11.3.2 BOD Model

It is generally assumed that the rate at which the oxygen is consumed is directly proportional to the concentration of degradable organic matter remaining at any time. The kinetics of BOD reaction can be formulated in accordance with first order reaction kinetics as:

$$d\,L_t\,/\,d\,t = -\,K\,L_t$$

Where, L_t = amount of first order BOD remaining in wastewater at time t

K = BOD reaction rate constant, $time^{-1}$

Integrating $\int_0^t dL_t = -KL_t\,.dt$

i.e., $\left[\log L_t\right]_0^t = -K\,t$

$Lt\,/\,Lo = e^{-K.t}$ or $10^{-K.t}$

Where Lo or BOD_u at time t = 0, i.e., ultimate first stage BOD initially present in the sample. The relation between K(base e) and K (base 10) is

K(base 10) = K(base e) / 2.303

The amount of BOD remaining at time 't' equals (Figure 11.1)

$Lt = Lo\,(e^{-k.t})$

The amount of BOD that has been exerted (amount of oxygen consumed) at any time t is given by

$BODt = Lo - Lt = Lo\,(1 - e^{-k.t})$

And the five day BOD is equal to

$BOD_5 = Lo - L_5 = Lo\,(1 - e^{-5k})$

For polluted water and wastewater, a typical value of K (base e, 20^oC) is 0.23 per day and K (base 10, 20^oC) is 0.10 per day. These values vary widely for the wastewater in the range from 0.05 to 0.3 per day for base 10 and 0.23 to 0.7 for base e.

The ultimate BOD (Lo) is defined as the maximum BOD exerted by the wastewater. It is difficult to assign exact time to achieve ultimate BOD, and theoretically it takes infinite time. From the practical point of view, it can be said that when the BOD curve is approximately horizontal (Figure 11.1) the ultimate BOD has been achieved. The time required to achieve the ultimate BOD depends upon the characteristics of the wastewater, i.e., chemical composition of the organic matter present in the wastewater and its biodegradable properties and temperature of incubation. At higher temperature for same concentration and nature of organic matter ultimate BOD will be achieved in shorter time as compared to lower

temperatures, where it will require more time. The ultimate BOD best expresses the concentration of degradable organic matter based on the total oxygen required to oxidize it. However, it does not indicate how rapidly oxygen will be depleted in receiving water. Oxygen depletion is related to both the ultimate BOD and the BOD rate constant (K). The ultimate BOD will increase in direct proportion to the concentration of biodegradable organic matter.

The BOD reaction rate constant is dependent on the following:

1. The nature of the waste
2. The ability of the organisms in the system to utilize the waste
3. The temperature

Nature of the waste: Thousands of organic matter exists with different chemical composition in nature. All organic matter will not have same degradation rate. Simple sugar and starches are rapidly degraded and will therefore have a very large BOD rate constant. Cellulose degrades much more slowly and hairs are almost undegradable during BOD test or during biological treatment of wastewater. Other compounds are intermediate degradable between these extremes. For complex waste, like sewage, the BOD rate constant depends upon the relative proportions of the various components. The BOD rate constant is high for the raw sewage (K (base e) = 0.35 -0.7 per day) and low for the treated sewage (K (base e) = 0.12 - 0.23 per day), owing to the fact that, during wastewater treatment the easily degradable organic matter will get more completely removed than the less degradable organics. Hence, in the treated wastewater, relative proportion of the less biodegradable organic matter will be higher, giving lower BOD rate constant.

Ability of organisms to utilize waste: Every microorganism is limited in its ability to utilize organic compounds. Many organic matters can only be utilized by particular group of microorganisms. In natural environment, where the water course is receiving particular organic compound, the microorganisms which have capability to degrade that organic matter will grow in predominant. However, the culture used during BOD test may have very small fraction of the organisms which can degrade that particular organic compounds in the waste. As a result the BOD value, for limited incubation duration, and the rate constant would be lower in the laboratory test than in the natural water where the waste is regularly discharged. Therefore, the BOD test should be conducted with organisms which have been acclimated to

the waste so that the rate constant determined in the laboratory can be compared to that in the river.

