CHAPTER 3.0

WASTEWATER (TYPES & CHARACTERISTICS)

TYPES OF WASTEWATER

Domestic	Industrial
• Houses • Schools • Offices	• Pharmaceutical • POME • Textile • Others …

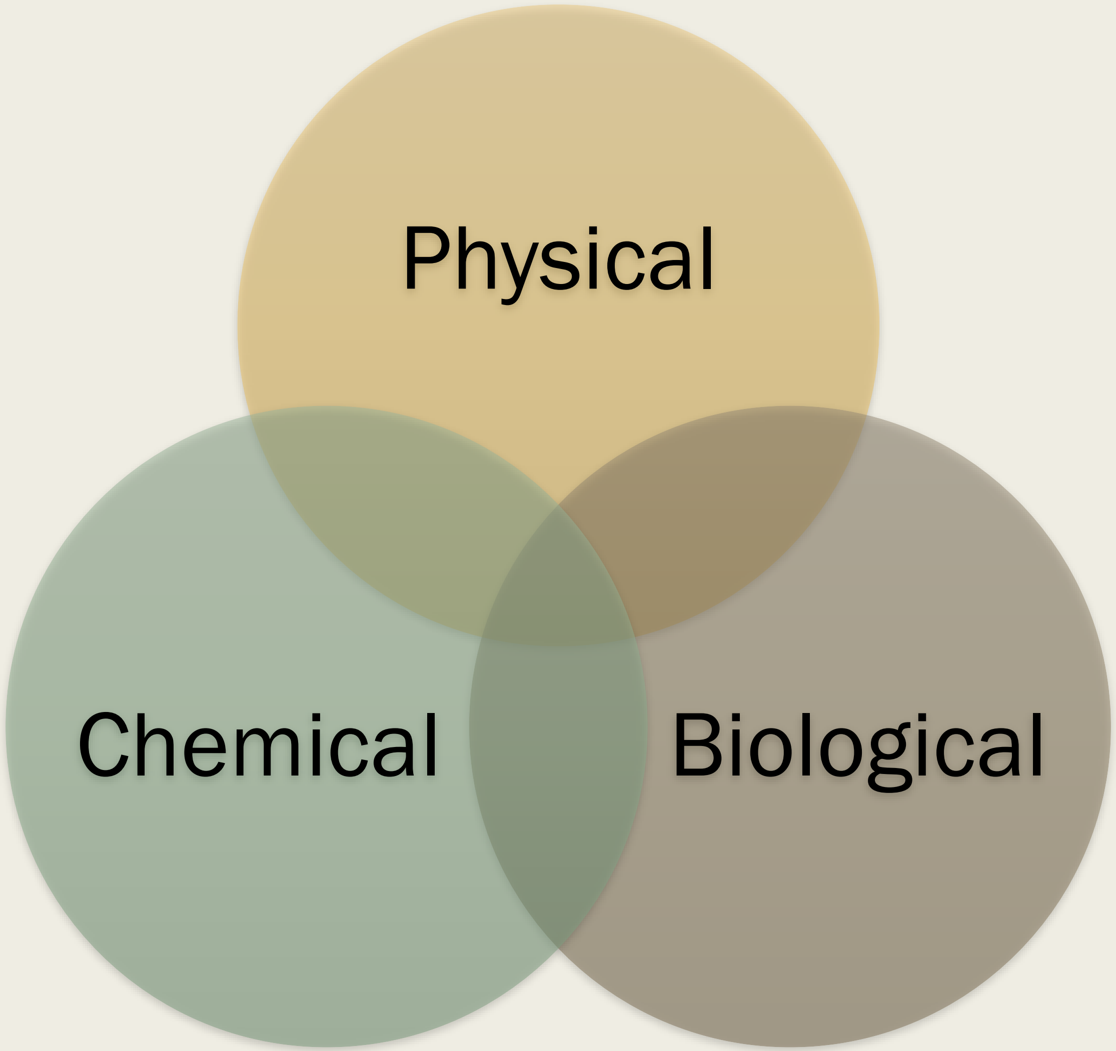
DOMESTIC WASTEWATER

- Wastewater by residential, shop houses, offices, schools etc.
- Normally generated from toilets, sinks and bathrooms.

INDUSTRIAL WASTEWATER

- Wastewater generated by industries.
- Quantity and quality depends on the type of industry.

WASTEWATER CHARACTERISTICS



PHYSICAL CHARACTERISTICS

A. Colour:

Depends mainly on the wastewater constituent

B. Odour:

Not significant if aerobic. Anaerobic wastewater release hydrogen sulphide (smells like rotten egg)

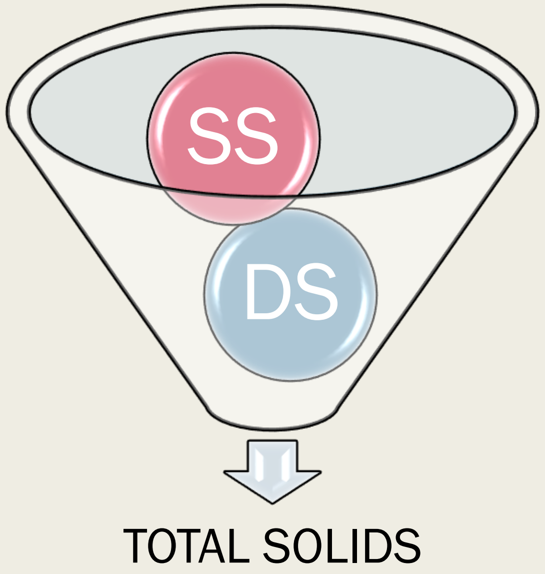
C. Temperature:

- Higher than water temperature due to the microbiological activities
- Effect of temperature on microbial growth rate - speed up as the temperature increases and slow down as the temperature drops

PHYSICAL CHARACTERISTICS (CONT’)

D. Solids:

- Caused by the presence of solids mainly suspended solids (SS) from clay, sand, human waste and plant fibres.
- Divided into two, suspended solids and dissolved solids (DS) which combined, forming Total Solids (TS).
- Common unit – mg/L



Dissolved Solids (DS)

Those solids which are in solution and are therefore filterable.

Suspended Solids (SS)

Those solids that are non-filterable with specified filters and are not volatilized at 103 degrees Celsius.

