



IIT ROORKEE



NPTEL ONLINE
CERTIFICATION COURSE

WASTE TO ENERGY CONVERSION

CHARACTERIZATION OF WASTES-3

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CHEMICAL ENGINEERING



Contents

- Characterization of solid wastes
 - Physical
 - Chemical
 - Proximate and ultimate analysis
 - Fusing point of ash
 - Lignocellulosic composition
 - Leaching properties
 - Energy content: Heating value
- Characterization of waste water



Characteristics of Wastewater

- Physical
- Chemical
- Biological



Physical Characteristics

- Total Solids -
 - Total Suspended solids - Turbidity
 - Fixed suspended solids
 - Volatile suspended solids
 - Total Dissolved solids
 - Fixed dissolve solids
 - Volatile dissolved solids
- Temperature
- Taste
- Odour
- Colour



Chemical Characteristics

- Hardness
- Biological oxygen demand
- Chemical oxygen demand
- Nutrients
 - Nitrogen & phosphorus
- Salts
 - Salts of Ca, Mg, Cl, HCO_3 , CO_3 etc.
- Heavy metals
- Total organic carbon (TOC)
- Dissolved oxygen (DO)



Biological Water Quality Parameters

- Aquatic Organisms: Single Cell – Fish: Trout:
- Pathogens: Capable of infecting or transmitting disease to Humans



Analytical methods

1. TSS – Turbidity meter
2. Colour – Spectrophotometer
3. Odour -Threshold odour number (TO)
Dilution of the sample till a barely perceptible odour is achieved.
4. TO - $[(\text{ml of sample} + \text{ml of odour free water}) / \text{ml of sample}]$
5. TDS- Gravimetric or conductivity meter
6. Alkalinity – pH meter
7. Inorganic substances (nitrate/ nitrite , sulphate/sulphite, phosphate, halides etc) – Chemical methods/ spectrometer
8. Trace metal – AAS / ICP-MS

➤ DO measurement

➤ BOD measurement

➤ COD measurement

➤ TOC measurement



- An excess of manganese(II) salt, iodide (I^-) and hydroxide (OH^-) ions is added to a water sample. DO converts from Mn^{2+} to MnO_2 (brown precipitate)



- The brown, Manganese-containing precipitate is dissolved back to the solution by addition of acid and under this condition iodide ion is converted into elemental Iodine.



Winklers Method

- Liberated I_2 is chemically equivalent to the original DO, which is determined by titration with sodium thio - sulphate with a starch indicator,



- After determining the number of moles of iodine produced, we can work out the number of moles of oxygen molecules present in the original water sample.
- Presence of **nitrites of iron in +2 state** in original solution can interfere with the original DO Determination. **Suspended solids** can also interfere.
- Use of azide, permanganate and alum are made to remove the interference due to nitrite, ferrous iron and suspended solid respectively.



DO measurement by membrane electrode method

In a typical dissolved oxygen sensor, two electrodes, a gold cathode and a silver anode, are immersed in a specially prepared electrolyte solution and separated from the sample to be measured by a gas permeable membrane.

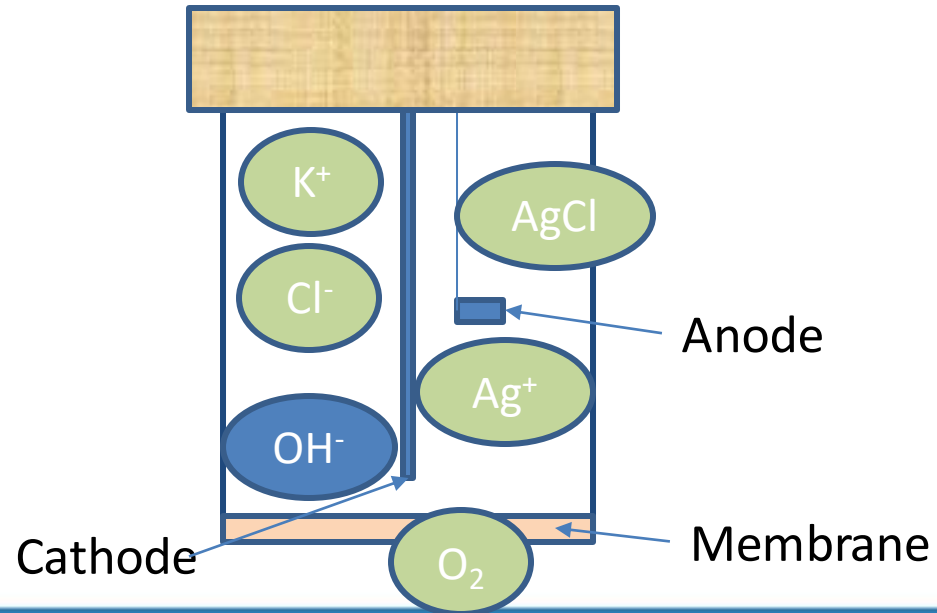
The transfer of oxygen across the membrane is proportional to the partial pressure of oxygen in the fluid.

