POTASSIUM PERMANGANATE AS OXIDANT IN THE COD TEST FOR SALINE WATER SAMPLES

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ABSTRACT

The objective of this study is to investigate the feasibility of applying potassium permanganate ($KMnO_4$) as the oxidant in the COD test for highly saline water samples. Initially, the COD values of various glucose standard solutions were determined by three methods, namely the standard closed reflux dichromate (COD_{Cr}), the acidic permanganate (COD_{Mn}) and the alkaline permanganate (COD_{OH}) methods. The results showed that at COD values lower than 20 mg/L, the standard dichromate method was not applicable due to its poor precision (RSD > 10%). The COD_{OH} method was less effective compared to the COD_{Mn} method as the recoveries were 0.71 and 0.89, respectively. The determination of COD_{OH} for the standard solutions of glucose in the presence of Cl^- and Br^-, respectively, or both Cl^- and Br^- ions were conducted. The results showed that the COD values only increased 5.1% with the increase in chloride concentrations up to 35000 mg Cl^-/L. This shows that the COD_{OH} method is a suitable method for determining the COD of highly saline water samples such as estuarine and coastal waters. The COD test was conducted for river, estuarine and coastal water samples. The results indicated that the COD_{OH} test correlates well with the COD_{Cr} test ($R^2 > 0.98$). The results also indicated that this COD_{OH} test can be applied in determining the pollution trends for estuarine and coastal waters.

Keywords: COD test; saline water sample; potassium permanganate

1. INTRODUCTION

Chemical oxygen demand (COD) is recognized as one of the most important parameters in assessing organic pollution in aquatic systems. The COD is defined as the amount of oxygen equivalent consumed in the oxidation of organic compounds by strong oxidants (such as dichromate and permanganate). Presently, the standard closed reflux dichromate (COD_{Cr}) method and the standard permanganate method are used in COD determination [1, 2]. The COD_{Cr} method is not applicable to highly saline water sample containing (after dilution) more than 2000 mg/L chloride [3]. On the other hand, the standard permanganate method is only applicable to potable and surface water of which the permanganate index is between 0.5 and 10 mg/L (about 2.5 mg/L COD) with a chloride ion concentration not exceeding 500 mg/L [2].

Over the years, much research work had been carried out in an attempt to correct for the chloride interference in the COD_{Cr} method by adding complexing agents such as $HgSO_4$ [4 - 7], Cr^{3+} and Al^{3+} ions, respectively, [8]. However, the dichromate method presents some environmental and health problems. First, chromium (VI) is a known carcinogen. Secondly, the

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discharge of mercuric ion which is needed to effect the removal of chloride may give rise to environmental problems. In terms of cost, silver sulphate is needed as a catalyst and it is expensive. As an alternative, the non-toxic cerium (IV) sulphate was used as the oxidizing agent for the determination of COD [9], but cerium (IV) sulphate was unsuitable for continuous monitoring over long periods because of its self-decomposition.

To date, no standard method has yet been suggested to determine the organic pollution in highly saline water samples (containing > 2000 mg/L chloride). The objective of this study is to develop a protocol for COD test for monitoring estuarine and coastal water pollution and to investigate the use of potassium permanganate ($KMnO_4$) as the oxidant in the COD test so that the use of toxic and carcinogenic compounds such as $HgSO_4$ and $K_2Cr_2O_7$ required in the standard dichromate method can be eliminated.

2. MATERIALS AND METHODS

A series of glucose standard solutions of 10, 20, 30, 40 and 50 mg/L COD were determined by three methods, namely the standard closed reflux dichromate (COD_{Cr}), the acidic permanganate (COD_{Mn}) and the alkaline permanganate (COD_{OH}) methods. Glucose solutions containing different concentrations of chloride and bromide, respectively, or both chloride and bromide ions were prepared for the study of the halide interferences in the COD test.

River, estuarine and coastal waters samples were collected from 15 sampling sites in Penang Island. Both river and estuarine water samples were collected from flowing water near midstream. In addition, the river water samples were collected during both high and low tides. The coastal waters sampling sites were all located in the surf zone at wading depth just off the coast.

