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Lecture - 07

Water Quality Monitoring: Biological/Biochemical Parameters - I

Good day everyone, and welcome to this lecture on Water Quality Monitoring. We will be continuing with the previous lectures, where we studied different parameters for water quality monitoring. And in the previous lecture like we studied the various chemical parameters which are used for estimating various properties of the wastewater or water.

Now, continuing in the same time, we will be now going to the third parameters, third set of parameters which are called as like biological or biochemical parameters. And they are essential parameters, because they estimate virtually what is the oxygen demand that will be there with respect to organics which are present in the water and when their natural degradation occurs in the natural requirement.

So, all those aspects will be discussing in this lecture. One of the foremost important parameters with respect to these biochemical parameters, it is called as biochemical oxygen demand.

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BIOCHEMICAL OXYGEN DEMAND (BOD)

- BOD is a method of determining the how much oxygen will be consumed during degradation of all the organic material present in the water in the natural environment when different types of biological organisms are present in aquatic system.
- BOD is considered as an indication of the quality of a water source.
- It is most commonly expressed in milligrams of oxygen consumed per litre of sample during 3 days of incubation at 27°C or 5 days of incubation at 20°C (old method).

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As such, whenever we are discharging any water into another aqueous stream, and that water contains some amount of organics, so, that organic will always naturally decay, and that decay happens because of the presence of microorganisms, which use that organic material as a nutrient and convert it into basic forms like carbon will be converted into CO2, etc.

And during that degradation process, they require a lot of oxygen. This type of decay we observe commonly on any soil surface also. So, any organic material if it is thrown on soil surface, so, its natural decay always happens. We do not foresee that, but always some amount of oxygen is required during the decaying process, which happens because of the presence of biological organisms in that system.

However, if that organic material is present in the water and that whole water is being discharged into another Aqueous stream. So, that means, the water which is there, it will be having a maximum oxygen availability depending upon the solubility of oxygen at that temperature. And if the oxygen demand is more than the what is present in that aqueous stream, then there will be anaerobic conditions will prevail.

And that decay process will be hampered, also oxygen level will also go down and it will cause effect on the aquatic life of both animals as well as plants. So, oxygen availability in the water is very, very important for the sustaining the life. And for doing this we must understand that any material which we throw into any water body, if it has some oxygen demand, that means the oxygen present in the water will be diminished and that will cause problem with respect to that Aqueous stream.

So, we always want the oxygen demand to be minimal, whenever we are discharging any water into another stream. So, that oxygen demand we need to determine beforehand. So, biochemical oxygen demand is one of the methods which actually helps in determining how much oxygen will be consumed during the degradation of all the organic material present in the water in the natural environment, when different types of biological organisms are present in that aquatic system.

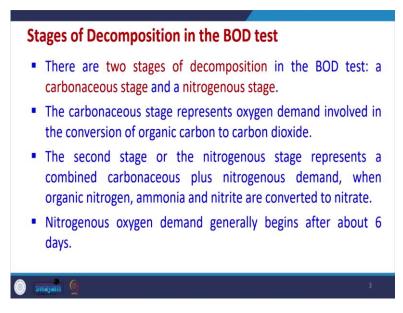
So, this BOD estimation helps in determining the oxygen demand in general. Now, it is any water stream it is having very high BOD value. That means, if it is mixed with another water stream or if that water will be discharged into another stream, so, the demand of oxygen will be more so, that means that the present water stream which is having high BOD, its water quality is bad. That means it contains a lot of organic material and which, during degradation will require a lot of oxygen.

So, we do not want BOD values to be higher, we always want BOD values to be minimum possible. So, if BOD value is very less, that means that the quality of water is good. There are

no organics present in the water and there will be no requirement or degradation of those organics present in that water.

So, this BOD is generally expressed in milligrams of oxygen consumed per liter of the whatever water sample. And there are two methods, earlier method it was in India, we used to do determine the BOD values by keeping the water sample for 5 days at 20 degrees centigrade. But now, since last few years, the new method has come under that we incubate the water sample for 3 days at 27 degrees centigrade for determining the BOD value.

