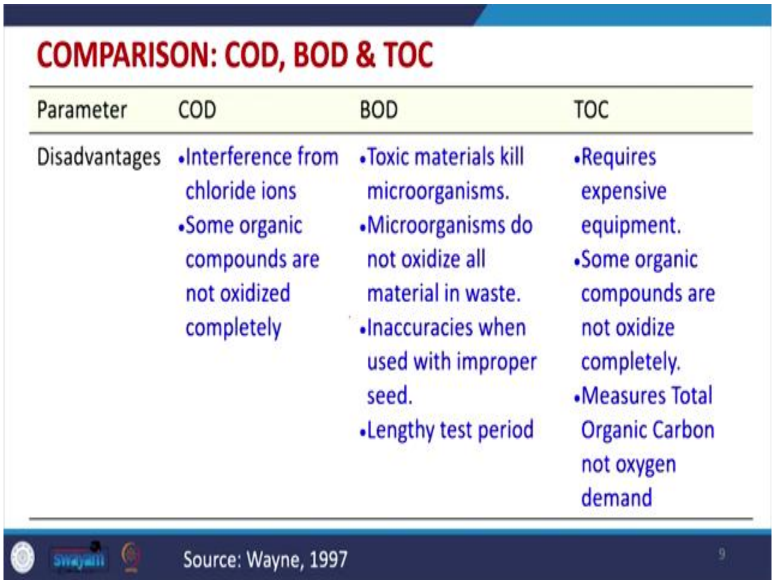
Source: Wayne, 1997

Now, certain advantages are there with each of the method and certain disadvantages are also there with each of the method. Now, with COD, the advantage is that it can be correlated with the BOD, and it is a faster method. So, some idea can be obtained for the BOD, also without estimating the BOD.

And any toxic material if it is present in the water sample during the COD test, it will not affect the COD, whereas it will affect the BOD estimation method. It is the disadvantage of the BOD method and the analysis time is also shorter with respect to BOD, but it is not as short as in that you see so TOC.

So, TOC has shortest estimation time and TOC can also be correlated with the BOD. So, we will solve some problems also to understand this. And BOD is most closely related model with respect to degradation that happens in the actual natural environment. So, this is very important so BOD estimation is the most correct method, but still the COD and TOC can be used for understanding the oxygen demand also and the degradation process.

(Refer Slide Time: 13:43)



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 Total Organic Carbon not oxygen demand

Source: Wayne, 1997

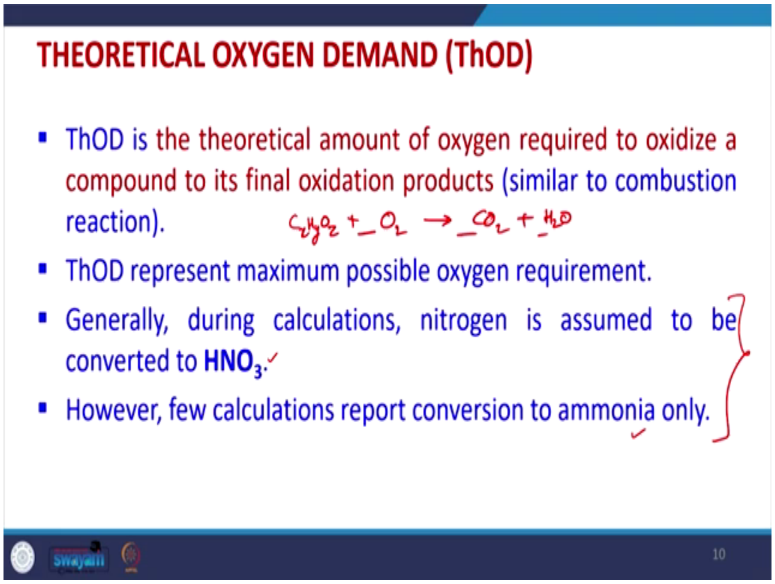
Then disadvantages are there. In the COD method, if chloride ions are present, they interfere also, some of the highly aromatic compounds may not get easily oxidised. In the BOD, the problem is that if toxic materials are present, they may kill the micro-organisms itself. So, micro-organisms will not be able to eat other materials. So, BOD estimated will be much lower than what is the value.

So, if there is no seeding we do not add micro-organisms from outside and we are assuming that micro organisms are already present in the water. So, in that case, also inaccuracies may exist. Also it is a less lengthy test period and during the preparation of water bottles sample waters lot of precautions have to be taken that there are no oxygen bubbles et cetera inside the water bottle. Otherwise, the BOD test fails after 3 days or 5 days.

So, we feel that, this is very bad and we have to do it again. So, lot of expertise are required for actually performing the BOD test and TOC requires TOC the disadvantage is that we require a very good TOC analyser and that will be very costly and then also some of the compounds may not also get oxidised during that process.

So, this is there and it does not measures the oxygen demand it measures TOC. So, from TOC we can tentatively calculate the oxygen demand, but it is not direct oxygen demand we are actually finding the carbon not the oxygen demand, whereas, the COD and BOD we find the oxygen demand this is the difference.