The chemical reactions that accompany this process are as follows:

Gold cathode: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \longrightarrow 4\text{OH}^-$

Silver anode: $\text{Ag} + \text{HCl} \longrightarrow \text{AgCl} + \text{e}^- + \text{H}^+$

The resulting current flow is directly proportional to the dissolved oxygen content of the stream.



BOD measurement

- Two standard 300 ml BOD bottles are filled completely with diluted waste water (waste water + dilution water) of which the BODs to be measured and the bottles are sealed.
- Another two bottles with dilution water only for blank test
- Dilution water contains CaCl_2 , MgSO_4 , FeCl_3 and phosphate buffer and may be dosed with microorganism seeds
- Oxygen content of one real and blank sample bottles are determined immediately.
- The other bottles of real and blank sample are incubated at 20°C for 5 days in total darkness, after which the oxygen content is measured.
- The incubation may be performed at 27°C for 3 days in total darkness, after which the DO content can be measured. This way BOD_3 equivalent to BOD_5 is calculated.



For unseeded samples the difference between the two DO values is the amount of oxygen that is consumed by micro-organisms during the 5 days and is reported as the BOD₅ (5 day BOD) value of the sample.

$$\text{BOD}_5 \text{ (in mg/L)} = D^* [\underbrace{[(\text{DO})_{t=0} - (\text{DO})_{t=5}]}_{\text{Sample}} - \underbrace{[(\text{DO})_{t=0} - (\text{DO})_{t=5}]}_{\text{Blank}}]$$

< 0.2 mg/l, may be neglected

For seeded samples

$$\text{BOD}_5 \text{ (in mg/L)} = D^* [\underbrace{[(\text{DO})_{t=0} - (\text{DO})_{t=5}]}_{\text{Sample}} - \underbrace{[(\text{DO})_{t=0} - (\text{DO})_{t=5}]}_{\text{Blank}}] * f]$$

Where D^* = dilution factor

f = ratio of seed volume in dilution solution to seed volume in BOD test on seed, normally f is near to 1

COD Measurement

Sample + excess of potassium dichromate and sulphuric acid + heating for 2 hr under total reflux conditions.



$$\text{Where } d = 2n/3 + a/6 - b/3 - c/2$$

Most commonly, a 0.25 N solution of potassium dichromate is used for COD determination,

A lower concentration of potassium dichromate is preferred for samples with COD below 50 mg/L



During digestion the chemically oxidizable material reduces a stoichiometrically equivalent amount of dichromate.

The amount of Cr^{3+} is determined after oxidization is complete, and is used as an indirect measure of the organic contents of the water sample.

The excess potassium dichromate is titrated with ferrous ammonium sulfate (FAS) until all of the excess oxidizing agent has been reduced to Cr^{3+} .

Once all the excess dichromate has been reduced, the Ferroin indicator changes from blue-green to a reddish-brown

A solution of 1.485 g 1,10-phenanthroline monohydrate is added to a solution of 695 mg $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in distilled water, and the resulting red solution is diluted to 100 mL.



The following formula is used to calculate COD:

$$\text{COD} = 8000(b-s)*n/\text{sample volume}$$

where b is the volume of FAS used in the blank sample,
 s is the volume of FAS in the original sample,
and n is the normality of FAS.

If mL is used consistently for volume measurements, the result of the COD calculation is given in mg/L.

Presence of chloride and nitrite can interfere the COD test since they are also oxidized by dichromate and creates an inorganic COD



COD Measurement

Nitrite interference can be eliminated by using sulphamic acid to the dichromate solution

Chloride interference can be eliminated by using mercuric sulphate prior to the addition of other oxidizing agent.



