Course Number : CE 332
Course Name : Environmental Engineering Lab
Course Credit : 1.50

Experiment No. 10
Determination of Biochemical Oxygen Demand (BOD)

INTRODUCTION

When biodegradable organic matter/waste (the most common category of pollutant affecting surface water) is discharged into a water body, micro-organisms (especially bacteria), fed on the wastes, breaking it down into simpler organic and inorganic substances. When this decomposition takes place in an aerobic environment (i.e. in presence of oxygen; Eq. 1), the process is termed as "Aerobic Decomposition", which produce non-objectionable stable products (e.g., CO_2, SO_4, PO_4, NO_3) and the process draws down the dissolved oxygen (DO) content of water.

$$\text{Organic matter} + O_2 \xrightarrow{\textit{Aerobic bacteria}} CO_2 + H_2O + \text{New cells} + \text{Stable products} \qquad (1)$$

When insufficient oxygen is available or when oxygen is exhausted by the aerobic decomposition of wastes, different set of microorganisms carry out the decomposition anaerobically (Eq. 2) producing highly objectionable products including H_2S, NH_3 and CH_4.

$$\text{Organic matter} \xrightarrow{\textit{Anaerobic bacteria}} CO_2 + CH_4 + \text{New cells} + \text{Unstable products} \qquad (2)$$

The amount of oxygen required by microorganisms to oxidize organic wastes aerobically called "Biochemical Oxygen Demand" (BOD). BOD may have various units, but most often it is expressed in mg of oxygen required per liter of water/ wastewater (mg/L). The total amount of oxygen that will be required for bio-degradation is an important measure of the impact that a given stream would have on the receiving water body.

Dissolved oxygen is the most commonly used indicator of the general health of a surface water body. If DO goes below 4 to 5 mg/L (due to decomposition of organic wastes), forms of life that can survive begin to be reduced. When anaerobic condition exists, higher life forms are killed or driven off. Noxious (unhealthy) condition, including floating sludge, bubbling, odorous gases, and slimy fungus growth prevails.

THEORY

The biochemical oxygen demand (BOD) determination is an empirical test, in which standardized procedures are used to determine the oxygen requirements of wastewater, effluents and polluted waters. It has become a standard practice to simply measure and report the oxygen

demand over a 5-day period, realizing that the ultimate oxygen demand (for complete degradation of organic matter) is considerably higher (and would take a much longer time to determine in the laboratory).

The 5-day BOD or BOD_5 is the amount of oxygen consumed by micro-organisms during the first 5-days of degradation. In its simplest form, BOD_5 test would involve putting a sample of water/ wastewater into a stoppered bottle, measuring the dissolved oxygen (DO) of the sample at the beginning of the test and again at the end of five days. The difference in DO would be the BOD_5 of the water/wastewater. Light must be kept out of the bottle to keep algae from adding oxygen by photosynthesis and the stopper is used to keep air from replenishing DO from outside.

To standardize the procedure, the test is run at a fixed temperature of 20°C. Since the oxygen demand of typical is several hundred mg/L and since the saturated value of DO of water at 20°C is only 9.1 mg/L, it is usually necessary to dilute the sample to keep the final DO above zero. If during the five days of experiment, DO drops to zero, then the test is invalid since more oxygen would have been removed had more been available.

The five-day BOD of a diluted sample is given by

$$BOD_5 = [DO_i - DO_f] \times DF \qquad (3)$$

where, DF = Dilution Factor = (Vol. of wastewater + dilution water)/ (Vol. of wastewater)

In some cases, it becomes necessary to seed the dilution water with microorganisms to ensure that there is an adequate bacterial population to carry out the biodegradation. In such cases, two sets of BOD bottles must be prepared, one for just the seeded dilution water (called the 'blank') and the other for the mixture of wastewater and dilution water. The change in DO for both is measured. The oxygen demand of the wastewater (BOD_w) is then determined from the following relationship:

$$BOD_m V_m = BOD_w V_w + BOD_d V_d \qquad (4)$$

where,
BOD_m = BOD of the mixture of wastewater and dilution water
BOD_d = BOD of the dilution water alone
V_w = Volume of wastewater
V_d = Volume of dilution water
V_m = Volume of the mixture = $V_w + V_d$