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Now, during the BOD test, there are or during any natural degradation of organic matter, there are two stages of decomposition. In the one stage, in the first stage, carbonaceous stage it is called. During that stage whatever oxygen demand is there, that is due to conversion of organic carbon into carbon dioxide.

And in the second stage, which is also called as nitrogenous stage, a combined demand is there which is of carbonaceous plus nitrogenous organic matter and because of their conversion into various other like carbon dioxide, ammonia, nitrite etc. So, during this nitrogenous demand, there will be always be organic nitrogen will be converted into ammonia nitrite further into nitrate.

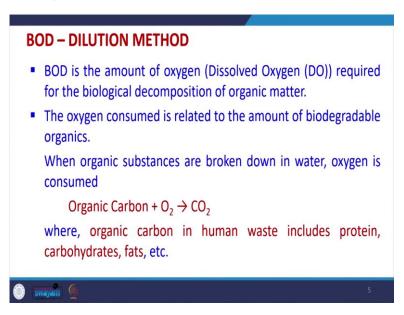
So, nitrogenous demand usually occurs much later than the carbonaceous demand and it may start occurring early as possible around 6 days. But, in the BOD test, we are usually inclined towards finding out the carbonaceous demand only we are not finding the nitrogenous demand in the water. Under some conditions, there is a possibility that ammonia nitrite and

nitrifying bacteria if they are present, this nitrification of nitrogenous organic matter may start occurring less than 5 days also.

So, we do not want because in the BOD, we want to estimate only the carbonaceous oxygen demand only. So, under that condition, we need to add some inhibitors during the BOD estimation, so that the only we can determine the carbonaceous demand, there is no nitrogenous demand, which comes into the BOD estimation. If we do not add that inhibitor, actually, our BOD values may be 10 to 40 percent higher than the carbonaceous oxygen demand, and that will be wrong.

So, the results of BOD tests are reported as carbonaceous BOD only and it may be BOD for 3 days, it may be 5 days when a inhibitor is added. Now, how do we determine the BOD? So, that we will, we are going to learn now.

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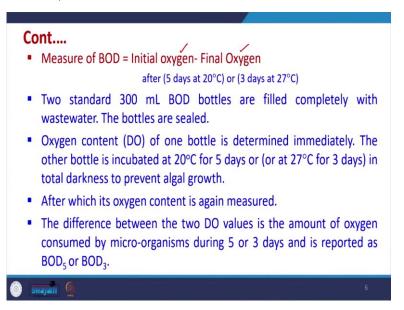


So, BOD is the amount of oxygen which is like dissolved oxygen required for the biological decomposition of organic matter, so this is very simple definition this is very simple definition. Now, the oxygen consumed is related to the amount of biodegradable organic, so, if organic matter is less.

So, amount of oxygen demand will be less and so, it depends upon the how much amount of organic substance is present in that water. And that organic carbon or organic substances which are present they may be because of the presence of protein, carbohydrates, fats or in the industrial wastewater, many other organic materials which are actually being used in that industry as a raw material or they are being produced.

So, are they are intermediate during the whole process. So, they may also come into the water and they may incur some oxygen demand. So, we need to find out the oxygen demand in the water. So, this is the BOD dilution method.

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Now, what we do is that measurement of BOD is done like finding out the initial oxygen and then finding out the final oxygen either after 5 days at 20 degrees centigrade or 3 days at 27 degrees centigrade. In India now, we prefer 3 day at 27 degrees centigrade, which is the standard. What we do is that we keep a number of standard 300 ml bottles are there, which are used during the BOD testing and they like 300 ml BOD bottles are filled completely with wastewater.

Now, if the overall demand is very less or the amount of organic matter present in the water is less than that what will happen? The oxygen content of one of the bottle is determined in immediately and that the DO value can be determined using a DO meter. There are many, many simple instruments which can determine the oxygen or we can determine the DO value using titration as well.

Now, the other bottle is incubated at 20 degrees centigrade for 5 days or at 27 degrees centigrade for 3 days in total darkness. So, it is kept in total darkness, so that there is no algal growth. And naturally it we are assuming here that some amount of microorganism is present already present in that wastewater.

