17. WATER QUALITY AND ESTIMATION OF ORGANIC CONTENT

17.1 Surface Water Quality: Rivers and Streams

Surface water is highly susceptible to contamination due to sewage, industrial waste discharge, and agricultural run-off apart from the recreational activities. The objective of the water quality management is to control the discharge of pollutants so that water quality is not degraded to an unacceptable extent below the acceptable level. To achieve this quantitative analysis of pollutants is must. It is necessary to understand the background water quality which would be present without human interventions, and decide the levels of pollutants acceptable for intended uses of the water. The impact of different pollutants joining the water body should be understood well for this purpose. The impact of the pollution on a river depends both on the nature of the pollutant and the characteristics of the individual river. Some of the important characteristics include velocity of water flowing in the river, depth of flow, type of river bottom, and surrounding vegetation. The other factors include, climate of the region, geological characteristics of the watershed, land used pattern, and aquatic life in the rivers. All these parameters must be considered in water quality management in the river.

It is understood that the water quality in the rivers will not remain same throughout the stretch of river i.e. from origin to the point where it meet to the sea. The water quality is best near the origin of the river and goes on deteriorating as the river flows and goes on assimilating the pollutant discharged in it. Proper management is necessary if the water quality is to remain usable for intended purpose. Oxygen demanding wastes and nutrients are among the common pollutant having profound impact on almost all types of rivers, hence they deserve special emphasis.

17.2 Effect of Oxygen Demanding Wastes on Rivers

Depletion of dissolved oxygen is a major problem due discharge of oxygen demanding organic or inorganic pollutant in the surface water. This poses threat to higher forms of aquatic life, if the concentration of oxygen falls below a critical point. To quantify how much oxygen will be depleted, it is necessary to know the quantity of oxygen demanding waste and how much oxygen will be required to degrade the waste. Although, oxygen is getting depleted for the degradation of organic matter, it is continuously being replenished from the atmosphere and through photosynthesis. The net concentration of oxygen in the water body is determined by the relative rates of these competing processes i.e. deoxygenation and reoxygenation.

17.3 Estimation of organic content of the wastewater

The organic matter present in the water body can be analyzed in laboratory by determining Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), and by determination of Total Organic Carbon (TOC). These test procedures and relevance of these tests are discussed below.

17.3.1 Biochemical Oxygen Demand (BOD)

The BOD can be defined as the oxygen required for biochemical oxidation of organic matter present in the water under aerobic conditions. This test is based on the premise that all the biodegradable organic matter contained in a water sample will be oxidized to CO_2 and H_2O by microorganisms using molecular oxygen. For example, the general overall oxidation reaction for glucose is

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

Thus, the theoretical oxygen demand would then be:

Oxygen demand = (Gram of oxygen used) / (Gram of carbon oxidized)

= 192 / 72 = 2.67 g/g of carbon

The actual BOD will be less than theoretical oxygen demand due to incorporation of some of the carbon into newly synthesized bacterial cells. The test is performed under the conditions similar to those in actual natural water to measure indirectly the amount of biodegradable organic matter present. A water sample is inoculated with bacteria (1 to 2 mL of sewage per liter) that consume the biodegradable organic matter to obtain energy for their life processes. The organisms also utilizes oxygen in the process of consuming the organic matter, the process is called as ‘aerobic’ decomposition. This oxygen consumption is measured; more is the organic matter concentration more is the amount of oxygen utilized. Thus, the BOD test is the indirect measurement of organic matter in terms of the oxygen requirement to convert them into stable end product. Although, not all organic matter is biodegradable within the stipulated incubation period, and the actual test procedure lack in precision due to different inoculum seed and many fold dilution required, it is still the most widely used method of quantifying organic matter because of the direct conceptual relationship between BOD and oxygen depletion in receiving waters.

The BOD test is performed for the following:

- To determine quantity of oxygen required for biochemical stabilization of organic matter.
- To determine suitability of biological treatment method, depending on COD/BOD ratio, and sizing the treatment units. For COD/BOD ratio less than 2 the wastewater is most suitable for biological treatment; for COD/BOD ratio between 2 to 6 acclimation of the inoculum is required for effective biological treatment; and for higher COD/BOD ratio biological treatment of such wastewater may not be suitable option.
- To monitor efficiency of the process.
- To determine compliance with wastewater discharge permits.

