COMPARATIVE ANALYSIS OF THE IODINE VALUE OF SUNLIGHT BLENDS USING WIJS METHOD AND GLC METHOD

&

TREND ANALYSIS OF ENVIRONMENTAL PARAMETER IN FATS AND OIL PROCESSING INDUSTRIAL EFFLUENT

By

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DECLARATION

The work described in this thesis was carried out by myself at the laboratory of Unilever Ceylon Ltd, under the supervision of H.I.S.C.Gunasekera (Laboratory manager) and Dr.Mrs.N.Wickramaratne,an industrial training project.

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Lovely dedicated to
Dear parents sisters & Brother

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ABSTRACT

TITLE.1

COMPARATIVE ANALYSIS OF THE IODINE VALUE OF SUNLIGHT BLENDS USING WIJS METHOD AND GLC METHOD

The iodine value (IV) is a measure of the unsaturation of fats and oils and is expressed in terms of the number of centigrams of iodine absorbed per gram of sample (% iodine absorbed).

The IV values for Sunlight Blend oil samples were calculated using two methods.

1.Wijs method

2.GLC method

Wijs method was allowed to calculate the number of double bond carbon (C=C) absorbed and remaining I_2 was calculated by iodomatric titration.

GLC method was used to analyze the methyl esters using fatty acid profile and IV was calculated theoretically.

The IV values of 30 Sunlight Blend oil samples were determined over a period of two months. The average % IV content from GLC Method was **34.43±2.1559**, average IV from Wijs Method was **34.44±2.4656**.

TITLE.2

TREND ANALYSIS OF ENVIRONMENTAL PARAMETER IN FATS AND OIL PROCESSING INDUSTRIAL EFFLUENT

Analysis of Environmental parameters in effluents from fats & oil processing industry is an important factor to measure the quality of effluents. The effluents are collect from varies departments. In Unilever Ceylon Ltd, the effluents are mainly containing fats, caustic, active detergent & shampoo. Firstly the effluents are collected in the large pans and the insoluble particals like fats are separated by physical separation. The pH of effluents is reduced by the addition of acids. Once the soluble parts are separated the effluents are chemically treated.

Three types of wastewater samples were collected daily from the effluent treatment plant as effluent,aeration tank and treated effluent sample. Two types of parameters are used to measure the quality of effluents. Chemical parameters such as COD, BOD, D.O &TDS and physical parameters such as temperature, pH & flow rate. COD, BOD, pH & TDS were measured in effluent & treated effluent samples while only pH & TDS in aeration tank.

The average pH/TDS values of effluent, treated effluent & aeration tank was 6.74/1080.5mg/l, 7.35/1148.7 mg/l and 7.16/1156.8 mg/l respectively. The average BOD/COD values of effluent & treated effluent was 546.44/1045 mg/l & 17.12/35.8 mg/l respectively. The Central Environmental Authority (CEA) specifications for pH, BOD & COD in treated effluent are 7, < 30 and < 250 respectively.

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CHAPTER.1

1.1.Introduction

Unilever Ceylon Ltd is one of the leading soap manufacturing company in srilanka. There is a range of different soap brands and sunlight is one of the most popular brand in srilanka. Sunlight blend is used to produce the sunlight soap. There are lot of parameters which are measure the quality of sunlight blend. The iodine value is one of the important parameter.
The iodine value (IV) is a measure of the unsaturation of fats and oils and is expressed in terms of the number of centrigrams of iodine absorbed per gram of sample.[1] The IV serves as an indicator of relative hardness or softness of fats & resulting fatty acids & soap products. In the most general sense, higher levels of unsaturation, reflected by higher iodine values, indicate a tendency toward softer material & subsequently, softer soap products. Lower IV indicating less unsaturation,will exhibit a higher melting point and will result in firmer soap than will lard.[4]

Sunlight blend is being mainly used to preparation of Hard Soap such as, Sunlight. In the preparation of Hard Soap the Iodine Value is an important parameter in the determining the hardness associated with Sunlight blend. The IV is going to be determined using two methods, the GLC and Wijs method. The IV is depend on the number of double bonds.

Since there are two accepted methods. It is important to find out the agreement of the results obtained by both methods. Therefore my study involve in comparison of results obtain for the iodine value from GLC & Wijs method.

1.2. Objectives

This study also focas on minimizing the cost and improvement of the accuracy of these methods.

CHAPTER.2

2.MATERIALS & METHADOLOGY

2.1.Sample collection

Sunlight blend samples from the bulk materials department were collected. 30 number of samples per batch was collected and analyzed for the iodine value using GLC & Wijs method.