Volatile Suspended Solids (VSS)

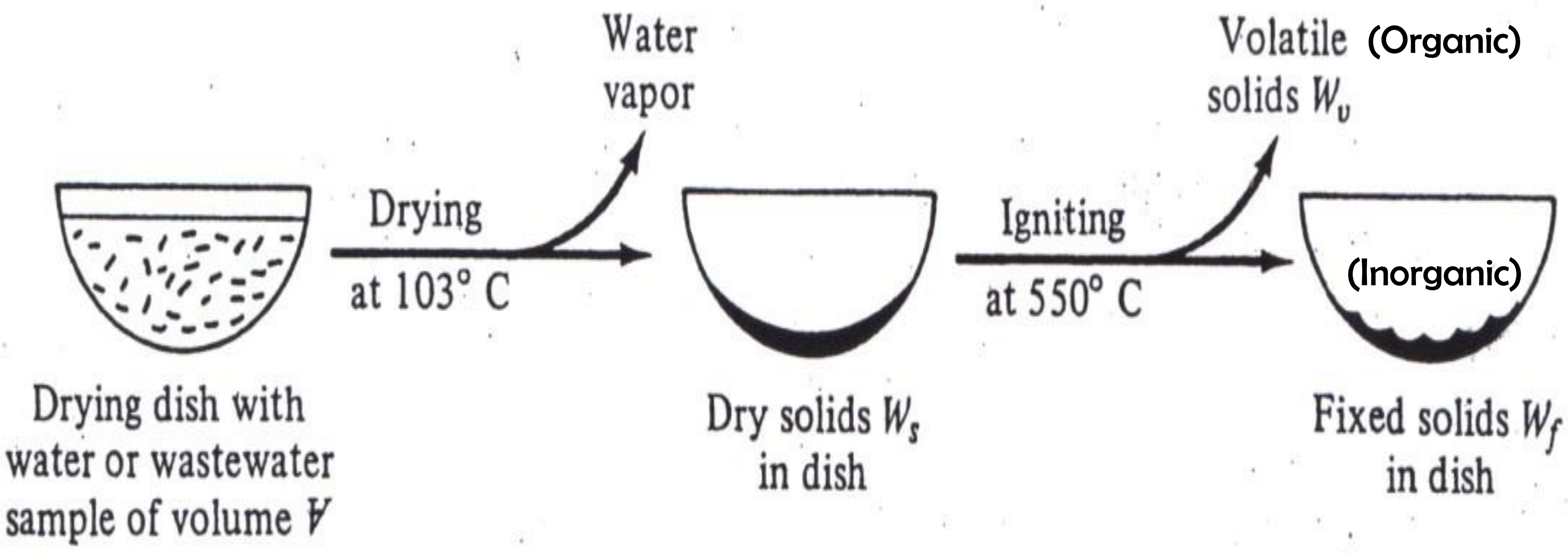
That portion of the suspended solids which are volatilized at 550 degrees C

Total Solids (TS)

All of the solids present whether suspended or dissolved.

Total Volatile Solids

That portion of the total solids which are volatilized at 550 degrees C.



$$\text{Total solids} = \frac{W_s}{V} \qquad \text{Total volatile solids} = \frac{W_s - W_f}{V} = \frac{W_v}{V}$$

Diagram of laboratory procedure to determine total solids and total volatile solids concentration of a water or wastewater sample.

MEASUREMENT OF TOTAL SOLIDS (TS)

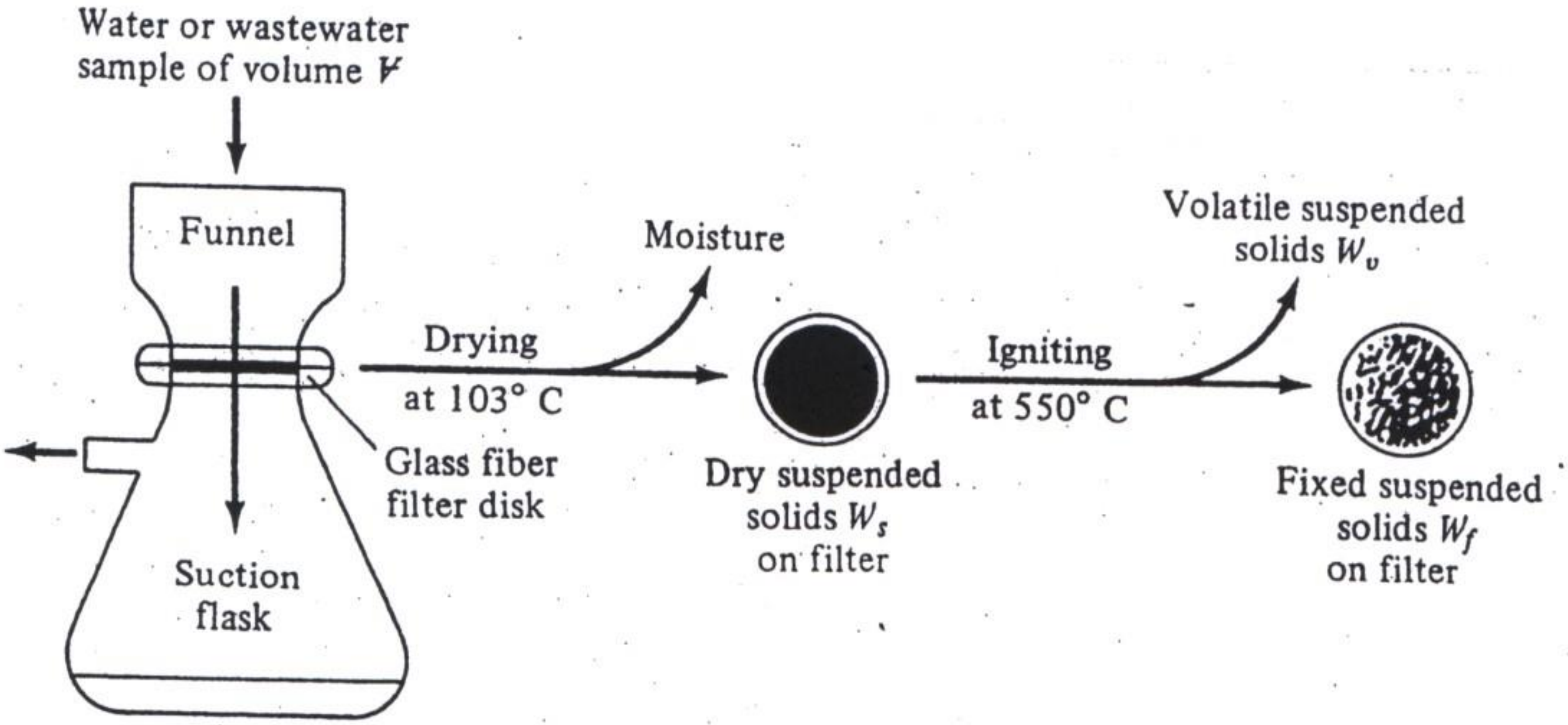
- Evaporate a known volume of sample to dryness and weigh the residue.
- The total solid is expressed as milligrams per litre (mg/L).