Dilution water and seed:

A wide variety of dilution waters have been used for BOD work. Natural surface waters have been used, but they suffer from a number of disadvantages including variable BOD, variable micro-organism population and variable mineral content. Tap water has also been used, but it also suffers from many of the limitations of the surface water plus the possibility of toxicity from chlorine residuals.
Synthetic dilution water prepared by adding different salts to distilled water has been found to be the most ideal for use as dilution water. The pH of the dilution water should be between 6.5 to

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8.5. K, Na and Mg salts are added to distilled water to give buffering capacity and proper osmotic pressure. Ferric chloride, magnesium sulfate and ammonium chloride are added to supply the requirements for iron, sulfur and nitrogen. The phosphate buffer provides phosphorus that may be needed. The dilution water is usually well aerated to raise its DO level before mixing with wastewater.

A wide variety of materials have been used for "seeding" purpose. Experience has shown that domestic wastewater, particularly from combined sewer systems, provide a well-balanced population of mixed micro-organisms. Usually 2 ml of wastewater per liter of dilutes wastewater is sufficient. Some river waters are also satisfactory, but care must be taken to avoid using waters containing algae or nitrifying bacteria in significant amount. The dilution water should always be "seeded" to ensure a uniform population of micro-organisms.

Modeling of BOD:

It is often assumed that the rate of decomposition of organic waste is proportional to the amount of waste available. If L_t represents the amount of oxygen demand left after time t, then, assuming a first order reaction, we can write,

$$\frac{dL_t}{L_t} = -kL_t \tag{5}$$

where, k = BOD reaction rate constant ($time^{-1}$)

Integrating Eq.5, we get, $L_t = L_0 e^{-kt}$ (6)

where, L_0 = ultimate carbonaceous oxygen demand, which is the total amount of oxygen required by micro-organisms to oxidize the carbonaceous portion of the waste.

Now, $L_0 = BOD_t + L_t'$ (7)

And combining Eq. (6) and Eq. (7), we get

$$BOD_t = L_0 (1-e^{-kt}) \tag{8}$$

Figure 1(a) and 1(b) show the graphical representations of Eq. (6) and Eq. (8) respectively.

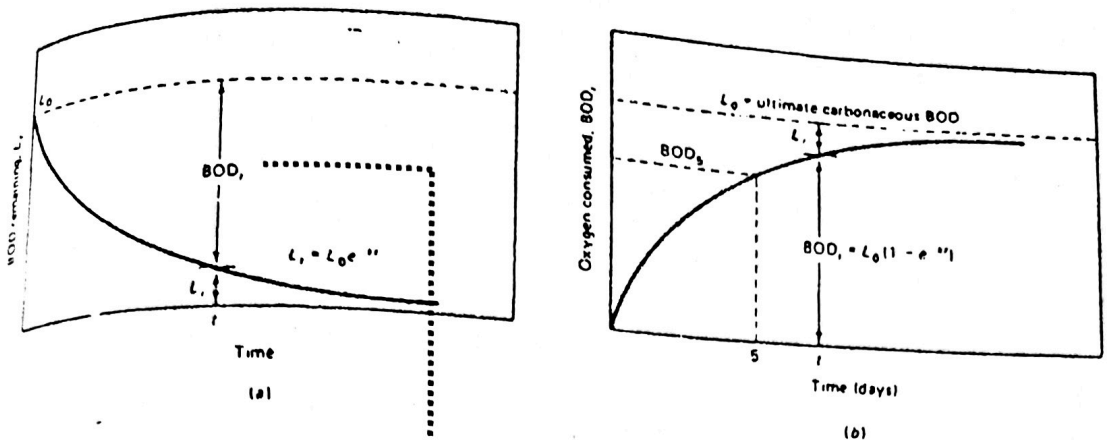


Figure 1. Idealized carbonaceous oxygen demand: (a) the BOD remaining as a function of time, and (b) the oxygen consumed or the biochemical oxygen demand as a function of time.