2.2.Iodine value (IV) analysis

2.2.1. Wijs method[1]

2.2.1.1. Apparatus & Reagents

Glass stoppered iodine flask 500ml,Pipet 20ml,Burrete, Filter paper.
0.2N ICl, CCl4/$CHCl_3$ (Carbon tetrachloride (or) chloroform), 10% Potassium iodide (KI) solution, Starch solution, 0.2N Na2S2O3,

2.2.1.2.Standardisation of sodiumthiosulphate solution[2]

The weight of 0.20 - 0.25g(Wg) of well dried $K_2Cr_2O_7$ was dissolved in distilled water. 5ml of conc. HCl & 25ml of 10%KI were added and Kept in a dark place for half-hour. Using starch as indicator, the sample was titrated with prepared sodium thiosulphate solution(Vml). Carryout three determination to get an average figure.

$K_2Cr_2O_7 + 6KI + 14HCl \rightarrow 8KCl + 2CrCl_3 + 3I_2 + 7H_2O$

$2\ Na_2S_2O_3 + I_2 \rightarrow Na_2S_2O_6 + 2NaI$

Normality = (1000*W)/(49.03*V)

2.2.1.3. Procedure

The prescribed amount of sample was weighed accurately into a iodine flask. Weight of sample can be determined as follows.

Weight = 20/Expected IV

The weighed sample was dissolved in an appropriate amount of solvent $CCl_4/CHCl_3$(10.00ml).20.00ml of Wijs solution and 10.00ml of 10% KI were added and mixed well. The mixture was kept in the dark for about 30-60 minutes. Distilled water was added and titrated with standardized 0.2N $Na_2S_2O_3$ solution, with constant & vigorous shaking. The starch indicator was added when the solution was turned to pale yellow (straw colour). Simultaneously a blank titration was carried out using the same quantity of reagents under same conditions

2.2.2. GLC Method[3]

2.2.2.1. Apparatus & Reagents

Gas Chromatograph,

Recorder, Integrater (or) Calculator, Syringe Chromatographic column.

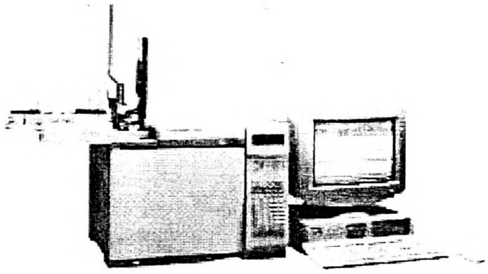


Fig.1. GLC Machine

Gases, Reference standards.

2.2.2.2. Procedure

The methyl esters was prepared and injected directly in a gas chromatograph.

2.2.2.2.1. Preparation of methyl esters

2.2.2.2.1.1. Apparatus & Reagents

125ml flat bottom boiling flasks, Water cooled condensers.

