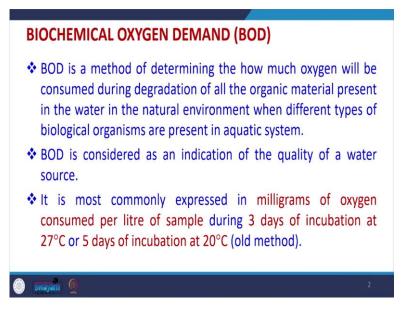
Biological Process Design for Wastewater Treatment Professor Vimal Chandra Srivastava Department of Chemical Engineering Indian Institute of Technology, Roorkee Lecture: 06 Wastewater Characterization-III

Welcome everyone in this NPTEL Online Certification Course on Biological Process Design for Wastewater Treatment. So, in today's lecture we will continue with the wastewater characterization. In the last lecture we studied regarding the chemical oxygen demand, which is one of the most important parameters, if we have to characterize any wastewater with respect to what is the oxygen demand in the aquatic bodies.

So, what will be the ultimate oxygen demand? When the all the organics get degraded that is always computed beforehand using the chemical oxygen demand as a parameter. There is another important parameter which is referred to as biochemical oxygen demand, or BOD.

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So, BOD is very very commonly evaluated in virtually all types of water or wastewater. BOD is a method of determining how much oxygen will be consumed during degradation of all the organic matter present in the water in its natural environment, when different types of biological organisms are present in the aquatic system.

So, all these biological organisms, they actually use the organic matter present in the water for their growth and their energy needs, and thus, they consume all the organic matter. During this consumption they require oxygen for various activities, including respiration and different reactions that happened during the degradation process. Thus, they require oxygen.

So, BOD essentially measures the oxygen when the microorganisms are present in the natural environment during the degradation of organic material present in the water itself. BOD itself is considered as an indication of the quality of a water source. So, if we can measure the BOD depending upon the standards, we can say that okay, what is the quality of water we know that we can use it for drinking or for bathing or for irrigation.

So, different aspects of water quality can be determined using BOD as a parameter. Now, BOD is expressed in milligram of oxygen consumed per liter of sample. Earlier the tests were conducted for 5 days with incubation of all the samples at 20 degrees centigrade, however in the recently, the 3 days of incubation is done and the water samples are kept at 27 degrees centigrade.

So, today we learn regarding how the BOD test is also conducted. So, that will come later in today's part of lecture.

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Stages of Decomposition in the BOD test

- There are two stages of decomposition in the BOD test: a carbonaceous stage and a nitrogenous stage.
- The carbonaceous stage represents oxygen demand involved in the conversion of organic carbon to carbon dioxide.
- The second stage or the nitrogenous stage represents a combined carbonaceous plus nitrogenous demand, when organic nitrogen, ammonia and nitrite are converted to nitrate.
- Nitrogenous oxygen demand generally begins after about 6 days.

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Now, coming there are during the BOD test, there are different stages of decomposition, there are essentially 2 stages of decomposition the BOD test in one of them the carbonaceous state under which the carbonaceous organic matter degradation happens and then there is a nitrogenous stage under which the nitrogenous compounds their the oxidation happens.

So, carbonaceous represent the oxygen demand involved in the conversion of organic carbon to carbon dioxide. Whereas in the second stage or the nitrogenous stage, it represents a combined carbonaceous plus nitrogenous demand when the organic nitrogen, ammonia and nitrite get converted into nitrate. So, nitrogenous oxygen demand generally begins after 6 days.

So, it was considered suitable to measure the BOD up to 5 days only, and that BOD 5 or BOD 3, actually, they essentially represent the carbonaceous stage of the BOD test, and they represent the carbonaceous oxygen demand they do not represent the nitrogenous oxygen demand along with the carbonaceous oxygen demand. So, this is there.

