

ENVIRONMENTAL SYSTEMS ENGINEERING

ENGI 9628

Winter Semester 2023

Term Paper

**A case study to interpret different methods for determination of
Chemical Oxygen Demand (COD) (Topic 29)**

23rd March 2023

Submitted by

Nahidul Kabir Siddiki #202291960

Md Sakil Ahmed #202196513

Submitted to

Dr. Noori Saady



**School of Graduate Studies
Memorial University of Newfoundland**

Table of Contents

Abstract	3
Chapter 1: Introduction	4
Chapter 2: Importance	6
Chapter 3: Review of the Case Studies	7
Chapter 4: Discussion.....	10
Chapter 5: Conclusion	12
Acknowledgement	14
Reference	15

Abstract

Global output rates of waste are rising. Once more, the mingling of garbage and water is becoming worse. Water quality is still a concern in many cities and developing countries, even though it is essential to assess it and treat it with effective waste management. Pollutants are typically difficult to remove, making water pollution remediation expensive and complicated. This pollution has an impact on creatures' quality of life and may harm all ecosystems. Water pollution has lately become a major worry due to the extraordinary number of organic compounds in wastewater, which are poisonous, nondegradable, and semi-volatile. An essential indicator of water quality, Chemical Oxygen Demand gives information on how wastewater discharge may affect the surrounding ecosystem. Significant environmental issues, such as high COD, might result from the massive volumes of chemicals in mineral processing effluent. For environmental monitoring and wastewater treatment operations, the traditional standard methods for COD analysis have been extensively utilized. However, these techniques do have a few drawbacks. In this essay, we have examined, evaluated, and critiqued many approaches to calculating the Chemical Oxygen Demand in the waterbody. We have read a few publications, cited them, and focused on and analyzed three important case studies in those papers.

Chapter 1: Introduction

Pollutants are typically hard to eradicate, making water pollution treatment costly and complex. All ecosystems may be harmed by this pollution, which reduces creatures' ability to survive. Due to the enormous number of organic compounds in wastewater and their inherent non degradability, toxicity, and semi-volatility, water pollution has lately become a major problem. According to Nijami (2017), there are several issues the globe is now confronting in order to address the expanding human population. As a result, there are a number of environmental problems, including the release of greenhouse gases and the massive creation of garbage from many different sources (i.e animal, agricultural, industrial, municipal wastes).

The elimination of organic pollutants from wastewater has drawn more and more attention. Water quality evaluation and pollutant management have become urgent global needs as a result of the significant problem that is water pollution. Aquatic systems, environmental deterioration, and human health are negatively impacted by organic pollutants, particularly phenolic chemicals, polycyclic aromatic hydrocarbons, and agricultural organic pollutants. The quantity of organic contaminants in wastewater is often estimated using the chemical oxygen demand (COD) metric. The COD is a measurement of the quantity of organic pollutants contained in the sample under test and is defined as the number of oxygen equivalents spent in the oxidation of organic compounds by potent oxidizing agents like dichromate and permanganates. Several research organizations and laboratories involved in the characterization of organic matter are now interested in developing reliable methods for measuring the COD of solid wastes.

The quantity of oxygen equivalents spent during the oxidation of organic compounds by potent oxidizing agents like dichromate and permanganate is the definition of the standard technique for COD detection. To obtain more thorough oxidation, this approach calls for the time-consuming

procedure of refluxing samples; nevertheless, the consistency of the findings depends on the operator's expertise and pricey reagent.

Rapidly creating innovative COD-determination techniques have received a lot of attention in recent years. Electrocatalytic or photocatalytic oxidation concepts have formed the foundation for all of these recent breakthroughs. As the high potentials necessary for the oxidation of organic compounds typically induce the oxidation of water, Claudineia (2008) pointed out that it is not possible to directly oxidize organic species in an aqueous solution using metal or carbon electrodes. Nevertheless, the oxidization of organic species like carbohydrates and amino acids, which is assumed to be primarily responsible for the COD, may be electro-catalyzed by the copper electrode in alkaline environments.

