Experiment 12
Determination of Chemical oxygen demand



Introduction:

The chemical oxygen demand (COD) test allows measurement of oxygen demand of the waste in terms of the total quantity of oxygen required for oxidation of the waste to carbon dioxide and water. The test is based on the fact that all organic compounds, with a few exceptions, can be oxidized by the action of strong oxidizing agents under acid conditions.

Organic matter + Oxidizing agent = $CO_2 + H_2O$ 12.1

The reaction in Eq.-1 involves conversion of organic matter to carbon dioxide and water regardless of the biological assimilability of the substance. For example, glucose and lignin (biologically inert substance) are both oxidized completely by the chemical oxidant. As a result, COD values are greater than BOD values, especially when biologically resistant organic matter is present.
Thus one of the chief limitations of COD test is its inability to differentiate between biodegradable and non-biodegradable organic matter. In addition, it does not provide any evidence of the rate at which the biologically active material would be stabilized under conditions that exist in nature.
The major advantage of COD test is the short time required for evaluation. The determination can be made in about 3 hours rather than the 5-days required for the measurement of BOO. For this reason, it is used as a substitute for the BOD test in many instances.

Environmental Significance:

"COD is often measured as a rapid indicator of organic pollutant in water; it is normally measured in both municipal and industrial wastewater treatment plants and gives an indication of the efficiency of the treatment process. COD has further applications in power plant operations, chemical manufacturing, commercial laundries, pulp & paper mills, environmental studies and general education.

Guideline:

According to Bangladesh Environment Conservation Rules (2023), drinking water standard for chemical oxygen demand (COD) is 10.0 mg/L. For wastewater effluent allowable concentration of CBOD set at a maximum of 125 mg/L depending on discharge point of the effluent (e.g., inland water, irrigation land, public sewer).

Principle:

Potassium dichromate or potassium permanganate is usually used as the oxidizing agent in the determination of COD. In this class potassium permanganate would be used in the determination of COD. Potassium permanganate is selective in the reaction and attacks the carbonaceous and not the nitrogenous matter.
In any method of measuring COD, an excess of oxidizing agent must be present to ensure that all organic matter is oxidized as completely as possible within the power of the reagent. This requires that a reasonable excess be present in all samples. It is necessary, therefore, to measure the excess in some manner so that the actual amount can be determined. For this purpose, a solution of a reducing agent (e.g., ammonium oxalate) is usually used.

Apparatus:

1. Beaker (250 mL)
2. Dropper
3. Stirrer

Reagent:

1. Diluted sulfuric acid solution
2. Standard potassium permanganate solution
3. Standard Ammonium Oxalate solution

Procedure:

1. Pipette 100 mL of the sample into a 250 mL Erlenmeyer flask.
2. Add 10 mL of diluted sulfuric acid and 10 mL of standard $KMn0_4$ solution.
3. Heat the flask in a boiling water bath for exactly 30 minutes, keeping the water in the bath above the level of the solution in the flask. The heating enhances the rate of oxidation reaction in the flask.
4. If the solution becomes faintly colored, it means that most of the potassium permanganate has been utilized in the oxidation of organic matter. In such a case, repeat the above using a smaller sample diluted to 100 mL with distilled water.
5. After 30 minutes in the water bath, add 10 mL of standard ammonium oxalate $[(NH_4)_2C_20_4]$ solution into the flask. This 10 mL ammonium oxalate, which is a reducing agent, is just equivalent to the 10 mL potassium permanganate (oxidizing agent) added earlier. The excess of reducing agent $[(NH_4)_2C_20_4]$ now remaining in the flask is just equivalent to the amount of the oxidizing agent ($KMn0_4$) used in the oxidation of organic matter.
6. The quantity of ammonium oxalate remaining in the flask is now determined by titration with standard potassium permanganate. Titrate the content of the flask while hot with standard potassium permanganate to the first pink coloration. Record the mL of potassium permanganate used.

Calculation:

$$\text{COD (mg/L)} = \frac{\text{mL of } KMnO_4 \text{ used in step 6} \times 100}{\text{mL of sample used}}$$

Assignment:

1. What are the principal advantages and disadvantages of the COD test over the BOD test?
2. Explain why COD values are greater than BOD values.

DATA SHEET

Experiment Name :
Experiment Date :

Student's Name :
Student's ID :
Year/ Semester :
Section :
Group :

Table

Sample No	Source of Sample	Temperature of Sample (°C)	COD (mg/L)

Signature of the course teacher and date