So, that microorganism will degrade the organic matter. And for that it will consume the oxygen which is already present in that water. So, after 5 days or 3 days, we determine the

oxygen content again. And the difference between the 2 DO values is the amount of oxygen consumed by microorganisms during the 5 or 3 days, and it is reported as BOD5 or BOD3.

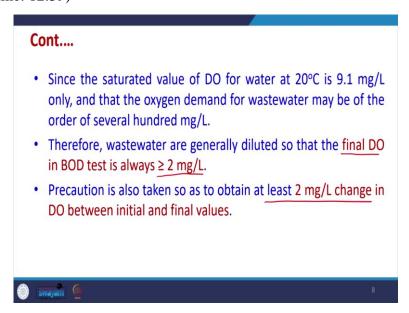
So, the simplest method, case first is when the amount of organic matter present in the water sample is very less we can determine by just finding out the initial DO and final DO after incubating the wastewater sample in a 300 ml bottles for 3 days or 5 days.

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Now, these are the simple DO bottles and we can use this instrument for finding out the DO very easily.

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Now, there is a certain limit, we can easily calculate this and in fact, this we will be doing that what is the saturated value of dissolved oxygen for water at any temperature. So, this we can determine very easily for the sake here it is reported that the saturated state value of DO for water at 20 degrees centigrade is approximately 9.1 milligram per liter.

So, that means, any water at 20 degrees centigrade will generally not contain more than this amount of oxygen. So, any extra oxygen will go out of the surface into the atmosphere. And if the water contains less DO some amount of oxygen will go into the water and so that the solubility limit is met again.

Now, the oxygen demand for wastewater it is possible that it is more than this requirement it may be several 100 milligram per liter. So, under that condition, this method which was given in the previous slide just finding the initial DO and final DO may not work because the oxygen demand is more, so the oxygen may become 0.

So, we do not know within 3 days whether whatever the actual demand. So, under that condition, what is done is that that we dilute the water with oxygen with the organic matter free water. So, that the overall demand overall amount of organic matter in the water sample becomes less and so that we can find out. So, always the dilution is done of the water sample itself.

And that we may know whether we require dilution or not. There are 2 methods for doing this. Any BOD test is considered to be okay. For that there are 2 conditions. One is that the final DO in the BOD test should always be less than or greater than 2 milligrams per liter, what does it mean?

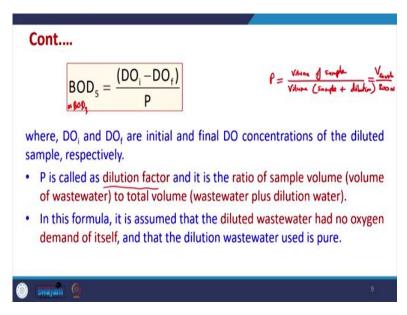
It means that after 3 days if the DO value in that water sample bottle is less than 2 milligram per liter we assume that we are not sure and it may be possible that oxygen demand was more, but it has not been properly given because availability was not there. So, it is possible that it may become 0 milligram per liter also.

So, if this happens that BOD at the DO value after 3 days or 5 days is less than 2 milligram per liter, we assume that the BOD test is not okay, we need to dilute the water further. So, that the final BOD or final DO value should always be greater than 2 milligram per liter. Also, it is possible that we might dilute the water so much that actually that we are not sure whether the change in DO which has happened is correct or not.

So, if the change in DO from initial and final values is less than 2 milligram per liter, the under that condition also, we assume that our BOD test has failed. So, we have to redo the BOD test. So, under this condition, actually, the dilution has been more. So, that is, why the demand of oxygen was very less, and there is absolutely virtually no change.

So less, if at least 2 milligram per liter change is not there, we assumed the BOD test to be failed. And similarly final DO should always be greater than 2 milligram per liter, then only the BOD test is assumed to be correct. So, these are the methods.