During the BOD test the organic matter will be converted into stable end product such as CO_2, sulphate (SO_4), orthophosphate (PO_4) and nitrate (NO_3).

The simple representation of carbonaceous BOD can be explained as below:

$$\text{Organic matter} + O_2 \xrightarrow{\text{microorganisms}} CO_2 + H_2O + \text{New Cells} + \text{Stable products}$$

This reaction continues till sufficient DO is available in the water. When DO is not available condition becomes anaerobic decomposition (fermentative reduction). The reaction under anaerobic conditions is as under:

$$\text{Organic matter} \xrightarrow{\text{microorganisms}} CO_2 + CH_4 + \text{New Cells} + \text{Other products } (NH_3, H_2S)$$

While biological oxidation of organic matter three distinct activities occur.

If sufficient O_2 is present, aerobic biological decomposition of an organic waste will continue until all of the waste is consumed.

Oxidation

$$COHNS + O_2 + \text{bacteria} \rightarrow CO_2 + H_2O + NH_3 + \text{other end products}$$

Portion of organic matter from waste is oxidized to end products to obtain energy for cell maintenance and the synthesis of new cell tissue.

Synthesis

$$COHNS + O_2 + \text{bacteria} + \text{energy} \rightarrow C_5H_7NO_2 \text{ (new cell tissue)}.$$

Simultaneously, some of the organic matter is converted to new cell tissue using part of the energy released during oxidation.

Endogenous respiration

$C_5H_7NO_2 + 5O_2 \longrightarrow 5CO_2 + NH_3 + 2H_2O$

When organic matter from waste is over, the new cells begin to consume their own cell tissue to obtain energy for cell maintenance.

BOD Test

Biochemical oxidation is slow process and theoretically takes an infinite time to go to completion i.e. complete oxidation of organic matter. During the first few days the rate of oxygen depletion is rapid because of the high concentration of organic matter present. As the concentration of organic matter decreases, so does the rate of oxygen consumption. Also initially concentration of easily biodegradable organic matter will be more and as the time proceeds fraction of this component will deplete faster as compared to total organic matter reduction. Hence, during initial days the rate of BOD exerted will be more as compared to later days. During the last part of the BOD curve, oxygen consumption is mostly associated with the decay of the bacteria that grew during the early part of the test. The oxygen consumption typically follows the pattern as shown in Figure 17.1. For wastewater like sewage, within 20 day period, the oxidation of carbonaceous organic matter is about 95 to 99% complete, and in the first five days, the period used for BOD determination, 60 to 70% oxidation is complete. The 20 ^oC temperature used is an average temperature value typically for slow moving streams in temperate climate. Different results would be obtained at different temperatures because biochemical reaction rates are temperature dependent.

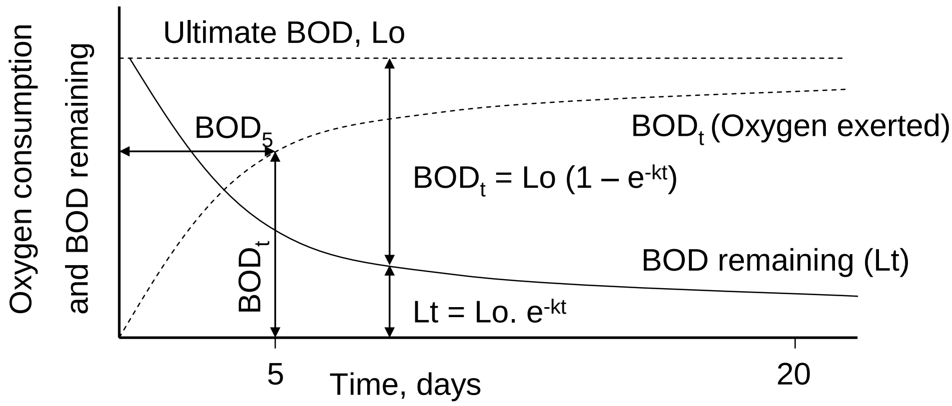

Figure 17.1 Variation in DO profile during BOD test with duration of incubation

The biochemical oxygen demand is represented as BOD_5 20^oC, which indicates the total amount of oxygen consumed for biochemical oxidation of organic matter for first five days at

20^oC incubation temperature. Under Indian conditions, the BOD values are acceptable for 3 days incubation at $27\,^oC$ temperature.