2.1   Closed reflux, titrimetric method

A 1.5 mL of 0.0333 M $K_2Cr_2O_7$ digestion solution was added into a 16 x 100 mm culture tube containing 2.5 mL sample. Subsequently, 3.5 mL H_2SO_4-Ag_2SO_4 solution was added carefully into the tube. The cap of the tube was tightly closed and then inverted for several times to mix completely. The tube was then placed in the aluminium block digester for 2 h at 150 °C. After digestion, the remaining dichromate was titrated with 0.0125 M ferrous ammonium sulphate (FAS) solution and the equivalents of oxidant consumed were converted to mg O_2/L of sample. The detailed procedure was described in the Standard Methods [1].

2.2   Modified permanganate method

Exactly 10 mL water sample was added with 1 mL of 9 M H_2SO_4 (for COD_{Mn} method) or 2.5 M NaOH (for COD_{OH} method) followed by 10 mL of 0.01 M $KMnO_4$ digestion solution. The sample was heated for 30 min in a water bath at 96-98 °C. After digestion, the sample was cooled immediately in an icebox to quench the reaction. The remaining permanganate in the sample solution was determined by titration.

2.2.1 Titration of an acidic sample solution

After a few grains of KI were added to the sample solution, the colour of the sample turned yellowish brown. The sample solution was titrated with 0.01 M $Na_2S_2O_3$ solution until the yellow solution turned pale straw colour. After that, 1mL of starch solution was added to turn the colour of the solution dark blue. The titration was continued until the solution was completely colourless. The above procedure was repeated for the blank test, with 10 mL of distilled water replacing the sample.

2.2.2 Titration of an alkaline sample solution

A few grains of KI were added to the sample solution, followed by adding 1 mL of 9 M H_2SO_4 to the solution. The sample solution was titrated with 0.01 M $Na_2S_2O_3$ solution until the yellow solution turned pale straw colour. After that, 1mL of starch solution was added to turn the colour of the solution dark blue. The titration was continued until the solution was completely colourless. The above procedure was repeated for the blank test, with 10 mL of distilled water replacing the sample.

3. RESULTS AND DISCUSSION

3.1 Effectiveness of permanganate method under acidic and alkaline conditions

The COD values of various glucose standard solutions were determined by the proposed permanganate methods. The results are given in Table 1. For comparison, the COD values determined by the standard closed reflux dichromate method [1] were also included in the results. The ratio of the mean measured COD and the theoretical COD were in the range of 0.71 to 0.75 for the COD_{OH} method and 0.89 to 0.92 for the COD_{Mn} method. Thus, the permanganate method in acidic condition has a better recovery. This is probably due to the fact that most of the organic matters were oxidized more completely in acidic than in alkaline conditions [10].

Table 1: *Comparison of COD values of glucose standards using different methods.*

Methods	Theoretical COD, mg/L	Mean measured COD, mg/L	Standard deviations, mg/L	Relative standard deviations, %	Recover, %
COD_{OH}	0.0	0.3	0.31	-	-
	10.0	7.5	0.23	3.07	75
	20.0	14.8	0.23	1.55	74
	30.0	21.6	0.40	1.85	72
	40.0	28.5	0.40	1.40	71
	50.0	36.1	0.46	1.27	72
COD_{Mn}	0.0	0.4	0.35	-	-
	10.0	9.2	0.23	2.50	92
	20.0	18.1	0.46	2.54	91
	30.0	27.6	0.40	1.45	92
	40.0	36.3	0.61	1.68	91
	50.0	44.7	0.46	1.03	89
COD_{Cr}	0.0	3.0	2.15	-	-
	10.0	11.0	3.05	26.99	110
	20.0	21.0	3.06	14.57	105
	30.0	28.0	1.15	4.11	93
	40.0	38.0	2.31	6.08	95
	50.0	48.0	0.58	1.21	96

The relative standard deviations for the COD_{OH} and COD_{Mn} methods were all below 5%. In contrast, the relative standard deviations for the COD_{Cr} method were higher than 10% for the determination of samples having COD value lower than 20 mg/L. The results in Table 1 indicate that the COD_{OH} and COD_{Mn} methods are more suitable for the COD determination of samples having COD value lower than 20 mg/L compared to the COD_{Cr} method.

