



Determination of chemical oxygen demand in water samples from automobile industry by open reflux method

Anosh Charles ^{1*}, Anubha Vijay Pandya ²

¹⁻² Department of Chemical Sciences, Christian Eminent College, Indore, Madhya Pradesh, India

* Corresponding Author: Anosh Charles

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Abstract

The Chemical Oxygen Demand is the evaluation of oxygen required for the portion of organic matter in wastewater that is exposed to oxidation and the amount of oxygen expended by organic matter from boiling acid potassium dichromate solution. It is a water quality measure used to determine the quantity of biologically active substances and biologically inactive organic matter in water. It is a rapidly measured variable for exemplifying industrial wastes, and treatment plant effluents. This test has the advantage of not being subjected to interference from toxic materials. For analysis, the water is subjected to reflux using potassium dichromate. Organic matter will partially reduce dichromate and the remainder can be measured after titrating with ferrous ammonium sulfate. Chemical Oxygen Demand is determined for both blank and samples, the difference between the volume of titrant gives the value of the particulate matter. Water samples from the automobile industry are collected and tested to check for the level of pollution for regulation and control. The results show that after treatment the water contains fewer pollutants in comparison with the untreated samples. The Chemical Oxygen Demand values are under the maximum limit given for the type of samples and are therefore permissible.

Keywords: oxygen, organic, reflux, wastewater

Introduction

Chemical oxygen demand (COD) is defined as the amount of a quantified oxidant that reacts with the sample under controlled conditions. The quantity of oxidant consumed is stated in terms of its oxygen equivalence. Because of its exceptional chemical properties, the dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) is the specified oxidant which is reduced to the chromic ion (Cr^{3+}) in these tests. Both organic and inorganic components of a sample are subject to oxidation, but in most cases, the organic component dominates and is of greater interest. COD is a distinct test; the amount of sample oxidation can be affected by digestion time, reagent strength, and sample COD concentration. COD often is used as a measurement of pollutants in wastewater and natural waters.

In a COD analysis, hazardous wastes of mercury, hexavalent chromium, sulfuric acid, silver, and acids are generated. The open reflux method is suitable for a wide range of wastes where a huge sample size is preferred. The closed reflux methods are more cost-effective in the use of metallic salt reagents and generate reduced quantities of hazardous waste, but require homogenization of samples containing suspended solids to obtain reproducible results. Ampoules and culture tubes with premeasured reagents are available commercially. Measurements of sample volumes as well as reagent volumes and concentrations are critical. Subsequently, obtain specifications as to limits of error for premixed reagents from the manufacturer before use. Most types of organic matter are oxidized by a boiling mixture of chromic and sulfuric acids. A sample is refluxed in a strongly acid solution with a known excess of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). After digestion, the remaining unreduced potassium dichromate is titrated with ferrous ammonium sulfate to determine the quantity of potassium dichromate consumed and the oxidizable matter is calculated in terms of oxygen equivalent. The ratios of reagent weights, volumes, and strengths are kept constant when sample volumes other than 50 mL are used.

The standard 2 hours reflux time can be decreased if it has been shown that a briefer period yields the same results. Some samples with very low COD or with highly heterogeneous solids content may need to be examined in replicate to yield the most reliable data. Results are additionally enhanced by reacting a maximum quantity of dichromate, provided that some residual dichromate remains. The oxidation of most organic compounds is 95 to 100% of the theoretical value. Pyridine and related compounds resist oxidation and volatile organic compounds will react in amount to their contact with the oxidant. Straight-chain aliphatic compounds are oxidized more effectively in the occurrence of a silver sulfate catalyst. The most common interferent is the chloride ion. Chloride reacts with silver ions to precipitate silver chloride, and thus inhibits the catalytic activity of silver. Bromide, iodide, and any other reagent that inactivates the silver ion can interfere similarly. Such intrusions are negative in that they tend to limit the oxidizing action of the dichromate ion itself.

However, under the severe digestion procedures for COD analyses, chloride, bromide, or iodide can react with dichromate to produce the elemental form of the halogen and the chromic ion. Results are then produced with many errors. The difficulties caused by the presence of the chloride can be overcome mostly, but not completely, by complexing with mercuric sulfate before the refluxing procedure. Even though 1 g mercuric sulfate is specified for a 20 mL sample, a lesser amount can be used where sample chloride concentration is known to be less than 2000 mg/L, as long as a 10:1 weight ratio of mercuric sulfate to chloride is sustained.