Since, the saturation value of DO for water at 20^oC is only 9.1 mg/L, it is usually necessary to dilute the samples to keep final DO level, at the end of incubation period, above 1.5 mg/L. Hence, according to BOD values expected for that wastewater appropriate dilution should be carried out. Thus, the actual BOD of the unseeded sample can be worked out as

$$\text{The 5 day BOD of sample} = \frac{DO_i - DO_f}{p}$$

Where, DO_i and DO_f are initial and final DO of diluted wastewater sample

$$p \text{ is the dilution fraction} = \frac{\text{Volume of wastewater}}{\text{Volume of wastewater + volume dilution water}}$$

The total volume of the BOD bottle used for test is usually 300 mL. The dilution water (distilled water) is aerated for sufficient time to correct DO close to the saturation value. Nutrients and buffer solutions are added to the dilution water to provide nutrient for bacterial growth and maintain pH near neutral. Sufficient amount of seed is added to the BOD bottle to ensure adequate concentration of bacterial population to carry out the biodegradation. Usually 1 to 2 mL of sewage per liter is considered as sufficient to act as a seed. In such case it is necessary to subtract the oxygen demand of the seed from the mixed sample, because organic matter present in this 1 to 2 mL of seed will also exert oxygen demand. Thus, the BOD of the wastewater with seeded sample can be worked out as below. The DO drop in blank is multiplied by (1- *p*) because this volume of blank is only present in the sample.

$$BOD_5 = \frac{(DO_i - DO_f) - (B_i - B_f)(1 - p)}{p}$$

Where,

DO_i an DO_f = DO of mixture, initial and final values, respectively,

B_i and B_f = DO of blank, initial and final values, respectively,

p = V_w/V_m = Volume of wastewater in mixture / Total volume of mixture.

Example:1

1. Dilution water requirement:

A wastewater is expected to have BOD_5 of about 200 mg/L. The initial DO of dilution water is 8.0 mg/L. Calculate the dilution requirement for BOD determination.

Solution

BOD = 200 mg/L; DOi = 8.0 mg/L,

Minimum DO that should be left after five days of incubation is 1.5 – 2.0 mg/L,

Say final DO = 2.0 mg/L

Hence, dilution required = 200 / (8.0 – 2.0) = 33.33 say 35 to 40 times.

Comments: To have accurate test result, the total DO drop during five days incubation should be 2.0 mg/L.

Example: 2. BOD determination

A test bottle containing only seeded dilution water has its DO level drop by 1.0 mg/L in a 5-day incubation. A 300 mL BOD bottle filled with 10 mL of wastewater and the rest seeded dilution water experiences a DO drop of 6.2 mg/L in the same time period. What would be five day BOD of the wastewater?

Solution:

Dilution factor p = 10/300

Therefore, BOD_5 = [6.2 – 1.0 (1 – (10/300))] / (10/300) = 157 mg/L

Example: A BOD bottle total 300ml capacity contains 15ml of waste sample and remaining dilution water. The initial DO of diluted sample was 8.8 mg/l and final DO after 5 days was 1.9mg/l. The corresponding initial and final DO of seeded dilution water were 9.1 and 7.9, resp. What is 5 day BOD of the wastewater sample?

