Oxygen Demanding Materials

Dissolved Oxygen

- Minimum concentration is required for the survival of higher aquatic life
- Significant discharges of organic wastes may depress the D.O. concentrations in receiving waters
  - microbially-mediated oxidation
  - each state has established ambient dissolved oxygen standards
- Another use of D.O. is the assessment of oxidation state in groundwaters and sediments
- also a very important parameter in biological treatment processes
  - indicates when aerobic and anaerobic organisms will predominate
- used to assess the adequacy of oxygen transfer systems
- indicates the suitability for the growth of such sensitive organisms such as the nitrifying bacteria.
- used in the assessment of the strength of a wastewater through the Biochemical Oxygen Demand (BOD)

Oxygen Demand is a measure of the amount of "reduced" organic and inorganic matter in a water. It relates to oxygen consumption in a river or lake as a result of a pollution discharge.

Measured in several ways

Experimental {
BOD - Biochemical Oxygen Demand
COD - Chemical Oxygen Demand
TOC-Total Organic Carbon
}
ThOD - Theoretical Oxygen Demand =Carbonaceous demand + Nitrogenous Demand

Theoretical Oxygen Demand

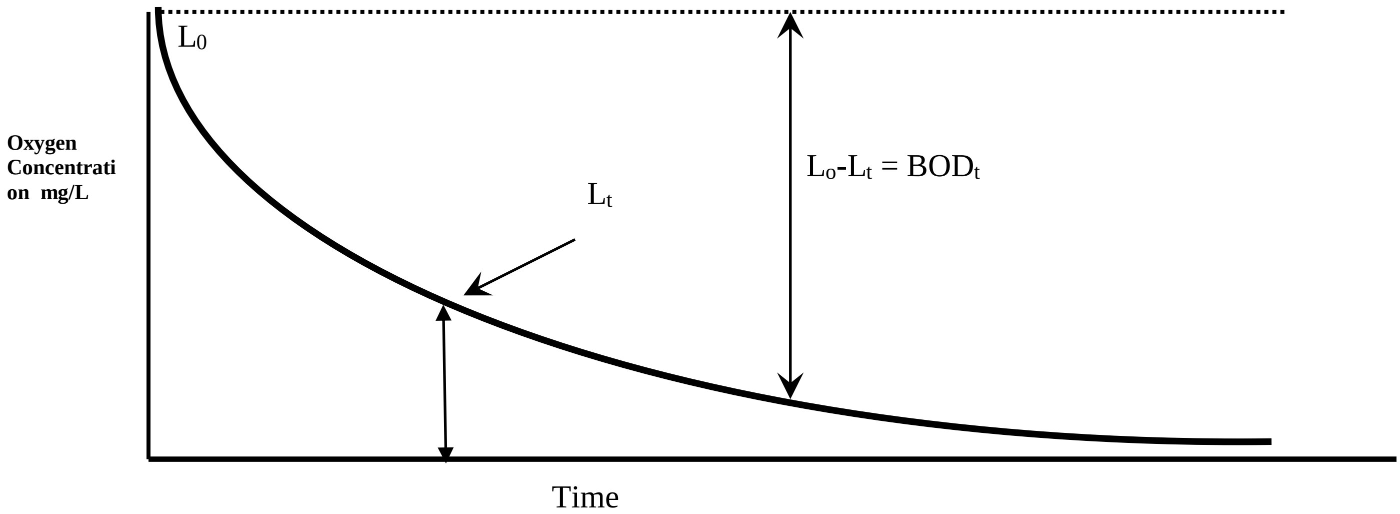
This is the total amount of oxygen required to completely oxidize a known compound to CO2 and H2O. It is a theoretical calculation that depends on simple stoichiometric principles. It can only be calculated on compounds of known composition. If N is present then it gets oxidized to NH3. NH3 can be further oxidized to nitrate. **Every mole of NH3 requires 2 moles of oxygen to get oxidized to nitrate.**

Chemical Oxygen Demand (COD)

This test determines the amount of oxygen needed chemically to oxidize organics in water or wastewater. The oxidizing agent is potassium dichromate ($K_2Cr_2O_7$) in an acid solution (typically 50% H_2SO_4) and in the presence of a Silver Sulfate (Ag_2SO_4) catalyst. This test is attractive because it takes only 2 hours. The major disadvantage is that some organics like detergents and aromatics may not be easily oxidized. COD's are always higher than BOD values. For municipal wastewater, $COD \approx 1.6BOD_5$.

Biological Oxygen Demand

BOD is a measure of the oxygen used by aerobic microorganisms while degrading and organic pollutant. Briefly, the BOD test employs a bacterial seed to catalyze the oxidation of 300 mL of full-strength or diluted wastewater. The standard test is run in the dark for five days at 20^{o}C in a glass bottle. This is known as the 5 day BOD or BOD_5. The oxygen consumption is easily measured by DO readings. The oxygen concentration in the BOD bottle typically follows the pattern as shown below:



The figure indicates that initially oxygen depletion is rapid because of high concentrations of organic matter present. As the concentration of organic matter decreases so does the rate of oxygen consumption. It has been noted that the curve in the above figure is mathematically denoted by a first order reaction.