Temperature: The biochemical reactions are temperature dependent and the activity of the microorganism increases with the increase in temperature up to certain value, and drop with decrease in temperature. Since, the oxygen utilization in BOD test is caused by microbial metabolism, the rate of utilization is similarly affected by the temperature. The standard temperature at which BOD is determined is usually 20^oC. However, the water temperature may vary from place to place for the same river; hence, the BOD rate constant is adjusted to the temperature of receiving water using following relationship:

$$K_T = K_{20} \theta^{(T-20)}$$

Where

T = temperature of interest, ^oC

K_T = BOD rate constant at the temperature of interest, day^{-1}

K_{20} = BOD rate constant determined at 20^oC, day^{-1}

θ = temperature coefficient. This has a value of 1.056 in general and 1.047 for higher temperature greater than 20^oC. This is because increase in reaction rate is higher when temperature increases from 10 to 20^oC as compared to when temperature is increased from 20 to 30^oC.

Example: 3

The wastewater is being discharged into a river that has a temperature of 15^oC. The BOD rate constant determined in the laboratory for this mixed water is 0.12 per day. What fraction of maximum oxygen consumption will occur in first four days?

Solution

Determine the BOD rate constant at the river water temperature:

$$K_{15} = K_{20} (1.056)^{(T-20)}$$
$$= 0.12 (1.056)^{(15-20)}$$
$$= 0.091 \text{ per day}$$

Using this value of K to find the fraction of maximum oxygen consumption in four days:

$$BOD_4 = Lo (1 - e^{-0.091 \times 4})$$

Therefore, $BOD_4 / Lo = 0.305$

Example: 4

The dissolved oxygen in an unseeded sample of diluted wastewater having an initial DO of 9.0 mg/L is measured to be 3.0 mg/L after 5 days. The dilution fraction is 0.03 and reaction rate constant k = 0.22 day^{-1}. Calculate a) 5 day BOD of the waste, b) ultimate carbonaceous BOD, and c) What would be remaining oxygen demand after 5 days?

Solution

a) Oxygen demand for first 5 days

$BOD_5 = (DO_i – Do_f) / p$ = (9.0 – 3.0) / 0.03 = 200 mg/L

b) Ultimate BOD

$BOD_u = Lo = BODt / (1 – e^{-kt}) = 200 / (1 – e^{-0.22 \times 5}) = 300$ mg/L

c) After 5 days, 200 mg/L of oxygen demand out of total 300 mg/L would be satisfied. Hence, the remaining oxygen demand would be 300 – 200 = 100 mg/L

Example: 5

Determine ultimate BOD for a wastewater having 5 day BOD at 20°C as 160 mg/L. Assume reaction rate constant as 0.2 per day (base 10).

Solution

$$BOD_5 = Lo (1 – 10^{-k.t})$$
$$160 = Lo (1 – 10^{-5 \times 0.2})$$

Therefore, Lo = 231.7 mg/L ~ 232 mg/L

Example: 6

The BOD of a sewage incubated for one day at 30°C has been found to be 100 mg/L. What will be the five day 20°C BOD? Assume K = 0.12 (base 10) at 20°C, and θ = 1.056

Solution:

BOD at 30°C = 100 mg/L

$K_{20} = 0.12$

Now $K_{30} = K_{20} \theta^{(T-20)}$

$K_{30} = 0.12 (1.056)^{30-20} = 0.207$ per day

$BOD_t = Lo (1 – 10^{-kt})$

$100 = Lo (1 – 10^{-0.207 \times 1})$

Lo = 263.8 mg/L

This is ulimate BOD, the value of which is independent of incubation temperature.

Now BOD_5 at 20^oC can be calculated as:

BOD_5 at 20^oC = Lo $(1 - 10^{-kt}) = 263.8 (1 - 10^{-0.12 \times 5}) = 197.5$ mg/L

Example: 7

Determine the 1 day BOD and ultimate first stage BOD for a wastewater whose 5 day 20^oC BOD is 200 mg/L. The reaction rate constant k (base e) = 0.23 per day.