MEASUREMENT OF SUSPENDED SOLIDS (SS)

- Weigh a filter paper on an analytical balance.
- Place the filter paper on the filter apparatus.
- Apply vacuum and filter 100 mL (or a larger volume if total suspended matter is low) well mixed sample.
- Dry the filter paper in an oven at 103^oC to 105^oC for at least 1 hour.
- After 1 hour, cool the filter paper in a desiccator and weigh.
- Repeat the drying cycle until a constant weight is attained or until weight loss is less than 0.5 mg.

Desiccator

Vacuum filter



$$\text{Suspended solids} = \frac{W_s}{V} \qquad \text{Volatile suspended solids} = \frac{W_s - W_f}{V} = \frac{W_v}{V}$$

Diagram of laboratory procedure to determine the suspended solids and volatile suspended solids concentrations of a water or wastewater sample.

DILUTION METHOD (IF NECESSARY)

- If samples contain high concentration of suspended solids it is recommended to dilute the sample.
- Dilute the sample using de-ionized or distilled water.
- Run the test using the diluted sample, and then multiply the result by the dilution factor to find the value in the sample before dilution.
- For example, for a 1/4 dilution multiply the result by 4 (the dilution factor).

CALCULATION EXAMPLE

A Total Solids and Suspended Solids were carried out on a wastewater sample.

The relevant information were as follows:

Weight of filter	=	0.1384 g
Weight of empty dish	=	45.4275 g
Weight of filter and residue	=	0.1759 g
Weight of dish and residue	=	45.4465 g
Volume of sample filtered	=	150 mL
Volume of sample dried	=	50 mL

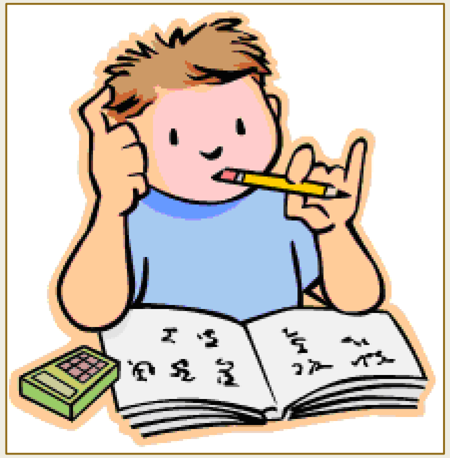
Calculate the concentrations of total solids, suspended solids and dissolved solids in mg/L.

SOLUTION

$$TS = \frac{(45.4465 - 45.4275)g}{50mL} \times 10^6 = 380mg / L$$

$$SS = \frac{(0.1759 - 0.1384)g}{150mL} \times 10^6 = 250mg / L$$

$$DS = 380 - 250 = 130\ mg/L$$



CHEMICAL CHARACTERISTICS

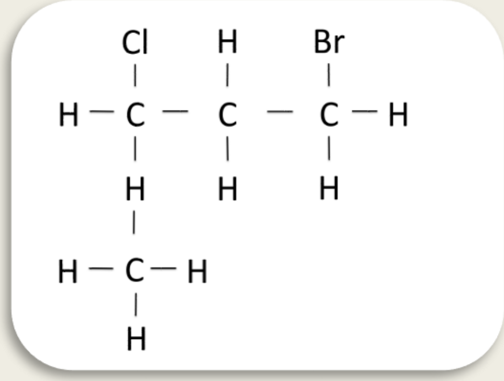
A. Organic compounds:

Definition

Compounds that contain carbon in combination with one or more elements.

A few exceptions are carbon monoxide, carbon dioxide and carbonates, which are considered inorganic

Properties of organic compounds



- Usually combustible
- Have lower melting and boiling points
- Less soluble in water
- Have very high molecular weight
- Most organic compounds can serve as a source of food for micro-organisms

Source(s):

- Natural: fibres, vegetable oils, animal oils and fats, cellulose, starch, sugar.
- Synthetic: a wide variety of compounds and materials prepared by manufacturing processes. E.g. DDT, polyvinyl chloride.
- Fermentation: Alcohols, acetone, glycerol, antibiotics, acids.

Classification of organic matter (difference in degradability)

- **Biodegradable organics**
- **Non-biodegradable organics**

Biodegradable organics

- Food for micro-organisms
- Fast and easily oxidized by micro-organisms
- e.g. starch, fat protein, alcohol, human and animal waste.