(Refer Slide Time: 15:42)

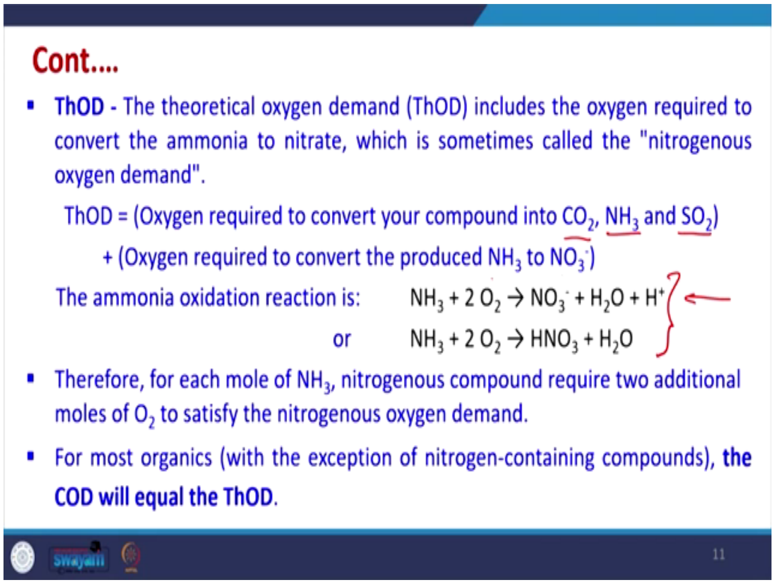


Now, there is another term which is actually can be used for estimating some of the things and it is useful in some other places, where like we have to do calibration and other things. So, it is called as theoretical oxygen demand. It is the theoretical amount of oxygen which will be required to oxidise a compound to its final oxidation state. So, it is like a similar to combustion reaction. So, we have a we if you are using any particular compound, so, we can write the similar to combustion reaction.

So, whatever is the compound for that CX HY OZ, something like this and we can write this type of balance equation and we have to balance here to find out the, what is the theoretical oxygen demand. So, this is there. So, it will be it is like maximum possible oxygen requirement, then there are certain precautions which have to be taken care. Generally whenever the ThOD value is reported. So, they assumed the nitrogenous any nitrogenous compound which is present.

So, it is nitrogen is assumed to be converted into HNO3, in few calculations, they report the conversion to ammonia only. In the second step actually ammonia gets converted into HNO3. So, this difference is there. So, whenever we are reporting theoretical oxygen demand, we should clearly state whether we have performed calculation up to HNO3 or up to ammonia only. But generally HNO3 is preferred calculation and this is reported more commonly.

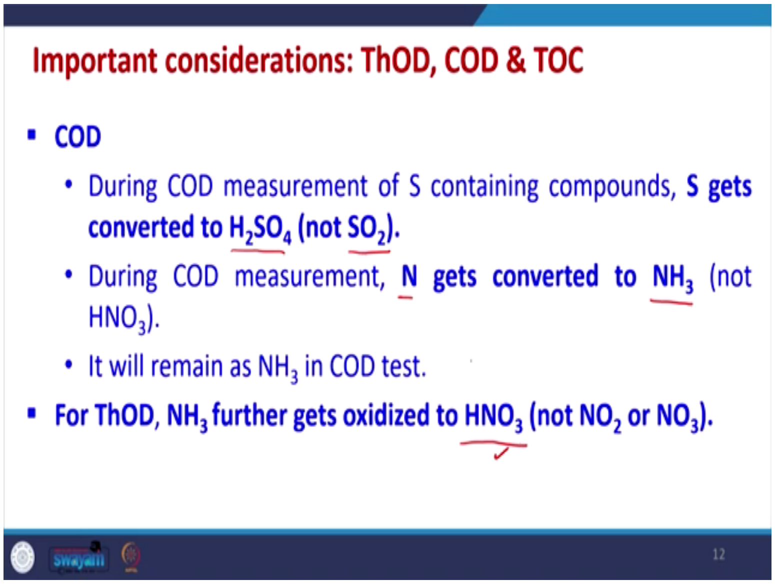
(Refer Slide Time: 17:41)



Now, theoretical oxygen demand actually it converts the compound into CO2, ammonia and SO2. So, if it contains sulphur, it contains carbon, nitrogen and sulphur. So, this and then second reaction where ammonia gets converted into nitrate. So, this is important and both generally both reactions are taken together, but some of the in literature some people report only up to this.

So, this precaution has to be taken and for most organics with the exception of nitrogen containing compound, if there is no nitrogen in the compound, then the COD value will always be equal to ThOD value. Otherwise, if we are reporting up to nitrate that THOD value will be higher than the COD value. So, this is the difference.