3.2   Effect of chloride and bromide ions on the determination of COD

One of the major difficulties encountered in COD_{Mn} and COD_{Cr} methods is the inability of the methods to compensate for positives interference caused by the oxidation of chloride present in water sample [4 - 7]. The standard method procedure for eliminating the chloride interference involves the addition of $HgSO_4$ to form a complex and thus prevent the oxidation of chloride [1, 7, 11]. As the main objective of this research is to develop a protocol for COD test for monitoring the estuarine and coastal water pollutions, both COD_{Mn} and COD_{Cr} methods are clearly not suitable for the analysis due to their low ability to compensate for the chloride interference.

The effects of chloride, bromide or both chloride and bromide, respectively, on the determination of COD_{OH} were investigated. Glucose standards of 20 mg/L COD were spiked with varying amounts of either chloride, bromide or both chloride and bromide in order to determine the limiting concentration at which the interference was significant. To prevent the oxidation of halogen compounds by permanganate solution in the test sample, the digestion reaction was carried out in alkaline condition first and then acidifying just before the titration.

The results are shown in Fig. 1, it was observed that the COD value increased about 5.1% with the increase in chloride concentrations up to 35000 mg Cl^-/L. The corresponding interferences of bromide or chloride together with bromide were, respectively, 5.9 and 6.7%. The results indicate that COD_{OH} method is a suitable method for analyzing high salinity water samples such as estuarine and coastal waters because the change of COD value against the interferences of halide ions was relatively minor.

The results compare quite favorably with the result reported by Fujimori [10] for the determination of COD for artificial seawater with salinity varying from 0 to 3.4%. Fujimori reported that the chemiluminescence signals increased about 10% with the increase in salinity. The results obtained by Fujimori were slightly higher than those obtained in this study probably because the experiment conducted by Fujimori et al. was in acidic condition. In acidic condition, the oxidizing ability of the $KMnO_4$ is stronger than in alkaline condition.

3.3 Determination of COD for environmental water samples

3.3.1 River water

Initial attempt for this study was to examine the correlation between COD_{OH} and COD_{Cr} for high salinity environmental samples, but the effort did not succeed because the oxidation of chloride was erratic. Alternatively, an effort to correlate between COD_{OH} and COD_{Cr} for river water samples was undertaken.

Samples were collected from Sungai Pinang the major river in Penang Island at five sampling points namely R1 to R5 (Fig. 2). All the sampling points were located in the urban area of Georgetown. Considering that sampling points R4 and R5 were located at the tidal part of Sungai Pinang, only samples collected from R1 to R3 were used to determine the correlation between COD_{OH} and COD_{Cr}. Nevertheless, the COD values determined at all the sampling points were used to study the pollution trend of Sungai Pinang.