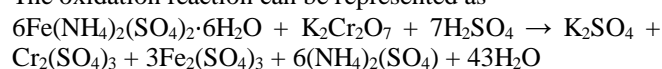
The test for samples containing more than 2000 mg Chloride ions per litre should not be done. Techniques designed to measure COD in saline waters are different. Halide interferences can be eliminated by precipitation with silver ions and filtration before digestion. This method may introduce many errors due to the obstruction and carry-down of COD matter from heterogeneous samples. Ammonia and its derivatives, in the waste or generated from nitrogen-containing organic matter, are not oxidized. Yet, elemental chlorine reacts with these compounds. Hence, corrections for chloride intrusions are difficult. Reduced inorganic species such as ferrous iron, sulfide, manganous manganese, etc., are oxidized quantitatively under the test conditions. For samples containing substantial levels of these species, stoichiometric oxidation can be presumed from the known initial concentration of the interfering species, and rectifications can be made to the COD value obtained. It is entirely artificial but is nonetheless considered to produce a result that may be used as the basis upon which to calculate a judiciously accurate and reproducible estimate of the oxygen-demanding properties of wastewater.

The silver, chromium, and mercury salts used in the COD determinations create dangerous wastes. The greatest problem is in the use of mercury. If the chloride concentration to COD is insignificant, Mercuric sulfate can be omitted. Smaller sample sizes reduce waste. Recovery of the waste material may be possible if permissible by the regulatory authority. The samples should be collected in glass bottles and the unstable samples must be tested without delay. Preservation can be done by acidification of the sample to pH ≤ 2 using concentrated Mercuric sulfate if a delay before analysis is inevitable. All samples should be homogenized holding suspended solids before analysis. If COD is to be related to BOD, TOC, etc., all tests should receive identical

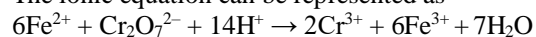
pre-treatment. Initial dilutions can be made for wastes containing a high COD to reduce the error typical in measuring small sample volumes, and requiring only two or three hours for test completion.

Standard potassium dichromate solution oxidizes the organic and inorganic oxidizable matter in an acidic medium. Oxidation is simplified by silver sulfate which acts as a catalyst. Oxidation of chloride is repressed by the addition of mercuric sulfate which forms a more stable and soluble mercuric chloride complex. In brief, in this method, a known volume of sample is refluxed with an excess of acidified standard dichromate solution for two hours. Where the oxidizable content of the sample is oxidized. Unreacted dichromate is back-titrated with a standard solution of ferrous ammonium sulfate. The test method does not homogeneously oxidize all organic materials. Volatile organic may partially be lost before oxidation is achieved.

The oxidation reaction can be represented as



The ionic equation can be represented as



This technique has the advantage of concentrating the sample without significant losses of easily digested volatile materials. Hard-to-digest volatile materials such as volatile acids are lost, but an improvement is gained over ordinary evaporative concentration methods.

Effluent Treatment Plant or ETP is one type of wastewater treatment plant that uses methods that are particularly intended to purify industrial wastewater for its reuse and its aim is to release safe water to the environment from the harmful effect caused by the effluent. Industrial effluents contain various materials, contingent on the industry. Some effluents contain oils and grease, and some contain toxic materials (e.g., cyanide). Effluents from food and beverage factories contain degradable organic pollutants. Meanwhile, industrial wastewater contains a diversity of impurities, and specific treatment technology called ETP is mandatory.

Sewage is the waste formed by residential, institutional, commercial, and industrial establishments. STP plant tests the sewage to make it appropriate for safe disposal, agricultural use or domestic use in toilets, etc. Sewage typically contains a high quantity of organic and inorganic wastes. It is essential to treat sewage before it enters any water body. If sewage, is permitted to enter the water sources without treatment, it will contaminate them; which is why it is vital to treat sewage properly before letting it into rivers or any other sources of water.

Reverse osmosis is one of the most active forms of water filtration because different chemical or carbon filtration systems, which use certain materials to attract or directly target the pollutants in the water, reverse osmosis works by forcing water through a microscopically small filter material. This semi-permeable membrane has a pore size of around 0.0001 microns, efficiently only letting the small water molecules through and catching any larger molecules of contaminants, organic materials, or even salt. Initially designed to desalinate seawater and decrease high chemical contaminant material such as heavy metals, reverse osmosis is now in use in numerous commercial, military, and even residential applications.

