

Wastewater Treatment and Recycling
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Lecture – 13
Waste water Characteristics: Quality Parameters (Contd.)

Hello friends and welcome back. So, previous lectures we were discussing some water quality parameters and we concluded the discussion on dissolved oxygen. We will continue the discussions on a few more water quality parameters in this lecture.

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The slide is titled "Water Quality Parameters" and features a handwritten chemical equation: $OM + O_2 \xrightarrow{C.O.C.} CO_2 + H_2O$. The equation is annotated with a checkmark and an arrow pointing to the text "Biochemical (or Biological) Oxygen Demand (BOD)". Below the equation, there are three bullet points:

- ❖ Organic matter (pollutants) present in water serves as substrate (food source) for the microorganisms present there. Often many of such compounds are broken to less complex organic substances and ultimately to simple compounds such as carbon dioxide and water.
- ❖ The wastewater receiving rivers and streams have some background DO, and aerobic microorganism present, consume the DO for decomposing the organic matter into simpler compounds. However DO keeps on getting replenished by natural atmospheric transfer and from photosynthesis.
- ❖ The amount of oxygen required by aerobic microorganisms to decompose the organic matter in a water sample (generally polluted) is typically referred as *Biochemical Oxygen Demand* or *Biological Oxygen Demand (BOD)*.

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The one that we are going to start with is one of the very common or very frequently quantum BOD. BOD is essentially the biochemical oxygen demand, some people refer it as a biological oxygen demand both are correct, ok. It is there is no preferential that whether, it should be called biochemical oxygen demand or biological oxygen demand. It is actually both are correct because pre-dominantly it is the demand is exerted by the microorganisms. So, it is biological oxygen demand, but it is from the biochemical reaction that is why it is referred as biochemical oxygen demand as well.

So, you see what happens when the organic matter or pollutant which are present in the water or which comes in the water through the waste disposal. So, this organic matter when it is present in the water and there are microorganisms also present in the water. So, microorganisms will have obviously, their natural growth in any system provided the

availability of food and nutrients are ensured. So, the microorganisms tend to grow, they in order to grow, in order to basically survive, in order to manage their food, how microorganisms survives? What is the food for microorganisms? Foods for microorganisms are the organic matter.

Now, when our waste has a lot of organic matter which are present in the water; so, when we are adding that waste to the water or we have or directly even if let us say waste water. So, in the wastewater, there is sample amount of organic matter present and when the bacteria gets in contact to that organic matter, they tend to utilise that organic matter as a substrate or as a food source ok. Many times they can actually utilise these substances for other requirements also like for nutrient source, for nitrogen or phosphorus source, for other elemental source.

So, they can utilise these some of these pollutants because the organic matter present in the water is a pollutant and for bacteria it is a food material there. So, bacteria utilise that as a substrate or microorganisms utilise that as a substrate. Now, often many of such compounds when they utilise what they do, how means because see our it may contain high end sugar, proteins, fatty acids, lipids. But, when the bacteria attacks these substances they break down these substances to smaller compounds and this breaking down could go as low as to the breaking in the carbon dioxide or water ok.

So, the complete breakage is called mineralization. So, bacteria tend to mineralize this mineralization always essentially may not be complete. So, it is not necessary that if there is a lipids of bacteria is going to break it down to a level of CO₂ and H₂O. But, they can at least or many a times, they can break it down to significant levels significant smaller compounds or simpler compounds and then another group of bacteria can so on work on that. It can actually completely mineralize it also, but that will required much larger time.

So, what happens that bacteria attacks the substrate; bacteria attacks this organic matter, utilise them as a substrate and in order to that the compounds are degraded and the bacteria grows. Because they get food, they get nutrients so, they multiply the new they synthesise new cells and for synthesis of new cells also, cells are made of what carbon, nitrogen, oxygen, phosphorus. So, all these things are required for synthesis of cells as well hydrogen. So, they synthesise cells out of this new cells and some of the sort of

mineralized or decompose degraded compounds are either left in the water or the complete mineralization can make it escape in the form of gas.

So, waste water receiving rivers and streams have some background dissolved oxygen ok. Normally, any river will have if river is flowing, it is open to the atmosphere and then through atmospheric exchanges, the river has significant quantity of oxygen dissolved in it near saturation level ok. At time even higher than saturation level particularly, if we see in the daytime when the photosynthesis and all those processes are occurring. So, level of dissolved oxygen could actually be supersaturated at those times.

