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ANALYTICAL WATER CHEMISTRY

Correlation of the Chemical Oxygen Demand of Water Using Hg and Hg-Free COD Vials

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Abstract—Chemical oxygen demand (COD) is regarded as a fast and economical way in determining organics present in water. This study clarified that reason of the chloride (Cl^-) could be act as the main interference when measuring the COD values, the effect of chloride on COD reading was measured by adding different amount of marine salt (0.600 g (1.125 wt %), 1.125 g (2.250 wt %) and 2.250 g (4.5 wt %) to simulate different concentration of artificial seawater, while the concentrations of chloride were 6788 mg Cl^-/L, 13 577 mg Cl^-/L and 27 156 mg Cl^-/L, respectively. The mean of COD values at ratio (1 : 25) with mercury vials and mercury free vials were ranged between (216, 658 and 1042 mg/L) and (1725, 2199 and 2550 mg/L), respectively. The results obtained using Hg-free vials method have been compared with the results obtained using Hg vials and titration method. Comparative data analyses of the COD results were carried out to detect the interference obtained by chloride ion. This study proposes that the Hg-free COD vials provide the likely solution to minimise risk of environmental damage and disposal expenses as compared with traditional mercury containing COD vials. In this study, a highly significant linear correlation ($r^2 = 0.939$) was determined between COD values using Hg and Hg-free vials for artificial seawater (4.500%), artificial seawater (2.250%) and artificial seawater (1.125%). Furthermore, a highly significant linear correlation ($r^2 = 1$) was found as well for oily wastewater (1 : 100) and oily wastewater (1 : 50). The COD test which is free from mercury has yet to be officially endorsed as such that can be accepted for mercury containing test. Therefore, mercury free COD vials could be successfully employed to in this project.

Keywords: COD, chloride ions, Hg-free vials, Hg vials, titration, interference

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INTRODUCTION

Chemical oxygen demand (COD) refers to a standard method commonly utilized in measuring indirectly the quantity of oxidizable organic substance in wastewater. The COD value outlines the oxygen equivalent of the organic content that can be oxidized to carbon dioxide and water by potassium dichromate ($K_2Cr_2O_7$) using silver sulfate (Ag_2SO_4) as a catalyst under acidic conditions (H_2SO_4). It is also used as an indication of the quantity of organic pollutants in the tested specimen [8]. However, there are a few shortcomings which exist in the conventional way of determining the level of dichromate. Among others, the conventional procedures require longer duration, demonstrate low sensitivity of detection, need complex procedures, must utilize the costly (Ag_2SO_4) and toxic (Cr and Hg) chemicals, and cause only partial oxidation of the pollutants [5, 14]. A number of researchers have found that this 10 : 1 ratio in samples containing chlorides higher than 2000 mg/L contributed to a major error at low concentration 50 mg/L, which allow the CODs value to be moderated [3, 6]. There are a few types of industry wastewaters with chloride concentrations in the excess of 15 g Cl/L, e.g. wastewater from petroleum and chemical industry [10]. [3] carried a study with the intention to utilize the open flux method using $HgSO_4$: Cl ratio of 10 : 1 for masking the chloride. To estimate the accurate value, he proposed to include the sample-specific chloride factors in the calculations. During this study, the COD data obtained by employing conventional commercially available COD kits containing free (approved by [4]) are compared against those that are Hg-free mercury.

EFFECTS OF CHLORIDES ON CHEMICAL OXYGEN DEMAND READINGS

For bounded seas and places where high drainage rate of saline water occurs, the salinity may show higher readings. For instance, the salinity of the Arabian Gulf Sea close to the Kuwait coastline and Saudi Arabia may amount to between 38 to 50 g/kg [1]. Generally, the natural seawater is very rich in chlorides, which in excess of half of the percent by weight of dissolved ions, therefore the major interference in the conventional dichromate method to determine the COD is from the chloride ions [9, 13], which could be act as the main interference when measuring the COD values. Therefore, the effect of chloride ions on the COD values was investigated in this project, as a result the interference of chloride ion could be reduced by several analytical methods [11].

MATERIAL AND METHOD

Colorimetric Measurements of COD

During this experiments, two different vials were used to check the COD values, such as mercury and mercury free vials (Hach). 100 mL of sample were homogenised for 5 min in overhead stirrer (CP Cole-Parmer). The oily wastewater was diluted (distilled water to oily wastewater, 100 : 1) in a 100 mL conical flask, and manually shaken for 5 min. The cap from a COD vial provided in the kit was removed and 2 mL of diluted sample was micro-pipetted into the vial. The lids were sealed tightly and the vial mixed gently several times to mix the contents. The vial was placed in the preheated digester block and allowed to react with COD vial (0–1500 ppm) containing 86% sulphuric acid and potassium dichromate. The vials were digested in a COD reactor hot block (DRB200, Hach, UK), and heated for 2 h at 150°C. The block was turned off and allowed to cool for 15 min. The digested samples and reagent blanks were measured in a pre-programmed colorimeter (DR890, Hach, UK) photometer.