The aim is to check whether the COD values of the water samples are within or above the normal limits for their respective sources.

Method and Materials

Apparatus

Reflux apparatus, consisting of COD digestion tubes and 300 mm jacket condenser with 24/40 ground-glass joint, Laboratory glassware, 500 mL conical flasks, and Digester.

Chemicals

Potassium dichromate, Ferrous ammonium sulfate, concentrated Sulphuric Acid, Silver sulfate, Mercuric sulfate, Ferroin indicator solution, and Potassium hydrogen phthalate.

Preparation of Standard Solutions

Standard potassium dichromate solutions, for 0.25N: The solution was prepared in a volumetric flask by mixing 12.259 g $K_2Cr_2O_7$ in 1000 mL distilled water.

For 0.025N: 100 mL of 0.25N standard potassium dichromate solution was taken in a volumetric flask and 900 mL of distilled water was added to it.

Sulfuric acid reagent: The reagent was made by adding 10.12 g Ag_2SO_4 to 1000 mL conc. H_2SO_4 .

Standard ferrous ammonium sulfate (FAS) titrant solutions, for 0.25N: The solution was prepared by mixing 98 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in distilled water with 20 mL conc. H_2SO_4 and diluted to 1000 mL.

For 0.025N: 100 mL of 0.25N ferrous ammonium sulfate solution was taken in a volumetric flask and 900 mL of distilled water was added to it.

Standardization of this solution was done using standard $K_2Cr_2O_7$ solution as follows:

The 0.25N standard $K_2Cr_2O_7$ solution of 25.00 mL was diluted with distilled water to about 100 mL. Then 30 mL conc. H_2SO_4 was added. It was titrated with FAS titrant using 0.10 to 0.15 mL (2 to 3 drops) ferroin indicator. Similarly, 0.025N FAS solution was standardized.

Sample Collection

The samples were taken from Mahindra and Mahindra Ltd. Pithampur, Dhar, Madhya Pradesh. It is an automobile manufacturing plant that has an effluent treatment plant from where five different water samples were collected.

Procedure:

The five samples were taken in the volume of 20 mL into five different COD digestion tubes.

In each tube, 1 g $HgSO_4$ and then 5 mL sulfuric acid reagent were mixed carefully. Then to the tube containing the RO drinking water sample 10 mL 0.025N $K_2Cr_2O_7$ solution was added.

To the rest of the four sample tubes, 10 mL of 0.25N $K_2Cr_2O_7$ solution and 30 mL of concentrated sulfuric acid were added to all the tubes, and the solutions were mixed properly.

The tubes were attached to the condenser and refluxed in the COD digester preheated to 150 °C for 2 hours.

After digestion, the tubes were cooled and 80 mL of distilled water was added from the vessel into each tube.

The solutions were then transferred in five different labeled 500 mL conical flasks. 2-3 drops of ferroin indicator were added to each flask.

The flask containing RO drinking water sample was titrated with 0.025N FAS solution. The rest of the four samples were titrated with 0.25N ferrous ammonium sulfate solution. The endpoint was blue-green to reddish brown.

In the same manner, a blank was refluxed and titrated containing the reagents and a volume of distilled water equal to that of the sample.

The observations were recorded and used to calculate COD values, which were analyzed to reach the conclusion.

Precautions taken during the experiment:

The refluxing mixture was thoroughly mixed before applying heat to prevent local heating of the flask bottom and a possible blowout of flask contents.

The open end of the condenser was covered with a small beaker to prevent foreign material from entering refluxing mixture and reflux for 2 hours.

The endpoint of the titration was taken as the first sharp colour change from blue-green to reddish brown that persisted for 1 minute.

Result and Discussion

The COD values of the samples were calculated in ppm using the formula:

$$\text{COD mg/L} = \frac{(V_1 - V_2) \times N \times 8000}{\text{Vol. of sample taken (mL)}}$$

Where:

V_1 = Volume of Ferrous ammonium sulfate solution required for the blank.

V_2 = Volume of Ferrous ammonium sulfate solution required for the sample.

N = Normality of Ferrous ammonium sulfate.