Now, what happens that there are dissolved oxygen. So, when bacteria tend to decompose the organic matter they need oxygen for that, they typically oxidize the organic carbon oxidized the organic materials and in the process of oxidation in the process of oxidising them they need dissolved oxygen present in the water. So, dissolved oxygen which is present in the water or in the background water gets consumed in the process. What will happen that when bacteria tend to decompose the organic matter, they will they will sort of if we see the reaction it is fairly simple reaction.

So, we have organic matter and we have a oxygen and then there are sort of cells ok. So, they gets decomposed here eventually converts to CO_2 plus H_2O or other kind of things can be made. So, these bacterial cells need dissolved oxygen and when this organic matter is broken down the dissolved oxygen is consumed in the process. So, dissolved oxygen is consumed is fine, but as discussed in the previous week that dissolved oxygen keeps on getting replenished also from the natural atmospheric transfers and from photosynthesis.

So, the amount of oxygen which is consumed in converting the organic matter by the is which is consumed in degrading or decomposing the organic matter can give us an idea of how much organic matter is present in the system or how much organic pollutant are present in the system. If there is no limitation of cell, if there are let us say enough amount of cell or bacteria present in the system. So, the amount of oxygen consumed in the system will be depending on how much organic matter is present because, the reaction is like this.

So, this amount of oxygen required by the aerobic microorganisms or amount of oxygen rather consumed by the aerobic microorganisms to decompose the organic matter in a

water sample, which typically is polluted because there has to be organic matter present in the water is referred as biochemical oxygen demand or biological oxygen demand. So, BOD is essentially an indirect estimate of organic matter organic pollution in the water ok. What we are essentially measuring is the how much oxygen is consumed in decomposing that organic matter and oxygen consumed is in a way is proportional to the organic matter present in the system. So, that way what essentially we are determining is how much organic pollution is there in the water.

How we are determining that? We are determining that considering that how much oxygen is getting consumed in order to decompose that organic matter. So, BOD is that estimation where we will we sort of observe or we see how much dissolved oxygen has been consumed over a period of time. Of course, because the oxygen consumed in 1 day is going to be obviously, less than the oxygen consumed in 2 day or 3 day. So, it is a time dependent process. So, how much oxygen is consumed in a given time by the aerobic microorganism is actually the BOD right.

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Water Quality Parameters

✓ **BOD:**

- ❖ BOD is a time dependent parameter, as oxygen consumed by bacteria would increase with the progress of time.
- ❖ When BOD levels are high, dissolved oxygen (DO) levels decrease because the oxygen that is available in the water is being consumed by the bacteria.
- ❖ If the quantity of organic waste present is sufficiently large, the rate of bacterial uptake of oxygen will outstrip that at which the DO is replenished, and ultimately the receiving water will become anoxic / anaerobic.

Microbiology of the BOD reaction

The diagram illustrates the following process:

- Organic Matter (Proteins, Carbohydrates, Lipids)** is consumed by **Bacteria + CO₂ + NH₃**.
- Protozoa** are shown consuming the bacteria.
- Nitrifying Bacteria** convert the released nitrogen into **Nitrates**.
- D.O.** (Dissolved Oxygen) is shown as a resource that is consumed in the process.

Source: <http://web.deu.edu.tr/atiksu/toprak/ani4024.html>

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So, if we see the microbiology of the BOD reaction we have organic matter, there has to be dissolved oxygen and there will be more bacteria will be synthesized and CO₂, NH₃ and this kind of things will be released. It is a time dependent parameter as oxygen consumed would increase with the progress of time, as the time changes oxygen consumed would also be changing. When BOD levels are high the dissolved oxygen

level decreases because, the oxygen that is available in the water is being consumed by the bacteria. Oxygen what is your oxygen amount is available is getting slowly and steadily consumed by the bacteria.

Now, if the quantity of organic waste present in the system is significantly large or very high, then the rate at which the oxygen is consumed is very high ok. If this organic matter is very high so, the rate at which DO consumes will also be very high. And probably the rate at which DO is replenished may not match that rate and then that typically results the depletion of the DO very rapidly and the water could become anoxic or anaerobic. Means, there would not be any dissolved oxygen present in the water and when there is not dissolved oxygen present in the water the aerobic processes will stop ok.