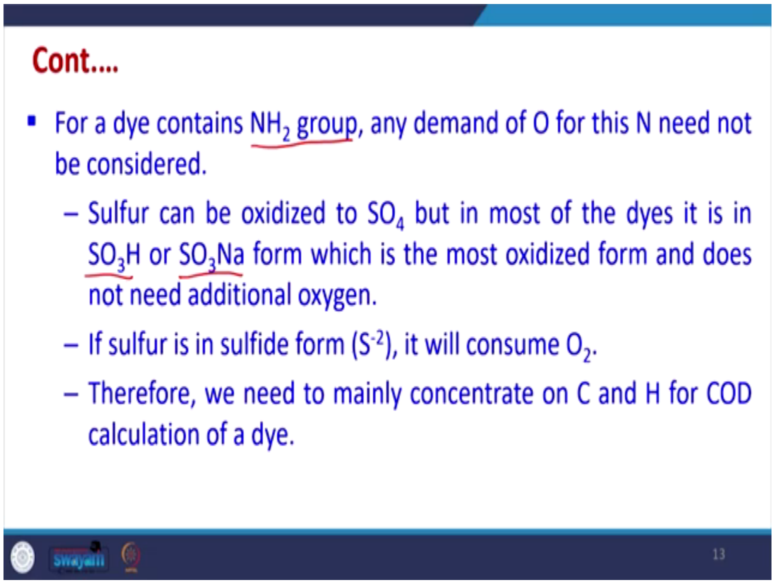
(Refer Slide Time: 19:10)



There are some important considerations that we should always be taken into account. In COD estimation, suppose, we take any compound and we want to estimate we take any compound some grams of that and dissolved in water and now, we can determine the theoretical COD also or theoretical to ThOD and now, during the COD measurements, if that compound contains sulphur as element, then during estimation or calculations sulphur should be converted into H2SO4 not SO2.

So, this we have to remember the equations we should write that S should be converted into H2SO4 for balance equation. During COD measurements S gets the nitrogenous compound they converted they get converted into ammonia not HNO3, but ThOD we convert them into a HNO3 not ammonia or any other. So, this is very important, we should in ThOD we nitrogen gets converted into HNO3 whereas in COD the nitrogen gets converted into ammonia. So, this will, this caution has to be taken.

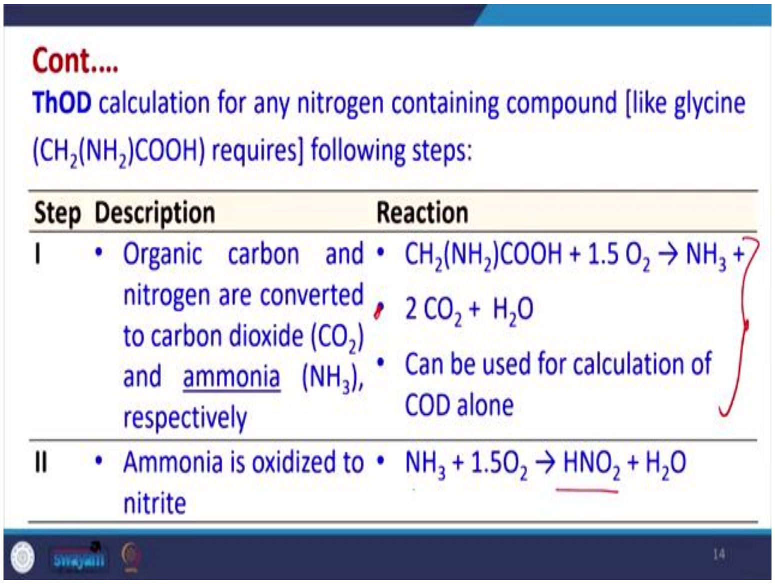
(Refer Slide Time 20:11)



Further, suppose any dye is there and it contains ammonia group. So, any demand for oxygen for this nitrogen need not be considered. So, if nitrogen is attached with NH2 group then we should avoid this group and if any other form of nitrogen is there, we can convert it into ammonia, but if nitrogen is there with respect to ammonia group that nitrogen should be left behind we do not take this into calculation during ThOD or otherwise. And sulphur can be oxidised to SO4 but in most of the dyes it is in SO3 H form or SO3 Na form which is most oxidised form and does not need additional oxygen.

So, for sulphur also if in the dye it is in this form or this form, we need not calculate the oxygen demand for this sulphur. So, if nitrogen is there in the NH2 group we need not find the oxygen demand for that, if sulphur is there in the SO3 H group or SO3 Na group we need not find the oxygen demand for that sulphur, if sulphur is in the sulphide form it will consume oxygen. So, this we have to take and we have to convert it into H2SO4. Therefore, we need to mainly concentrate on carbon and hydrogen for COD calculation of a dye and this actually is the mistake done by many persons while calculating the COD or ThOD in the usual case.

