

## Comparison of Different Methods of Chemical Oxygen Demand (COD) Using the Gara-Tie-Dye Wastewater

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### Abstract

This study investigates the suitability of various types of dichromate (photometric and titrimetric) and permanganate (acidic titrimetric and alkaline titrimetric) methods of determining COD in three different samples A, B and C of gara-tie-dye wastewater. Results indicate that the photometric and titrimetric dichromate methods gave higher COD concentration because of complete oxidation of the organic matter in the gara-tie-dye wastewater than the permanganate methods. For samples A and C, results of the dichromate method was significantly higher ( $p > 0.05$ ) than the permanganates. The acidic and alkaline permanganate gave comparable results and within the same order of magnitude but were lower than both the dichromate methods. The photometric and titrimetric dichromate methods were comparable and were found to be more suitable for the determination of the COD of gara-tie-dye wastewater.

**Keywords:** *Chemical Oxygen Demand, gara-tie-dye wastewater, dichromate method, permanganate method*

### Introduction

The gara-tie dye industry operates on a small scale in Sierra Leone and quite a few people operate at a cottage industry scale. Although the industry has long been in existence, the zest for income to meet family needs and to make business profit has attracted many people to the industry and the trade of the dyed fabric. The industry is more predominant in the North of the country.

Gara - tie – dying is a type of dying textile that makes use of several coloured dyes. In Sierra Leone cotton is the most common

fabric used. The process of tie-dye typically consists of folding, twisting, pleating, or crumpling the fabric and binding with string or rubber bands, followed by application of dye(s)/ink. Several materials are required for gara tie-dye making such as ink, powder, soda (NaOH) and hot water. The powder is mainly composed of sodium hydrosulphite ( $(\text{Na}_2\text{S}_2\text{O}_4)$ , 85% wt. and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) of 15% wt). Details of the dying process are described in Frazer-Williams (2014). The gara-tie -dye industry operates in a batch system rather than a continuous flow of automated steps

observed in a conventional high-tech textile industry. Consequently, the industry production stages are much shorter than the conventional method.

Wastewater generated from textile industry has a distinctive characteristic that distinguishes it from common municipal wastewater or other industrial wastewater. This is because textile industry wastewater contains large amount of dyes and chemical additions that are organic in nature such as sequestering agents, leveling agents and finishing agents. These organic compounds are of a complex organic structure. Consequently, textile industry effluents are characterized with high pollutant concentration as follows: COD ( $\approx$  400-3.000 mg/L), BOD5 ( $\approx$  200-2.000 mg/L), Total Solids ( $\approx$  1.000-10.000 mg/L), Suspended Solids ( $\approx$  100-1.000 mg/L), TKN ( $\approx$  10-100 mg/L), Total Phosphorus ( $\approx$  5-70 mg/L) ((Mahmoodi, and Arami 2010; Yonar, 2010 and Yonar *et al.*, 2005).

The main pollutants in textile waste water came from dyeing and finishing processes as not all chemicals and dye added are used. Dae-Hee *et al.*, (1999) reported that the major pollutants and their levels in textile wastewaters are high suspended solids, COD, colour, heat and other soluble substances whilst the gara-tie-dye

wastewater is often alkaline with sometimes a choking and irritating smell/odor. Pagga and Brown (1986) reported that only about 47% of 87% of dyestuff are biodegradable. In a country like Sierra Leone where wastewater treatment facilities seldom exists, such wastewater poses a threat to treatment plants, pollute receiving water bodies and contaminate land.

The gara-tie-dye wastewater poses a wide range of environmental challenges to land and receiving water bodies. This is because although they generally constitute a small fraction of total liquid effluent compared to other industries, yet they contribute a high proportion of total contaminants since their effluent are often more concentrated compared to other types of wastewater. This is particularly true for the first rinse wastewater of the gara cloth after the dyeing process.