BOD, mg/l= $\frac{(D_1-D_2)-(B_1-B_2)f}{P}$

f = $\frac{300-15}{300} = 0.95$

P=$\frac{15}{300}$=0.05

BOD_5=$\frac{(8.8-1.9)-(9.1-7.9)\times 0.95}{0.05} = 115.2\text{ mg/l}$

17.3.2 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 = First order BOD reaction rate constant, $time^{-1}$

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

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

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

Where Lo or BOD_u at time t = 0, is the 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^{o}C) is 0.23 per day and K (base 10, 20^{o}C) is 0.10 per day. These values vary widely for the wastewater in the range from 0.05 to 0.3 per day for K (base 10) and 0.23 to 0.7 for K (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 the 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 matters exist 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 high value of 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 biodegradable organic matter will get more completely removed than the less biodegradable 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 environment 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°C. 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, °C

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

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

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

Example: 3

The treated wastewater is being discharged into a river that has a temperature of 15°C. 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:

$$BOD_4 = Lo\,(1 - e^{-0.091x4})$$

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 = 177.8 mg/L ~ 178 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

$K_{20} = 0.12$ per day

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 ultimate BOD, the value of which is independent of incubation temperature.

Now BOD_5 at 20°C can be calculated as:

BOD_5 at 20°C $= Lo\ (1 - 10^{-kt}) = 263.8\ (1 - 10^{-0.12 \times 5}) = 197.5$ mg/L = 198 mg/L

Example: 7

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

Solution

Ultimate BOD

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

Therefore, one day BOD

$Y_1 = Lo – L1 = Lo (1 – e^{-kt}) = 293 (1 – e^{- 0.23 x 1}) = 60$ mg/L

Example: Determine the 1- day BOD and ultimate first order BOD for a wastewater whose BOD5, 20°C is 200mg/l. the reaction constant $k_{(base)}= 0.23\ d^{-1}$. what would have been BOD5 at 27°C? What will be BOD at 27°C?

Solution

1. Ultimate carbonaceous BOD

BOD_5= BODu (1- $e^{-k.t}$)

200= BODu (1-$e^{-5\times0.23}$)

BODu= 293mg/l

2. 1- Day BOD

   BOD_1=293 (1- $e^{-1\times0.23}$) =60.1 mg/l.

3. BOD_5 at 27°C

   $K_{27}= K_{20}\ \theta^{(T-20)}= 0.23(1.047)^{(27-20)} = 0.317$

   BOD_5 at 27°C= 293 (1- $e^{-0.317\times5}$) = 233 mg/l

   BOD_3= 293(1-$e^{-0.317\times5}$) =233 mg/l

17.3.3 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.

The BOD reaction rate coefficient affected significantly by the size of the particles in wastewater. Hence treatment of wastewater can be affected by modifying the particle size distribution.

Table 17.1 Particle size of biodegradable particle and reaction rate

Fraction	**Size range,µm**	**K (base 10), d^{-1}**
settleable	>100	0.08
super colloidal	1-100	0.09
colloidal	0.1 to 1.0	0.22
soluble	<0.1	0.39

Limitation in BOD test:

Test suffers from several deficiencies.

- No stoichiometric validity, i.e. 5 days does not correspond to consumption of all organic matter.
- Five day is used since most of the river meets sea in 4.8 day in England.
- Potential for nitrification to occur.
- The general limits on the precision of the test and test results are not highly reproducible.
- No correlation exists when organic matter is present in suspended form.

Despite its limitations, use of BOD as regulatory parameter is acceptable because the test represents the potential oxygen depletion effect the wastewater may have on the receiving water body.

17.3.4 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 17.2). 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.