The goal of this study was to create a quick, cheap, safe, and easy-to-use COD determination procedure that could be used to small projects as well as larger businesses with the highest level of accuracy and cost-effectiveness. It will be contrasted and shown how the industrial KIT, a modified version of the standard process, and the basic COD determination technique differ from one another.

Chapter 2: Importance

COD is a very essential parameter to understand the outcome will be received from the water, which is about to get attached as it reacts, similarly prioritized as BOD determination of water. Higher COD levels mean a greater amount of oxidizable organic material in the sample, which will reduce dissolved oxygen (DO) levels. A reduction in DO can lead to anaerobic conditions, which is deleterious to higher aquatic life forms. COD determination has become very popular by the time pollutant level in water, effectiveness of wastewater treatment solution, disposal effects of wastewater on environment and so many. It is not so unbelievable that it is a big concern to have the result of COD level on time and mostly with maximum accuracy.

According to the report by Realtechwater.com named “*COD Parameter*”, it has so many applications which can be stated as below,

- a) Air circulation Advancement
- b) Optimizing the dose of minerals
- c) Handling of Industrial Effluent Discharges
- d) Comprehensive Therapy for Product Loss Monitoring & Protection
- e) Optimization of Water Reuse
- f) Monitoring Wastewaters Pollution

As the fields are not very short, the importance of more research to improve COD determination is extensively needed.

Different methods bring out the potential according to duration, accuracy, availability and accessibility of different material to attempt different determination process of Chemical Oxygen Demand.

Chapter 3: Review of the Case Studies

There are several case studies available that outline various alternate approaches to calculating COD levels. Although some broke out of the box before being noticed, others have already demonstrated promising outcomes. As is previously known, an aliquot of the sample must be digested for two hours at 150°C with sulfuric acid and dichromate in order to determine COD. Using a ferroin indicator or a spectrophotometer reading at the proper wavelength, the resultant solution is titrated to a colored endpoint. Sometimes the conditions for determining COD might be varied depending on the sample's kind, source, equipment that is accessible, or substance. If lab access is flexible, the conventional procedure is often advantageous. Other approaches are recalled and adopted when the circumstance is different. It is undeniable that the majority of them were influenced by and somewhat modified from the previous standard operating procedure.

Three strategies were mentioned in the first research we chose from Sluiter et al. (2008). Methods 2 (sample dilution and sampling with a pipette) and 3 (sample dilution and sampling with a pipette cut at the tip) were less than ideal for figuring out the COD, though. In actuality, COD estimates by techniques 2 and 3 considerably deviated from the theoretical value for 8 out of the 9 samples (Tukey HSD test, $p < 0.05$). Only the cow manure COD measured by technique 3 (Tukey HSD test, $p = 0.098$) sample was comparable to the theoretical value. The mean absolute errors were found to be 39% and 31%, respectively, for the samples produced by Methods 2 and 3.

Case Study 1:

The level of COD was measured using an alternate technique. Method 1 was to be modified to hydrolyze agricultural biomasses and control material. Samples weighing 80 mg were put in 35 mL Pyrex glass tubes. The tubes were then heated to 30 °C for an hour while being stirred

magnetically. 0.85 mL of H₂SO₄ was added to each tube at that point (300 rpm). The tubes were filled with 23.8 mL of distilled water, and they were then heated for 1 hour at 121 °C. Following cooling, commercial kits were used to determine the COD levels in the supernatant liquids. The range of values was 500 to 10,000 mg COD.L⁻¹. For each sample, all the analyses were carried out in quadruplicate. In the shortest possible time, 1 mL aliquots of supernatant liquids were put in the disposable tubes. The tubes were subsequently heated for 120 minutes in a preheated thermoreactor to 148 °C. An automated spectrophotometer was used to measure the COD in the end. As of 2016, André et al.

2nd method was to dilute a solid input of 3.5 g TS.L⁻¹ of agricultural biomasses in distilled water. Each combination was manually stirred before a pipette sample of the supernatant liquid was taken for COD determination as previously mentioned. 3rd method was almost same, to dilute a solid input of 3.5 g TS.L⁻¹ of agricultural biomasses in distilled water. Each combination was manually stirred, and the supernatant liquid was then sampled with a pipette whose tip had been previously cut (0.3 cm) to minimize blockage by large-sized particles before to COD measurement.