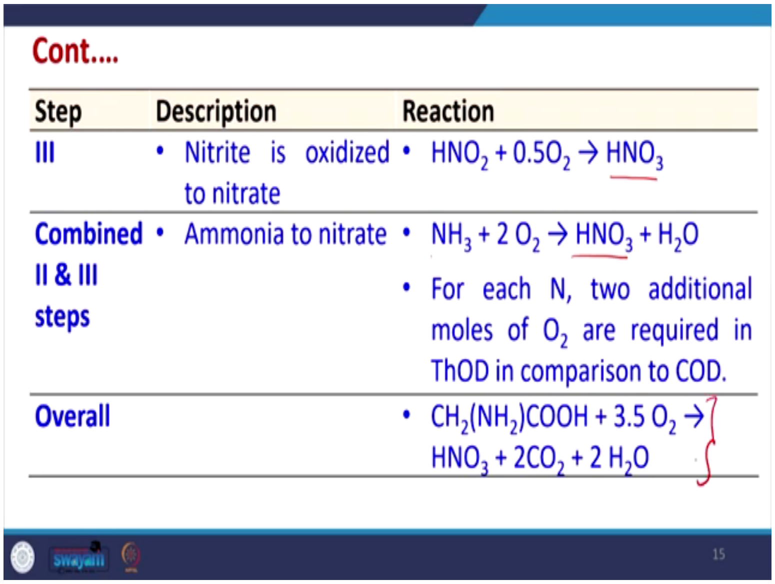
(Refer Slide Time: 21:43)

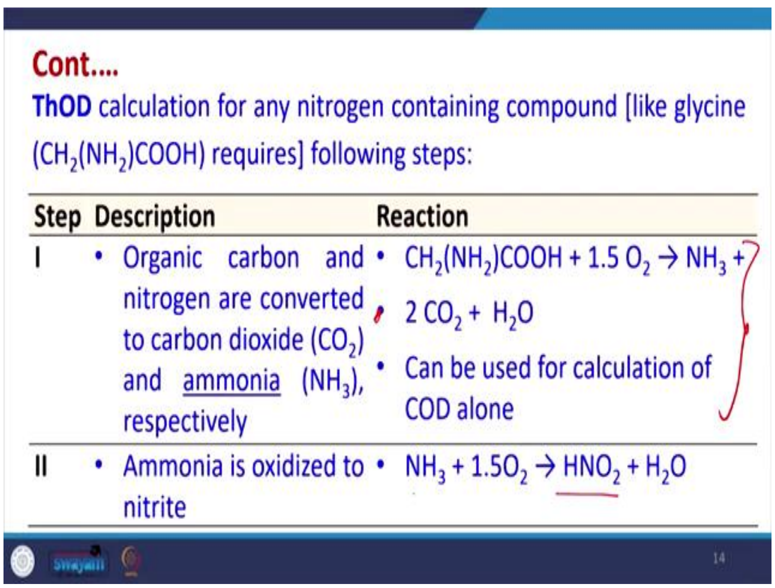


Now, ThOD calculation for any nitrogen containing compound like glycine requires following a step. So, these steps are there, in the step one organic compounds and nitrogen are converted into CO2 and ammonia. So, nitrogen will be converted into ammonia in the first step and the second step ammonia will be converted into HNO2.

So, this is there for ThOD, but this step will be valid for COD also, but this additional step will be there for the ThOD. So, this is glycine is getting converted sorry this getting converted into ammonia, CO2 and H2O and this equation can be used for COD alone and this second step is used additionally in addition to the first step for ThOD.

(Refer Slide Time: 22:36)

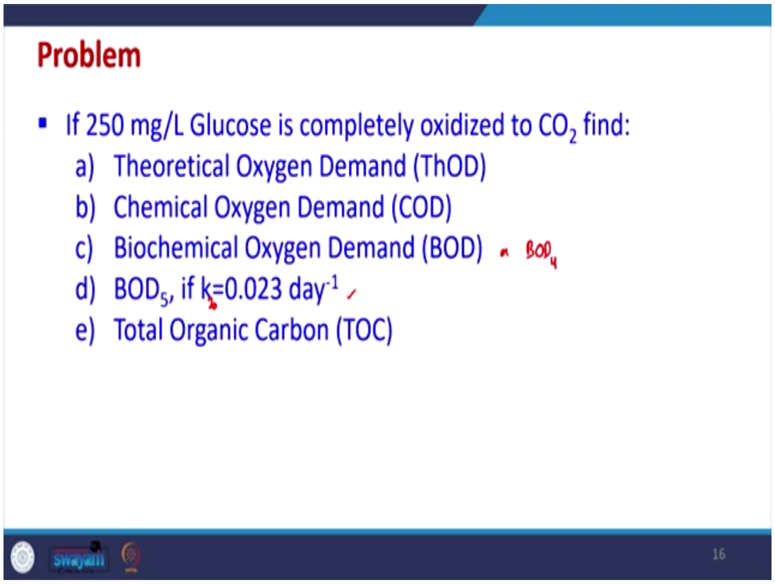




Now, in the third step, the nitride is oxidise into nitrate. So, this is there. So, this also we have to combine. So, also ammonia has to be converted into nitrite if you combine the second and step together, so, for each N at least we cross check this reaction ammonia getting converted to a HNO2 then as HNO2 getting converted into HNO3.