(a)
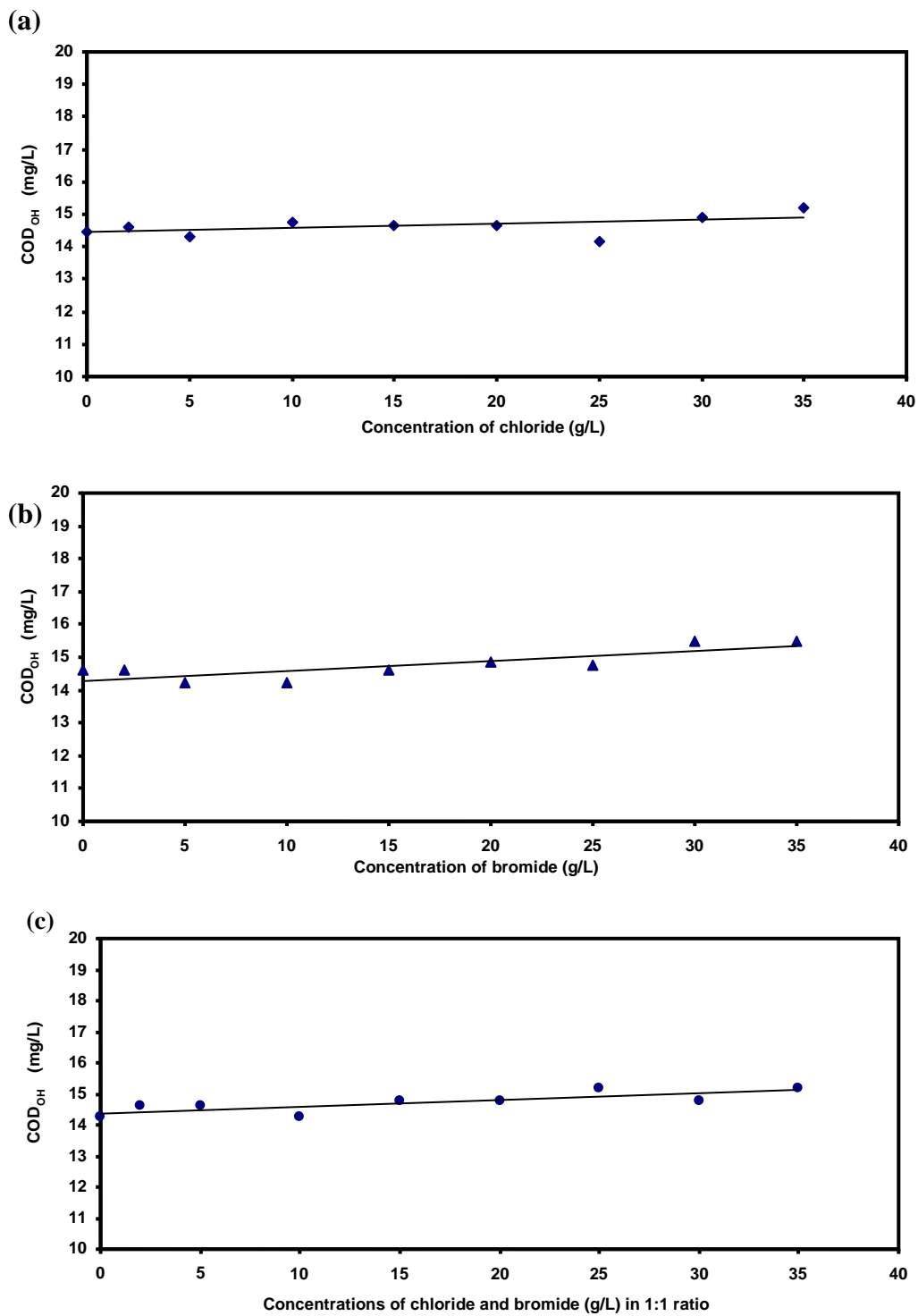

(b)

(c)