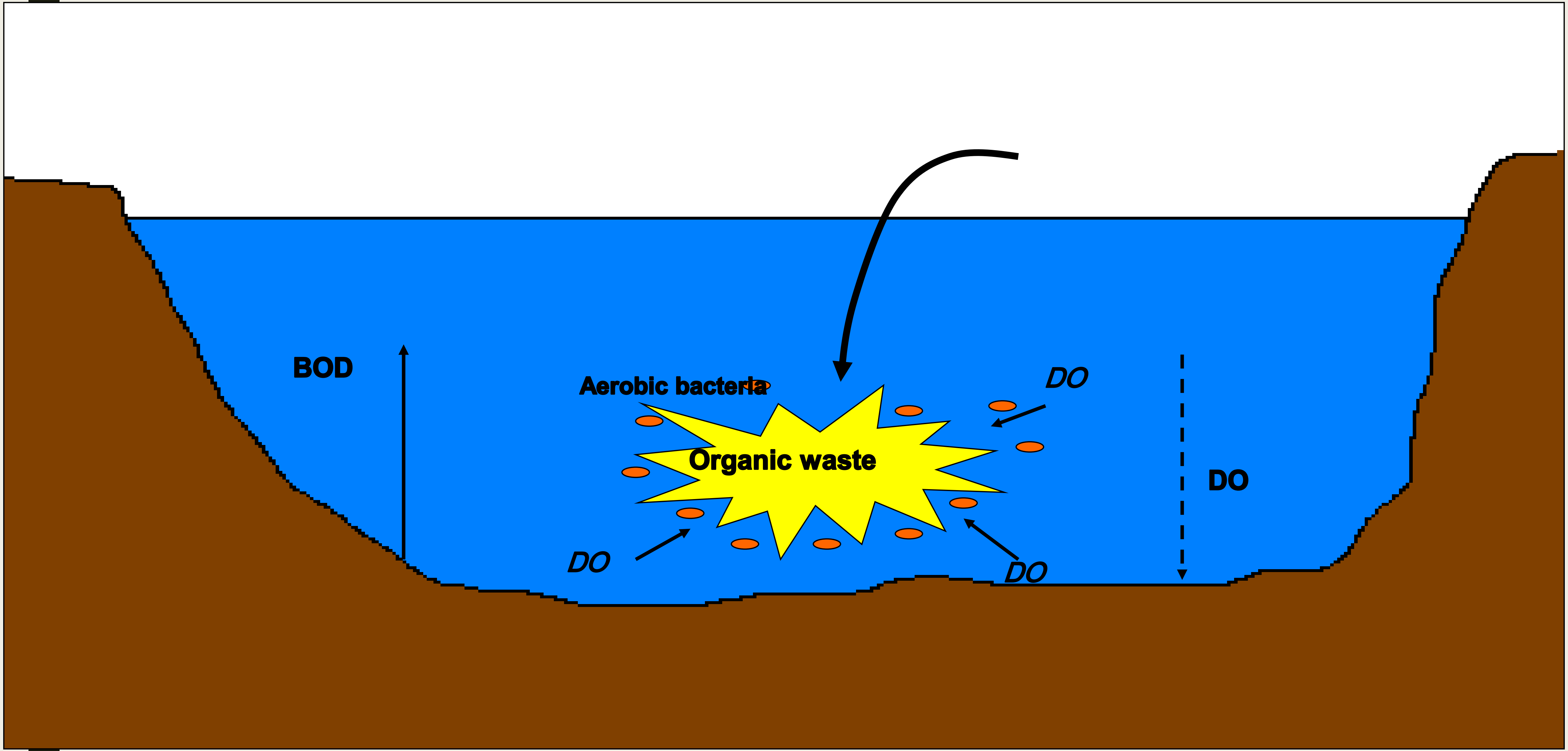
Non-biodegradable organics

- Difficult and much more longer to biodegrade
- Or toxic to micro-organisms
- e.g. PVC, pesticide, industrial waste, cellulose, phenol, lignic acid.

Effect(s):

- Depletion of the dissolved oxygen in the water
  - Destroying aquatic life
  - Damaging the ecosystem

- Some organics can cause cancer
  - Trihalomethanes (THM-carcinogenic compounds) are produced in water and wastewater treatment plants when natural organic compounds combine with chlorine added for disinfection purposes.



BOD
Aerobic bacteria
Organic waste
DO
DO
DO
DO
DO

Normally, wastewater has high organic content. The organic content is measured by Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) and the value is about 100 to 400 mg/L.

BIOCHEMICAL OXYGEN DEMAND (BOD)

Definition

The quantity of oxygen utilised by a mixed population of micro-organisms to biologically degrade the organic matter in the wastewater under aerobic condition.

Another definition:

The amount of dissolved **oxygen** needed (i.e. demanded) by aerobic **biological** organisms to break down organic material present in a given water sample at certain temperature over a specific time period

BOD is the most important parameter in water pollution control

It is used as a measure of organic pollution as a basis for estimating the oxygen needed for biological processes, and as an indicator of **process performance**.

BOD test can be 5-day at 20^{o}C OR 3-day at 30^{o}

$$\text{Organic matter} + O_2 \xrightarrow{\text{microorganisms}} CO_2 + H_2O + \text{new cells}$$

Note:

- 5 days test is for domestic and industrial WW (*Global standard*).
- 3 days test is specially for POME and rubber manufacturing WW (*Malaysia standard)*.

Calculation of BOD,

$$BOD_t = \frac{DO_i - DO_t}{P}$$

Where

BOD_t = Biochemical oxygen demand (mg/L)

DO_i = Initial DO of the diluted wastewater sample at 15 min. after preparation (mg/L)

DO_t = Final DO of the diluted wastewater sample after incubation for 5 days (mg/L)

P = Dilution factor

$$P = \frac{\text{Volume of sample}}{\text{Volume of sample} + \text{Volume of distilled water}}$$

BOD TEST METHOD (BOD_5 @ 20^{o}C)

a) A water sample containing degradable organic matter is placed in a BOD bottle.

b) If needed, add dilution water (known quantity).

c) Dilution water is prepared by adding phosphate buffer (pH 7.2), magnesium sulphate, calcium chloride and ferric chloride into distilled water. Aerate the dilution water to saturate it with oxygen before use.

d) Measure DO in the bottle after 15 minutes (DO_i)

e) Closed the bottle and placed it in incubator for 5 days, at temperature 20^{o}C

f) After 5 days, measure DO in the bottle (DO_t).

WHY DILUTION IS NEEDED?

- For a valid BOD test, the final DO (DO_t) should not be less than 1 mg/L. BOD test is invalid if DO_t value near zero.

- Dilution can decrease organic strength of the sample. By using dilution factor, the actual value can be obtained.

Dilution of wastes:

- By direct pipetting into 300 mL BOD bottle

Volume of sample (mL)	Range of BOD value (mg/L)
0.02	30,000-105,000
0.05	12,000-42,000
0.10	6,000-21,000
0.20	3,000-10,500
0.50	1,200-4,200
1.00	600-2,100
2.00	300-1,050
5.00	120-420
10.00	60-210
20.00	30-105
50.00	12-42
100.00	6-21
300.00	0-7

BOD ANALYSIS

- In aerobic processes (O_2 is present), heterotrophic bacteria oxidise about 1/3 of the colloidal and dissolved organic matter to stable end products ($CO_2 + H_2O$) and convert the remaining 2/3 into new microbial cells that can be removed from the wastewater by settling.
- The overall biological conversion proceeds sequentially, with oxidation of carbonaceous material as the first step (known as carbonaceous oxygen demand):