Titration Analysis

The conventional procedure using dichromate was employed as a reference to detect the values of the COD of a number of samples. The chemicals used were H_2SO_4 (98%), $C_6H_{12}O_6$, $K_2Cr_2O_7$, Ag_2SO_4, $HgSO_4$ and $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$. Specific details of the test procedure are as follows:

Reagents. The preparation for the digestion solution was arranged by adding 12.2588 g $K_2Cr_2O_7$, which was dried beforehand for 2 h at 103°C in oven and diluted to 1000 mL. The preparation for the sulfuric acid reagent (H_2SO_4) was performed in accordance with the standard methods, which approved by American Public Health Association [2] for the open colorimetric technique.

RESULT

The impacts of the salt concentrations exceeding 2000 mg/L was determined by using open-reflux digestion methods and colorimetrically (photometrically). Hach approved Method 8000 [4, 12] was utilised in analyzing saline water, which contain the excess of 50 mg/L COD, and below 2000 mg/L of chloride concentration. Generally, Hg-free vials can avoid the risks of the toxic mercury. It also reduces the disposal cost of test vials in comparison with test vials containing mercury, unlike COD results obtained by using Hg-free. In order to detect the interference generated, relationship of COD data using Hg vials compared with those of Hg-free vials needs to be established for this particular waste. This interference can be prevented by adding excess mercuric sulfate to a maximum concentration of 5000 mg/L. The accuracy of the results obtained were confirmed in comparative experiments to ensure the validation of results. This way would support the results, further the results obtained using titration method were considered as reference to confirm the data. The measurements of COD were carried out on (COD; 96 samples), the number of corresponding samples analysed at various stages were tested. Further, there are various range of COD (Hach) testing vials such as ultra-low range, low range, high range and high range plus. Therefore, the percent of chlorides ion in the tested samples were determined to select the accurate range of COD testing.

COD for artificial seawater. It has been shown that chloride ions should be considered as the most significant interference for the determination of COD by dichromate method. Table 1 shows the COD of artificial sea water prepared using 2.250 g (4.500%), 1.125 g (2.250%) and 0.560 g (1.125%). These samples were prepared to investigate the interference by oxidizing different concentration of chloride ions. Dilution was performed appropriately in accordance with the range specified by Hach Handbook [4].

Table 1 shows the comparison between Hg and Hg-free COD vials. The outcome of this study shows that the COD values decreased dramatically by decreasing the amount of marine salt. It can be seen that

Table 1. COD of artificial seawater with different ratios by using mercury and mercury free vials ($n = 3$)

Marine salt in (50 mL)	Concentration of chloride ion mg Cl^-/L	Type of vial	Ratio (mL : mL)	Mass of chloride ion (mg)	Mean	Standard deviation
COD of artificial seawater 4.500 %	27 156	Mercury	1 : 25	1.086	1042	14
			1 : 50	0.543	1217	29
		Mercury free	1 : 25	1.086	2550	25
			1 : 50	0.543	2907	45
COD of artificial seawater 2.250 %	13 577	Mercury	1 : 25	0.543	658	14
			1 : 50	0.272	776	29
		Mercury free	1 : 25	0.543	2199	44
			1 : 50	0.272	2533	101
COD of artificial seawater 1.125 %	6788	Mercury	1 : 25	0.272	216	14
			1 : 50	0.136	283	28
		Mercury free	1 : 25	0.272	1725	66.1
			1 : 50	0.136	2150	132.3

there are major differences in COD values, when measured with Hg and Hg-free COD vials (Post-hoc Scheffe test, $P < 0.05$). To examine the statistical difference of the colorimetric method, three concentrations of salinities were tested, 27 156 mg Cl^-/L, 13 577 mg Cl^-/L and 6788 mg Cl^-/L. The mean difference between Hg and Hg-free COD vials at ratio (1 : 25) with mercury vials were 1508, 1541 and 1509 mg/L, repetitively. While at ratio (1 : 50) the difference values were increased to 1690, 1757 and 1857 mg/L, repetitively. Table 1 indicated that the mean of COD using Hg vials were reduced about (50%) by reducing the mass of marine salt from (2.250, 1.125 and 0.560 g), further, Hg-free vials were reduced about (25%). The interference generated by oxidising various mass of chloride ions was investigated in this section. Based on Table 1 the mass of chloride ion was 0.543 mg Cl^- in both 2.25% of marine salt with ratio 1 : 25 and 4.5% of marine salt with ratio 1 : 50. With regard to dilution ratio, the mean of COD using mercury vials were 658 and 1217 mg/L, respectively. This point shows that the COD values was increased about double by adding twice of marine salt. The result shown a significant linear correlation between Hg and Hg-free COD vials for various concentration of artificial seawater such as 1.125, 2.250 and 4.500% of marine salt at ratio 1 : 25. This suggests that the chlorides cause the most serious problem because of their normally high concentration in wastewater samples. This interference was eliminated by the addition of mercuric sulphate to the sample, prior to addition of other chemicals.