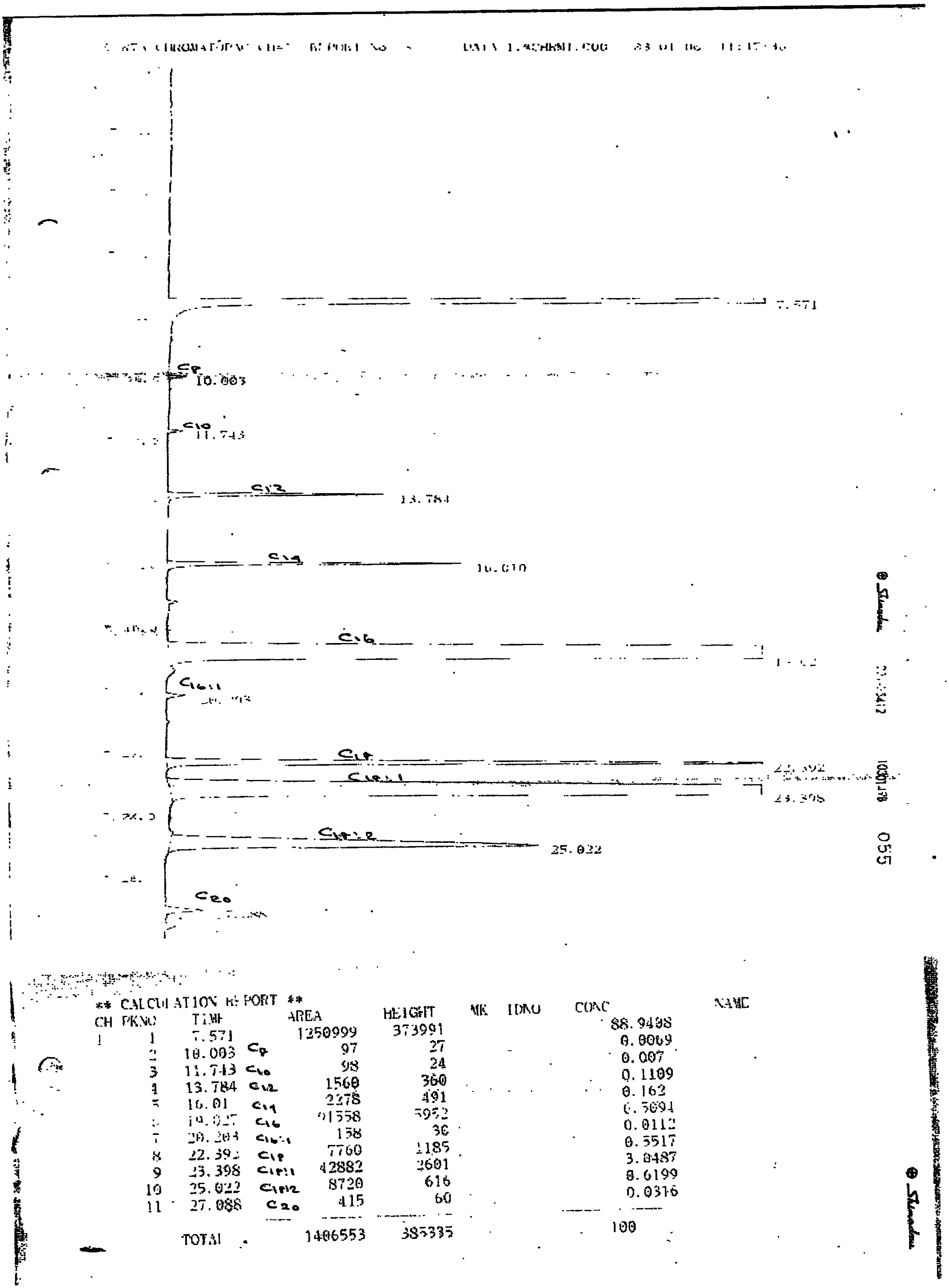
BF3-Methanol, 0.5N methanolic sodium hydroxide, Sodium chlorite (NaCl), Saturated solution in water, Isooctane.

2.2.2.2.1.2. Procedure

The oil (filtered oil) was introduced into flat bottom boiling flask (Accurate weighing is not required about 8 drops). The specified amount of (5ml) 0.5N methanolic sodium hydroxide was added and a boiling chip was added. A condencer was attached and the mixture was heated on a steam bath until the fat globules went into solution(5-10 minutes). 3.00ml of BF3-Methanol was added through the condenser and boiled for two minutes.Two to 5ml of isooctane was added through the condencer and boiled for one minute longer. The flask was removed from heat and condenser. And the enough amount of saturated salt solution was added to float the isooctane solution of the methyl esters into the neck of the flask. About 1ml of the isooctane solution was transferred into a test tube. The isooctane solution was injected directly in to the gas chromatograph.

2.2.2.2.1.3. Identification of peaks

The reference standard mixture of known composition was analyzed under the same operating conditions as those employed for the sample and retention distances (or retention time) was measured. Construct graphs showing the logarithm of the retention time as a function of the number of carbon atoms of the acids.Under isothermal conditions, the graphs for straight chain esters of the same degree of unsaturation should be straight lines.[3]The peaks of the sample from chromatogram was identified by comparing the retention time of the standard mixture.



```
** CALCULATION REPORT **
CH PKNO    TIME          AREA     HEIGHT   MK  IDNO    CONC          NAME
 1    1    7.571       1250999    373991               88.9498
      2   10.003 C8         97        27                0.0069
      3   11.743 C10        98        24                0.007
      4   13.784 C12      1560       360                0.1109
      5   16.01  C14      2278       491                0.162
      6   19.027 C16     91558      5952                6.5094
      7   20.203 C16:1     158        36                0.0112
      8   22.392 C18      7760      1185                0.5517
      9   23.398 C18:1   42882      2601                3.0487
     10   25.022 C18:2    8720       616                0.6199
     11   27.088 C20       415        60                0.0316

           TOTAL       1406553    385335              100
```

Fig.2.Example of chromatogram

CHAPTER.3

3.RESULTS

3.1. Calculated iodine values from Wijs method

Weight of sample in grams = W,

Volume of thiosulphate used for sample = V_S,

Volume of thiosulphate used for blank = V_B.