Table 1: Observation table for chemical oxygen demand values of water samples

S. No.	Name of water samples	Volume of FAS Solution used in titration	FAS Volume difference between blank and sample
1.	Untreated ETP	13 mL	2.8 mL
2.	Treated ETP	11.3 mL	1.1 mL
3.	Untreated STP	12.1 mL	1.9 mL
4.	Treated STP	10.7 mL	0.5 mL
5.	RO drinking water*	10.8 mL	0.6 mL

The titration value of Blank is 10.2 mL of FAS.

RO drinking water is titrated with 0.025 N potassium dichromate

Using the data in table 1, a graph is made by taking sample numbers on the x-axis and the volume of FAS solution on the y-axis.

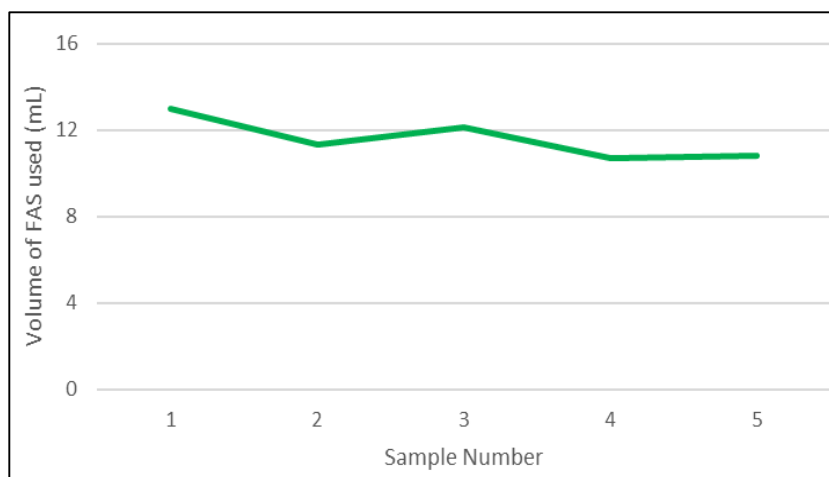


Fig 1: Shows the decrease in the volume of FAS going from samples 1 to 5

Table 2: Result table for chemical oxygen demand values of water samples

S. No.	Name of water samples	COD values of the sample	Normal range
1.	Untreated ETP	280 mg/L	<500 mg/L
2.	Treated ETP	110 mg/L	<150 mg/L
3.	Untreated STP	190 mg/L	<400 mg/L
4.	Treated STP	50 mg/L	<100 mg/L
5.	RO drinking water	6 mg/L	<10 mg/L

Using the data in table 2, a graph is made by taking sample numbers on the x-axis and the chemical oxygen demand

values on the y-axis.

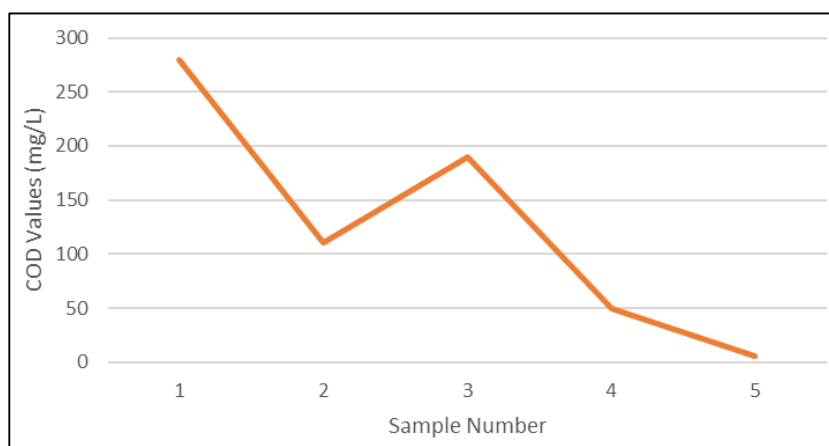


Fig 2: shows the decrease in the COD Values going from samples 1 to 5.

Conclusion

The samples of water gave a variety of COD values. The untreated ETP samples had the highest COD value of 280 mg/L whereas the RO drinking water has the least COD value of 6 mg/L. The COD value of untreated STP 190 mg/L was less than the COD value of untreated ETP 280 mg/L. The COD value of treated ETP 110 mg/L is more than the COD value of treated STP 50 mg/L. From these results, it can be concluded that there are no exceeding COD values in the water samples and that they are below normal values for their respective source of collection.

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