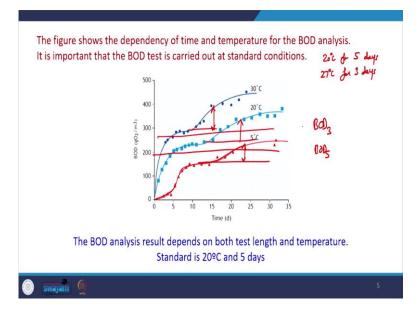
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Cont.... Under some conditions, if ammonia, nitrite, and nitrifying bacteria are present, nitrification can occur in less than 5 days. The BOD test must be inhibited to prevent oxidation of ammonia. If the inhibitor is not added, the BOD will be between 10% and 40% higher than can be accounted for by carbonaceous oxidation [Russell, 2006]. The results of BOD test are reported as carbonaceous BOD (CBOD) or as CBOD₃ when a nitrification inhibitor is used.

Under some conditions if ammonia nitrite and nitrifying bacteria are present nitrification can occur in less than 5 days also. So, it is possible and in the natural environment it is possible. However, during the BOD test, we add some inhibitors so as to prevent the oxidation of ammonia. And if the inhibitor is not added the BOD which actually represents the carbonaceous oxygen demand in a way will be at least 10 to 40 percent higher than that accounted by actually the carbonaceous oxidation.

So, we always add inhibitor so as to minimize the nitrogenous oxidation, so as to not to add the demand of nitrogen into the carbonaceous oxidation. The results of BOD tests are reported as carbonaceous BOD, or as CBOD₃ when nitrification inhibitor is used.

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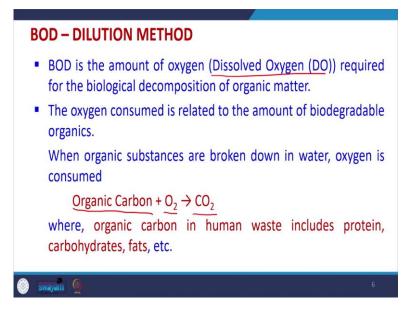
Now, this is the figure actually, which represents the dependency of time and temperature for the BOD analysis. And it may be noted that BOD test is carried out either at 20 degrees centigrade, this was for 5 days, this was earlier in standard. Nowadays it is conducted at 27 degrees centigrade for 3 days. Now, we can see the effect of temperature here. Now, earlier what we found it out that there are 2 stages of demand.

So, one is stages like up to 5 days or 6 days, we can see here the demand is there. And after that again the demand is increasing. So, the second part of demand is basically carbonaceous plus nitrogenous. So, here in this case, we can see the demand is increasing. So, this section is nitrogenous demand in the, at 20 degree centigrade this is the nitrogenous demand, in this figure it seems this is the nitrogenous demand.

And whereas the lower part represents the carbonaceous demand, so we always represent either BOD, we report either BOD₃, or BOD₅ depending upon the standards which are prevailing in their respective countries. In India, currently, the standard is with respect to BOD₃. And in this figure, what we can see is that, that if we measure the demand BOD value for the same water sample at different temperatures, we can essentially see that the oxygen demand the BOD value increases with increase in temperature.

And this is because the microorganisms have increased, their tendency to degrade the organic matter in enhances and their metabolic all the metabolics increase with increase in temperature because of which the BOD also increases with increasing temperature.

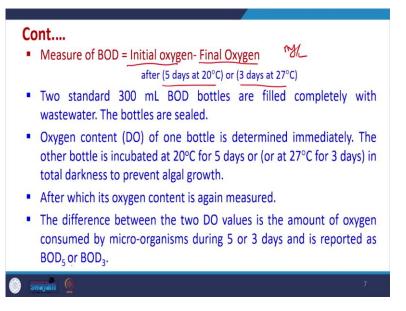
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Going further, what are the methods of measuring the BOD? So, BOD can be measured very easily by 2-3 methods. The BOD already we have told that it is the amount of oxygen which is essentially the dissolved oxygen required for the biological decomposition of organic matter. The oxygen consumption is related to the amount of biodegradable organics.