Fig. 1: *Effect of (a) Cl⁻, (b) Br⁻ and (c) both Cl⁻ and Br⁻ concentrations on the determination of COD_OH for the standard solutions of 20 mg/L theoretical COD.*
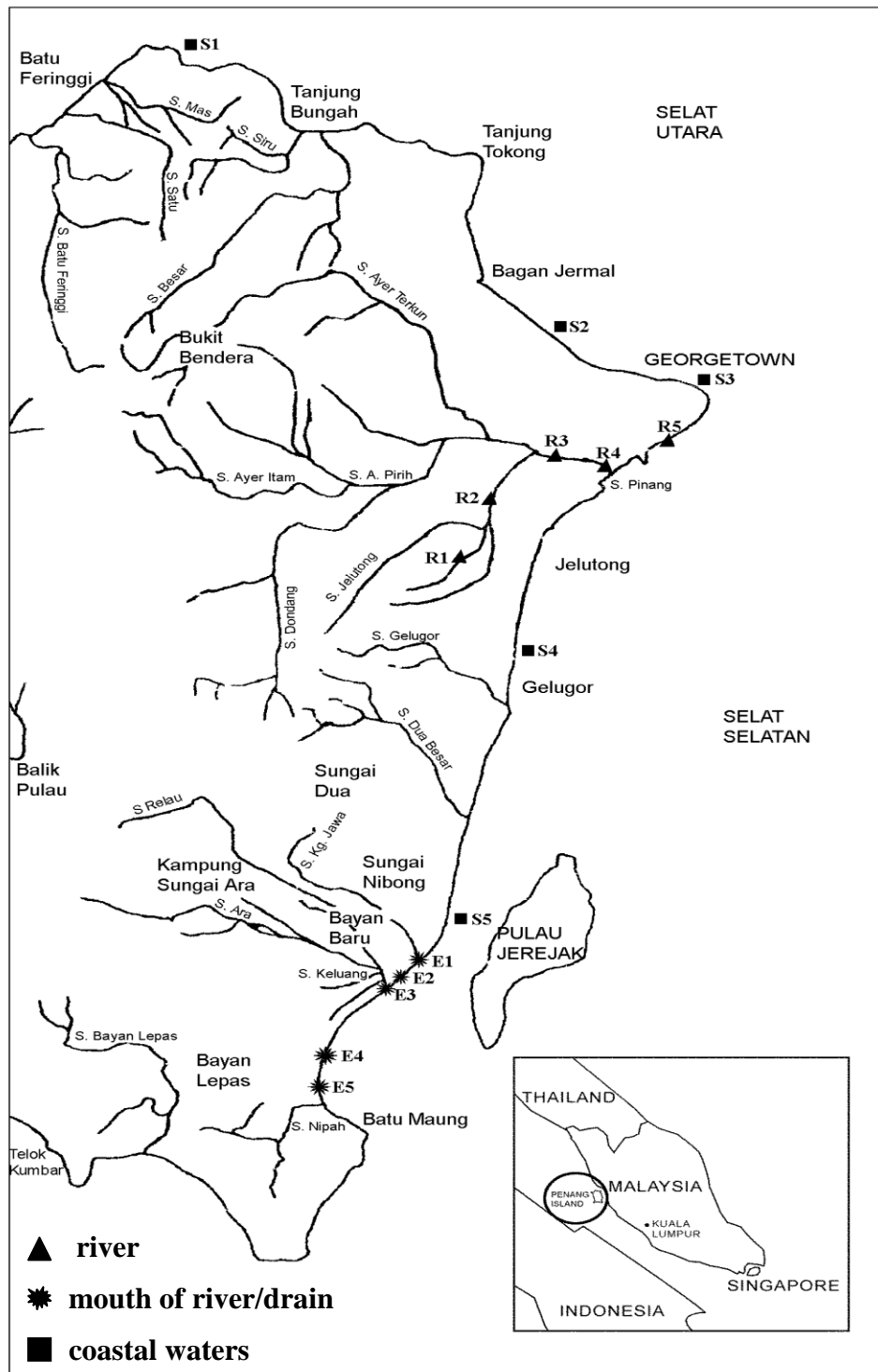
Fig. 2:   *Sampling locations for environmental water samples.*
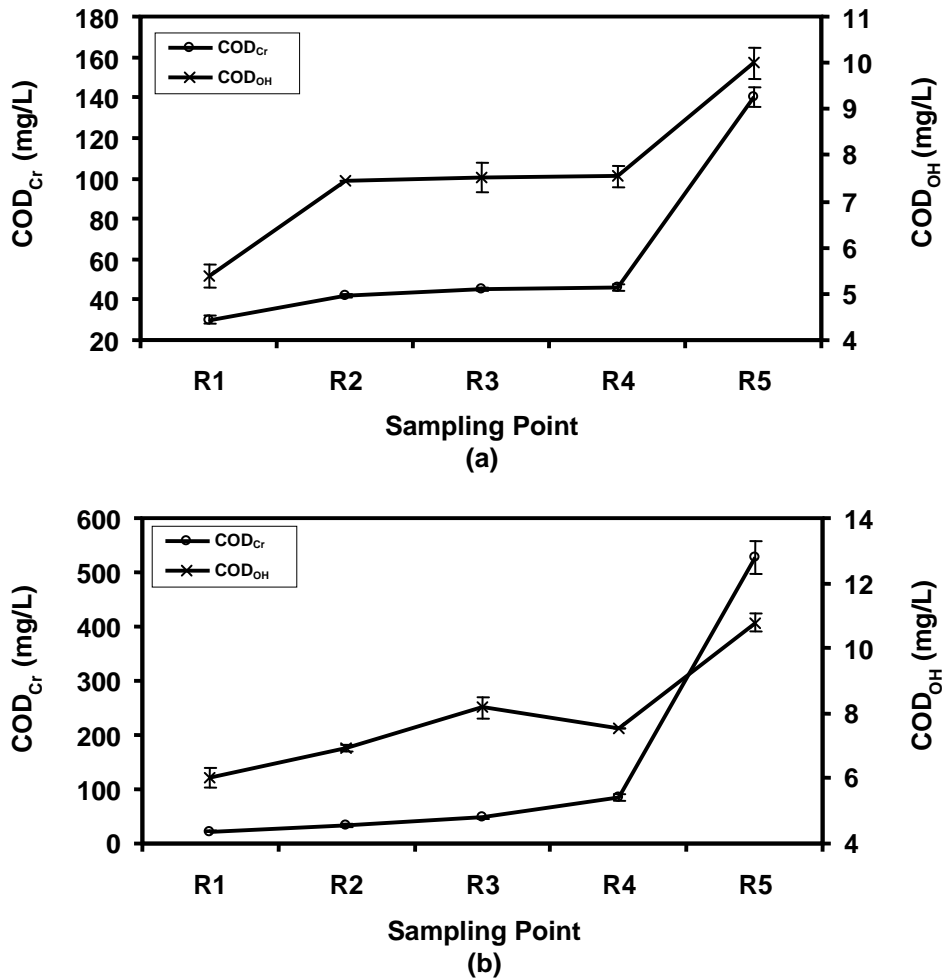
Fig. 3: *Determination of COD values for river water samples during (a) low tide and (b) high tide.*