Solution

Ultimate BOD

BOD_u = Lo = $BODt$ / $(1 - e^{-kt}) = 200 / (1 - e^{-0.23 \times 5}) = 293$ mg/L

Therefore, one day BOD

Y_1 = Lo – L1 = Lo $(1 - e^{-kt}) = 293 (1 - e^{-0.23 \times 1}) = 60$ mg/L
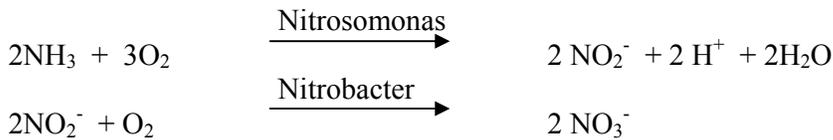
11.3.3 Interpretation of the BOD test Result

Following factors must be considered in the interpretation of the BOD for industrial wastewaters:

1. The seed is acclimated to the wastewater and lag period required for acclimation is eliminated.

2. The rate constant should be established based on long term BOD tests on both wastewater and treated effluents. The rate constant for untreated and treated wastewater is not same for many wastewaters. The rate constant value is higher for untreated wastewater and lower for treated wastewater. For example, for raw sewage rate constant is about 0.15 to 0.3 and that for treated sewage it is around 0.05 to 0.15 (base 10). Hence, direct comparison of BOD may not be valid. The value of K (base e) for raw sewage varies in the range 0.35 to 0.7 and that for treated sewage it will be 0.12 to 0.23.

3. In case of acidic waste, all samples must be neutralized before incubation.

4. When organic matter is present in suspended form, interpretation of the test result is difficult due to lag time involved in hydrolysis of organic matter before actual oxidation starts during BOD test.

11.3.4 Nitrification in BOD Test

Non-carbonaceous matter, such as ammonia is produced during the hydrolysis of proteins. In addition, when the living things die, excreta waste, and nitrogen organic compounds, the nitrogen tied to organic molecule is converted to ammonia by bacterial and fungal action. Under aerobic conditions, this ammonia will be converted to nitrate, called as nitrification as per the reactions given below:

$$2NH_3 + 3O_2 \xrightarrow{\text{Nitrosomonas}} 2\,NO_2^- + 2\,H^+ + 2H_2O$$

$$2NO_2^- + O_2 \xrightarrow{\text{Nitrobacter}} 2\,NO_3^-$$

Hence, the organic matter containing nitrogen will have oxygen requirement for nitrification. The oxygen demand associated with the oxidation of ammonia to nitrate is called the nitrogenous BOD. Due to low growth rate of nitrifying bacteria, this BOD demand normally occurs from 6 to 10 days (Figure 11.2). This is one of the reasons to use incubation period of 5 days for BOD determination to eliminate oxygen demand for nitrification and to find out only carbonaceous oxygen demand. Incidentally, the five day period was chosen for the test because the Themes River requires five days from its origin to join sea, and if oxygen demand for these five days is determined and satisfied the river water quality can be protected.
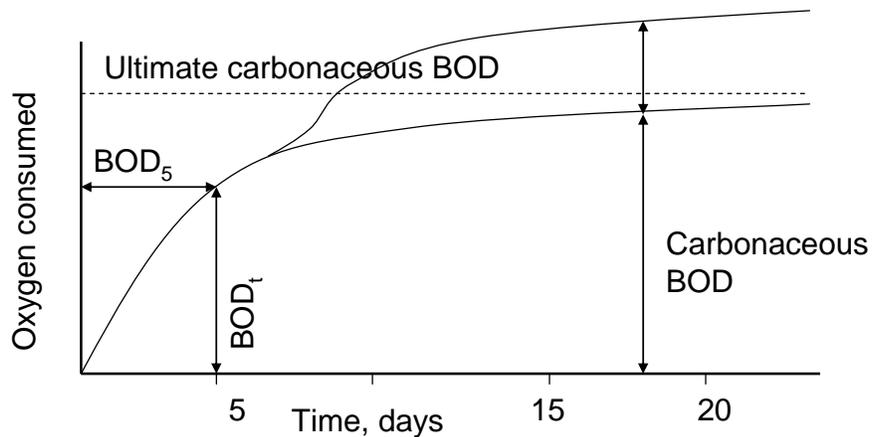

Figure 11.2 Nitrification during BOD test

11.3.5 Other Measures of Oxygen Demand

Chemical Oxygen Demand (COD)

During COD determination total organic content of the waste is oxidized by dichromate in acid solution.

- In this test to determine the oxygen requirement of the wastewater, strong oxidizing agent 'potassium dichromate' is used.

- Acidic environment is provided to accelerate the reactions by addition of sulphuric acid.

- The reflux flasks (closed reflux vials), used for the test, are heated to 150^oC for two hours with silver sulphate as catalyst. When silver sulphate catalyst is used, the recovery of most organic compounds is greater than 92 percent.