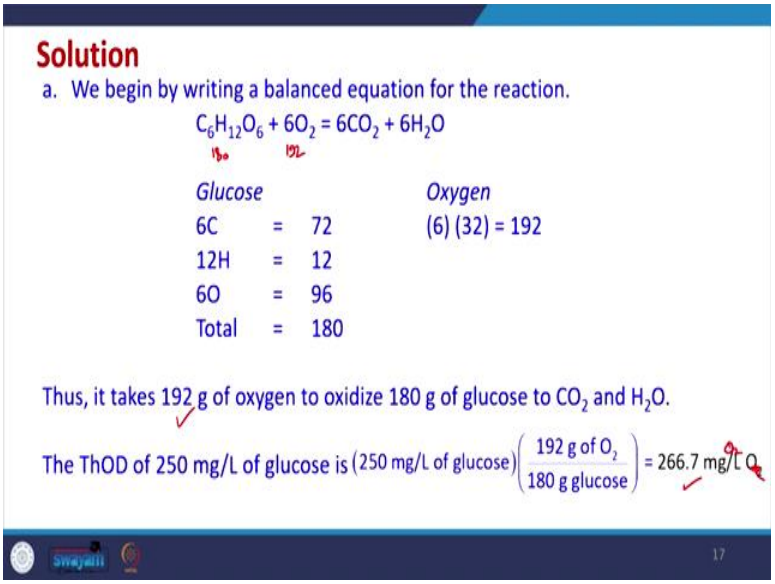
So, if you add second and step, so, ammonia if it is getting converted to HNO3 for each N, we require two additional moles of oxygen as are required in ThOD calculation as compared to in a COD calculation. So, overall if for ThOD, this will be the reaction for glycine. So, this is the difference which is there.

(Refer Slide Time: 23:28)



Now, we will solve one problem to further understand the differences and if suppose 250 milligram per litre of glucose is completely oxidised to CO2. Now, we have to find out that theoretical oxygen demand, chemical oxygen demand by biochemical oxygen demand, BOD5 it is given that k value is this at 20 degrees centigrade. So, this is at 20 degrees centigrade and we have to find out that total organic content. So, we had to find out ThOD, COD, BOD, BOD5, whenever there is only BOD term is written it means we are asking for BODu the ultimate oxygen demand. So, this is there. Now, let us calculate it.

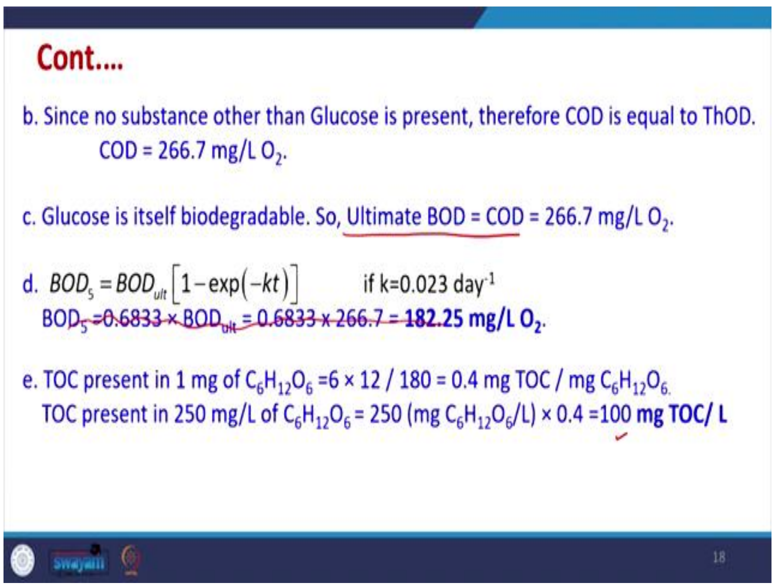
(Refer Slide Time: 24:25)

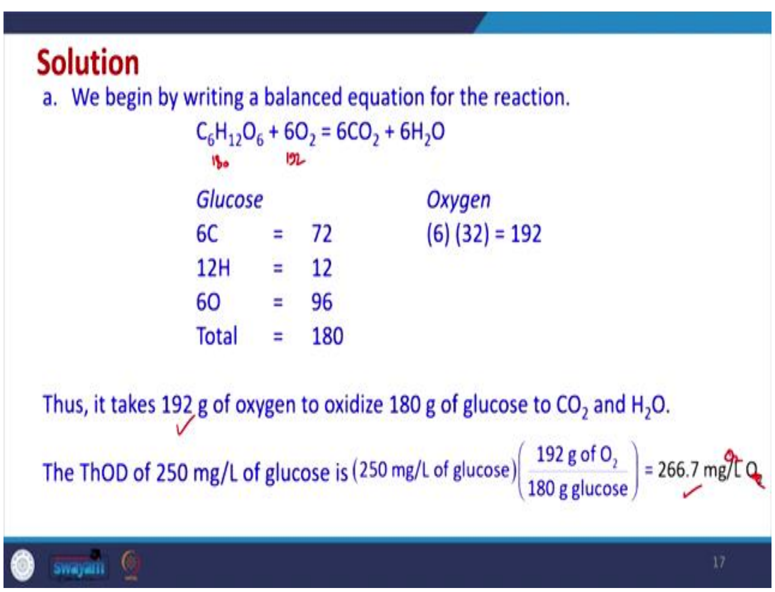


Now, we begin by writing a balance equation for the reaction. So, this is a simple balanced equation which we can write very easily and so, the what we infer from here is that the glucose 192 gram of oxygen is required for oxidising 180 gram of glucose to CO2 and H2O. So, if you write here, for glucose, it will be 180 and here it will be 6 into 32 it will be 192, that means 192 gram of oxygen is required to oxidise 180 gram of glucose.