Ratio of BOD to COD indicates the bio-treatability of the wastewater; Ratio higher than 0.8 indicates wastes are highly amenable to biochemical treatment



COD measurement by colorimetric method

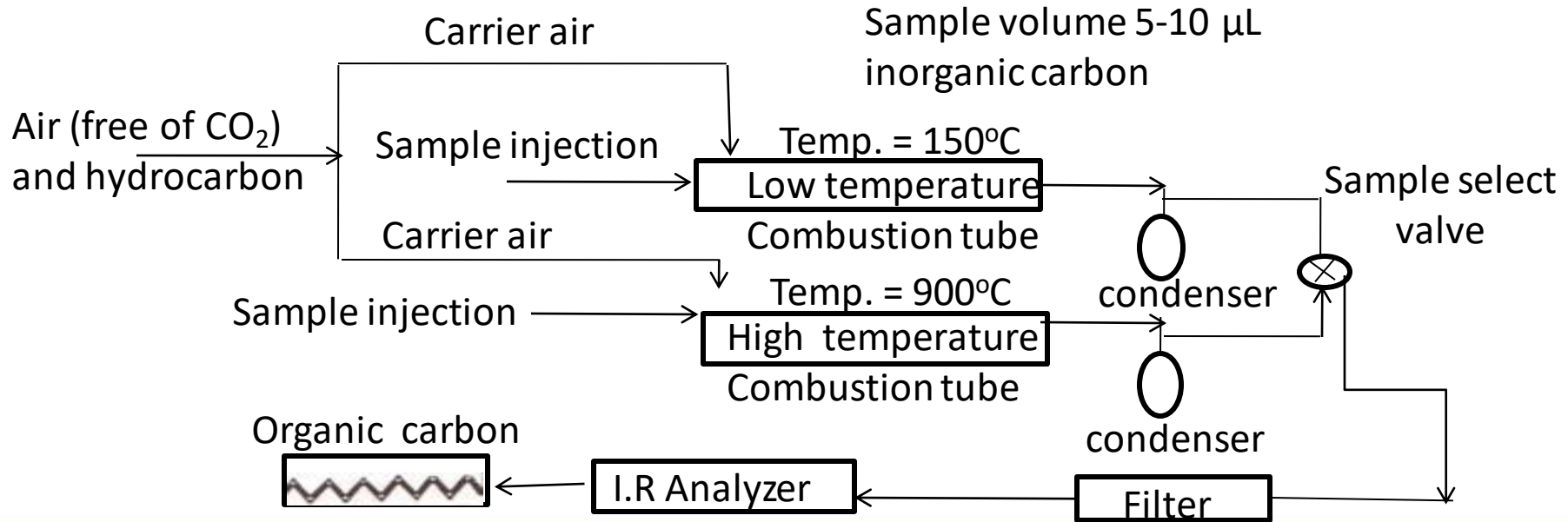
Reagents

- H_2SO_4 reagent (Concn. H_2SO_4 + silver sulphate)
- K-dichromate reagent (K-dichromate + mercuric sulphate)
- Digestion of blank and real sample with the reagents for 2 h at 150 °C
- Colour change due to reduction of dichromate and formation of Cr^{3+}
- Absorbance measurement at 350 - 654 nm for various range of COD (0-40, 0-150, 0-1500 mg/l)
- COD for blank sample is set at zero
- COD of real sample is determined directly (direct reading)

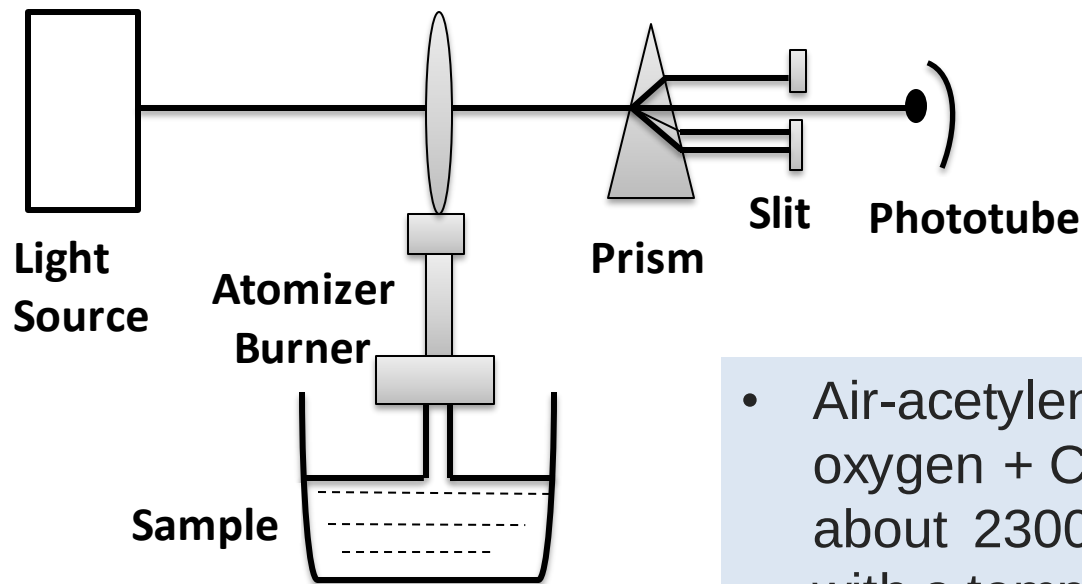


TOC measurement

The organic carbon test is based on the oxidation of the carbon of the organic matter to carbon dioxide, which is measured by a non dispersive infrared analyzer. Alternatively the carbon dioxide can be reduced to methane, which is then measured by a flame ionization detector