Normality of thiosulphate = N,

IV = $[(V_B-V_S)*N*126.9*100]/[W*1000]$

IV = $[12.69*N*(V_B-V_S)]/W$

Example

IV = $[12.69*N*(V_B-V_S)]/W$
V_S=22.4ML,
V_B=16.8ML,
W=0.3662g,
N=0.1939,
IV = [12.69*0.1939*(22.4-16.8)]/0.3662
IV=37.6,

Table.1. Used for the Calculations of iodine values from GLC method

SAMPLE SL Blend 14/11/02

SOURCE BMD

CONDITIONS

Initial Temperature:100 0C/ Rate: 09 0C per min/Split ratio: 1:100

Final Temperature:200 0C/Attenuation: 1/Range :2/ BF3 Method

METHOD OF ESTERIFICATION :

ANALYST	IG	AREA	% by mass
Component in Ref. Mixture	**No of C atoms**	**0**	**0.000**
Caproic acid	C6	0	0.000
Caprylic acid	C8	0	0.000
Capric acid	C10	512	0.443
Lauric acid	C12	1589	1.375
Miristic acid	C14	0	0.000
Miristoleic acid	C14 : 1	70993	61.423
Plastic acid	C16	113	0.098
Palmitoleic acid	C16:1	5093	4.406
Stearic acid	C18	30891	26.727
Oleic acid	C18 : 1	6139	5.311
Linoleic acid	C18 :2	251	0.217
Arachidic acid	C20	0	0.000
Linolenic acid	C18 : 3	115581	100.000
	IV	33.78	

Table.2. Used for the Calculations of iodine values from GLC method

Formula			Mol Wt.	IV	
C	H	O			
6	12	2	116	0.00	0.00
8	16	2	144	0.00	0.00
10	22	2	174	0.00	0.00
12	24	2	200	0.00	0.00
14	28	2	228	0.00	0.00
14	26	2	226	0.00	0.00
16	32	2	256	0.00	0.00
16	30	2	254	99.92	0.10
18	36	2	284	0.00	0.00
18	34	2	282	90.00	24.05
18	32	2	280	181.29	9.63
20	40	2	312	0.00	0.00
18	30	2	278	273.88	0.00
					33.78

Table.3.Used for the Iodine values from Wijs and GLC method

DATE	IV [WIJS METHOD]	IV [GLC (CALCULATED) METHOD]
02/OCT/02	32.82	33.78
03/OCT/02	30.68	31.75
05/OCT/02	30.30	31.59
06/OCT/02	32.69	32.00
07/OCT/02	31.93	31.25
08/OCT/02	31.63	30.47
10/OCT/02	32.60	31.86
11/OCT/02	30.29	31.61
12/OCT/02	33.72	34.32
14/OCT/02	33.60	33.78
16/OCT/02	33.37	33.87
21/OCT/02	34.01	33.20
25/OCT/02	35.82	35.02
25/OCT/02	32.57	33.87
02/NOV/02	33.22	32.73
02/NOV/02	33.12	33.87
09/NOV/02	33.46	34.32
13/NOV/02	35.91	35.47
16/NOV/02	35.12	35.32
21/NOV/02	35.05	35.27
25/NOV/02	37.08	36.98
29/NOV/02	35.02	34.75
05/DEC/02	35.78	35.47
09/DEC/02	34.46	35.60
09/DEC/02	37.06	36.79
10/DEC/02	36.36	35.33

10/DEC/02	36.36	35.33
13/DEC/02	35.47	35.07
17/DEC/02	37.6	37.23
21/DEC/02	38.3	37.25
27/DEC/02	38.38	38.79
31/DEC/02	40.3	38.69