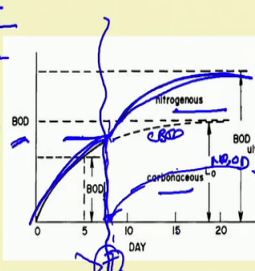
And new resume or new type of bacteria may take up the anaerobic processes may take up the degradation is still possible by anaerobic bacteria where, electron acceptor changes instead of dissolved oxygen something else become in the electron acceptor. Particularly, the ions like sulphate and nitrate and those kind of things start acting as electron acceptors and the organic matter still get decomposed, but it no more decomposes to this thing it rather started producing methane and H₂S and those kind of things are started coming in the system.

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Water Quality Parameters

✓ **BOD: Carbonaceous and Nitrogenous BOD**

- ❖ The oxygen demand could also arise from nitrification requirements where the nitrogenous waste such as ammonia is converted to nitrates by autotrophic bacteria using oxygen as an energy source.
- ❖ The requirement of DO for the process is called Nitrogenous Biochemical Oxygen Demand (NBOD) while requirement of oxygen for degrading carbonaceous organic matter is referred as Carbonaceous Biochemical Oxygen Demand (CBOD).
- ❖ Generally, the nitrifiers have slower growth rates and do not flourish until the food supply for the heterotrophic (CBOD consuming) microbes has diminished, therefore NBOD does not become discernable until approximately 7 days of incubation have occurred.



Source: https://www.tankonyvtar.hu/en/tartalom/tamop412A/2011_0009_Juhasz_Csaba-Environment...

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So, further, now the oxygen which is consumed in the water could arise from two different sources. So far we have been talking about the organic matter gets decomposed. And in the process the oxygen is consumed, but there is a possibility that oxygen demand could arise from the nitrification requirements as well nitrification requirement could also lead to the some oxygen demand the nitrifiers or nitrifying bacteria which because, there is lot of nitrogenous waste that comes in the form of proteins and amino acids amines and all those things. So, the ammonia present is converted to the nitrates through the process of nitrification by the autotrophic bacteria and these autotrophic bacteria use oxygen as a energy source. So there will be oxygen consumed in this process as well.

Now, the requirement of dissolved oxygen for this process for the process of nitrification or the for the process of where ammonia is getting converted to nitrate is called nitrogenous biochemical oxygen demand or NBOD while. So, far we have been referring BOD, BOD, BOD is actually gets a new name as the carbonaceous biochemical oxygen demand or CBOD. So, CBOD is the one which is the oxygen demand which arise for the degradation of carbonaceous organic matter or organic matter simply where as NBOD is the oxygen demand required for the nitrification or required for the conversion of ammonia to the nitrate.

There are two different types of oxygen demand or biological oxygen demand that are coming out of the system this both are the biological process. So, the both are the biochemical or biological oxygen demands which are coming and if we see the total BOD total BOD is the summation of CBOD plus NBOD, right. However, normally the rate at which nitrifiers grow is very slow they have much slower rate and generally they do not flourish till significant amount of time till around it has been observed that around 7 the nitrifiers in the system start flourishing only after 7 days until unless, we are amending them, we are talking about mostly the natural system.

So, till 7 days, there would not be like any demand for the nitrification purpose. So, whatsoever we get till this period is mostly CBOD and beyond that beyond the 7 day period we start seeing the nitrogenous build up as well. So, if you see you will see like if you see the oxygen demand is specially for nitrifiers. It will be something like this you will get some demand like this and this in addition added to the because what is ever the your CBOD or carbonaceous biological oxygen demand, if we add this NBOD to that; what we get is this total curve like this.

So, this is our oxygen this is our total BOD which contains carbonaceous oxygen demand as well as nitrogenous oxygen demand. But generally if we analyse the system before 7 day, we often overlooked the nitrogenous the NBOD part and what we get usually is the CBOD part and the conventional BOD determination processes are for determining BOD up till day 5 ok.