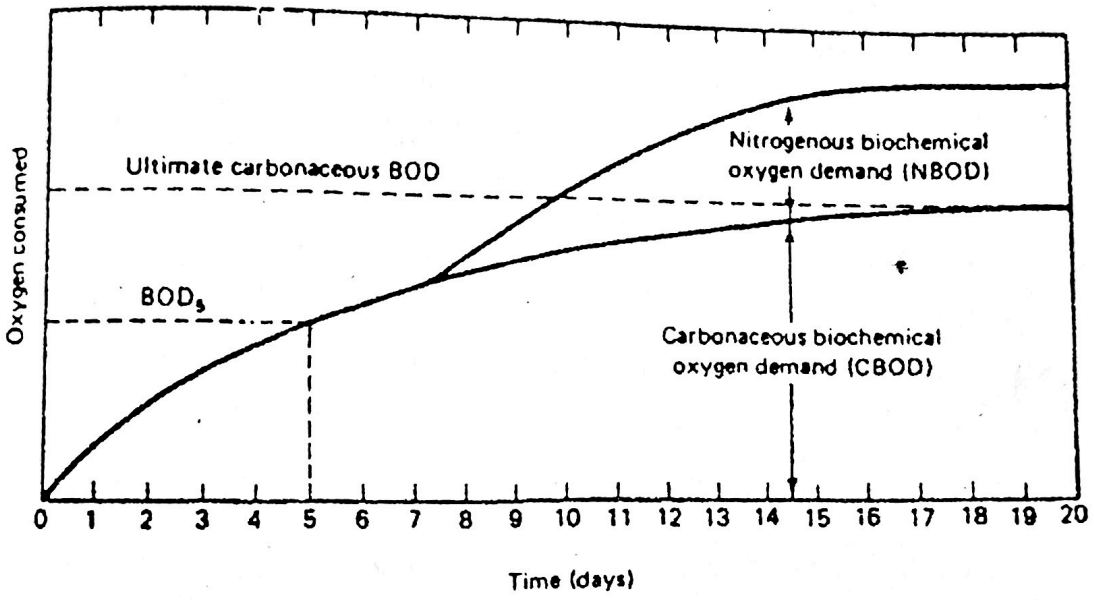


Figure 2. Illustration of Carbonaceous and Nitrogenous Biochemical Oxygen Demand

BOD reaction rate constant, k

The BOD reaction rate constant, k, is a factor that indicates the rate of biodegradation of wastes. As k increases, the rate at which dissolved oxygen is used increases, although the ultimate amount required, L_o, does not change.

$$K = k_{20}\,\theta^{(T-20)}$$

where, k_{20} is the reaction rate constant at standard 20°C.

The most commonly used value for θ is 1.047.

Beside the oxidation of carbonaceous organic matter, a significant additional demand may be caused by the oxidation of nitrogenous compounds. To distinguish this nitrogenous biochemical oxygen demand from the carbonaceous biochemical oxygen demand, the two are sometimes referred as NBOD and CBOD respectively. Figure 2 illustrates the two demands for a typical

municipal waste. Note that the NBOD does not begin to exert itself for at least 5 to 8 days. Therefore, most 5-day BOD tests are not affected by the nitrification process.