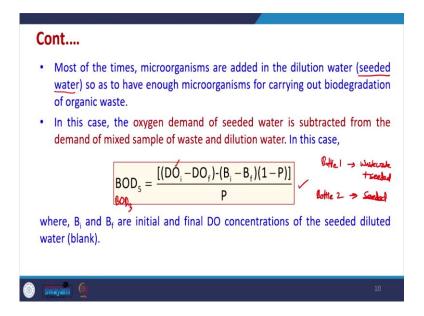
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BOD could be calculated as follows:

$$BOD_5 = \frac{(DO_i - DO_f)}{P}$$

where, DO_i and DO_f are initial and final DO concentrations of the diluted sample, respectively. P is called as dilution factor and it is the ratio of sample volume (volume of wastewater) to total volume (wastewater plus dilution water).



Now, this dilution if when we are doing the dilution, we can find out the BOD using this method it may be BOD5 or BOD3 also depending upon whether it is 3 day test or 5 day test, so, it is found out by using this formula BOD is equal to DO initial minus DO final divided by P where P is the dilution factor.

And which is defined as the ratio of volume of sample of wastewater to the total volume of wastewater that means wastewater plus dilution water. So, P is like P is equal to volume of sample, volume of sample and it is volume of sample plus dilution water. So, and generally this whole thing is at the bottom it is 300 ml. So, and this is the volume of the sample, so, this is how P is defined.

The oxygen demand of seeded water is subtracted from the demand of mixed sample of waste and dilution water. In this case

$$BOD_5 = \frac{[(DO_i - DO_f) - (B_i - B_f)(1 - P)]}{P}$$

where, B_i and B_f are initial and final DO concentrations of the seeded diluted water (blank).

So, because we always do the test in 300 ml BOD bottles, which are also called as Meyer flask, so, we use them. So, for this it is there. Now, in this formula there is presumption. Presumption is that, that dilution wastewater which has been used, it has no oxygen demand of itself. But it may be possible that dilution water that we are using it has some oxygen demand.

And also there is a second case that sometimes it is possible that water samples that we are

using it has no microorganism. So, sometimes what we do is that we use the dilution water

which is seeded water, dilution water which is seeded water what does it mean? That dilution

water that we are using is already seeded with some microorganisms.

So, if they are seeded with some microorganisms, they will also incur some demand. And this

is done, so that we always have some micro exam present during the BOD test. So, this is

done. And during that condition, it is most likely that, that dilution water also has some BOD

demand. So, under that condition, we use this formula which is given here for finding out the

BOD.

Again, it may be BOD5, or BOD3, depending upon the number of days for which the BOD

bottles are kept. Most of the times micro-organisms are added in the dilution water and it is

referred to as seeded water. So, as to have enough micro oxygen for carrying out

biodegradation of organic waste. So, in this case, the oxygen demand of seeded water has to

be subtracted from the demand of mixed the samples of waste plus dilution water.

So, and Bi and Bf are the initial and final DO concentration. So, in this case, we keep at least

3 bottles, one is initially will find out that DO of the sample. Second case, will find that DO

of the sample. So, one bottle, bottle one will contain wastewater plus seeded water. So, both

will be there and then there will be at least one another bottle, which will be containing only

seeded water.

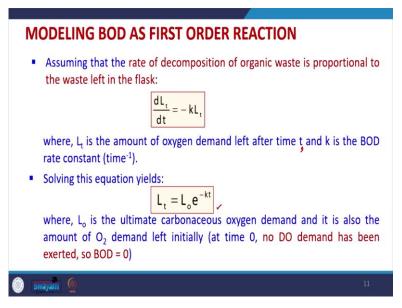
And it will also be kept for that many days, 3 days or 5 days inside the incubator at that

particular temperature. So, if it is kept it for 3 days it will be holding incubator will be kept at

3 days and at 27 degrees centigrade and everything will be in the dark. So, this is the method

and we can find out the BOD via this method.

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Now, these there are some other important things, DO can be modelled as a first order reaction. And this is very important, because many times we need to determine the carbonaceous oxygen demand for maybe 8 days, 10 days or at any other temperature also. So, we have performed the test suppose that 27 degrees centigrade, but actual degradation is going to occur at 15 degrees centigrade.