Case Study 2:

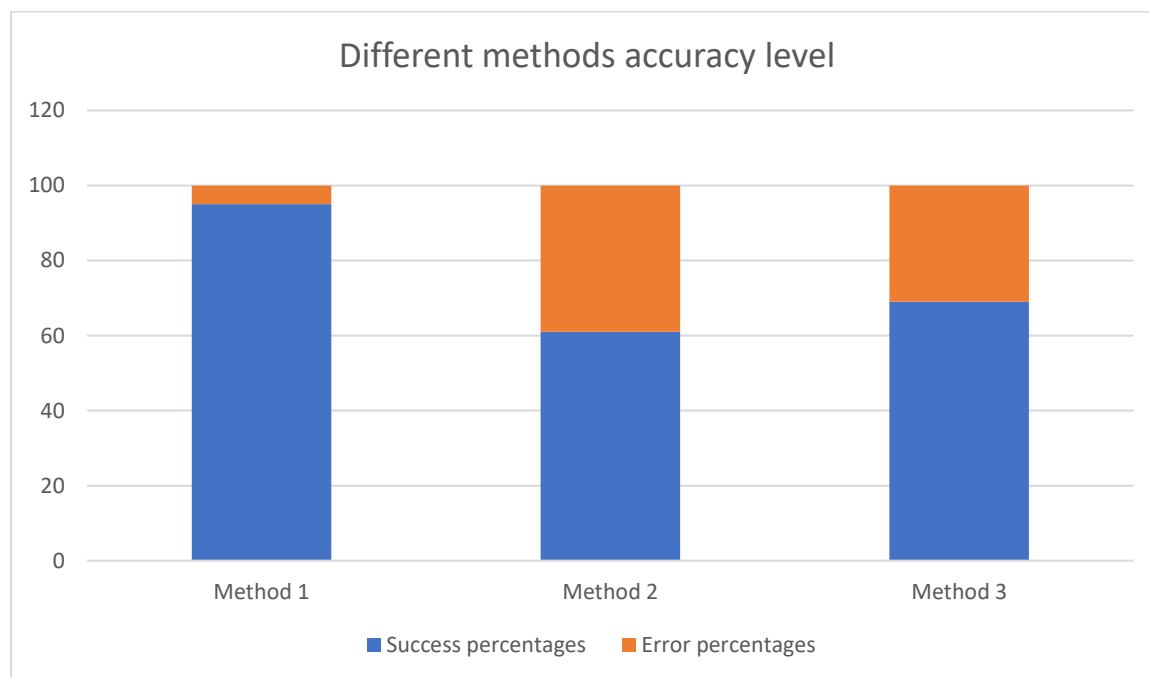
500 ml of distilled water, 167 ml of concentrated H₂SO₄, and 33.3 HgSO₄ were combined to create the digestion solution. 3 g of K₂Cr₂O₇ that had been dried for two hours at 103 C beforehand was also added. After being dried at 110 C, potassium hydrogen phthalate (KHP) was dissolved in distilled water and diluted to a volume of 1000 ml, giving the solution a theoretical COD of 500 mg/L. The following COD standards (mg COD/L) were created by diluting this solution with distilled water: 20, 50, 90, 140, 190, and 230. By adding 20 g and 40 g of sodium chloride per liter, respectively, to the aforementioned standard KHP solutions, two saline standards were created. After removing each (10 ml) standard saline solution, HgSO₄ was added at a 20:1 ratio

(HgSO₄:Cl). With the 20 g NaCl/L saline sample, this concentration was equivalent to 2.42 g HgSO₄ and for the 40 g NaCl/L sample, it was equal to 4.85 g HgSO₄. Following the precipitation of HgC₁₂, 2 ml of the sample was taken out and combined with 1.2 ml of the digestion solution (K₂Cr₂O₇-H₂SO₄-HgSO₄) and 2.8 ml of the sulfuric acid reagent (Ag₂SO₄-H₂SO₄) before being added to Hach reflux tubes that had been correctly mixed and firmly sealed. The mixtures were refluxed for two hours at 150 C in a Hach COD reflux reactor. The samples were examined using a spectrophotometer at a wavelength of 600 nm after cooling to 4 C for a few hours. To achieve the final concentrations of 130 mg COD/L, 70 mg COD/L, and 35 mg COD/L, synthetic sewage was also generated and diluted.