The results in Fig. 3 indicate that there was an increasing pollution trend from the upstream to the estuary of Sungai Pinang. Besides, they also indicate that the COD_{OH} method can accommodate the chloride interference in the environmental samples such as river water with tidal effect. The decrease of COD_{OH} for R4 [Fig. 3(b)] was probably due to the intrusion of seawater during high tide. Surprisingly, the COD_{OH} for R5 which was expected to be lower due to greater intrusion was higher than R4. One reason for this might be that sample collected at R5 was more polluted due to the location of R5 near the residential houses built on the reclaim land along the estuary. Owing to the absence of proper sanitation system, most of the wastes were directly discharged into the river.

The coefficient of determination (R^2) for the COD_{OH} and COD_{Cr} was calculated. The R^2 value was 0.997 for the samples collected during high tide. For the samples collected during low tide

the R^2 was 0.983. As the values of R^2 obtained were all close to 1.00, this indicates that both the COD_{Cr} and COD_{OH} methods correlate well (Fig. 3).

3.3.2 Estuarine and coastal waters

Figure 4(a) shows the results of COD for samples collected at the mouths of the waterways draining into the coastal waters. The samples were collected at five sampling points namely E1 to E5 (Fig. 2). The results from the study show that the COD_{OH} method is applicable in indicating the pollution trend of estuarine waters, the COD results from the dichromate method was quoted for comparison. The results also show that the standard method was unable to compensate for the chloride interference.

