

Measurement of organic content in wastewater

There are three common laboratory methods used for measurement of organic content in wastewater:

- 1) Biological Oxygen Demand(BOD)
- 2) Chemical Oxygen Demand (COD)
- 3) Total Organic Carbon (TOC)

Biological oxygen demand (BOD)

The most widely used parameter of organic pollutants is 5-day BOD (BOD₅). This determination involves the measurement of the dissolved oxygen used by micro-organisms in the biochemical oxidation of organic matter.

Despite this test is widely used, it has a lot of limitation. The question now is why we used it if it has limitation? The answer is there are four reasons for that:

- 1) To determine the approximate quantity of oxygen that will be required to biologically stabilize the organic matter in wastewater.
- 2) To determine the size of waste treatment facilities.
- 3) To measure the efficiency of some treatment processes.
- 4) To determine compliance with wastewater discharge permits.

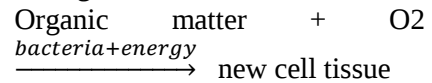
Base of BOD test:

If sufficient oxygen amount is available the aerobic biological decomposition of organic waste will be occurred. This process includes three distinct activities:

- 1) Oxidation: A portion of organic matter is oxidized to end products to obtain energy for cell maintenance and synthesis of new cell tissue.

$$\text{Organic matter} + \text{O}_2 \xrightarrow{\text{bacteria}} \text{CO}_2 + \text{H}_2\text{O} + \text{energy}$$
- 2) Synthesis: Some of organic waste converted into new cell tissue

using part of the energy released during oxidation.



- 3) Endogenous: When organic matter is used up, the new cells begin to consume their own tissue to obtain energy for cell maintenance

$$\text{Cell tissue} + \text{O}_2 \longrightarrow \text{CO}_2 + \text{NH}_3 + \text{H}_2\text{O}$$

BOD test procedure:

- 1) A small sample of waste water is placed in 300 ml bottle.
- 2) Fill the bottle with dilution water saturated with oxygen and essential nutrients for biological growth.(the sample must be suitably diluted with saturated water so that adequate amount of oxygen and nutrients are available during incubation period, the table 1 shows the ranges of BOD can be measured and the direct pipetting method)
- 3) Measure the oxygen concentration (D₁)
- 4) Stop the bottle and incubate for 5 days at 20°C
- 5) After incubation period measure again the oxygen concentration (D₂)

$$\text{BOD mg/L} = \frac{D_1 - D_2}{P}$$

When testing water with low concentration of micro-organisms, a seeded BOD test is conducted. When using seeded diluted water another 300 ml bottle is filled with seeded water without sample and then measure the dissolved oxygen at this bottle before(B₁) and after (B₂) incubation.

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

f is the fraction of seeded dilution water volume in sample to volume of seeded dilution water in seeded control

Range of BOD mg/L	Volume of sample mL
30,000 – 105,000	0.02
12,000 – 42,000	0.05
6,000 – 21,000	0.01
3,000 – 10,500	0.2
1,200 – 4,200	0.5
600 – 2,100	1
300 – 1,050	2
120 – 420	5
60 – 210	10
30 – 105	20
12 – 42	50
6 – 21	100
0 – 7	300

Table 1

Remains two points before leaving this part:

- 1) Ultimate biological oxygen demand(UBOD) this is the amount of oxygen required to complete the three reactions(oxidation, synthesis, endogenous).
- 2) During the 5-day period only 60-70% of organic matter oxidized and this point is important for design facilities.

Modeling of BOD reaction:

The amount of organic matter remaining at any time t is governed by a first – order reaction as given below:

$$\frac{d BOD_r}{dt} = -k BOD_r$$

Integration between the limits of UBOD and BOD_r and $t = 0$ and $t = t$ yields:

$$BOD_r = UBOD (e^{-k_1 t})$$

Where:

- BOD_r is the amount of waste remaining at time t (days)

expressed in oxygen equivalents mg/L

- K is first order reaction rate constant 1/d
- UBOD is ultimate BOD
- t is time (days)

so the BOD exerted up to time t is given up

$$BOD_t = UBOD - BOD_r = UBOD - UBOD(e^{-k_1 t}) = UBOD (1 - e^{-k_1 t})$$

This is the slandered expression for defined the BOD in water.

The value of K_1 at 20°C can be determined experimentally by observing the variation of the dissolved oxygen with time in a series of incubated samples. To determine the reaction constant k_1 at any temperature other than 20°C we use the following equation:

$$K_{1T} = K_{120} \Theta^{T-20}$$

Where:

The value of Θ is 1.056 at temperature between 20°C to 30°C and 1.135 at temperature between 4°C to 20°C.

Example 1:

A t 5-days Bod test 15ml of sample was added to 300ml BOD bottle and incubated at 20°C. the DO values before and after incubation were 8.8 mg/L and 1.9 mg/L respectively. The corresponding intial and final DO at the seed bottel were 9.1 mg/L and 7.9 mg/L respectively. what is the 5-day BOD?

Solution:

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

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

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

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

Example 2:

Determine the 1-day BOD and UBOD for a wastewater whose 5-day 20°C BOD is 200mg/L. the reaction constant K is 0.23 d⁻¹. What would the 5-day 25°C BOD?

Solution:

1) Determination of UBOD

$$\text{BOD}_5 = \text{UBOD}(1 - e^{-k_1 t})$$

$$200 = \text{UBOD}(1 - e^{-0.23 \times 5})$$

$$\text{UBOD} = 293 \text{ mg/L}$$

2) Determination of 1-day BOD

$$\text{BOD}_1 = \text{UBOD}(1 - e^{-k_1 t})$$

$$\text{BOD}_1 = 293(1 - e^{-0.23 \times 1}) = 60.1 \text{ mg/L}$$

3) Determination of 5-day 25°C BOD

$$K_{1_T} = k_{1_{20}} \Theta^{T-20}$$

$$K_{1_{25}} = 0.23(1.056)^{25-20} = 0.30 \text{ d}^{-1}$$

$$\text{BOD}_5 = \text{UBOD}(1 - e^{-k_1 t}) = 293(1 - e^{-0.3 \times 5}) = 227.6 \text{ mg/L}$$

References:

- Metcalf & Eddy in wastewater engineering treatment and reuse 2003
- Wikipedia website.
- Makenzie L.Davis in water and wastewater engineering design principles and practice 2003