So, when any organic is present in water, this is used by microorganisms in presence of oxygen to convert into CO_2 , some part of the organic matter is used for biomass growth also. Now, what we do is that we try to measure the BOD by measuring the dissolved oxygen before and after that test.

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So, initially what we do is that we measure the initial oxygen and then we measure the final oxygen. So, difference between both in terms of milligram per liter, either 5 days or 3 days gives the measurement of BOD. During this test what is done is that, we use 2 standard 300 ml bottles, which are filled completely with wastewater, the bottles are sealed.

The oxygen content of one bottle is determined immediately and the other bottle is incubated at 20 degree centigrade for 5 days or at 27 degrees centigrade for 3 days in total darkness to prevent algal growth. After 5 days or 3 days as respective temperatures, the oxygen content is again measured. The difference between the two DO values is the amount of oxygen consumed by microorganism during 3 days or 5 days and is reported as BOD₅ or BOD₃.

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Now, these are the bottles we can see the initial these are the 300 ml bottle, they essentially when we fill the water in this water bottle sample in this water bottle actually they when the cap is kept, they measure 300 ml exactly. So, we keep these bottles inside this incubator depending upon the temperature for that respective number of days and we measure the DO using the DO meter either 3 days or 5 days, we can use the titration method also for determining the dissolved oxygen.

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 Since the saturated value of DO for water at 20°C is 9.1 mg/L only, and that the oxygen demand for wastewater may be of the order of several hundred mg/L.
 Therefore, wastewater are generally diluted so that the final DO in BOD test is always ≥ 2 mg/L.
• Precaution is also taken so as to obtain at least 2 mg/L change in DO between initial and final values. (1) Find DO $\ge 2 \text{ g/L}$ (2) $(00_{\tilde{L}} - 00_{\tilde{J}}) \ge 2 \text{ g/L}$
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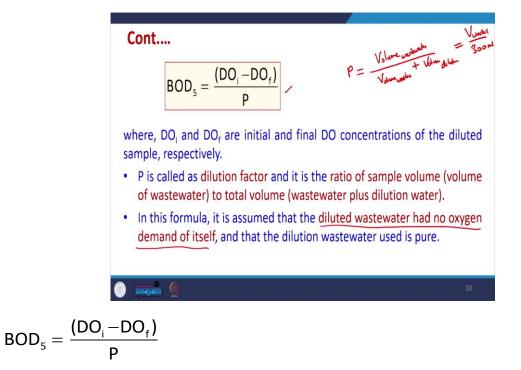
Since the saturated value of DO for water at 20 degrees centigrade is around 9.1 milligram per liter only that means the oxygen demand for wastewater may be of order of several 100 many a times. So, therefore, what we do is that wastewaters are generally diluted. So, that the final DO in the BOD test is always greater than 2 milligram per liter. So, in the any wastewater sample, the dilution is very necessary.

And until and unless we perform dilution, we cannot measure the BOD directly, because the BOD may be much higher, whereas, the DO saturation level is only 9.1 milligram per liter. So, when we perform the test, we cross check two things and if any of the two things fail, we consider the test to be filled and then we had to dilute the water.

So, what is done is that precaution is taken so as to obtain at least 2 milligram change in the DO between initial and final values. So, there are two conditions that have to be cross checked that after the test is completed, the final DO value should be at least 2 milligram per liter or more, if it is less than that, that means, there is a possibility that total oxygen may have gone and we are measuring incorrect value.