Principle of atomic absorption spectrophotometer (AAS)



Works on Lambert–Beer law

$$A = \epsilon * b * c$$

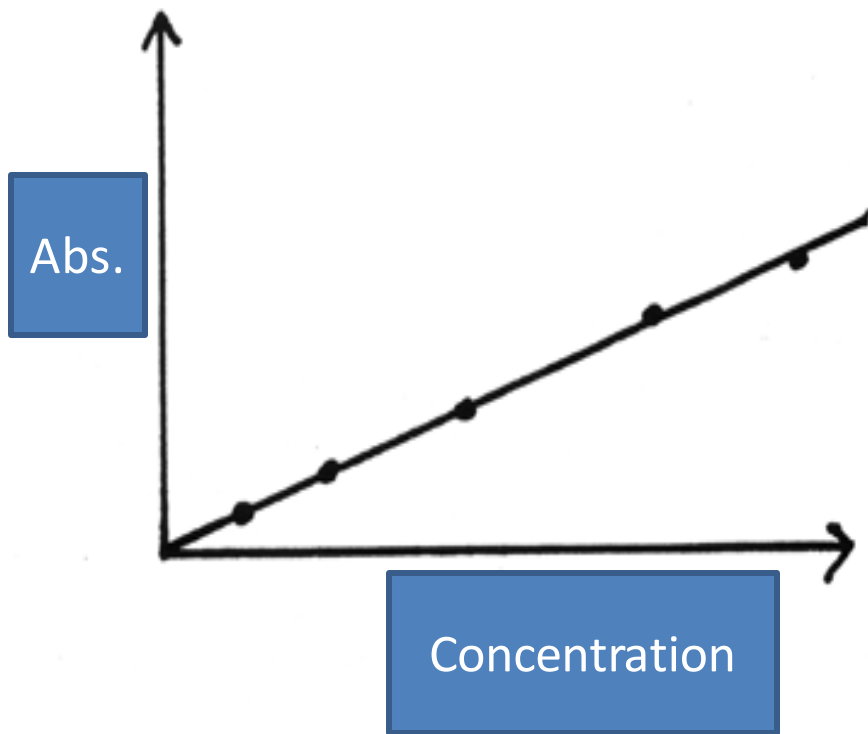
ϵ is the wavelength-dependent molar absorptivity coefficient, b is path length, c is analyte conc.

Flame atomizers

Electrothermal atomizers

(Graphite tube)

- Air-acetylene (compressed high-purity oxygen + C_2H_2) flame with a temperature of about $2300^\circ C$ and (N_2O) -acetylene flame with a temperature of about $2700^\circ C$.
- The latter flame, is ideally suited for analytes with high affinity to oxygen.



Calibration curve

Atomic absorption detection limit

Element	Detection limit, ppm	Wave length (nm)
Arsenic	0.1	1937
Barium	0.05	5536
Cadmium	0.001	2288
Chromium	0.005	3579
Mercury	0.5	2537
Lead	0.03	2833
Silver	0.005	3281

Bacteriological Measurement

- **Membrane filter technique**

Known value of water sample is passed through the filter having very small pores. Coliform bacteria are captured in filter and the filter is then exposed to nutrients which promote the growth of coliform while inhibiting that of other organisms. After 24 or 48 h of incubation, the number of coliform colonies is counted and their density is determined in terms of total coliforms per 100 ml. The coliform colonies appear pink color and their count is made with the aid of an optical device.

Total and volatile solids

- **Total Solid (TS):** Total solid is determined by drying the sample at 105°C in the hot air oven till it attains the constant weight.

$$\text{Total Solid (mg/L)} = \frac{A - B}{\text{Sample Volume, ml}} \times 1000$$

where: A = weight of dried residue + dish, mg, and

B = weight of dish, mg

- **Volatile solid (VS):** Ignite the residue obtained by drying the sample at 105°C for total solid calculation to a constant weight in a muffle furnace at a temperature of 550°C. 15 to 20 min ignition are required for 200 mg residue.

$$\text{Volatile Solid (mg/L)} = \frac{A - B}{\text{Sample Volume, ml}} \times 1000$$

A = weight of residue + dish before ignition, mg,

B = weight of residue + dish or filter after ignition, mg, and

Thanks...