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Water Quality Parameters

✓ **BOD:**

- ❖ BOD is a time dependent parameter, as oxygen consumed by bacteria would increase with the progress of time.
- **BOD₅:** Quantifies the oxygen consumed in a sample within a five-day period
- **Ultimate BOD (UBOD or BOD_∞):** Quantifies the oxygen required for the total biochemical degradation of organic matter.
- ❖ Generally the five-day period is not long enough for complete oxidation, but it provides sufficient time for microbial acclimatization and for substantial oxidation.
- ❖ The BOD test is a standardized test where final DO (say after 5 days) is subtracted from the initial DO to know the oxygen consumed during the period of incubation.

Source: <http://web.deu.edu.tr/>

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So, the conventional BOD measurements that we do is actually only the CBOD part because NBOD starts after day 7 and generally, we overlooked that for most cases BOD is determined up till 5 day is because, it is a standard test and it is generally believed that 5 day is long enough period for acclimatization and substantial oxidation, it is not long enough for complete oxidation. So, in 5 day, oxidation is not complete the process of oxidation does not get complete in the 5 days, but significant amount of oxidation or significant amount of oxidation is complete within that 5 days including the initial microbial acclimatization.

There has been some historic prospective as well the process when it was developed. So, since then only the 5 days is coming and it is in the train one of the theories is that in the Britain no river takes more than 5 day to reach to the ocean. So, whatsoever biological decomposition process has to be take play has to be there is often, there only for 5 day. So, the BOD 5 was used as in standard and it is basically coming since then only. So, what BOD 5 is as we were saying that if we try to see let us say we are having we are

starting a sample we have a sample and we are starting with the dissolved oxygen level D_0 ok. Say initial DO was 8 milligram per litre ok.

Now if we incubate this sample for one day and then next day, we try to monitor at day one DO 1. So, some amount of oxygen would have been consumed in the process may be very little maybe very high let us say it has come down to 7 milligram per litre if we do it on the second day again we will see further decay let us say a 5.55 milligram per litre. Similarly, DO 3; we will see for the decay, let us say 4 milligram per litre ok. DO 4 again, we saw that 3.2 milligram per litre.

DO 5; we saw 2.5 milligram per litre, we did DO 6, we again saw 2 point; let us say 2 milligram per litre. DO 7 say 2 milligram per litre or 2.1 mili 2 milligram per litre. So, that way this is obvious that as the time progress the dissolved oxygen level will keep on decreasing and if you try to plot this, you will see that your initial DO is somewhere here and with time, it will keep on decreasing and then it reaches the saturation value or somewhere there.

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The slide is titled "Water Quality Parameters" and focuses on BOD. It includes a handwritten equation $BOD_5 = \frac{[DO_0] - [DO_5]}{D_5}$ circled in blue. To the right is a graph showing a curve that starts at a high point on the y-axis and decays towards the x-axis, with a vertical line at day 5 and a horizontal line from the curve to the x-axis. The slide lists several points about BOD:

- ✓ **BOD:**
 - ❖ BOD is a time dependent parameter, as oxygen consumed by bacteria would increase with the progress of time.
 - **BOD_5 :** Quantifies the oxygen consumed in a sample within a five-day period.
 - **Ultimate BOD ($UBOD$ or BOD_u):** Quantifies the oxygen required for the total biochemical degradation of organic matter.
 - ❖ Generally the five-day period is not long enough for complete oxidation, but it provides sufficient time for microbial acclimatization and for substantial oxidation.
 - ❖ The BOD test is a standardized test where final DO (say after 5 days) is subtracted from the initial DO to know the oxygen consumed during the period of incubation.

Source: <http://web.deu.edu.tr/>

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Now, let us say this is my day 5 and this is for say; let us say any day x ok. Now, for typically reporting purpose, the 5 day DO is used which quantifies the oxygen consumed in a sample within a 5 day period, how much oxygen is consumed in a 5 day period. So, the procedure is simple. So, like we have listed different DO. So, you take DO_5 minus DO_0 ; what was the initial 0? So, this is the amount of dissolved oxygen that has been

consumed in 5 days, you divide it with the sample volume. So that means, you get this much milligram of oxygen has consumed per unit you that you put it with the dilution factor or what is ever appropriately eventually, you want to convert it to the per litre of sample.