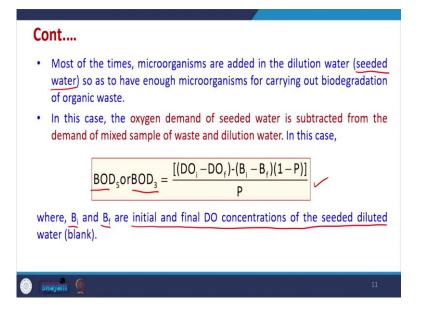
So, considering this condition we always try to see that the final DO value should always be greater than 2 milligram per liter. The second condition is that that the difference in the initial value and the final value that should also be greater than or equal to 2 milligram per liter. If both these test conditions are satisfied, we considered the BOD test to be satisfactory, and then we report the BOD value. If any of these conditions fail, we use the diluted water for diluting the water sample and then only we determine the BOD.

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Under that condition when we do the dilution of the sample then we use this particular formula where DO_i and DO_f are the initial and final DO concentration of the diluted sample and where the P actually represents the ratio of sample volume, volume of wastewater taken so we can say that this is a volume of wastewater and divided by volume of wastewater plus volume of dilution water which is used.

So, here the dilution water which is used. And generally this will be 300 ml because we are using the 300 ml water bottle and the here the volume of wastewater is there. So, this is the P value. So, in this formula it is assumed that that diluted wastewater had no oxygen demand of itself. So, whichever diluted wastewater we use, it has no oxygen demand by itself and this dilution wastewater is pure.



In this case,

$$BOD_{5}orBOD_{3} = \frac{[(DO_{i} - DO_{f}) - (B_{i} - B_{f})(1 - P)]}{P}$$

Now, there is another condition which may happen that most of the times the microorganisms may have to be added the wastewater sample itself may not contain microoganism. So, under those conditions, we need to add microorganism from outside and if we have to add microorganisms from outside so what we do is that in place of pure dilution water we use seeded dilution water.

Seeded dilution water means the water which contains microorganism and this is done so as to have enough microorganisms for carrying out the biodegradation of organic waste. So, if the wastewater may not contain any microorganism, we dilute that sample with seeded water which contains microorganism and in this case, because we are using some dilution water which may itself incur some oxygen demand.

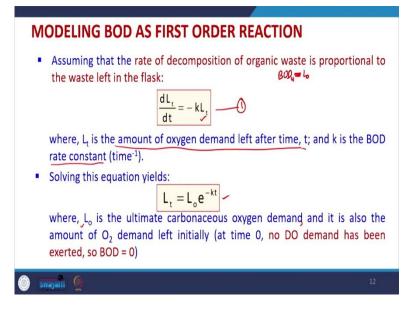
So, in that case we determined the DO level in this dilution water also. So, B_i and B_f actually represent the initial and final DO concentration of seeded dilution water because they will be incurring some demand itself. So, what we do is that we subtract the oxygen demand of the diluted water sample and the formula, the revised formula becomes like this.

So, we can find out BOD_5 or BOD_3 depending upon the number of days and temperature at which test is carried out. And we use this particular formula for determining the biological

oxygen demand or biochemical oxygen demand of the water sample. So, we have learned that, that the BOD can be determined by 3 methods.

One, under one case, we do not require any dilution water, and we essentially determine the BOD value using the initial DO and final DO. There is a second case in the water sample may have to be diluted if the value of BOD is little higher. Under those conditions, we use dilution water which does not contain any microorganism.

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Assuming that the rate of decomposition of organic waste is proportional to the waste left in the flask:

 $\frac{dL_t}{dt} = -kL_t$

Solving this equation yields:

$$L_t = L_o e^{-kt}$$

In the third case, the microorganisms may have to be required because the water sample may not contain any microorganism by itself. So, under those conditions, we use a dilution water which is essentially called as seeded dilution water, and which itself incurs some demand for oxygen. So, under those conditions, we use this formula for determining the BOD value.

Now, we have seen earlier that the BOD is a function of time, also as temperature. So, let us model BOD using some equations so that we can determine the BOD value. If one of the

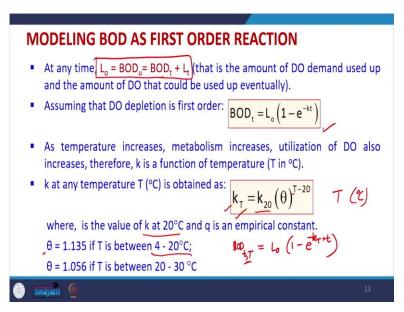
values at any temperature is known, we can easily find out the value at any other temperature and time. So, this is possible.