The level of organics in wastewater is normally determined by either Chemical Oxygen Demand or Biological Oxygen Demand (BOD). Chemical Oxygen Demand may be defined as the amount of oxygen equivalents consumed in oxidizing the organic compounds of samples by strong oxidizing agents such as dichromate ( $K_2Cr_2O_7$ ) or permanganate ( $KMnO_4$ ). Potassium dichromate is a hexavalent

chromium salt that is bright orange in color and is a very strong oxidant. Between 95-100% of organic material can be oxidized by dichromate. Once dichromate oxidizes a substance, it is converted to a trivalent form of chromium, which is a pale green color. Biochemical oxygen demand (BOD) contrast with COD in that it requires the use of microorganisms to break down the organic material in the sample by aerobic respiration over the course of a fixed incubation period usually 5 days (i.e. BOD<sub>5</sub>). BOD is always lower than COD (generally about 2 -3 times lower than COD) as the biochemical breakdown of organics in BOD is often not as complete as the chemical method. Both COD and BOD are expressed in milligrams per liter (mg L<sup>-1</sup>). Furthermore, unlike BOD, COD does not differentiate between the stable organic matter from the unstable form during determination.

The greater the chemical oxygen demand level, the greater the amount of water pollutants wastewater in samples (Trivedy and Goel, 1986). Depending on the type and nature of wastewater, COD or BOD may be preferred. In the case of gara-tie-dye wastewater wherein most of the parameters are not biodegradable, COD may be more preferable than BOD. Furthermore, because the gara-tie-dye

wastewater contains a high sodium chloride content, whichever method is used to determine the amount of COD must be able to overcome chloride interference. In view of the foregoing, this study was therefore aimed at investigating the suitability of the various types of dichromate and permanganate methods in determining the amount of COD in gara-tie-dye wastewater in Sierra Leone.

## **Materials and Methods**

### **Sample collection and preparation**

Three different gara-tie-dye wastewater samples A, B and C were collected from 19 Davis street, 16 Dan street, and 28 Oxyle street respectively in Freetown, the capital city of Sierra Leone for COD and chloride analysis. Samples were collected in a plastic sample containers previously cleaned according to standard method (APHA, 1998) in order to avoid contamination from unwanted substances and other foreign materials. Further, the bottle caps were securely screwed to prevent oxygen entering into the sample (as this might influence biodegradation since microbes degrade organics under aerobic conditions) thereby decreasing the COD concentration. Following collection, the samples were transported to the laboratory and stored in a refrigerator at ~5°C prior to analysis.

Due to the high pollutant load of gara-tie-dye wastewater (Frazer-Williams, 2014), 5ml of each of the three different samples were diluted to 250ml in an Erlenmeyer flask and a further 10ml from the 250 ml flask was further diluted in a 100ml Erlenmeyer flask. This second diluted sample was used in all analysis. Chloride was determined by the Palintest Chloridol PHOT.46.AUTO photometric method. The test is based on the principle of the reaction between chloride and silver ions to form the insoluble silver chloride similar to the standard argentometric (Mohr) method (APHA, 1998). The turbidity of the insoluble silver chloride formed is proportional to the concentration which is measured using a Palintest Photometer.

COD was analysed using four different types of methods ((i). Photometric Dichromate, (ii) Titrimetric Potassium Dichromate, (iii) Acidified Titrimetric Potassium permanganate and (iv) Alkaline Titrimetric Potassium permanganate and results obtained were compared with each other.

**(i) The Plain Test Photometric Dichromate method**

The test tubes heater was turned on, heating control set to 150°C and allowed to heat up to 150°C. The tubes containing

reagents for the COD test were shaken vigorously to obtain a homogeneous mixture. The caps of the COD test tubes were removed and 2ml of sample was added using plain test pipette. The caps were returned, screwed tightly and inverted several times in order to obtain a homogeneous mixture. For the reagent blank, 2ml of distilled water was used instead of the samples. The tubes were digested for two hours. After the two hour period, the test tubes were allowed to cool to room temperature in a test tube rack. The test tubes were placed on the photometer and the Phot 82 was selected on the photometer which displayed the COD result in mg/L.