Average from Wijs method=34.44±2.466,

Average from GLC method =34.43±2.156,

Correlation Co-efficient=0.944668953,

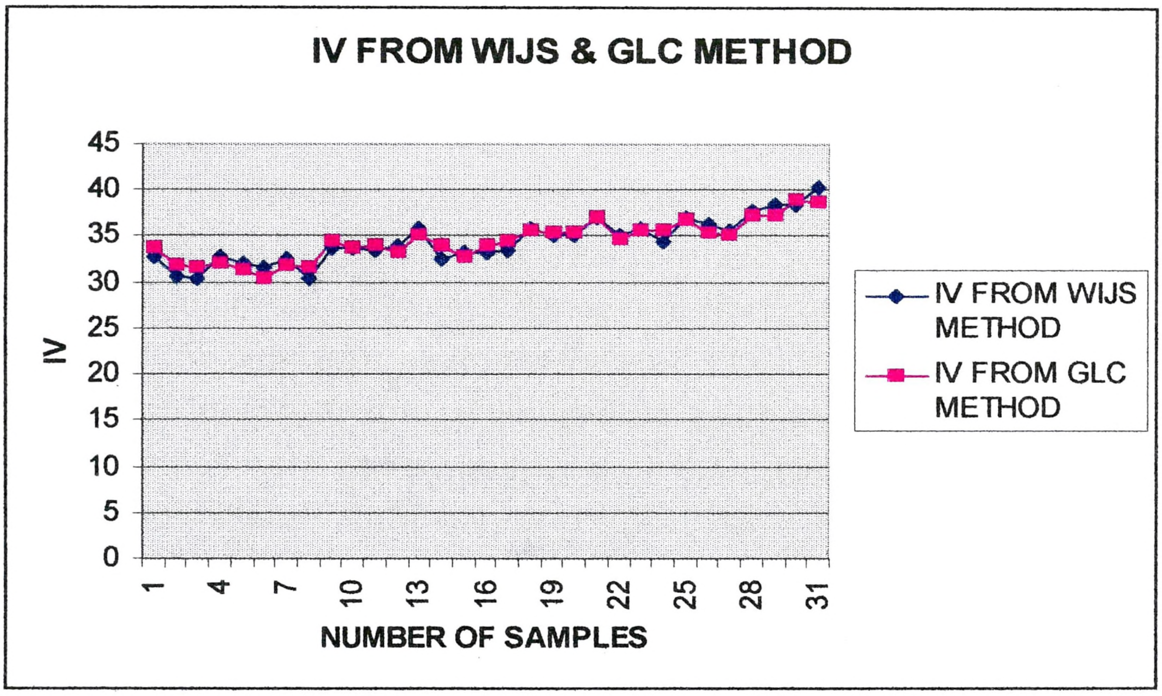


Fig.3.Variation of IV from Wijs & GLC method

CHAPTER.4

4.DISCUSSION

4.1 Wijs method

The sample to be investigated is treated with an ICl solution (Wijs solution). The I_2 is liberated from excess ICl and KI and is titrated with standardized thiosulphate solution.

$ICl + I_2 \rightarrow 3ICl$

$ICl + KI \rightarrow I_2 + KCl$

$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$

Standardization of the sodium thiosulphate solution is very important in Wijs method. Here the strength is obtained to four decimals. If the strength is varies slightly,the iodine value also changed.

Before weighing the sample it should be filtered through filter paper to remove any solid impurities and the last traces of moisture. The mechanical stirring was very satisfactory for agitating during the addition of thiosulphate. Then only we can get the sharp end point. And also we should keep the sample with Wijs solution in dark room, because of Wijs solution is sensitive to temperature, moisture, and light, for 1 hour at room temperature for complete absorption of iodine.

4.2.GLC (Calculated) method

Methyl esters of fatty acids are separated and determined quantitatively by GLC using a packed column. The method is applicable to methyl esters of fatty acids having 8 to 24 carbon atoms and to animal fats, vegetable oils, marine oils and fatty acids after their conversion of methyl esters. The method permits quantitative separation of mixtures containing saturated & unsaturated methyl esters. The conditions specified in this method are not suitable for determining epoxy (or) oxidized fatty acids (or) fatty acids that have been polymerised.[3]

Preparation of methyl esters (which due to their greater volatility) of long-chain fatty acids is very essential for further analysis by gas liquid chromatography method.

In this method, if polyunsaturated components with more than three double bonds are present, they may decompose in a stainless-steel column.[3]

The required reaction time appears to increase as both the carbon number and degree of unsaturation increase. For longer chain and more unsaturated fatty acids, a general observation is that the reaction should be allowed to proceed just untill there is no visual evidence of oil globules in the reaction mixture. The methyl esters should be analyzed as soon as possible.[3]

All glassware must be absolutely clean and completely dry.

Fresh cyclohexane (or) chloroform should be used when prepared the Wijs solution. Erratic results may be obtained if old cyclohexane (or) chloroform is used.

CHAPTER.5

CONCLUSION

According to the results there is no significant difference between two iodine values obtained from Wijs and GLC methods.

REFERENCES

1.A.O.C.S.Official Method Cd 1-25,

2.A.O.C.S.Official Method Cd 1b-87,

3.A.O.C.S. Official Method Ce 1-62,

4. Luis Spitz , A.O.C.S.Champaign Illinois, Soap Technology for the 1990, PP 262(Iodine number),

TREND ANALYSIS OF ENVIRONMENTAL PARAMETER IN FATS AND OIL PROCESSING INDUSTRIAL EFFLUENT.