So, for modeling the BOD we assume that the rate of decomposition of organic waste inside the water sample is proportional to the waste which is left in the flask itself. Now, if suppose L t is the amount of oxygen demand left after time t, so the rate of oxygen demand will be proportional to the oxygen demand itself. So, we assumed this to be first order. And thus the proportionality rate constant k is called the BOD rate constant and its unit is time inverse.

Now, if we try to solve this equation, we assumed that at time t is equal to 0 the amount of oxygen demand is L_0 is the ultimate carbonaceous oxygen demand and so we can find out the L_0 value. So, integrating this particular equation 1 with respect to the condition that L_0 is the ultimate carbonaceous oxygen demand or the oxygen demand at time t equal to 0. So, it is we can find out this particular equation and at time is equal to 0 no demand has been exerted. So, BOD is essentially 0, but after some time the BODs values be there.

Now, when we model such equation, there are two important thing that has to be considered. There is always the BOD value, BOD ultimate demand or the oxygen demand left is this is they are essentially 0, and they are essentially same.

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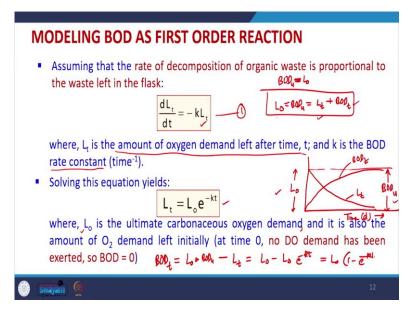
At any time, , $L_o = BOD_u = BOD_t + L_t$

Assuming that DO depletion is first order:

$$BOD_t = L_o(1 - e^{-kt})$$

k at any temperature T (oC) is obtained as:

$$\mathbf{k}_{\mathrm{T}} = \mathbf{k}_{\mathrm{20}} \left(\boldsymbol{\theta} \right)^{\mathrm{T-20}}$$



Assuming that the rate of decomposition of organic waste is proportional to the waste left in the flask:

$$\frac{dL_t}{dt} = -kL_t$$

Solving this equation yields:

$$L_t = L_o e^{-kt}$$

And at any time that the amount of oxygen demand which is represented by this equation, where L_0 or BOD_u there are 2 terms which are related. So, we will explain this using a figure. Actually, this is a figure suppose, and we want to measure the BOD now BOD if you want to measure it will be like suppose for 5 days only carbonaceous BOD, we are measuring. So, the BOD will increase like this.

So, at any time t, here this is the equation time t in terms of days, this is there. And this is the, this curve actually represents the BOD at any time t. Now, opposite the oxygen demand will always be represented by this equation, where L_0 is the initial oxygen demand which are very high and which will go on decreasing depending upon the oxygen demand left.

And similarly, the BOD_u, the BOD_u represent the ultimate oxygen demand, the demand of BOD which will be there after ultimate time or infinite time. So, we can see from this figure and some of these, some of this represents L_t . Now, we can see from the figure that either L_0 this one or BOD_u, they are essentially same that was written earlier and they are essentially equal to L_t any oxygen demand left and the oxygen demand which has been incurred already.

So, this is BOD_t . So, this is the ultimate formula which represent this. So, from this figure we can find out that we can find out the BOD_t by subtracting the L_t value from L_0 . So, the equation for BOD_t from this represents the BOD_t is equal to L_0 or we can see BOD_u minus L_t and if we represent L_t itself, so this is L_0 minus L_0 e raised to minus kt. And that means L_0 1 minus e raise to minus kt. So, this is the equation which is given here.