Theory of DO Determination:

The reactions involved in the various steps of the **Winkler Method** of dissolved oxygen (DO) determination are presented below:

Manganous sulfate reacts with potassium hydroxide in the alkaline potassium iodide solution to produce a white precipitate of manganous hydroxide.

$$MnSO_4 + 2KOH = \underset{\text{(white precipitate)}}{Mn(OH)_2} + K_2SO_4 \quad (9)$$

If the white precipitate is obtained, there was no dissolved oxygen in the sample and there is no need to proceed further. A brown precipitate shows that oxygen is present and reacted with the manganous hydroxide. The brown precipitate is manganic basic oxide and formed as follows:

$$2Mn(OH)_2 + O_2 = \underset{\text{(brown precipitate)}}{2MnO(OH)_2} \quad (10)$$

Upon the addition of (sulphuric) acid, this precipitate is dissolved, forming manganic sulfate:

$$MnO(OH)_2 + 2H_2SO_4 = Mn(SO_4)_2 + 3H_2O \quad (11)$$

This compound immediately reacts with potassium iodide, liberating iodine and resulting in the typical iodine (blue) coloration of the water.

$$Mn(SO_4) + 2KI = MnSO_4 + K_2SO_4 + \underset{\text{(blue)}}{I_2} \quad (12)$$

The quantity of iodine liberated by these reactions is equivalent to the quantity of oxygen present in the sample. The quantity of iodine is determined by titrating a portion of the solution with a standard solution of sodium thiosulfate solution.

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI \quad (13$$

REAGENTS

1. Manganous sulfate solution
2. Alkaline potassium iodide solution
3. 0.025N sodium thiosulfate
4. Starch solution (indicator)
5. Concentrated sulfuric acid.

APPARATUS

1. BOD bottle	: 3 nos.
2. Beaker (250 ml)	: 1 no.
3. Measuring cylinder	: 1 no.
4. Dropper	: 1 no.
5. Stirrer	: 1 no.

PROCEDURE (for determination of DO)

Fill two BOD bottles with sample (or diluted sample); the bottles should be completely filled. Determine initial DO (DO_i) in one bottle immediately after filling with sample (or diluted sample). Keep the other bottle in dark at 20°C and after particular days (usually 5-days) determine DO (DO_f) in the sample (or diluted sample). Dissolved oxygen (DO) is determined according to the following procedure:

(1) Add 1 ml of manganous sulfate solution to the BOD bottle by means of pipette, dipping in end of the pipette just below the surface of the water.

(2) Add 1 ml of alkaline potassium iodide solution to the BOD bottle in a similar manner.

(3) Insert the stopper and mix by inverting the bottle several times.

(4) Allow the "precipitates" to settle halfway and mix again.

(5) Again allow the "precipitates" to settle halfway.

(6) Add 1 ml. of concentrated sulfuric acid. Immediately insert the stopper and mix as before.

(7) Allow the solution to stand at least 5 minutes.

(8) Withdraw 100 ml of solution into an Erlenmeyer flask and immediately add 0.025N sodium thiosulfate drop by drop from a burette until the yellow color almost disappears.

(9) Add about 1 ml. of starch solution and continue the addition of the thiosulfate solution until the blue color just disappears. Record the ml. of thiosulfate solution used (disregard any return of the blue color).

CALCULATION

Dissolved Oxygen, DO (mg/L) = mL of 0.025N sodium thiosulfate added x 2

Calculate BOD of the sample according to Eq. 3 or Eq. 4.

ASSIGNMENT QUESTIONS

(1) A sample of sewage is mixed with water (no seeding done) in the ratio of 1:20 (i.e., 1 mL of sewage diluted to 20 mL by adding water) for BOD test. The initial DO is 8.5 mg/L and final DO, after 5 days, is 3.1 mg/L. Calculate BOD_5 of the sewage.

(2) A test bottle containing just seeded dilution water has its DO level drop by 0.8 mg/L in a 5-day test. A 300 ml BOD bottle filled with 30 ml of wastewater and the rest with seeded dilution water experiences a drop of 7.3 mg/L in the same period (5-day). Calculate the BOD_5 of the wastewater.

(3) In a BOD test on a diluted wastewater sample (1:20 dilution, but not seeded), the initial DO is 8.4 mg/L and final DO after 5 days is 4.2 mg/L. If the reaction rate constant is 0.22/day, calculate: (a) 5-day BOD of the wastewater, (b) ultimate carbonaceous BOD of the wastewater, (c) remaining oxygen demand after 5-days.