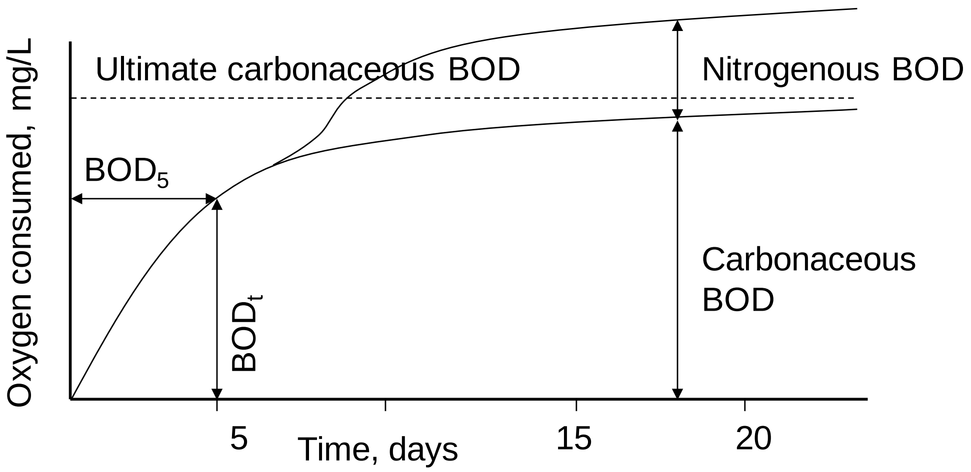

Figure 17.2 Nitrification during BOD test

Overall conversion of ammonia to nitrate

$NH_3 + 2O_2 \longrightarrow HNO_3 + H_2O$

- Oxygen required for conversion of ammonia to nitrate is known as nitrogenous oxygen demand.
- Typically it may occur on 5 to 8 days; however, if sufficient nitrifying organisms are present it may start early.

Oxygen and alkalinity requirement for nitrification

O_2 requirement

$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O$

O_2 required = 64/14 = 4.57 mg O_2/mg N

Alkalinity required = 100/14 = 7.14 mg as $CaCO_3$/mg. N

Comment: Due to high ammonia in septic tank effluent, nitrification may not be possible completely because of insufficient alkalinity.

17.3.5 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 (or closed reflux vials), used for the test, are heated to 150^{o}C 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 soluble 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 17.3 (Haandel and Lettinga, 1994).

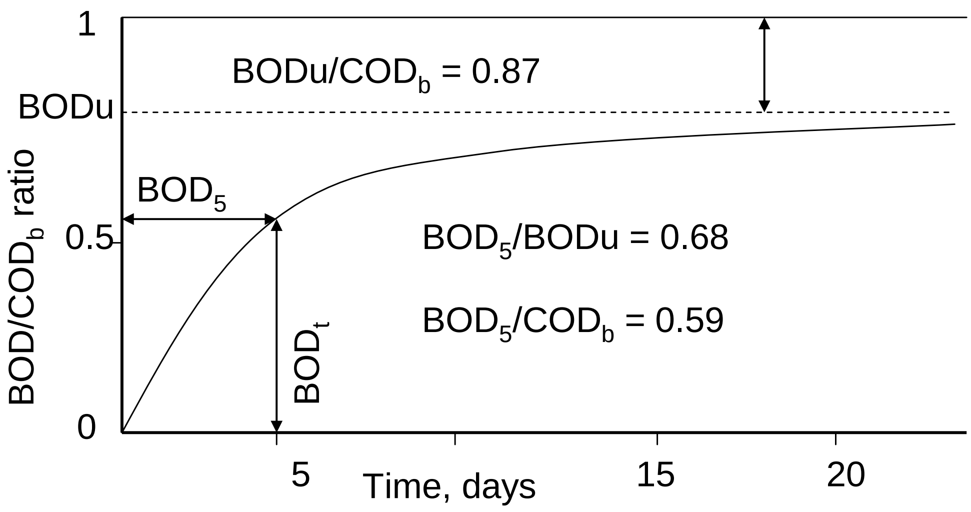

Figure 17.3 Correlation between BOD and COD for sewage at 20^{o}C incubation and k = 0.23 per day.

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 resisting dichromate oxidation) 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.

Interrelationships of BOD, COD, and TOC

Comparison of ratios of various parameters used to characterize wastewater

Type of wastewater	BOD_5/COD	BOD_5/TOC
Untreated	0.3-0.8	1.2-2.0
After primary sedimentation	0.4-0.6	0.8-1.2
Final effluent	0.1-0.3	0.2-0.5

$BOD_5/COD > 0.5$ easily biodegradable; $BOD_5/COD > 0.3$ acclimated seed required

Example: determine BOD/COD, BOD_5/TOC ratios for $C_5H_7NO_2$ consider BOD first order reaction rate constant 0.23 d^{-1}(base e).