So, per litre of sample how much dissolved oxygen has been consumed that will give you the BOD value ok; so, BOD 5 is equal to this minus this divided by the dilution factor and volume similar that way right. So, that that is how we can get the value of BOD. Now, coming to the this point again in five-day period, we can get certain DO, this will keep on decrease, but it would not decrease beyond a time. By this time all the possible oxygen consumption, all the possible reactions which need oxygen has taken place. And since, those reaction are complete, either the organic matter is completely sort of degraded decomposed or it has decomposed to a level beyond which there would not there is no further decomposition is possible.

So, there after you keep it for what how so, ever long your sample is not going to decrease, dissolved oxygen is not going to decrease further. So, this is called ultimate BOD or BOD u and this quantifies the oxygen requirement for a total biochemical degradation of organic matter what is ever possible degradation.

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The slide is titled "Water Quality Parameters" and contains the following content:

- Handwritten formulas: $[DO_0] - [DO_5]$ and $(DO_0) - (DO_5)$ with arrows pointing to the right.
- Section: **✓ BOD:**
- List of points:
 - ❖ BOD is a time dependent parameter, as oxygen consumed by bacteria would increase with the progress of time.
 - **BOD₅**: Quantifies the oxygen consumed in a sample within a five-day period
 - **Ultimate BOD (UBOD or BOD_u)**: Quantifies the oxygen required for the total biochemical degradation of organic matter.
 - ❖ Generally the five-day period is not long enough for complete oxidation, but it provides sufficient time for microbial acclimatization and for substantial oxidation.
 - ❖ The BOD test is a standardized test where final DO (say after 5 days) is subtracted from the initial DO to know the oxygen consumed during the period of incubation.
- Source: <http://web.deu.edu.tr/>
- Footer: IIT KHARAGPUR, NPTEL ONLINE CERTIFICATION COURSES, MANOJ KU SCHOOL OF W, IIT KMA

So, similarly for ultimate BOD, you will have to use DO final for what is ever long it takes and you need to subtract that DO final from initial DO DO_0 minus DO_{final} . So,

initial DO minus final DO will give you the how much dissolved oxygen has been consumed because this has been left over similarly like as we are discussing initial DO minus DO on day 5.

So, this will give you 5 day indicate the 5 day BOD, this will indicate the final BOD or ultimate BOD and most commonly 5 day period is used this BOD test is standardized test where we take this DO and substrate from the initial DO and know the oxygen consumed during this period of incubation and that is how the BOD tests are done.

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Water Quality Parameters

✓ **Chemical Oxygen Demand (COD):**

- ❖ COD is measure of organic materials in a wastewater in terms of the oxygen required to oxidize the organic materials chemically.
- ❖ Chemical oxygen demand is measured as a standardized laboratory assay in which a closed water sample is incubated with a strong chemical oxidant, potassium dichromate ($K_2Cr_2O_7$), which is used in combination with boiling sulfuric acid (H_2SO_4).
- ❖ COD along with BOD are two different ways to measure how much oxygen the water will consume when it enters the recipient. In both the COD and BOD tests, the organic material concentration is calculated from the oxidant consumption necessary for the oxidation of the organic material.
- ❖ Since biologically or biodegradable organic matter can be oxidize while chemically almost all oxidizable matters could be oxidized, COD values are always higher than BOD.

Handwritten notes: OM (Biodegradable) and Non-biodegradable

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The next parameter is chemical oxygen demand which is COD, we just discussed the BOD. Now with BOD, one criteria is that we are trying to see how much organic matter gets decomposed by the bacteria. Now, the organic matter; there are it is not that it is not possible that all the organic matter can be decomposed by the bacteria ok, we know that polythanes are also organic, but bacteria cannot decompose polythene.

So, similarly there are variety of other complex organic matters which are non biodegradable. So, you can say that waste or organic matter could be biodegradable or could be non biodegradable. So, the BOD only targets the biodegradable part because your aerobic bacteria or group of bacteria or biomass can actually decompose only organic matter which is biodegradable, they cannot degrade non biodegradable compounds or non biodegradable elements.

So, then how we estimate the non biodegradables well then other parameter is the chemical oxygen demand where the organic matter in waste water is estimated in terms of oxygen required to oxidize the organic matter chemically. So, earlier we are doing it biological now biologically it may not be possible to degrade all the organic matter. But chemically, it is possible to degrade majority or almost all of the organic matter because we use very strong oxidant strong chemical oxidant potassium dichromate in the boiling sulphuric acid. So, we use it at a high temperature in acidic medium with a very strong chemical oxidant. So, that almost all the oxidizable compounds are oxidized.