So, theoretically for ThOD because the value is 250 milligram per litre of glucose. So, we perform this calculation, so, this much amount of oxygen will be required per litre of the water. So, this O2 should be here not here milligram per litre. So, this is we can do.

(Refer Slide Time: 25:24)





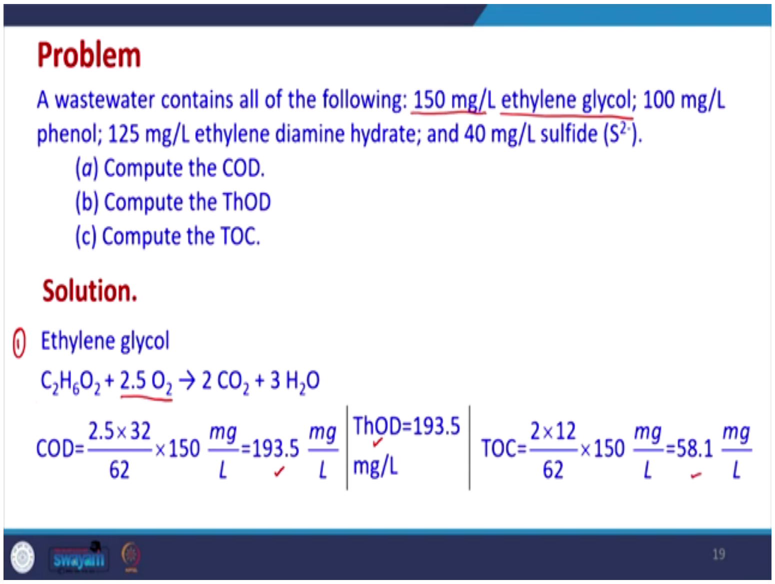
Now, since, no other substance other than glucose is present, therefore, COD will be equal to ThOD itself. So, that means, the COD and because there is no nitrogenous element, no sulphur, so, there is no additional requirement of oxygen. So, this is only 266.6 milligram O2 per litre of so COD will be same as ThOD.

Now, glucose is itself biodegradable. So, that means, glucose is totally biodegradable. So, if only glucose solution is there, whatever is the COD value that will be the BOD value also, because there is no difference is there with respect to so, ultimate BOD will be same as COD and it is written here.

Now, if you have to find out BOD5, then we have to use the BOD this ultimate BOD and this is actually we can calculate it this is wrongly written we can actually find out the value and we can perform the calculations also directly. Now, TOC if it is now 1 milligram for the same reaction, if we see here, what is the organic content.

So, this is with respect to for organic content 6 into 12 that means 72. So, 180 gram of glucose contains 72 gram of carbon. So, for TOC 1 milligram of this glucose contains 0.4 milligram of TOC per milligram of glucose. So, that means, if TOC is 250 milligram per litre. So, overall value you can be estimated and it will be 100 milligram of TOC will be there per litre of the this. So, we can easily calculate this way and find out the values. So, this is there and now, we will go ahead further.

(Refer Slide Time: 27:34)

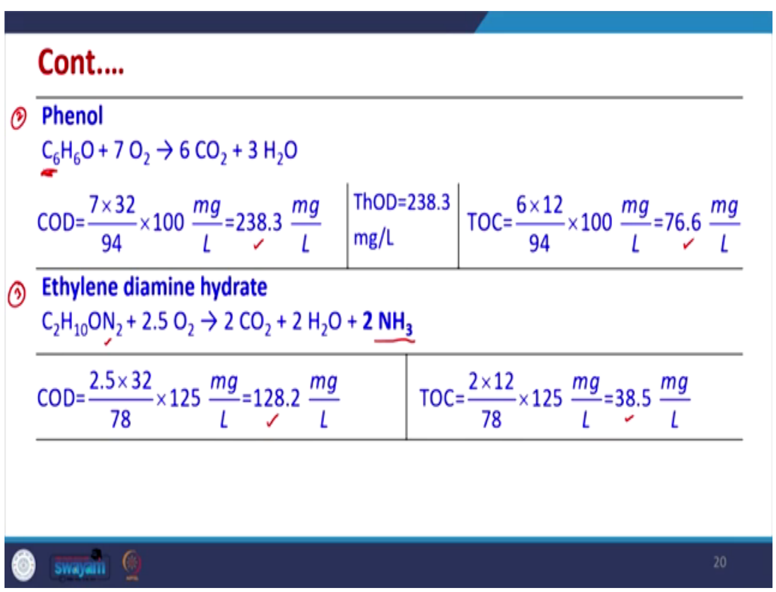


So, a wastewater contains, this is second problem and it for this come we have a mixture of compounds. So, a wastewater contains all of the following, 150 milligram per litre of ethylene glycol, 100 milligram per litre of phenol, 125 milligram per litre of ethylene dynamin hydrate and 40 milligram of sulphide. So, we have to compute the COD, ThOD and TOC.