As it has been proven that the COD_{Cr} is not suitable for the monitoring of water pollution for estuarine waters, only the COD_{OH} method was used to determine the COD for coastal waters. The coastal water samples were collected at five sampling points namely S1 to S5 (Fig. 2). The results indicate that the water at S2 had a higher COD value compared to other sampling points (Fig. 4(b)). The location of S2 was off Gurney, a popular tourist spot for hawker food which might be a source for pollution.
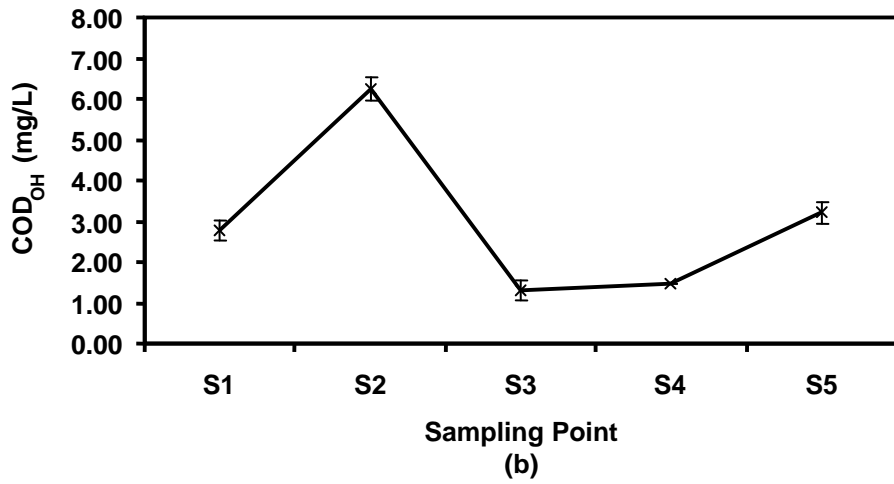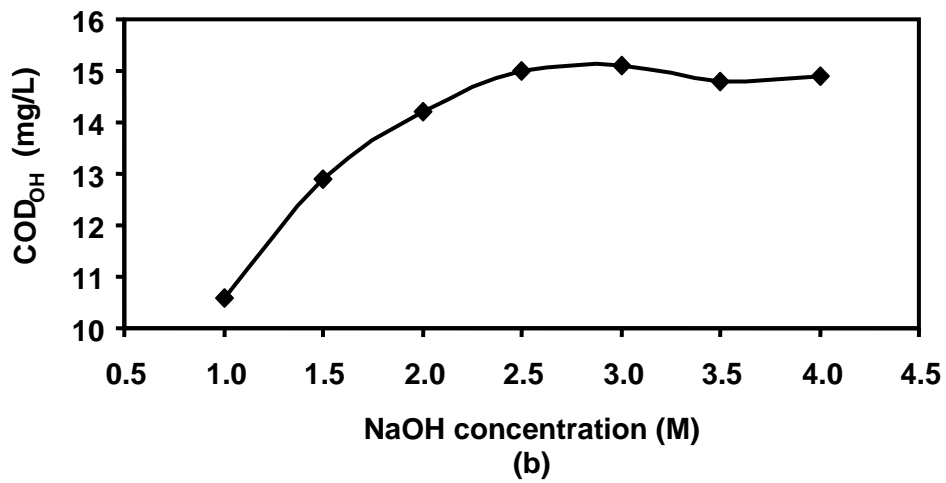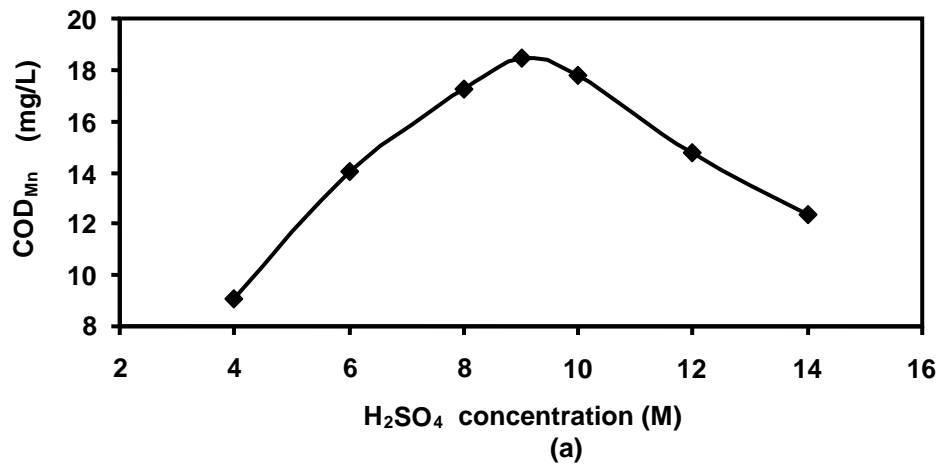