CHAPTER.1

1.Introduction

The disposal of waste waters is of widespread national concern. In the chemical field alone there is a large volume of literature. The problem of adequately handling industrial waste water is more complex and much more difficult than sewage. In factories having both acid & basic wastes. It reduces the cost of neutralization. In plant having waste water containing large amount of organic material this results in a decrease in suspended matter and a reduction of the BOD.[3]

Analysis for organic matter in water and waste water can be classified into two general types of measurements.Those that quantity an aggregate amount of organic matter comprising organic constituents with a common characteristic and those that quantify individual organic compounds.[1]

Methods for total organic carbon and chemical oxygen demand are used to assess the total amount of organics present. Gross fractions of the organic matter can be identified analytically. As in the measurement of BOD in an index of the biodegradable organics present oil and grease, which represents materials extractable from a sample by a nonpolar solvent (or) totaorganic halide(TOX),which measures organically bound halogens.Trihalomethane formation potential is an aggregate measure of the total concentration of trihalomethane formed upon chlorination of a water sample.[1]

Analyses of organics are made to assess the concentration and general composition of organic matter in raw water supplies waste water,treated effluents and receiving water and to determine the efficiency of treatment processes.[1]

Parameters which measure the quality of effluents. Chemical parameters are COD, BOD, DO (Dissolved Oxygen), & Total Solids [TS]/Suspended Solids [TSS]/Dissolved Solids [TDS]. Physical parameters are Temperature & pH.

CHAPTER.2

2.MATERIALS & METHADOLOGY

2.1.Sample collection

Three types of wastewater samples were collected from the effluent treatment plant and used for analysis.

1.Effluent sample,
2.Aeration tank sample,
3.Treated effluent sample.

2.2. pH value

pH value of samples were determined using Orion 410.A pH meter.[4]

2.3. Total Dissolved Solids [TDS]

TDS values of samples were determined using ORION 115 conductivity meter.[5]

2.4. Biochemical Oxygen Demand [BOD][6]

2.4.1. Apparatus & Reagents

Incubation bottles, Air incubator & Ordinary laboratory apparatus,

Seeded dilution solution(one ml of each Ferric chloride stock solution, $CaCl_3$ stock solution, Magnesium sulphate stock solution, Phosphate buffer solution [pH 7.2], Seeding solution were mixed with 1L of Water-distilled (or) deionised), Dissolved Oxygen Reagents(see.2.4.2.2.1).

2.4.2. Procedure

2.4.2.1. Sample Preparation

The sample was neutralized with H_2SO_4(0.5M) and 1M NaOH. The pH was monitered using a pH meter (or)pH paper between 6.5 and 8.5 if necessary.500ml of seeded dilution solution was transfered into cylinder(1L),ensuring no air was mixed into the liquid.One ml of mixed sample was added to the cylinder and fill to the 1Litre mark with seeded dilution solution and stirred with a glass rod(No air bubbles trapped).The diluted samples were transfered to incubation bottles,The bottles were completely filled to the brim and let them for few minutes.To remove all air bubbles, the bottles were tapped gently and carefully stopper taking care that no air bubbles were trapped under the stopper.Two bottles of blank were prepared using the same seeded dilution solution.[Fill 2 bottles of each sample one to be used for initial dissolved oxygen(D.O) test and other for final D.O test after incubation]

Determine the initial D.O of one set[Sample & Blank] immediately after completing the preparation.

2.4.2.2.Determination of D.O[6]

2.4.2.2.1. Apparatus & Reagents

Incubation bottles, Air incubator & Ordinary laboratory apparatus,

Manganous sulphate, Alkaline Iodide Azide reagent, Conc.H_2SO_4, 10%V/V Sulphuric acid, Accurately standardised 0.0250N $Na_2S_2O_3$ solution

2.4.2.2.2.Standardisation of sodium thiosulphate solution[6]

The 5g of KI was dissolved in 100ml of distilled water. 10ml of diluted sulphuric acid and exactly 40ml of standard $K_2Cr_2O_7$ solution were added and Stand for 5 minutes. Then 200ml of distilled was added and titrated with prepared $Na_2S_2O_3$ adding starch indicator near the endpoint where the liquid is pale yellow. Titration was continued until the blue colour developed by the starch has changed to light green. The volume of $Na_2S_2O_3$ added was noted.