Solution:

1) Determine COD

$C_5H_7NO_2 + 5O_2 \longrightarrow 5CO_2 + NH_3 + 2H_2O$

2) Determine BOD_5

$BOD_5/BODu$

$= (1- e^{-k.t})=(1- e^{-0.23\times5}) = 0.68$

$BOD_5 = 0.68 \times 1.42$ mg O_2/mg $C_5H_7NO_2$ (considering BODu = COD)

= 0.97 mg BOD_5/mg $C_5H_7NO_2$

3) Determine TOC of the compound

$TOC = \frac{12\times5}{113} = 0.53$ mg TOC/mg $C_5H_7NO_2$

$\frac{BOD_5}{COD} = 0.97/1.42 = 0.68$

$\frac{BOD_5}{TOC} = \frac{0.68\times1.42}{0.53} = 1.82$

$\frac{TOC}{COD} = \frac{0.53}{1.42} = 0.37$

Example: Wastewater contains the following:

150mg/L ethylene glycol ($C_2H_6O_2$)

100 mg/l phenol (C_6H_6O)

40 mg/L sulphide (S^{2-})

125 mg/L ethylene diamine hydrate (essentially non biodegradable)

a) Compute the COD and TOC

b) Compute the BOD_5 if the K_{10} is 0.2/day

c) After treatment, the BOD_5 is 25 mg/L. estimate the COD (K_{10} = 0.10/day), consider BOD_u = 0.92 COD for wastewater.

Solution:

a) Computation of COD

Ethylene glycol

$C_2H_6O_2 + 2.5\ O_2 \longrightarrow 2CO_2 + 3H_2O$ (12×2+1×6+32)=62

$COD = \frac{2.5 \times 32}{62} \times 150\ \frac{mg}{L} = 194\ mg/L$

Phenol

$C_6H_6O + 7O_2 \longrightarrow 6CO_2 + 3H_2O$ (12×6+1×6+16)=94

$COD = \frac{7 \times 32}{94} \times 100\ \frac{mg}{L} = 238\ mg/L$

Ethylene diamine hydrate

$C_2H_{10}N_2O + 2.5O_2 \longrightarrow 2CO_2 + 2H_2O + 2NH_3$

$COD = \frac{2.5 \times 32}{78} \times 125\ \frac{mg}{L} = 128\ mg/L$ (2×12+10+14×2+16)=78

Sulfide $S^{2-} + 2O_2 \longrightarrow SO_4^{2-}$

$COD = \frac{2 \times 32}{32} \times 40\ \frac{mg}{L} = 80\ mg/L$

Total COD = 194 + 238 + 128 + 80 = 640 mg/L

b) Computation of TOC of glycol

$$\frac{2 \times 12}{62} \times 150\ \frac{mg}{L} = 58\ mg/L$$

Phenol $\frac{12 \times 6}{94} \times 100\ \frac{mg}{L} = 77\ mg/L$

Ethylene diamine hydrate

$$\frac{2 \times 12}{78} \times 125\ \frac{mg}{L} = 39\ mg/L$$

Total TOC is 58 + 77 + 39 = 174 mg/L.

c) The ultimate BOD can be estimated as BODu = 0.92COD

(194+238+80)× 0.92 mg/L = 471 mg/L

$BOD_5 = BOD_u\ (1\text{-}10^{-kt})$

$= 471(1\text{-}10^{-0.2 \times 5})$

= 424 mg/L

d) The BODu of the effluent is

$$\frac{25\ mg/L}{1-10^{-5\times0.1}} = 25/0.7 = 36 \text{ mg/L}$$

The COD is 36/0.92 = 39 mg/L

Effluent COD = 128 mg/L+ 39 mg/L+ residual byproducts.

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.
8. Describe the limitations of BOD test, how particle size of biodegradable particle will affect the rate of reaction?

9.

Answers:

Q 5: Lo = 179 mg/; BOD_5 at 20^{o}C = 122 mg/L