- COD test measures virtually all oxidizable organic compounds whether biodegradable or not, except some aromatic compounds which resists dichromate oxidation.

- The COD is proportional to BOD only for readily assimilable organic matter in dissolved form e.g. sugars.

- No correlation between BOD and COD exists when:
    - Organic matter is present in suspended form, under such situation filtered samples should be used.
    - Complex wastewater containing refractory substances.

- For readily biodegradable waste, such as dairy COD = BODu/0.92

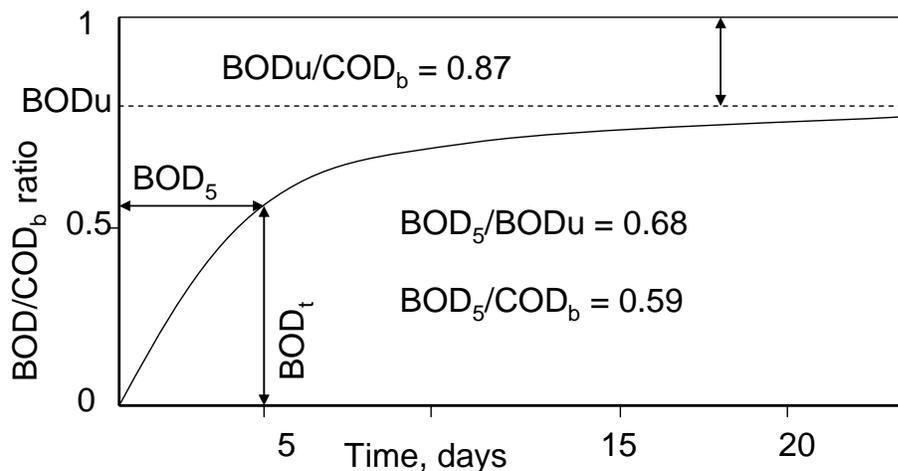The correlation between BOD and COD for sewage is presented in the Figure 11.3.

Figure 11.3 Correlation between BOD and COD for sewage at 20^oC incubation and k = 0.23 per day.

The COD is faster determination but does not give idea about the nature of organic matter whether biodegradable or biorefractory organic matter. Hence, determination of BOD is necessary for the wastewater to know biodegradable organic matter fraction. The BOD is not very useful test for routine plant control due to long incubation period required, hence

requiring long time (5 days) to obtain results. Thus, it is important to develop correlation between BOD and COD (or TOC), so that COD (or TOC) can be used as a parameter for routine analysis and control of the treatment plant. Once COD values are known, the BOD can be estimated using correlation. The test results are more reproducible for COD.

Theoretical Oxygen Demand (ThOD)

Theoretical oxygen demand for the wastewater is calculated as oxygen required for oxidizing the organic matter to end products. For example, for glucose, the theoretical oxygen demand can be worked out as below:

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$$

$$ThOD = (6\ M_{o2}) / (M_{C_6H_{12}O_6}) = (6 \times 16 \times 2) / (12 \times 6 + 1 \times 12 + 6 \times 16) = 1.07$$

For most of the organic compounds (except aromatics) COD is equal to ThOD.

TOC is related to COD through carbon-oxygen balance.

$$COD/TOC = (6\ M_{o2}) / (M_C) = 2.66$$

Depending on the organic matter in question COD/TOC ratio may vary from zero (for organic matter resistant to dichromate oxidation) to 5.33 for methane (most reduced organic compound).

Since, organic content undergoes changes during biological oxidation, COD/TOC and BOD/TOC, BOD/COD values will change during treatment.

Questions

1. Explain objectives of conducting BOD test.

2. Explain BOD reaction rate constant and parameters on which it is dependent.

3. Draw a curve for BOD exerted and remaining with respect to time for organic wastewater and derive mathematical expression for both.

4. Why only about 60% BOD is satisfied during BOD test determination, whereas during actual wastewater treatment in aerobic process more than 90% of BOD can be removed during 5 to 6 hours of retention time in biological reactor?

5. BOD of a sewage incubated for 3 days at $27^{o}C$ was measured 110 mg/L. Calculate BOD5 at $20^{o}C$. Consider k = 0.23 per day (base e) and temperature coefficient = 1.047.

6. Describe nitrification during BOD test.

7. Explain correlation between BOD, BODu and COD for sewage.