2.4.2.2.3.Procedure

The sample was poured directly into the glass stoppered bottle in such a way that no air bubbles were trapped in the liquid and stoppered the bottle.The stopper was removed and 2.00ml of manganese sulphate solution was added from a pipette.The tip of the bottle was placed below the surface of the liquid.2ml of alkaline azide reagent was added in the same manner.The stopper was replaced without trapping air bubbles.The bottle was shaked for 20-25 seconds by inverting the bottle about once each second.The bottle was let to stand until the brown precipitate has settled leaving a clear supernant.The stopper was removed and 2ml of conc.H_2SO_4 was added.The stopper was replaced and mixed well.200ml was measured to a conical flask and titrate with standard $Na_2S_2O_3$ solution until a pale straw colour was obtained.The starch was added as indicator and the titration was continued till a pale green endpoint was obtained.The volume of used $Na_2S_2O_3$ was noted.

The other two (Sample & Blank) bottles were kept in an incubator at 30°c for 3 days. The final D.O was determined as mentioned in above and the volume of $Na_2S_2O_3$ added for blank & samples were noted.

2.5. Chemical Oxygen Demand(C.O.D)[2]

2.5.1. Apparatus & Reagents

Round borrom flask, Condenser with ground-glass joint, Hot plate.

N/16 $K_2Cr_2O_7$, N/200 FAS (Ferrous Ammonium Sulphate), H_2SO_4/ $AgSO_4$ solution, 20% W/V $HgSO_4$ solution in 10% V/V sulphuric acid,. Ferric indicator (O.Phenanthroline).

2.5.2. Procedure

The sample was homogenised for 2 minutes.0.5ml of effluent sample and 5.0ml of treated effluent sample were placed separately in a 50ml round borrom flask and distilled water was added up to 5ml.If C.O.D values were suspected to be greater than 400mg/l a smaller aliquot of the sample can be taken.1.00ml of $HgSO_4$ and 4.00ml of $K_2Cr_2O_7$ were added.12.0ml of $AgSO_4$ /conc. H_2SO_4 was added carefully and mixed well. A blank was prepared using 5ml of distilled water.

The sample and blank were refluxed for 2 hours. The condenser was rinsed with distilled water and allowed to cool. The flask was removed from condencer and 2 drops of ferroin indicator was added. Titrated with N/200 FAS to a colourless of faint pink end point. The FAS solution was standardized by using 2.5ml of distilled water, 0.5ml of $HgSO_4$, 2.00ml of $K_2Cr_2O_7$ and 6.0ml of $AgSO_4$/conc.H_2SO_4 solution without refluxing.

CHAPTER.3

3.RESULTS

Table.4.Used for the pH Values of Effluent Samples

DATE	INEFFLUENT (EFFLUENT) SAMPLE	TREATED EFFLUENT SAMPLE	AERATION TANK SAMPLE
01/NOV/2002	6.2	7.3	7.05
02/NOV/2002	6.0	7.3	7.1
04/NOV/2002	6.85	7.25	6.9
05/NOV/2002	6.7	7.0	6.8
06/NOV/2002	6.1	7.3	7.1
07/NOV/2002	5.3	7.1	7.0
08/NOV/2002	7.45	7.3	7.25
09/NOV/2002	6.35	7.4	7.2
10/NOV/2002	6.4	7.35	6.9
12/NOV/2002	8.5	7.35	7.1
13/NOV/2002	6.7	7.2	7.1
14/NOV/2002	7.0	7.35	7.0
15/NOV/2002	6.7	7.3	7.1
16/NOV/2002	7.4	7.4	7.1
18/NOV/2002	6.2	7.4	7.1
20/NOV/2002	6.7	7.5	7.15
21/NOV/2002	6.7	7.3	7.15
22/NOV/2002	7.3	7.5	7.3
23/NOV/2002	6.5	7.5	7.15
25/NOV/2002	6.5	7.2	7.15
26/NOV/2002	6.15	7.4	7.1
27/NOV/2002	7.3	7.2	7.1

28/NOV/2002	6.6	7.25	7.1
29/NOV/2002	7.05	7.4	7.1
30/NOV/2002	6.5	7.4	7.2
02/DEC/2002	7.25	7.3	7.2
03/DEC/2002	6.7	7.4	7.3
04/DEC/2002	7.05	7.3	7.2
05/DEC/2002	7.05	7.3	7.3
06/DEC/2002	7.3	7.4	7.25
07/DEC/2002	7.1	7.3	7.2
09/DEC/2002	9.3	7.4	7.3
10/DEC/2002	6.0	7.45	7.1
11/DEC/2002	6.8	7.4	7.3
12/DEC/2002	6.5	7.6	7.3
13/DEC/2002	6.3	7.5	7.2
14/DEC/2002	6.95	7.5	7.3
16/DEC/2002	6.8	7.2	7.2
17/DEC/2002	7.3	7.4	7.2
18/DEC/2002	6.25	7.3	7.2
20/DEC/2002	6.5	7.5	7.3
21/DEC/2002	6.4	7.2	7.3
23/DEC/2002	6.8	7.5	7.4
24/DEC/2002	6.6	7.55	7.15
26/DEC/2002	6.6	7.3	7.3
27/DEC/2002	6.35	7.4	7.4
28/DEC/2002	6.2	7.3	7.0
30/DEC/2002	6.3	7.5	7.2