So, what we do is that, we try to calculate the for each of the compound individually. So, remember ethylene glycol. The first is it ethylene glycol, the formula is written here and we can write this equation. So, it does not contain any sulphur or nitrogen. So, it is very very straightforward and the as earlier the COD value, ThOD value will be same. Because it does not contain any nitrogen and sulphur.

So, for COD we estimated 2.5 moles of oxygen is required per mole of ethylene glycol. So, 2.5 mole into 32 divided by 62 which is the molecular weight of ethylene glycol into 150 because 150 is the amount of ethylene glycol present in the water. So, we calculate it and it will be 193.5 milligram per litre. So, we can calculate that ThOD also it will be same and TOC also we can determine because it will be 2 into 12. So, 2 into 12 divided by 62 into 150. So, this is the amount of TOC for ethylene glycol. Now, we go for second which is phenol.

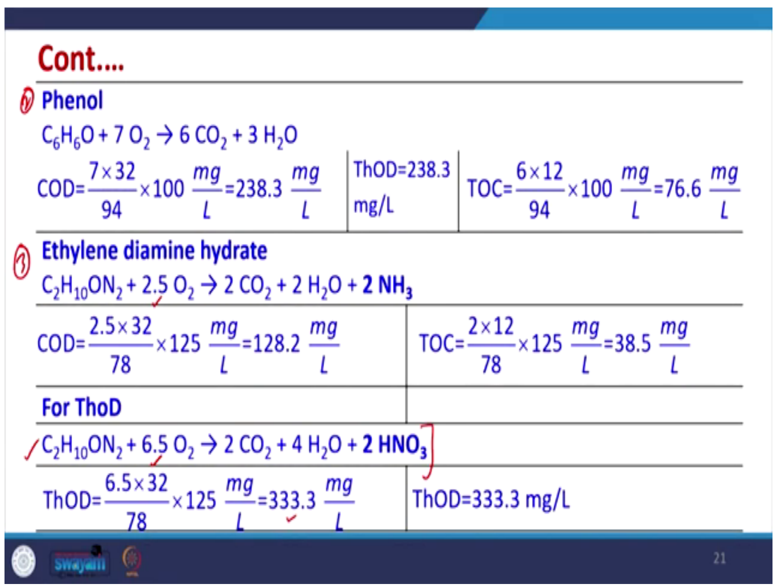
(Refer Slide Time: 29:22)

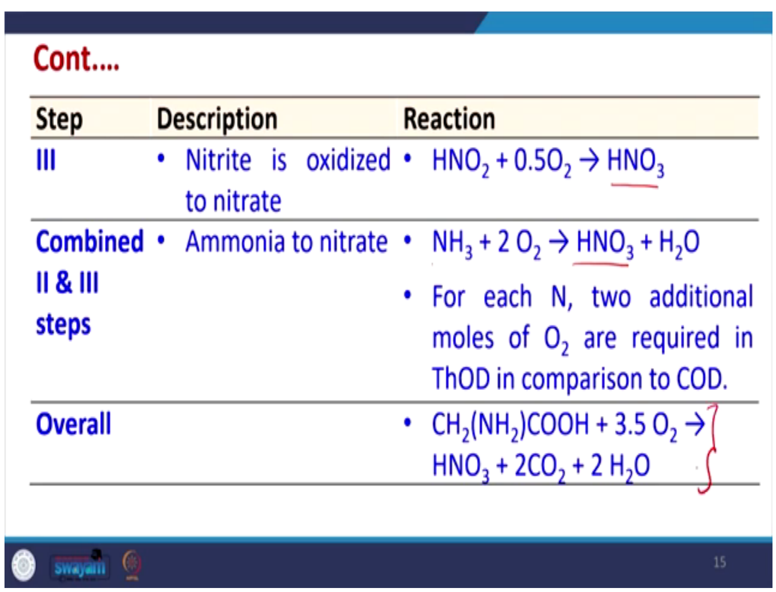


So, for phenol which is the second compound present in the water, we write the equation again and again there is no sulphur, no nitrogen. So, we easily performed the calculation 7 into 32 divided by 94 which is the molecular weight of phenol. So, we can calculate 238.3 milligram per litre, we can calculate the THOD value and we can calculate the TOC because 6 into 12 divided by 94 because this is the only carbon matter. So, we can calculate it is 76.6.

Now, coming to the third because third is tricky. It is ethylene diamine hydrate and it contains nitrogen. So, what we do is that we perform the calculation in the two steps, in the one step, we only convert this into ammonia. Remember first COD we convert the reaction is written in terms of ammonia not HNO3. So, this is first thing and we balance it and we find out, perform the calculation the COD value will be 128.2 and the TOC value will be 38.5. We have not performed calculation for ThOD.