So, at any time, L_0 or BOD_u they are equal to BOD_t plus L_t that is the amount of DO demand used up at any time. And the amount of DO that could be used up eventually. So, we have already derived equation, so we can model the BOD using this equation. Now, in this case, there is a parameter with respect to k, the k which is represented by the BOD rate constant.

Now, this BOD rate constant k is a function of temperature as temperature increases, we have seen the metabolism increases and utilization of DO also increases therefore, k is a function of temperature. So, k at any temperature t can be written by this equation, combining both equation together, we can always write the BOD in terms of temperature and time. Now, the k at this is the k at 20 degrees centigrade.

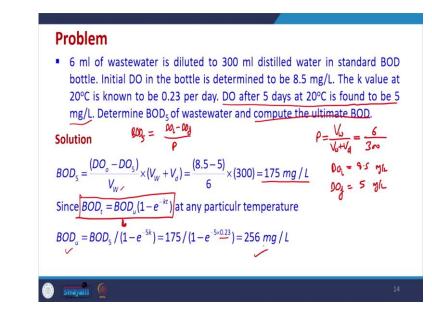
Remember the t value given here is always in degree centigrade, we have to write the value in degree centigrade we cannot represent by any other Kelvin or Rankine etcetera. Now, that theta value is an empirical constant and is a function of temperature. So, generally like in the range of 4 to 20 degree centigrade, theta can be written as 1.135 and between 20 to 30 degrees centigrade 1.056.

There are different theta values depending upon the type of wastewater also. So, but generally they will fall in this range one point something so this is there. Now, for simplicity we can write another trick we can use is that we can always remember the BOD_t at any temperature is a function of this L_0 1 minus e raise to k at temperature whatever temperature it is being measured into time.

So, this is the good formula to remember and where kt is equal to this. So, through this formula we can use the t term is also coming where the temperature at which the k value has

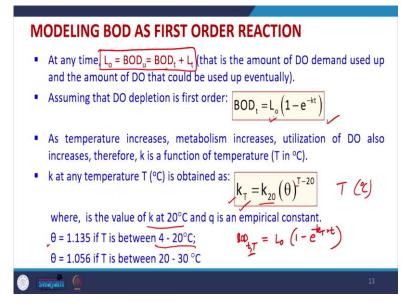
been determined. So, we will try to solve some question so as to further understand how to go ahead in determining the BOD values.

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$$BOD_{5} = \frac{(DO_{o} - DO_{5})}{V_{w}} \times (V_{w} + V_{d}) = \frac{(8.5 - 5)}{6} \times (300) = 175 \ mg \ / L$$

Since $BOD_t = BOD_u (1 - e^{-kt})$ at any particulr temperature $BOD_u = BOD_5 / (1 - e^{-5k}) = 175 / (1 - e^{-5 \times 0.23}) = 256 mg / L$



At any time, , $L_o = BOD_u = BOD_t + L_t$

Assuming that DO depletion is first order:

$$BOD_t = L_o(1 - e^{-kt})$$

k at any temperature T (oC) is obtained as:

$$\mathbf{k}_{\mathrm{T}} = \mathbf{k}_{\mathrm{20}} \left(\boldsymbol{\theta} \right)^{\mathrm{T-20}}$$

The 6 ml of wastewater is diluted to 300 ml of distilled water in the standard 300 ml BOD bottle. The initial DO in the bottle is determined to be 8.5 milligram per liter. And the k value is known to be this. So, k value is given. But, there is another thing is given that DO after 5 days at 20 degrees centigrade is find to be 5 milligram per liter.

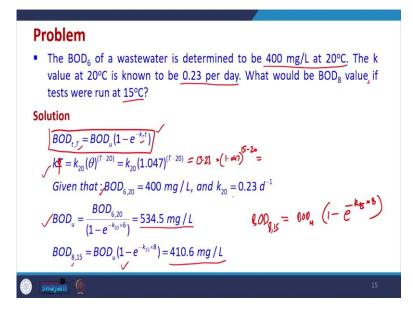
So, we have few things which are given here. First thing is that we have been given the dilution factor, because we have the value of 5-6 ml of wastewater is diluted to 300 ml of distilled water. So, you have volume of wastewater, volume of wastewater plus volume of dilution water and this is given to be 6 ml by 300 ml.