**(ii) Titrimetric Potassium Dichromate Method**

The standard potassium dichromate titrimetric method according to procedure outlined in Standard methods for the Examination of Water and Wastewater (APHA, 1998) was used with slight modification. The modification was sodium diphenylamine sulfonate indicator was used instead of ferroin indicator.

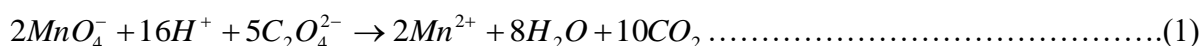
The acidic and alkaline titrimetric permanganate methods were generally as outlined in Goh and Lim (2008).

**(iii) Acidified Potassium permanganate method**

100ml of the sample was pipetted into an Erlenmeyer flask. 10ml each of the 2M sulfuric acid and the 0.05M standard potassium permanganate solution was added into the flask. The flask was heated in a boiling water bath for exactly 30 minutes keeping the water in the bath

above the level of the solution in the flask. After 30 minutes in the water bath, 10 ml of the 0.125M ammonium oxalate was added. The quantity of ammonium oxalate remaining in the flask was determined by titrating with 0.05M potassium permanganate to the first pink coloration and the ml of potassium permanganate from the burette was recorded.

The equation for the reaction is given below:



**(iv) Alkaline Potassium permanganate method**

100ml of the sample was pipetted into an Erlenmeyer flask. 10ml each of 2M sodium hydroxide and 0.05M potassium permanganate was added into the flask. The flask was heated into a boiling water bath for exactly 30 minutes keeping the water in the bath above the level of the solution in the flask. After 30 minutes in the water bath, 10 ml of the 0.125M ammonium oxalate was added. The

quantity of ammonium oxalate remaining in the flask was determined by titrating with 0.05M potassium permanganate to the first pink coloration and the ml of potassium permanganate from the burette was recorded.

**Results**

Results of COD and chloride determined in all three samples are presented (Tables 1 and 2).

**Table 1: Concentration (mg L<sup>-1</sup>) of COD (mean ±standard deviation) in the three samples of gara – tie - dye wastewater using different methods**

Sample	Photometric		Titrimetric		
	Plain Photometric Dichromate	Test Photometric Dichromate	Potassium Dichromate	Acidified Potassium permanganate	Alkaline Potassium permanganate
A	22500		20000 ± 4,000	7150.0 ±50.0	5503.33 ± 5.77
B	7500		8000 ± 4,000	6350.0 ± 50	3706.67 ± 525.40
C	65000		65866.67 ± 230.9	8003.33 ± 5.77	5100.0 ± 50.0

**Table 2: Concentration (mg L<sup>-1</sup>) of chloride in the three samples of gara – tie - dye wastewater**

Sample	Free Chloride	Total Chloride
A	220	240
B	100	125
C	30	60

For all samples generally, the photometric and titrimetric dichromate methods gave higher COD concentration than the permanganate methods. For samples A and C, results of the dichromate method was significantly higher (p>0.05) than the permanganate methods. Furthermore, the acidic and alkaline permanganate gave results within the same order of magnitude. Chloride concentration of all three samples ranged from 30 to 240 mg L<sup>-1</sup>.

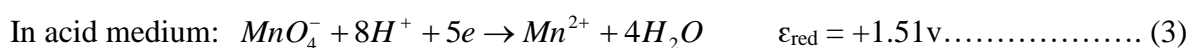
**Discussion**



Several reasons account for the higher concentration obtained for acidic titrimetric permanganate over the alkaline titrimetric permanganate. To illustrate, for many oxidants, the pH of the medium is of great importance and hence their oxidizing

In this study, the acidic and alkaline permanganate methods both gave comparable results although for all samples, the acidic titrimetric permanganate method gave a higher COD concentration than the alkaline titrimetric permanganate method. No clear trend was however observed between the photometric and titrimetric dichromate methods possibly because the principle involved in both methods is the same in which the dichromate ion is reduced to the chromite ion (equation 2).