COD of seawater. Seawater obtained from Portsmouth seafront was used as the reference method to detect the COD values by using mercury and mercury free vials, as illustrated in Fig. 1.

As can be seen from Fig. 1, COD values using mercury vials at ratios (1 : 25) and (1 : 50) were 36 and 44%, respectively, less than the generated result using mercury free vials. Moreover, the mean of COD values by using mercury vials at ratios (1 : 25) and (1 : 50) were 937 mg/L and 1283 mg/L, respectively (paired sample test, $p < 0.05$). While, the mean of COD by mercury free vials at ratios (1 : 25) and (1 : 50) were 2608 mg/L and 2930 mg/L, respectively (paired sample test, $p < 0.05$). Comparison of this study with the previous Section (5.1), the COD values at ratios (1 : 25) were reduced about 36 and 40% by using mercury vials for Portsmouth seawater (38 000 ppm) and artificial seawater (45 000 ppm). This highlights the fact that a lower ratio (1 : 25) and mercury vials are essential for the analysis of high COD at high salinity.

COD for glucose. The COD values detected using the colorimetric procedures were correlated with those determined by the titration method. While, the titration dichromate method was used as the reference method to detect the COD values of the glucose. This section examines the normality test of COD values obtained by using mercury vial, mercury free vials and titration method on glucose sample. The normality test was examined based on [10]. A Shapiro–Wilk's ($p > 0.05$) and exam scores were approximately normal distributed for all conducted method. Another test was carried out to confirm the normality and to show whether samples data are fit or differ from a normal distribution. As such, a Skewness and kurtosis shows that the data is normally distributed. The outcomes for the mercury vial, mercury free vials and titration method were 1.44 and 0.81, 1.55 and 0.94 and 0.66 and 0.24, respectively. It has been found

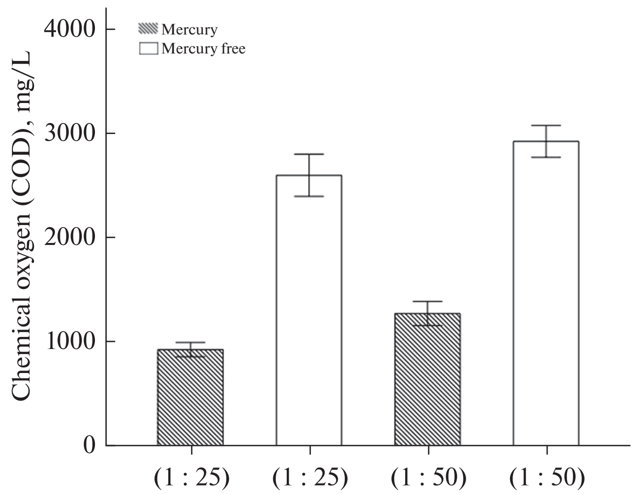

Fig. 1. Mean of COD for Portsmouth seawater measured by using mercury and mercury free COD vials at ratio (1 : 25) and (1 : 50) (error bars are indicative of the standard deviation of the mean (n = 3)).

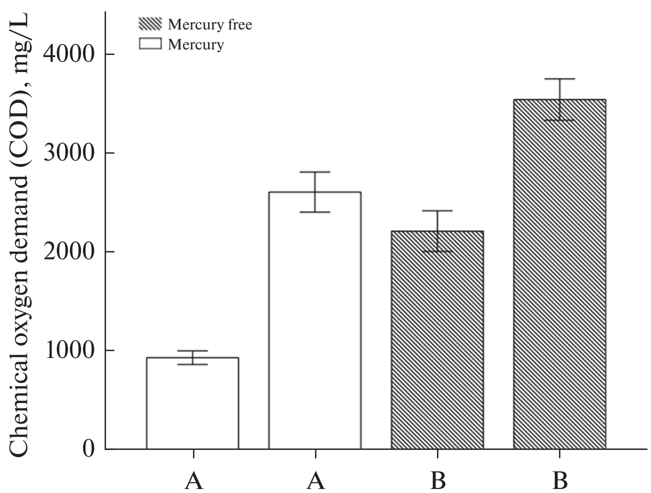

Fig. 2. Mean of COD values for (A) seawater; (B) seawater with glucose by using conventional mercury and mercury free COD test vials at ratio (1 : 25) (error bars are indicative of the standard deviation of the mean (n = 3).

that the mean of COD values for glucose sample using Hg vial, Hg-free vial and titration method were 1060 mg/L, 1054 mg/L, and 1065 mg/L, respectively. The outcome indicated that there was insignificant effect with the mercury free as compared to the mercury vial or titration method on the COD values for glucose sample. Another experiments were carried out on artificial seawater with glucose using the colorimetric procedures. The glucose was used as the reference to detect the COD values (Fig. 2).