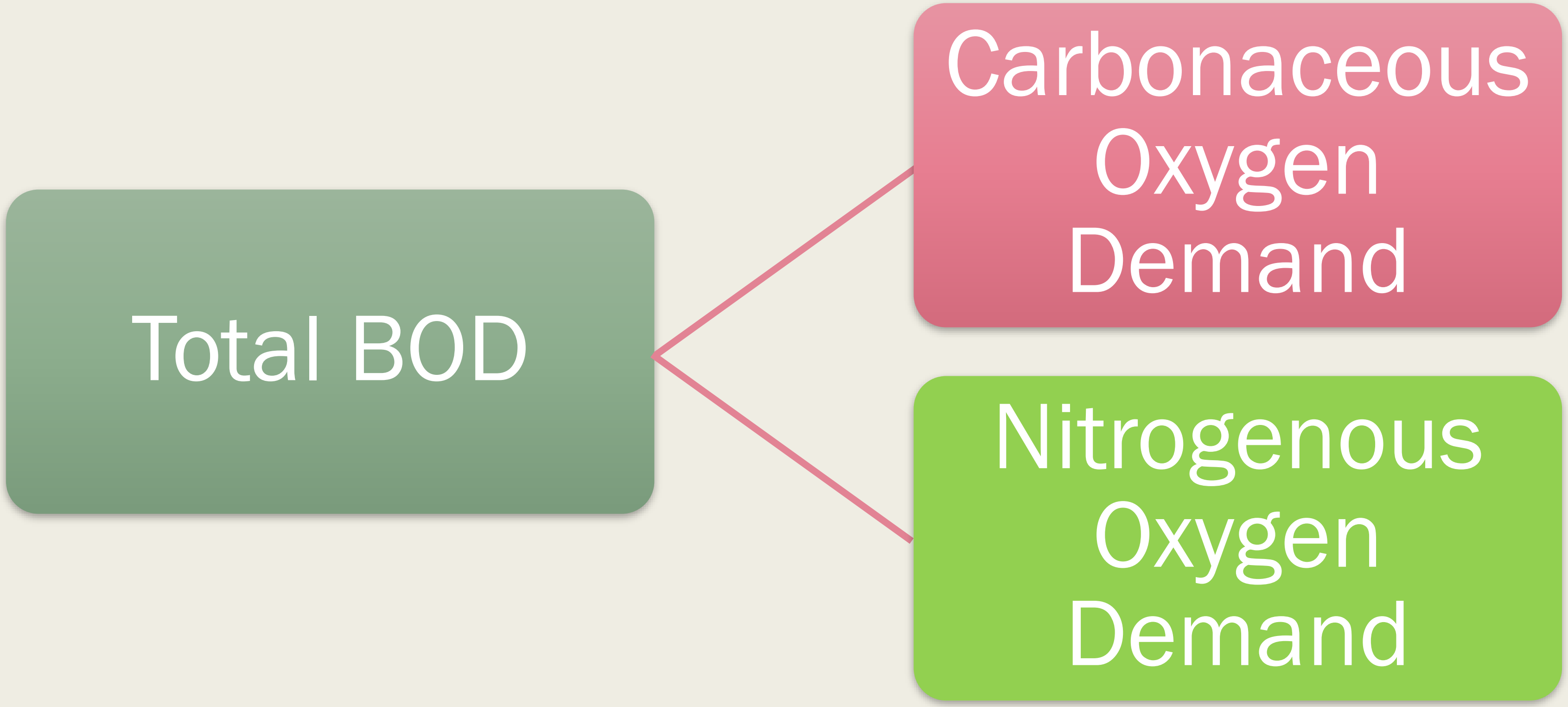
$$\text{Organic matter} + O_2 \xrightarrow{\text{microorganisms}} CO_2 + H_2O + \text{new cells}$$

- Under continuing aerobic conditions, autotrophic bacteria then convert the nitrogen in organic compounds to nitrates (known as nitrification oxygen demand):

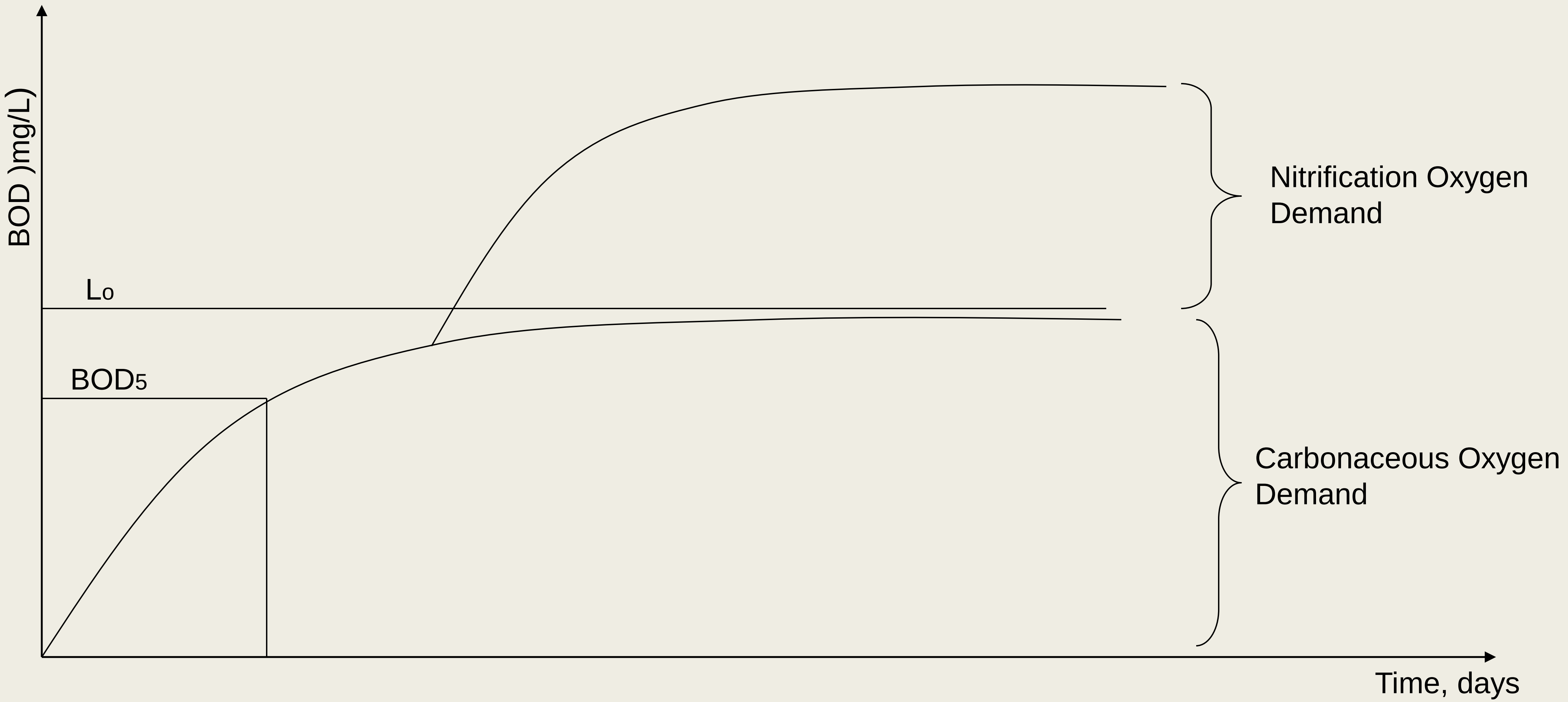
Organic-Nitrogen $\longrightarrow$ Ammonia-Nitrogen (Decomposition)