(a)
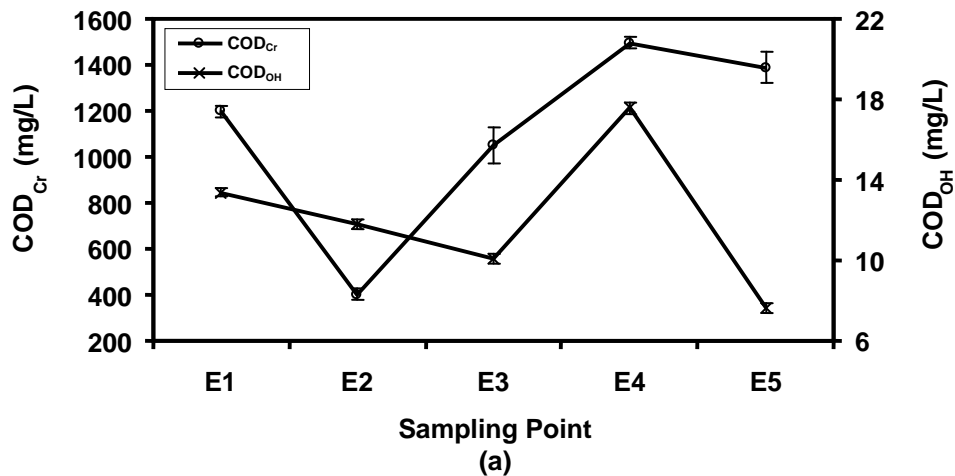
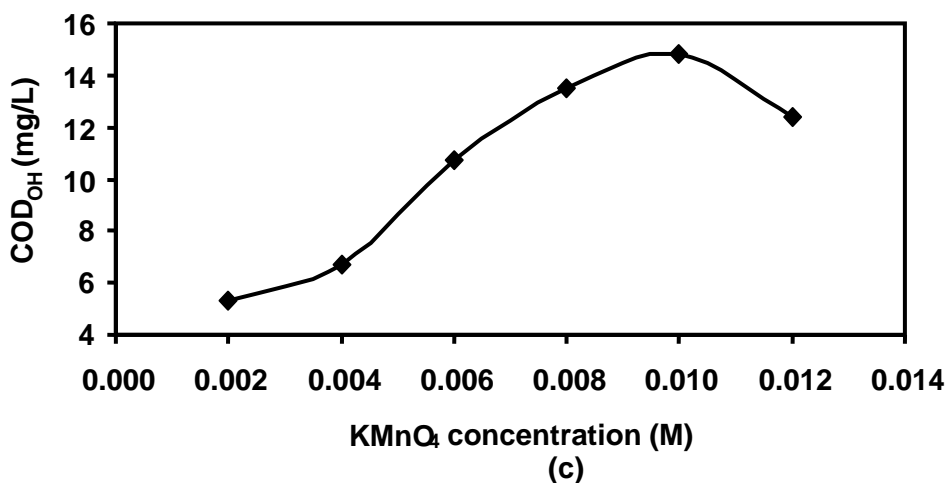*Fig. 4: Determination of COD values for (a) estuarine waters and (b) coastal waters.*

Fig. 5: *Effects of (a) H_2SO_4 concentration on COD_{Mn}, (b) NaOH concentration on COD_{OH} and (c) $KMnO_4$ concentration on COD_{OH}.*

3.4   Optimum conditions for COD_{Mn} and COD_{OH} tests

Over the years, research had been done to study the effect of H_2SO_4 concentration on the COD_{Mn} test [10, 12]. Figure 5(a) shows the effect of H_2SO_4 concentration on COD_{Mn} analysis and the results indicate that 9 M H_2SO_4 was the optimum concentration. The effect of NaOH concentration on the determination of COD_{OH} was also examined in the range of 0 to 4.0 M. Figure 5(b) shows that 2.5 M NaOH was the optimum concentration. Some researchers [10, 12] had reported that $KMnO_4$ concentration affects the digestion reaction. The results in Fig. 5(c) indicate that 0.010 M $KMnO_4$ was the optimum concentration for the determination of COD_{OH}. In addition, the effects of the digestion period and the digestion temperature on the COD_{OH} test were also studied. It was observed that 30 min of digestion period was sufficient and there was an increase of 9.0% in the recovery of COD_{OH} test when the samples were heated at 96 - 98°C compared to that at 80°C [2, 13].

4.   CONCLUSIONS

The COD_{OH} method yielded COD values which exhibited similar trend as the COD values obtained from the standard test for river water samples. The COD_{OH} test is applicable regardless of the tidal effects making it a better monitoring parameter for river water pollution. With this COD_{OH} test, the COD for the estuarine and coastal waters can be determined easily without additional procedure to correct for the interference of chloride.

Over the years, the consumption of expensive reagents such as $AgSO_4$ and the difficulty of disposing of highly toxic mercury, silver and chromium waste is a serious problem faced by most analytical laboratories. The use of $KMnO_4$ as an oxidizing agent in the COD test can help to avoid the use of toxic compounds such as $HgSO_4$ and $K_2Cr_2O_7$ which are required in the standard method. Thus, this COD_{OH} test is considered a low cost and environmentally friendly method.

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