Based on Fig. 2, the mean values of COD readings for Hg and Hg-free vials for seawater at ratio 1 : 25 were 1042 and 2550 mg/L, respectively. The average of COD values for seawater with glucose using Hg and Hg-free vials were increased about 1171 and 992 mg/L, respectively, than seawater samples (see Fig. 2). These results suggest that increasing of COD values were reflected to the COD values of glucose.

COD for oily wastewater sample. COD vials, which are available commercially containing Hg and Hg-free were employed in assessing the COD values. Results obtained from the tests were compared against the values obtained from the titration method (Fig. 3).

As can be seen from Fig. 3, the mean of COD values for oily wastewater using mercury vials and titration method were 35 500 and 33 759 mg/L, respectively (paired sample test, $p > 0.05$). However, this study indicated that the mean of COD values was increased to 48 107 and 47 673 mg/L, by using mercury free vials and titration with mercury free, respectively (paired sample test, $p > 0.05$). The existing methods have

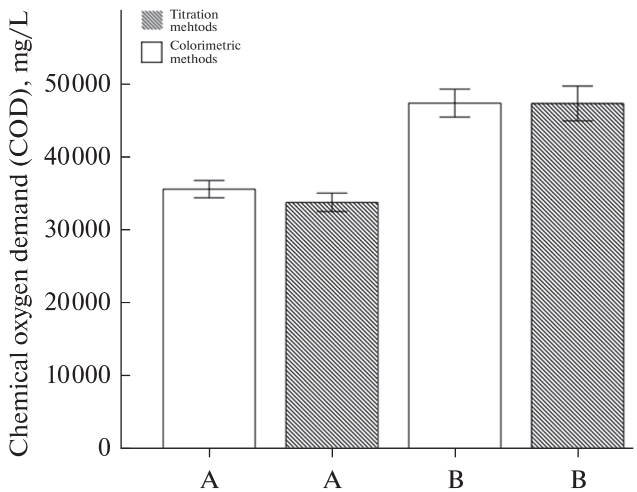

Fig. 3. Mean of COD values for oily wastewater by using: (A) mercury vials, (B) mercury free (error bars are indicative of the standard deviation of the average (n = 3).

substantial challenges, mainly in high organic concentrations, high salinity and high dilution. This highlights the fact that a high ratio 1 : 100 and mercury vials are essential for the analysis of high COD at high organic concentrations with high salinity. The outcome of this study established a linear correlation between mercury and mercury free vials for different sample such as oily wastewater with ratio of 1 : 100, oily wastewater ratio of 1 : 50. The tested samples suggest that there is a strong linearity with high correlation factor between Hg vials and Hg-free vials.

DISCUSSION

Oily wastewater is produced which contain high percentage of organics with a comparatively high salinity. The samples were diluted enough to bring the COD results in range of 20 to 1500 mg/L. Measured values of diluted samples were adjusted based on the dilution factor however, major errors can be found as a result of high dilution. According to [7], the low oxidation capabilities of the chemicals involved, due to the sort of organic pollutants in the wastewater leads to issues of poor reproducibility and accuracy. In reality, a COD test assesses the content of carbon based materials through measurement of quantity of oxygen that will react with the sample. The transaction of oxygen is where the name is taken from, hence chemical oxygen demand. This work have utilised the standard open reflux and the colorimetric method for analysis of samples containing high salinity and high COD value up to 48 107 mg COD/L for oily wastewater sample using mercury free vials. Comparison of standard opened reflux with mercury and colorimetric COD vials that contain mercury shows that our COD results are more reliable. Further, these results suggest that the colorimetric method with mercury vials can be reliable for high salinities.

CONCLUSIONS

In general, employing colorimetric method is more appealing to most researchers than using titration methods, as the latter would require skills and expensive equipment. The titration test for COD utilised a few chemicals for example acid, chromium, silver and mercury which resulted in the production of liquid hazardous waste which have to be properly disposed. It has been found that the mercuric ion combines with the chloride ion to form a poorly ionised mercuric chloride complex, which causes threat to human health and environment. This study proposes that the Hg-free COD vials provide the likely solution to minimise risk to environmental and disposal expenses compared with traditional mercury containing COD vials. Therefore, mercury free COD vials could be successfully employed to in this project.

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