Determination of Chemical Oxygen Demand (COD) of Waste Water

By
Munde Walters

Ganesh Raj Osti

Nguyen Diem Hang

1. Introduction:

In any water system, microorganism will consume any organic & inorganic matter added to it and will produce biomass using oxygen present in the water. The oxygen required for the degradation of the organic matter biologically is called the Biochemical Oxygen Demand (BOD).
The industrial and municipal waste water effluents may contain very high amounts of organic matter and if discharged into natural water bodies, it can cause complete depletion of dissolved oxygen leading to the mortality of aquatic organisms.
The amount of oxygen needed to consume the organic and inorganic materials is called the Chemical Oxygen Demand (COD). There exists a definite correlation between the COD and BOD under certain conditions and by determining the COD, the information about the BOD of the water/waste water can be derived.
Potassium dichromate is considered the best oxidant due to its strong oxidizing ability, its applicability to a wide variety of samples and ease of manipulation makes it very efficient.

2. Reagents used:

1. Potassium dichromate (Standard solution): $K_2Cr_2O_7$ – 0.004167 M (0.0250 N)
2. Mohr's Salt: Ferrous ammonium sulphate (Standard solution): $FeSO_4.(NH_4)_2SO_4$ (0.025 M)
3. Mercuric Sulphate: Powdered $HgSO_4$
4. Silver Sulphate: Powdered Ag_2SO_4
5. Phenanthroline ferrous sulphate indicator solution
6. Concentrated Sulphuric acid: H_2SO_4 18 M

3. Procedure:

50 ml of sample was taken into a refluxing flask and several boiling stones were added. 0.1 g $HgSO_4$ was added to the solution. 5 ml of concentrated H_2SO_4 was also added to the solution. To ensure that $HgSO_4$ dissolved completely, the solution was swirled slowly while adding Sulphuric acid. 0.1 g of Ag_2SO_4 was added to this solution. Finally Potassium dichromate was added. Thorough mixing of the solution was ensured by swirling the flask in a water bath to recover any volatile substances that may have escaped from the liquid state. The flask was then attached to the condenser and further cooling was done. 20 ml of Sulphuric acid was added to the solution in the flask continuing cooling and swirling to mix the solution. The solution was refluxed for 1 hour.
A blank run (using 50 ml distilled water instead of sample) was simultaneously conducted with the same procedure after cooling; the solution was transferred to an Erlenmeyer flask. The reflux flask was rinsed thrice, pouring the rinsing water to the Erlenmeyer flask. The

solution was diluted to about 300 ml and about 8 drops of Phenanthroline ferrous sulphate was added to the solution as an indicator.
The solution was titrated against the Mohr's salt and the titer volume required for the color change from blue-green to reddish blue was noted.
The procedure was repeated for the blank run.

4. Observations:

Solution	Initial Reading (ml)	Final Reading (ml)	Titer volume (ml)
Sample	0.00	21.60	21.6 - V_s
Blank	0.00	23.2	23.2 - V_{bl}

5. Calculations:

COD = 8000 * (V_{bl} – V_s)* M/ original volume of sample taken mg/l

Where,

V_{bl} = Titer volume for the blank
V_s = Titer volume for the sample
M = Molarity of Mohr's solution

COD = 8000 * (23.2-21.60) * 0.025/ 50
= 6.4 mg/l

6. Discussions and Results

Potassium dichromate acts as a strong oxidizing agent and oxidizes the organic and inorganic matter in the waste water. The reaction can be expressed as -

$$\mathbf{Cr_2O_7^{2-} + 14\ H^+ + 5\ e^- = 2\ Cr^+ + 7\ H_2O}$$

If chlorides are present in the sample it will interfere with the oxidation of the organic matter. To ensure non-interference of chlorides **Mercury Sulphate** is added which will form complex of mercuric chloride. An amount of 10 g of Mercury Sulphate is required for 1 g of Chlorides to form complex.

Sulphuric acid is added to the mixture so that the mercury is completely dissolved. Besides, it assists in oxidizing the nitrogen compounds in the sample and the increased heat will accelerate the reaction rate.

Silver Sulphate catalyses the reaction and also assists in the oxidation of the nitrogen compounds.

Mercury sulphate is added first in order to allow the chlorine atoms to combine with mercury. If Silver Sulphate is added first, the chlorine would bind with the silver. Mercury sulphate may be added after; however it will take some time for the chlorine to detach from the silver and bind to mercury. Thus, it is best to add mercury sulphate first.

The titer volume of the sample gives the volume of Ferrous Ammonium Sulphate required to react with the excess potassium dichromate in the solution. Similarly, the titer volume for the blank (distilled water) gives the volume of Ferrous Ammonium Sulphate required to react with the excess potassium dichromate in the blank. The equation for the titration can be expressed as:

$$\mathbf{Cr_2O_7^{2-} + FeSO_4\,(NH_4)_2SO_4 = Cr^{+} + NH_4^{+} + Fe^{3+}}$$

From above equation it can be seen that one molecule of dichromate corresponds to one molecule of Mohr's salt. Thus, the difference in volume of excess $K_2Cr_2O_7$ reacting with Mohr's solution can be calculated from the expression:

= (Original vol. $K_2Cr_2O_7$ – vol. of $K_2Cr_2O_7$ used for oxidation)$_{solution}$ - (Original vol. $K_2Cr_2O_7$ – vol. of $K_2Cr_2O_7$ used for oxidation)$_{blank}$

= (Vol. of $K_2Cr_2O_7$ used for oxidation)$_{blank}$ **- Vol**. of $K_2Cr_2O_7$ used for oxidation)$_{solution}$

Hence, the difference in the titer volume for the solution and the blank is used to find out the Chemical Oxygen Demand directly.

The resulting COD value of the sample was 6.4 mg/l. According to VLAREM II Basic Environmental Quality Standards for Surface Water, the range of COD should be < 30 mg/l. Thus, the sample is within the standard COD value.

7. Conclusion

This project was to determine the COD of a given sample using the method of titration. The COD value of the sample was found to be 6.4 mg/l.