and

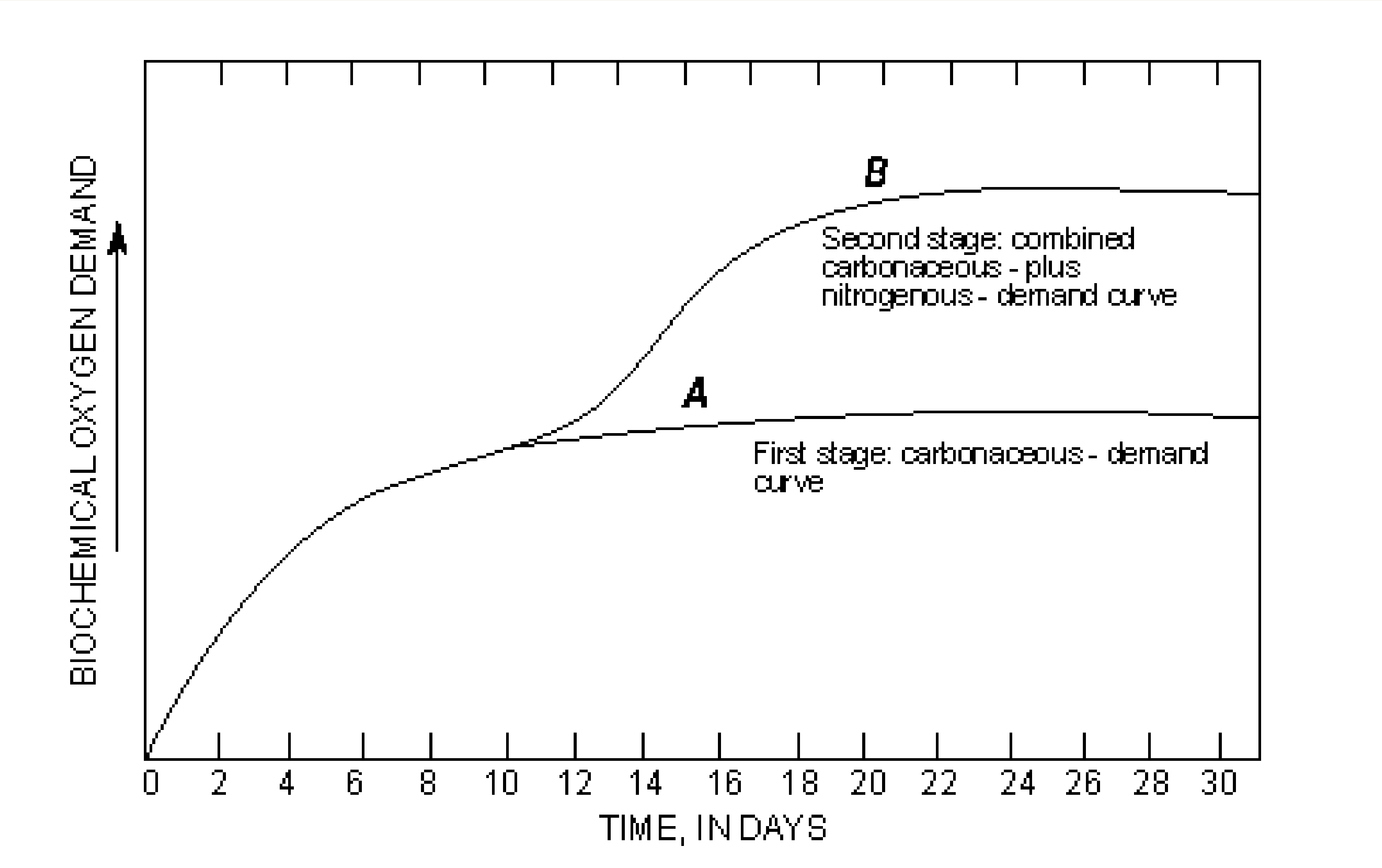
$NH_3 - N + O_2 \xrightarrow{\text{Nitrifying bacteria}}$ Nitrate-Nitrogen (Nitrification)



Traditionally, because of the slow growth rates of those organisms that exert the nitrogenous demand, it has been assumed that no nitrogenous demand is exerted during the 5-day BOD_5 test.



The ultimate BOD (Lo) is defined as the maximum BOD exerted by the waste.



BIOCHEMICAL OXYGEN DEMAND
B
Second stage: combined carbonaceous - plus nitrogenous - demand curve
A
First stage: carbonaceous - demand curve
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
TIME, IN DAYS

The carbonaceous oxygen demand curve can be expressed mathematically as:

$$BOD_t = L_o (1-10^{-Kt})$$

Where

BOD_t = Biochemical oxygen demand at time t (mg/L)

L_o = Ultimate BOD (mg/L)

t = Time (days)

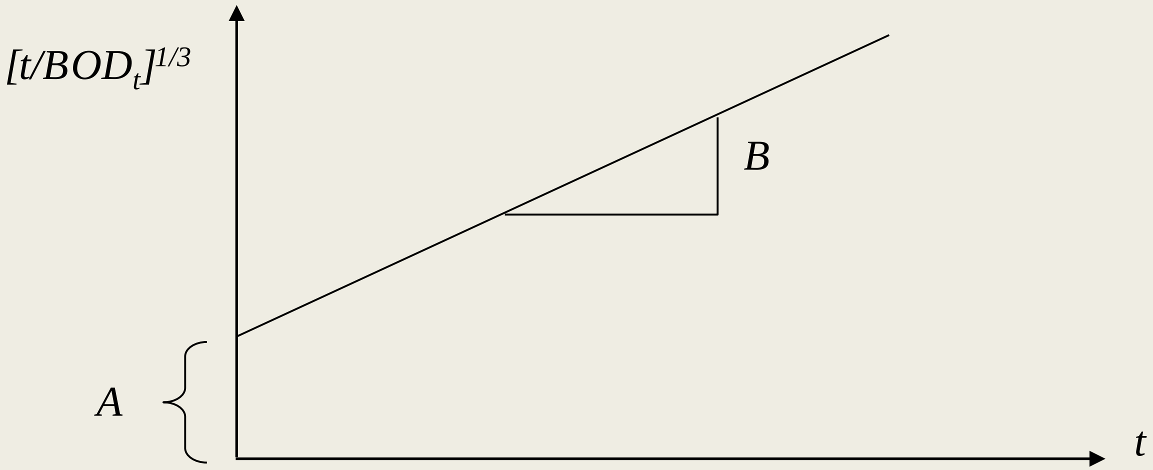
K = Reaction rate constant (day^{-1})

Determination of BOD K-Rate

Time (day)	BOD_t (mg/L)	$[time/BOD_t]^{1/3}$
1	W	$[1/W]^{1/3}$
2	X	$[2/X]^{1/3}$
3	Y	$[3/Y]^{1/3}$
4	Z	$[4/Z]^{1/3}$