(Refer Slide Time: 30:39)

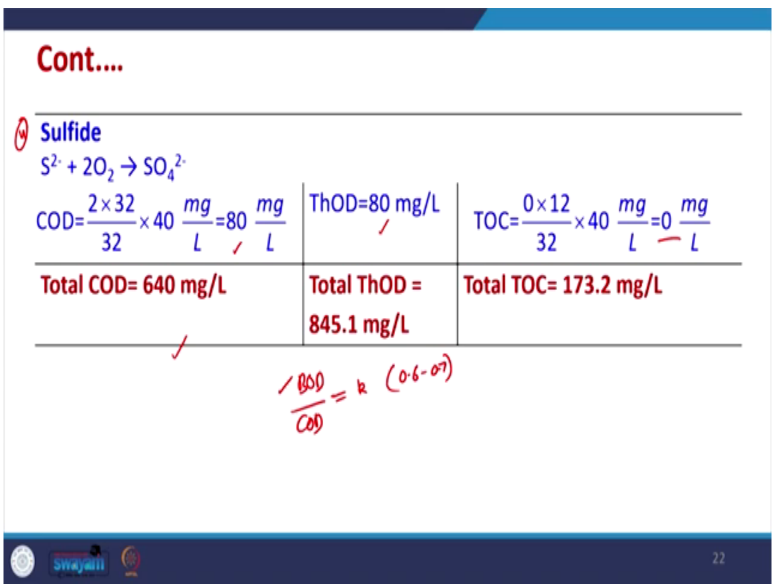


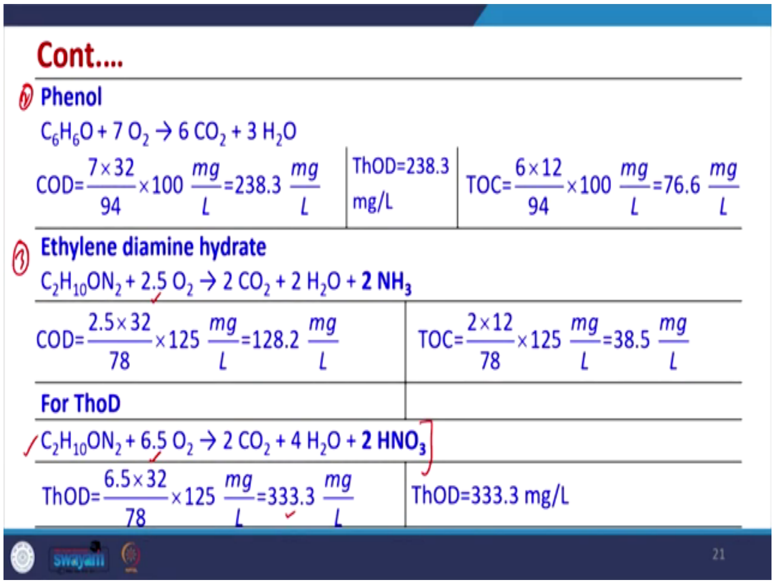


Now, for ThOD actually this is step, for ThOD we have to add additional this reaction where HNO it is written in terms of HNO3 not in terms of ammonia. So, if you write in terms of HNO3. So, we will be having the oxygen demand will increase remember for each N, it was earlier told for each N we required two additional moles of oxygen.

So, it was shown in one of the slides. So, for each N we require two additional moles of oxygen and here also in the equation, we can be very easily see that for each N because 2 N is there so, the difference is 4 6.5 minus 2.5. So, we require 4 additional moles of oxygen and because of that the ThOD will be 333.3 for this for ethylene diamine which is our third compound, phenol was our second compound.

(Refer Slide Time: 31:45)





Now, going further for sulphide which is our fourth compound, we find out, write the reactions like this the COD will be 80, ThOD will be 80 and TOC will be 0, because there is no carbon in this. Now, we add together all the COD values, ThOD values and TOC values the final will be total COD will be 640 milligram per litre, the ThOD value will be 845.1 milligram per litre and total TOC value for this case after adding will be 173.2 milligram per litre.

So, this way we can perform the calculations, if we can, we have the idea of BOD to COD of similar wastewater, we can tentatively calculate if we know what is the this k value. So, like it was given in the range of 0.6 to 0.7 for some of the wastewater. So, it we can estimate the BOD also from here without performing the test or we can have tentative idea of the BOD also.

So, this is how we can estimate the oxygen demand beforehand actually doing or also these methods can be used for performing the calibrations of our systems. So, we should periodically cross check, we can add these type of compound in our usual system of determining the COD, ThOD or TOC and through that we can perform the calibration and we can cross check whether our system is working properly or our method is working properly or not.

So, this may be end today's lecture and we will learn regarding the chemical oxygen demand, theoretical oxygen demand and total organic matter. We will continue with the estimating the parameters in the next lecture. Thank you.