Technically COD and BOD are the two different ways to measure; how much oxygen the water will consume when it enters to the recipient water body ok. Since, the biological only biodegradable organic matter can be oxidized and while chemically almost all oxidizable matter could be oxidized. The COD values are always higher than the BOD because, in as we were discussing we BOD we are targeting only this while in COD, we are targeting all the oxidizable matter which is present in the system which can be oxidized by the dichromate or by the presence of oxygen typically dichromate is used as we are discussing.

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Water Quality Parameters

✓ **Chemical Oxygen Demand (COD):**

Dichromate COD Chemistry:

- ❖ When organic matter is oxidized by dichromate in sulfuric acid, most of the carbon is converted to CO₂. Hydrogen present is converted to H₂O. The reaction is illustrated using the primary standard, potassium acid phthalate (KHP):

$$2 \text{KC}_8\text{H}_5\text{O}_4 + 10 \text{K}_2\text{Cr}_2\text{O}_7 + 41 \text{H}_2\text{SO}_4 \longrightarrow 16 \text{CO}_2 + 46 \text{H}_2\text{O} + 10 \text{Cr}_2(\text{SO}_4)_3 + 11 \text{K}_2\text{SO}_4$$

- ❖ Dichromate ions ($\text{Cr}_2\text{O}_7^{2-}$) form orange-coloured solutions.
- ❖ Chromic ion (Cr^{3+}) turns the solution becomes green.

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So, for the measurement purpose, when organic matter is oxidised by dichromate and sulphuric acid most of carbon is converted to CO₂ hydrogen present is converted to H₂O, the reaction illustrate the primary standard potassium acid phthalate. So, this is

your KHP which is typically reacts with the dichromate in the presence of H₂SO₄ and it actually mineralize this.

So, here what happens that the dichromate ions are orange coloured solution while the chromic ions which are there basically turns the solution green. So, when this reaction is completes the solution turns green and then by titration or by the spectrophotometric colour measurement as we discussed earlier, we could actually determine the COD could determine theoretically also because it is a chemical oxidation procedure.

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Water Quality Parameters

✓ **Chemical Oxygen Demand (COD):**

Theoretical COD:
 $(\text{M.W. KHP}) \text{ g} \times 7.5 = 16 \times 2 \text{ g}$

$$\text{KC}_8\text{H}_5\text{O}_4 + 7.5 \text{ O}_2 \rightarrow 8 \text{ CO}_2 + 2 \text{ H}_2\text{O} + \text{KOH}$$

$$\text{C}_x\text{H}_y\text{O}_z + \frac{1}{4}(4x+y-2z) \text{ O}_2 \rightarrow x \text{ CO}_2 + \frac{y}{2} \text{ H}_2\text{O}$$

So, $\text{COD} = \frac{8(4x+y-2z)}{(12x+y+16z)} \text{ g COD/g}$

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So, for our standard which is potassium hydrogen phthalate the reaction the governing reaction is this. So, this reacts with 7.1 mole of KHP reacts with 7.5 mole of oxygen ok. So, correspondingly we can see how much is the theoretical COD of KHP ok, we know that this is 7.5 into 16 into 2. So, this much gram of oxygen is required in let us say, if the molecular weight of this is KHP is M KHP. So, MKHP gram of this needs this much of oxygen.

So, how much is the oxygen requirement for 1 milligram or 1 gram of KHP can be estimated theoretically. Conceptually all organic matter which are made of C H and O ok so, if it is C x, H y, O z they will need this much moles of oxygen for degradation and decomposition and then we can get the COD value for this compounds using this. So, it is we can write equation and see based on the molecular weights how much it is coming and that way, we can estimate the theoretical COD of these compounds.

So, this way BOD and COD both are very important parameter very critical parameter. We the body water bodies that gets polluted because, of organic matter and the DO depletion are also primarily because of the organic matter present. And these are the indicators of the organic pollution, primarily organic pollution in the water and all though the procedure for measurements are different since, COD is more closer towards the towards the measurement of total organic carbon.

So, COD can nicely be correlated with the total organic carbon as well. So, with this we conclude this session and we will continue the discussion of the remaining water quality parameters in the next lecture.

Thank you.