1. From the experiment results of BOD for various values of t, calculate $[time/BODt]^{1/3}$ for each day.

2. Plot $[t/BODt]^{1/3}$ versus t



3. Determine the intercept (A) and slope (B) from the plot.
4. Calculate K = 2.61 (B/A)

BOD RATE CONSTANT (per day)

- K (base 10)

$$L_o = \frac{BOD_t}{1-10^{-Kt}}$$

- k (base e)

$$L_o = \frac{BOD_t}{1-e^{-kt}}$$

- K = k/2.3

- Simple compounds such as sugars and starches are easily utilized by microorganisms
  - ➢ have high k rate
- More complex materials such as phenols and cellulose are difficult to assimilate
  - ➢ have low k values.
- Typical values of K for various water:

Water Type	K, per day (base 10)
Tap water	0.04
Surface water	0.04 – 0.1
Raw sewage	0.15 – 0.30
Well-treated sewage	0.05 – 0.10

EFFECTS OF TEMPERATURE ON REACTION RATES

Reaction Rate Constant, K

- Most biological processes speed up as the temperature increases and slow down as the temperature drops. The rate of utilization is affected by temperature
- The relationship for the change in the reaction rate constant (K) with temperature is expressed as:

$$K_T = K_{20} \times \theta^{(T-20)} = K_{20} \times 1.047^{(T-20)}$$

θ = temperature coefficient = 1.047

EXAMPLE

A BOD test was conducted on a domestic wastewater at 30^oC. The wastewater portion added to a BOD bottle was 20 mL and the dissolved oxygen values listed below were measured.

Time (days)	DO (mg/L)
0	7.4
1	5.5
2	4.5
3	3.7
4	2.5
5	2.1

a) Calculate values of BOD_3

b) Determine the BOD rate constant, K_{30}

c) Calculate values of BOD_5 at 20^oC

SOLUTION:

a) $$BOD_3 = \frac{DO_0 - DO_3}{P} = \frac{7.4 - 3.7}{20/300} = 55.55 mg/L$$

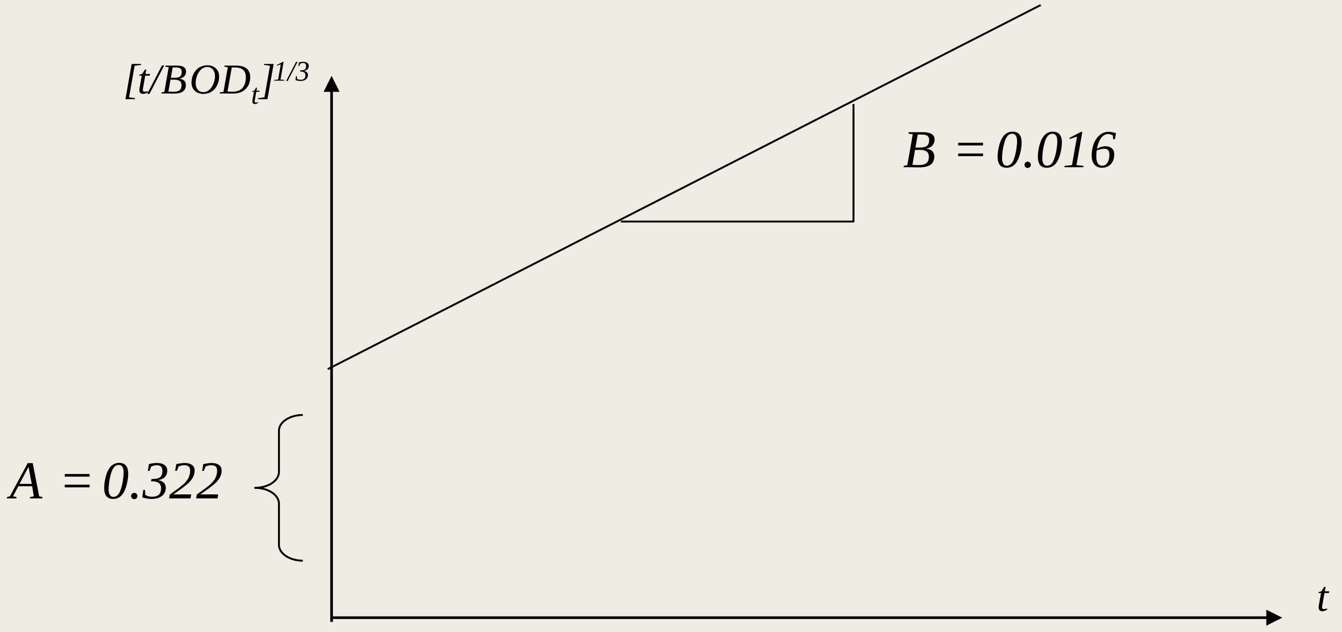
b) Determine the BOD rate constant, K_{30}

(i)

Time	DO	BOD	$[time/BOD]^{1/3}$
0	7.4	-	-
1	5.5	28.5	0.33
2	4.5	43.5	0.36
3	3.7	55.5	0.38
4	2.5	73.5	0.38
5	2.1	79.5	0.40

SOLUTION (CONT’)

(ii) Plot [time/BOD]$^{1/3}$ versus time



K_{30} = 2.61 (B/A)

= 2.61 (0.016/0.322) = 0.13 per day

SOLUTION (CONT')

c. BOD_5 @ 20ºC

(i) $K_{30} \rightarrow K_{20}$

$$K_{20} = \frac{K_{30}}{1.047^{(30-20)}} = \frac{0.13}{1.047^{10}} = 0.08 day^{-1}$$

(ii) L_o – ultimate BOD

$$L_o = \frac{BOD_3}{1-10^{-K_{30}x3}} = \frac{55.5}{(1-10^{-0.13x3})} = 93.7 mg/L$$