So, under that condition, the values will change, the demand will change. So, for doing all these studies, it is very important to model the BOD. Now, as usual, since most of the biological reactions can be modelled as first order reaction here also BOD is also modelled as first order reaction assuming that the rate of decomposition of organic waste it is proportional to the whatever is the waste left.

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

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

where, L_t is the amount of oxygen demand left after time t and k is the BOD rate constant (time⁻¹).

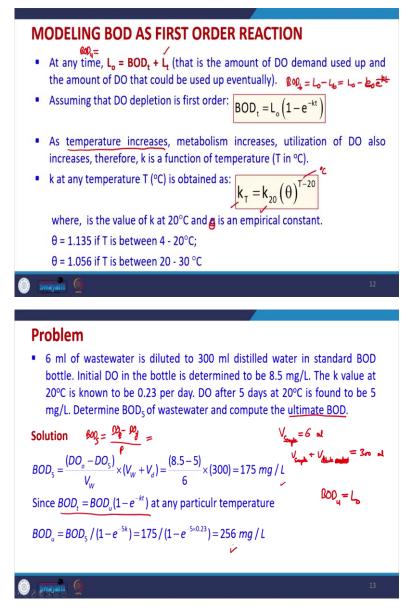
$$L_{t} = L_{o}e^{-kt}$$

where, L_0 is the ultimate carbonaceous oxygen demand and it is also the amount of O_2 demand left initially (at time 0, no DO demand has been exerted, so BOD = 0)

So, it is the traditional simple concepts, so we are putting dL by dt is directly proportional to Lt and where Lt is the amount of oxygen demand left. So, after time t, and k is the BOD rate constant and its unit is time inverse. So, if it is kept in days it is will be day inverse.

Now, if you solve it assuming that at time t is equal to 0, the demand left is 0. So, under that condition we can easily solve and this equation we will get. And here, there are few things more that will understand may be in the.

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Now at any time, whatever is the total oxygen demand? So, that demand is equal to the BOD already used up and whatever is left. So, that means L0 is equal to BODt plus Lt. So, always L0 at time t, at initial BOD and it is also sometimes that what will be the ultimate oxygen demand this is equal to L0, they both are same and they are equal to BODt plus Lt.

Assuming that DO depletion is first order:

$$BOD_{t} = L_{o} \left(1 - e^{-kt} \right)$$

k at any temperature T (°C) is obtained as:

$$k_T = k_{20} \left(\theta\right)^{T-20}$$

Now, if this is there, then we can find out the BODt very easily because BODt will be at any time t will be equal to L0 minus Lt and Lt is already known, because it is Lt is like L0 e raise to minus kt. So, we have BODt is equal to L0 1 minus e raise to minus kt. So, this is there. Now, here the these parameters the k value is highly dependent upon the temperature and as the temperature increases, we know very well that metabolism increases, so, utilization of DO also increases.

So, that is why k is a function of temperature in degree centigrade and its relationship with k20. So, whatever is the value of constant at 20 degrees centigrade, it is related to at any other temperature and theta is one of the constants which is used and remember the t which is given here it has to be in degrees centigrade, so t minus 20.

And this theta value have been reported differently and they may vary with respect to water also, type of water whether it is municipal wastewater, industrial wastewater, etc., but generic values are given here. So, this is theta. So, theta is an empirical constant here and theta value may be 1.135 if temperature is between 4 to 20 degrees centigrade.

It may be 1.056 if the temperature is between 20 to 30 degrees centigrade. The, this is very, very important and this is used many times for various uses and it has a lot of value. Now, we are taking few problems for better understanding, so how to solve these problem.

First problem is like we perform a test and we use a 6 ml of wastewater and it is diluted to 300 ml of distilled water in standard BOD bottle. So, what we have taken? We have taken the volume of sample which has been taken here is 6 ml. So, this is one thing and now, after using the dilution water, so, volume of sample plus volume of diluted water, so, I am just writing diluted seeded water.

And this will always be equal to 300 ml as earlier told. Now initial DO in the bottle is determined to be 8.5 milligram per liter. So, as soon as water and both the things are mixed

together, so, the initial demand was only 8.5 milligrams per liter DO was this. Now, k value

at 20 degrees centigrade is given already given 0.23 per day, now, DO you after 5 days at 20

degrees centigrade is found to be 5 milligram per liter.