Chapter 4: Discussion

Case study 1

Method 1 developed in this study, which consisted of a double acid hydrolysis followed by COD analysis using commercial kits significantly improved the results. The mean of the absolute error ranged from 4% to 7% with reliable repeatability of the measure (± 1 –5%). The double acid hydrolysis adapted from Sluiter et al. (2008) allowed for the hydrolysis of cellulose and hemicelluloses, thereby resulting in an improvement of the homogeneity of the solid wastes during the sampling. The validity of the acid hydrolysis method was verified on cellulose and cellobiose powders, for which the recovery yields reached 103% ($\pm 0.7\%$) and 100% ($\pm 1.2\%$) of the theoretical COD. Noguero-Arias et al. (2012) and Raposo et al. (2008) had developed two different titrimetric methods adapted to COD determination of solid samples. These two methods reported high accuracy and precision. Noguero-Arias et al. (2012) had reported an accuracy of 1.9% and a precision of 1.4% (RSD) measured on two certified reference materials. In regard to the operating time, the main procedures comprise the weighing (5 min per sample), the double acid hydrolysis (5 min per sample), the tube cleaning (5 min per sample), and the analysis using COD kits (5 min per sample), which amount to approximately 20 min of labor per sample.



Case Study 2:

Two salinity concentrations, 12.19 g Cl/L and 24.39 g Cl/L, were evaluated in a COD range between 0 mg COD/L and 230 mg COD/L to examine the statistical error of the improved approach. The same COD level but samples devoid of chloride were tested using the standard technique as a control. At COD levels between 20 mg COD/L and 190 mg COD/L, the improved approach had an error of less than 10% at 12.19 g Cl/L, while it had an error of less than 10% at 24.39 g Cl/L for COD levels between 230 mg COD/L and higher.

The inaccuracy of the standard technique was less than 3% for samples containing 50-230 mg COD/L and less than 8% for those containing chloride. When the recommended approach was followed, the error for samples without chloride was less than 3% for samples with 50-230 mg COD/L and less than 8% for samples with 20 mg COD/L. The standard deviation for the traditional approach with samples devoid of chloride was up to 3.5, in contrast to the modified technique's standard deviations of 1.2-4.5 and 2-4.9 with 12.19 g Cl/L and 24.39 g Cl/L, respectively. Results show that the modified method may be reliable for COD concentrations between 20 and 230 mg/L and salinities up to 40 g NaCl/L. To compare this study to the conventional procedure, synthetic sewage was utilized when the same amount of Hg was used as in the recommended improved methodology. The findings showed that even when using a ratio of 20 HgSO₄:1 Cl, the inaccuracy did not significantly decrease (by more than 40%) when using the conventional method. This underlines the necessity of measuring low COD at high salinity with a lower K₂Cr₂O₇ concentration.

According to the results, a modification to the conventional closed reflux colorimetric approach is suggested for the measurement of samples with high salinity (40 g NaCl/L) and low COD (up to

230 mg COD/L). Comparing the suggested improved approach to the conventional method utilizing synthetic sewage reveals that the new method is significantly more trustworthy. When the salinity was high (40 g NaCl/L), the modified method's error was less than 10% whereas the regular method's error was larger than 50%. A lesser quantity of chromium is necessary for more accurate findings at high salinity and low COD, as shown by the fact that the error did not decrease much (more than 40%) when the same amount of Hg was used in the conventional approach as in the suggested modified method.