So, this is there, so this is the dilution. P is given here. Now the DO initial is also given, DO initial is 8.5 and DO final is this is milligram per liter and DO final is 5 milligram per liter. So, if we use the formula earlier, which was given that BOD at any time since this is 5 days, so this is 5, this is equal to DO initial minus Do final upon P.

So, the same formula is given here, in place of P it is written in terms of volume of wastewater volume of wastewater plus dilution water. So, if we use the formula, we can find out that BOD₅ is 175 milligram per liter. Now, we have to compute the ultimate BOD. And already we know this is the formula. So, sometimes in the formula in place of BOD_u, it is L_0 which is given in the previous case, we can see that here L_0 is given but it is L_0 or BOD_u both are same, so there is no difference.

So, this is the formula which is given here. And using this formula, we can find out the BOD_5 is equal to the k value since it is given we can find out the BOD_5 to be 256 milligram per liter using this formula and after putting all the values, so thus the maximum amount of oxygen demand that will be incurred by this wastewater sample will be 256 milligram per liter.

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$$BOD_{t,T} = BOD_{u} (1 - e^{-k_{T}t})$$

$$kT = k_{20}(\theta)^{(T-20)} = k_{20} (1.047)^{(T-20)}$$
Given that : $BOD_{6,20} = 400 \text{ mg} / L$, and $k_{20} = 0.23 \text{ d}^{-1}$

$$BOD_{u} = \frac{BOD_{6,20}}{(1 - e^{-k_{20} \times 6})} = 534.5 \text{ mg} / L$$

$$BOD_{8,15} = BOD_{u} (1 - e^{-k_{15} \times 8}) = 410.6 \text{ mg} / L$$

Now, there is another thing, another question is given here that BOD_6 of a wastewater is determined to be 400 milligram per liter at 20 degrees centigrade. The k value at 20 degrees centigrade is known to be 0.23 per day, what will be the BOD_8 value? Suppose the tests were conducted at 15 degree centigrade. So, we have the BOD_6 is given already at 20 degrees centigrade and k value is also given.

So, using this, so earlier I had given this particular formula where the temperature was also written. Now, we use this particular trick to find out the value of ultimate BOD, so BOD_6 at 28 degree centigrade is given to be 400 milligram per liter k 20 is also given. So, if we keep both the values BOD_6 and k value, we can determine the ultimate BOD and that will be 534.5 milligram per liter.

So, once BOD has been determined, we can again use back this formula to find out the BOD_8 at 15 degree centigrade. Now, we have to find out the BOD_8 at 15 degree centigrade that means, we should know the k value also at 15 degree centigrade. So, because we have to

ultimately use this formula, so if we have to determine the 15 degree centigrade value into 8, so for this we have to find out k 15.

So, we can find out the k 15 using this particular formula, and the k 15 value will be 0.23 into theta value is given suppose it is given as 1.047 and then we can find out 15 minus 20 degrees centigrade and through this we can find out the k_{15} value. And once k_{15} value is determined, we can find out the BOD₈ at 15 degrees centigrade and this will be 410.6 milligram per liter.

So, this way we can find out the BOD values at any temperature and for any number of days. So, this formula gives lots of ideas with respect to converting the BOD values from one value to another value at different temperature and time. So, today we have learned regarding the BOD, everything was described with respect to BOD.

In the next lecture, we will try to learn the difference between BOD and COD, because we have done both COD as well as BOD. And then there are other parameters also like Total Organic Carbon, then theoretical oxygen demand and the difference between the two. So, we will continue the wastewater characterization aspects with respect to biological or biochemical parameters. So, thank you very much for today's lecture.