So, we have to find out the BOD5. Now, in this case it is not given that whether it is seeded

water or not. So, that means, here there is no seeded water only dilution water without any

oxygen demand was there. So, that means the, it is simple water otherwise the data may have

been given for seeded dilution water also that for seeded dilution waters bottle the initial

value was this and final value was this.

So, if it is not given that this here we are assuming that the seeded dilution water had no

oxygen demand by itself. So, in this case, the BOD5 will be the formula that earlier was

written the BOD5 is equal to DO initial whatever is that DO initial minus DO final. So, like i

and f divided by P.

And that P can further be written. So, we have this formula DO 0 or DO initial minus DO 5

upon Vw into this. So, all the values are kept and we can see here it is 175 milligram per liter

for 5 days. So, this is there. And if it is also many times required to find out that what is, what

will be the ultimate BOD, what will be the maximum BOD that will be required. So, ultimate

BOD remember ultimate BODu it is written or L 0. Both are same.

So, BODu, we can find out the formula with respect to BODt was BODt is equal to L0, 1

minus e raise to minus kt. So, the same thing is written here. And we just find out the BODu

value by dividing and it is 256 milligram per liter.

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Problem

■ The BOD<sub>6</sub> of a wastewater is determined to be 400 mg/L at 20°C. The k value at 20°C is known to be 0.23 per day. What would be BOD<sub>8</sub> value if tests were run at 15°C?

Solution

\begin{bmatrix}
BOD_{t,T} = BOD_{u}(1 - e^{-k_{t}t}) \\
kT = k_{20}(\theta)^{(T-20)} = k_{20}(1.047)^{(T-20)}
\end{bmatrix}

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BOD_{t,T} = k_{20}(\theta) \\
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Then, there is another question which is written here, the BOD6 of a wastewater is determined to be 400 milligram per liter at 20 degrees centigrade. The k value is 20 degrees at 20 degrees centigrade is 0.23, per day, what will be the BOD8 value if the test runs were conducted at 15 degrees centigrade. So, remember, we use the generic formula is written like this, the BOD at for t days is equal to L0, 1 minus e raise to minus kt.

But we can modify this formula, L0 is always equal to BODu, this was highlighted. So, there is no change here. But we can use a trick at what temperature we are writing. So, this formula can be rewritten like this. So, BOD for time t, at what temperature we are finding, then L0 and BODu they do not have any effect with respect to temperature because ultimate demand will be always be the same.

Only rate by which we are reaching that ultimate demand will be different. And similarly for the k term because k term is temperature dependent, we can write k capital T, where T represents the temperature multiplied by time. So, this is there. So, and this is the same formula that is written here.

Now, already for k, we know that k at any temperature T is equal to k20 and theta raise to t minus 20. Now, for this case, we are assuming that theta value to be 1.047. So, we can find out at any temperature, so at 15 degrees centigrade, we can find out what is the value of k. So, from here using this formula we can find out the value at 15 degrees centigrade. So, this will be the first step, we can use, so k15 can be found out using the k20 value.

And so, this already this is 047 raise to 15 minus 20. So, this we can solve and this the value we can find out here. And now BOD 6, we have to find out the BOD 6 at 20 degrees

centigrade is given to be 400 milligram per liter, k20 is given. Now, by using this value and implying this formula we can find out in the first step what is BODu.

So, in the first step this BODu or ultimate BOD has been found out and all the, we are using the same formula which is given by equation 1 and we can find out okay ultimate oxygen demand is this. Now, later on, since we have to find out the BOD at 15 degrees centigrade, we are using this same equation 1 only we have to use the k15.

So, k15, we can find out from here and we can solve, the answer will be this. So, we can see that, we can find out the BOD at any temperature or any number of days if we know the value at some specific temperature and day. And we can use this modified formula always along with the second formula.

So, both in combination can be used for finding out the BOD for at any number of days for any number of days at any temperature. So, with this we end today's lecture and will continue in the next lecture. Thank you very much.