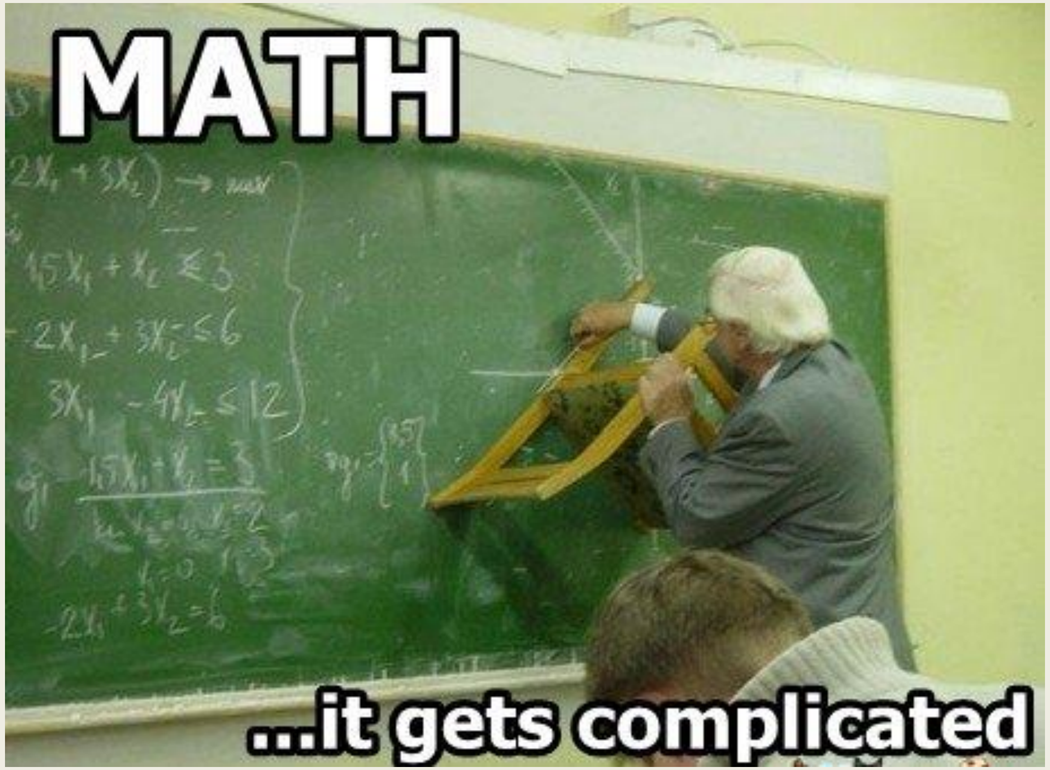
SOLUTION (CONT’)

(iii) BOD5 @ 20°C

$= L_o (1-10^{-K20x5})$

$= 93.7 (1-10^{-0.08x5})$

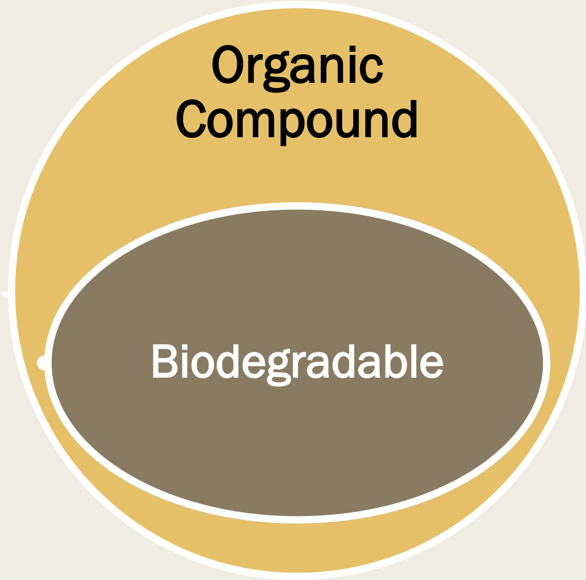
$= 56.4$ mg/L



CHEMICAL OXYGEN DEMAND (COD)

Definition

- The quantity of oxygen needed to chemically oxidize the organic compound (Biodegradable+Non-biodegradable) in sample, converted to carbon dioxide and water.
- Commonly used to define the strength of industrial wastewaters



TEST PROCEDURE

- Add measured quantities of potassium dichromate, sulphuric acid reagent containing silver sulphate, and a measured volume of sample into a flask.
- The mixture is refluxed (vaporized and condensed) for two hours. The oxidation of organic matter converts dichromate to trivalent chromium,

TEST PROCEDURE (CONT')

$$\text{Organic matter} + Cr_2O_7^{2-} + H^+ \longrightarrow CO_2 + H_2O + 2Cr^{3+}$$

- The mixture is titrated with ferrous ammonium sulphate (FAS) to measure the excess dichromate remaining in sample.
- A blank sample of distilled water is carried through the same COD testing procedure as the wastewater sample.

COD is calculated from the following equation:

$$COD = \frac{8000(a-b)}{\forall} \times Normality of Fe(NH_4)_2(SO_4)_2$$

Where:

COD = Chemical oxygen demand (mg/L)

a = Amount of ferrous ammonium sulphate titrant added to blank (mL)

b = Amount of titrant added to sample (mL)

$\forall$ = Volume of sample (mL)

8000 = Multiplier to express COD in mg/L of oxygen

EXAMPLE

The results of a COD test for raw wastewater (50 mL used) are given. Volumes of FAS used for blank and the sample are 24.53 mL and 12.88 mL, respectively. The normality of FAS is 0.242. Calculate the COD concentration for the sample.

SOLUTION:

- Using the equation:

$$COD = \frac{8000(a-b)}{\forall} \times Normality of Fe(NH_4)_2(SO_4)_2$$

$$= \frac{8000 \times (24.53 - 12.88) \times 0.242}{50}$$

= 451 mg/L

SIMPLIFIED COD ANALYSIS

RELATION BETWEEN COD AND BOD

- COD > BOD which means that COD >= L_0
- COD/BOD ≈ 2, biodegradable organic
- COD >> BOD, non-biodegradable organic
- Ratio of COD/BOD is approximately 2 before wastewater treatment. After the treatment, the ratio increases.
- *If COD/BOD = 1 , What does that mean ??*

COD vs BOD

COD

- Process Performance testing
- Takes 2.5 hrs

BOD

- Compliance testing
- Takes 5 days

CHEMICAL CHARACTERISTICS (CONT')

B. Inorganic compounds:

Definition

- When placed in water, inorganic compounds dissociate into electrically charged atoms referred to as ions.
- All atoms linked in ionic bond.

$NaCl \rightarrow Na^{+} + Cl^{-}$

$Ca(OH)_2 \rightarrow Ca^{2+} + 2(OH)^{-}$

$AlCl_3 \rightarrow Al^{3+} + 3Cl^{-}$

Source(s):

May cover nutrients (nitrogen and phosphorus), alkalinity, chlorides, sulphur, and other inorganic pollutants.

Effect(s):

Nitrogen and phosphorus

- excessive algae breeding and aquatic plants
- eutrophication

- Nitrogen presence in wastewater as organic nitrogen, ammoniacal nitrogen, nitrite nitrogen and nitrate nitrogen.
- The presence of ammonia indicates fresh wastewater.
- Under aerobic conditions, ammonia is oxidised to nitrite and then to nitrate. This process is known as nitrification.

Organic Nitrogen → Ammonia → Nitrite → Nitrate