Chapter 5: Conclusion & Recommendation

Water pollution is a serious problem that affects not only the environment but also human health. Organic pollutants, such as phenolic chemicals, polycyclic aromatic hydrocarbons, and agricultural organic pollutants, are some of the major contributors to water pollution. Measuring the chemical oxygen demand (COD) is an essential parameter to determine the amount of oxidizable organic material in a sample, which can reduce dissolved oxygen levels in water and negatively impact aquatic life.

The traditional method for determining COD is time-consuming, requires costly reagents, and depends on the operator's expertise. Several alternative methods have been developed, such as electrocatalytic or photocatalytic oxidation, to overcome these drawbacks. However, each method has its advantages and disadvantages, and it is essential to choose the best method based on the sample's kind, source, available equipment, or substance.

Based on the findings of the study, we recommend further research to validate the proposed electrocatalytic method for COD determination. It is important to test the proposed method on a wide range of wastewater samples and compare the results with the conventional COD determination technique. Additionally, further research is needed to determine the potential of the electrocatalytic method for industrial applications. Furthermore, more research is needed to develop cost-effective and reliable methods for COD determination that can be used in small projects as well as large businesses. This can help address the challenges faced in water pollution management and improve the accuracy and cost-effectiveness of COD determination.

Acknowledgment

For his unwavering support and inspiration during this semester, Dr. Noori Saady, our lecturer at Memorial University of Newfoundland for the ENGI 9628 Environmental Laboratory course, has earned our sincere gratitude. We want to express our deep gratitude to Dr. Noori Saady for his excellent manners and compassion, as well as for the educational possibilities he gave us during the course.

Second, we would like to express our sincere gratitude to the teaching assistant (TA) for helping us with this course's completion and for providing us with real-time data. We also value his time and support throughout the semester.

We have worked hard to finish this term paper. But without the kind help and support of many people, including our lecturer, our guides, and Memorial University, we would not have succeeded. We wish to express our sincere gratitude to each one of them.

References

- Cazaudehore, G. et al. (2019) “Determination of chemical oxygen demand of agricultural wastes by combining acid hydrolysis and commercial cod kit analysis,” *Journal of Environmental Management*, 250, p. 109464. Available at: <https://doi.org/10.1016/j.jenvman.2019.109464>.
- Jing, G. et al. (2020) “Electrocoagulation: A promising method to treat and reuse mineral processing wastewater with high cod,” *Water*, 12(2), p. 595. Available at: <https://doi.org/10.3390/w12020595>.
- Li, J. et al. (2009) “A spectrophotometric method for determination of chemical oxygen demand using home-made reagents,” *Desalination*, 239(1-3), pp. 139–145. Available at: <https://doi.org/10.1016/j.desal.2008.03.014>.
- Miandad, R. et al. (2017) “Effect of plastic waste types on pyrolysis liquid oil,” *International Biodeterioration & Biodegradation*, 119, pp. 239–252. Available at: <https://doi.org/10.1016/j.ibiod.2016.09.017>.
- Silva, C.R. et al. (2008) “Determination of the Chemical Oxygen Demand (COD) using a copper electrode: A Clean Alternative Method,” *Journal of Solid State Electrochemistry*, 13(5), pp. 665–669. Available at: <https://doi.org/10.1007/s10008-008-0580-9>.
- Sousa, A.C. et al. (2007) “A method for determination of cod in a domestic wastewater treatment plant by using near-infrared reflectance spectrometry of Seston,” *Analytica Chimica Acta*, 588(2), pp. 231–236. Available at: <https://doi.org/10.1016/j.aca.2007.02.022>.
- Vyrides, I. and Stuckey, D.C. (2009) “A modified method for the determination of Chemical Oxygen Demand (COD) for samples with high salinity and low organics,” *Bioresource*

Technology, 100(2), pp. 979–982. Available at:

<https://doi.org/10.1016/j.biortech.2008.06.038>.

- Yao, N., Wang, J. and Zhou, Y. (2014) “Rapid determination of the chemical oxygen demand of water using a thermal biosensor,” *Sensors*, 14(6), pp. 9949–9960. Available at: <https://doi.org/10.3390/s140609949>.