Therefore, $\frac{dL}{dt} = -kL$ Integrating $\int_{L_o}^{L_t} \frac{dL}{L} = -k\int_0^t dt$ yields $L_t = L_o e^{-kt}$

Where L_0 = oxygen concentration at time 0
L_t = oxygen concentration at time t

Since BOD is defined as the oxygen used, the total oxygen used in time t = $L_0 - L_t$

Therefore, $BOD_t = L_0 - L_o e^{-kt} = L_0 (1- e^{-kt})$

L_0 is often referred to as the ultimate BOD

BOD rate depends on

- nature of waste
- ability of microorganisms to degrade the waste
- Temperature- Corrections to k can be made as follows $k_T = k_{20^o C}\theta^{T-20^o C}$
  θ = 1.135 for temp between 4 and 20°C and 1.056 for temp between 20 and 30°C.

Nitrogenous Oxygen Demand

Oxygen consumption due to carbon is called carbonaceous biological oxygen demand (CBOD) and oxygen consumption due to nitrogen oxidation is called nitrogenous biological oxygen demand (NBOD). Bacteria that oxidize organic compounds typically convert the nitrogen in these compounds to ammonia. The ammonia is further biodegraded by nitrifying bacteria (two kinds) in two steps:

$$NH_3 + 1.5O_2 \xrightarrow{Nitrosomonas} NO_2^- + H_2O + H^+$$

$$NO_2^- + \frac{1}{2}O_2 \xrightarrow{Nitrobacter} NO_3^-$$

The overall reaction is $NH_3 + 2O_2 = 2HNO_3 + H_2O$

SAMPLE PROBLEMS

1. The BOD_5 of a sewage sample is 200 mg/L. What is the ultimate BOD_u at 20°C if k_{20} = 0.16 day^{-1}? What is the BOD_5 and BOD_u of the sample at 30°C if k_{30} is 0.25 day^{-1}?

$L_t = L_o (1-e^{-kt})$ Given Lt = 200 Lo=? k_{20} = 0.16 day^{-1} t= 5 days

$200 = Lo(1-e^{-.16*5})$ or Lo = 363.19 mg/L = BODu

Note BODu is not a function of temperature. Therefore same BODu will be used at 30°C

BOD_5 =Lt = $363.19 (1 - e^{-.25*5})$ = 259.13 mg/L

2. The BOD3 of a wastewater is 120 mg/L while the BOD_7 of the wastewater is 217 mg/L. What is the value of the ultimate BOD (BODu) in mg/L and the biodegradation rate constant k in day^{-1}? Also calculate the value of the 5 day BOD. Assume temperature of 20°C.

The biodegradation rate of a wastewater at 20°C is 0.12 day^{-1} while the rate is 0.24 day^{-1} at 30°C. What is the value of O if the following relationship holds $k_1 = k_2 O^{T1-T2}$?

3. Dr. Jahan's class is preparing a harmless potion for engineering students for a Halloween event. The organic chemical being used is totally harmless, non toxic, **highly biodegradable and readily oxidized chemically.** The chemical formula of the compound is $C_{10}H_{20}$ and the concentration prepared is 150 mg/L.

What are the THOD, BOD and COD of the sample? Justify the values of the BOD_u and COD values. Assume BOD_u is 0.85*COD. If the biodegradation rate k is 0.25day-1 what is the BOD_5 in mg/L?

PROBLEMS FORM TEXTBOOK

5-1 Theoretical oxygen demand of glutamic acid

Given: 63 mg/L of glutamic acid and oxidation reactions

Solution:

a. Compute the gram molecular weights of glutamic acid and oxygen consumed

GMW of $C_5H_9O_4N$ = 147

GMW of oxygen ($4.5\ O_2 + 2\ O_2$) = 208

b. Calculate the ThOD

$$\text{ThOD} = (63\,\text{mg/L})\frac{208}{147} = 89.15\,\text{mg/L}$$

5-2 Theoretical oxygen demand of bacterial cells

Given: 30 mg/L of bacterial cells and oxidation reactions

Solution:

a. Compute gram molecular weights

GMW of $C_5H_7NO_2$ = 113

GMW of oxygen ($5\ O_2 + 2\ O_2$) = 224

b. Calculate the ThOD

$$\text{ThOD} = (30\,\text{mg/L})\frac{224}{113} = 59.47\,\text{mg/L}$$

5-3 Theoretical oxygen demand of acetic acid

Given: 300 mg/L of acetic acid and oxidation reaction

a. Compute gram molecular weights

GMW of CH_3COOH = 60

GMW of oxygen = 64

b. Calculate ThOD

$$\text{ThOD} = (300\,\text{mg/L})\frac{64}{60} = 320\,\text{mg/L}$$

5-23 Theoretical NBOD of bacterial cells

Given: Problem 5-2, 30 mg/L of bacterial cells. (NOTE: the concentration is not specified in the first printing of the 3rd edition.)

Solution:

a. Calculate the amount of nitrogen that is oxidized.

$$(30\,\mathrm{mg/L})\left(\frac{14\mathrm{gN}}{113\mathrm{gC_5H_7NO_2}}\right) = 3.72\,\mathrm{mgN/L}$$

b. Using the relationship from Eqn 5-20

Theo. NBOD = (3.72 mg N/L)(4.57 mg O_2/mg N) = 16.99 or 17 mg O_2/L

5-24 Theoretical NBOD of casein

Given: 200 mg/L of casein ($C_8H_{12}O_3N_2$) and reactions

Solution:

a. Calculate amount of nitrogen oxidized

$$(200\,\mathrm{mg/L})\left(\frac{28\mathrm{gN}}{184\mathrm{gC_8H_{12}O_3N_2}}\right) = 30.43\,\mathrm{mgN/L}$$

b. Using the relationship from Eqn. 5-20

Theo. NBOD = (30.43 mg N/L)(4.57 mg O_2/mg N) = 139.07 or 140 mg O_2/L