strength may vary depending on the medium in which its reaction is studied; and permanganate oxidizing power is strongest in acid medium as illustrated in the half reactions below:

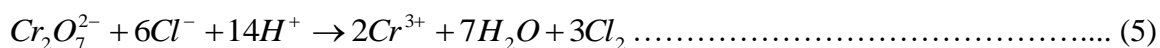


In a study to investigate the feasibility of applying potassium permanganate as the

oxidant in COD test for highly saline waters, Goh and Lim (2006) compared the

acidic permanganate, the alkaline permanganate and the closed reflux dichromate methods on glucose standards. He reported that at COD values lower than 20 mg L<sup>-1</sup>, the dichromate method was not applicable due to poor precision and concluded that the alkaline COD method was suitable for determining the COD of highly saline water samples such as coastal and estuarine waters. However, there is a paucity of work done on comparative study of determining COD in highly saline wastewater under varied acidic and alkaline conditions.

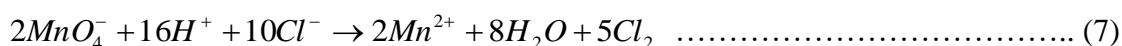
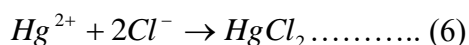
Gara-tie-dye wastewater however is different from sea, coastal and estuarine waters and sometimes have very high chloride levels in addition to various other organic contaminants (Frazer-Williams, 2014). High chloride concentration has long been identified to interfere in the determination of COD of wastewater (Chin-Ping and Lim, 2008; APHA, 1998; Baumann, 1974; Cripps and Jenkins, 1964). This is because chlorides are quantitatively oxidized by dichromate and thus represent a positive interference (equation 5):



To correct for chloride interference in the dichromate method therefore, a complexing agent such as HgSO<sub>4</sub> was used. The HgSO<sub>4</sub> dissociates into Hg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> ions. The Hg<sup>2+</sup> ion reacts with chloride ion (equation 6) present in the gara-tie-dye wastewater sample in order to reduce the interference of chloride in the determination during the process.

Sulfuric acid was used in the dichromate method which also serves as a primary catalyst in the digestion stage.

No chloride correction was done in the permanganate methods. In the presence of chloride ions under acidic medium, permanganate can oxidize chloride to chlorine, which can be a source of positive errors as permanganate is consumed in this reaction (equation 7):



Compared to the dichromate method, chloride does not interfere and is not consumed in the reaction. This may

possibly account for the difference in COD concentration obtained in the permanganate method compared to the

dichromate methods although the chloride concentration of the gara-tie-dye wastewater was not extremely high (Table 2).

In this study, both dichromate (photometric and titrimetric) methods gave comparative results. Other than the fact that the photometric dichromate is faster, the titrimetric is a good alternative to measure COD of concentrated samples with high chloride concentration. For sample B, there is no significant difference between the dichromate methods and the acidified permanganate method.

The use of  $HgSO_4$  and  $Ag_2SO_4$  in the dichromate method is less favoured nowadays. This is because  $Ag_2SO_4$  is expensive and  $HgSO_4$  poses some environmental health problems as mercuric compounds are carcinogenic and causes kidney tumors. As a result, disposing toxic mercury and silver wastes is a serious challenge faced by most analytical laboratories in developing countries where facilities hardly exist. Hence, few researchers have tried the alternative permanganate which does not require the use of mercury (Goh and Lim, 2008; Ho *et al.*, 2003; Vaidya *et al.*, 1997). However, the eventual method used for the determination of the COD content in a

wastewater will depend on the characteristic of the wastewater.

### Conclusion

The dichromate method gave a higher COD concentration than the permanganate as a result of complete oxidation of organics in the gara-tie-dye wastewater. The acidic and alkaline permanganate gave comparable results albeit lower than the dichromate methods. Similarly, both dichromate (photometric and titrimetric) methods gave comparative results. Other than the fact that the photometric dichromate is faster, the titrimetric dichromate method is a good alternative to measure COD of concentrated samples with high chloride concentration.

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