Average pH of effluent sample=6.74± 0.635,

Average pH of Treated effluent sample =7.35 ±0.119

Average pH of Aeration tank sample =7.16±0.125,

Table.5.Used for the TDS Values of Effluent Samples

DATE	INEFFLUENT (EFFLUENT) SAMPLE[mg/l]	TREATED EFFLUENT SAMPLE[mg/l]	AERATION TANK SAMPLE [mg/l]
01/NOV/2002	977	1330	1290
02/NOV/2002	1290	1350	1230
04/NOV/2002	1600	1770	1840
05/NOV/2002	1750	2160	2140
06/NOV/2002	994	2000	1900
07/NOV/2002	1240	1760	1740
08/NOV/2002	994	1670	1600
09/NOV/2002	2330	1520	1460
10/NOV/2002	548	1490	1440
12/NOV/2002	1150	1350	1310
13/NOV/2002	1570	1260	1230
14/NOV/2002	937	1210	1150
15/NOV/2002	1210	1150	1100
16/NOV/2002	981	1130	1110
18/NOV/2002	2130	1100	1090
20/NOV/2002	534	1060	1030
21/NOV/2002	766	982	957
22/NOV/2002	762	942	903
23/NOV/2002	1100	903	880
25/NOV/2002	1940	1040	1040
26/NOV/2002	1300	1240	1240
27/NOV/2002	1170	1190	1180
28/NOV/2002	1150	1200	1150
29/NOV/2002	831	1080	1070
30/NOV/2002	1060	1140	1080

02/DEC/2002	1100	1100	1090
03/DEC/2002	478	1130	1110
04/DEC/2002	1030	1060	1030
05/DEC/2002	1050	1170	1200
06/DEC/2002	995	1050	1030
07/DEC/2002	470	1000	1010
09/DEC/2002	802	960	970
10/DEC/2002	1020	1030	957
11/DEC/2002	1350	906	891
12/DEC/2002	912	926	931
13/DEC/2002	659	880	894
14/DEC/2002	990	822	872
16/DEC/2002	538	866	853
17/DEC/2002	835	871	879
18/DEC/2002	936	989	983
20/DEC/2002	1520	927	930
21/DEC/2002	282	943	922
23/DEC/2002	2110	915	953
24/DEC/2002	1100	1120	1130
26/DEC/2002	1370	1150	1170
27/DEC/2002	907	1080	1330
28/DEC/2002	510	836	870
30/DEC/2002	590	767	974

Average TDS of effluent sample=1080.6± 448.99,

Average TDS of Treated effluent sample =1148.7±302.07,

Average TDS of Aeration tank sample =1156.8±287.62,

3.1. BOD Values of Effluent Samples

D.O in mg/litre =[40*B*40*0.004167*6]/A

= 40B/A

A-Volume of $Na_2S_2O_3$ used in the standardization test

B-Volume of $Na_2S_2O_3$ used for the sample

D.O concentration [mg/l] in sample before incubation-S_1

D.O concentration [mg/l] in sample after incubation-S_2

D.O concentration [mg/l] in blank sample before incubation-B_1

D.O concentration [mg/l] in blank sample after incubation-B_2

V_{EF}= Amount of effluent taken before dilution with aerated water.

$\{[S_1-S_2]-[B_1-B_2]\}$ = Volume of $Na_2S_2O_3$ required for V_{EF} volume of effluent.

$$B.O.D = \{[S_1-S_2]-[B_1-B_2]\}\ N/1000*1/4*32/V_{EF}*1000*10^3$$

$$B.O.D = \frac{\{[S1-S2]-[B1-B2]\}*N*1000}{V_{EF}*0.0125}$$

Example-1.BOD for effluent sample

S1=7.3ml,

S2=5.65ml,

B1=7.4ml,

B2=6.9ml,

VEF for effluent sample = 1/600*1000

= 1.667,

N =0.0115M,

$$\mathrm{BOD} = \frac{\{[7.3-5.65]-[7.4-6.9]\}*0.0115*1000}{1.667*0.0125}$$

BOD = 635mg/litre,

Example-2.BOD for treated effluent

T1=7.3ml,

T2=6.35ml,

B1=7.4ml,

B2=6.9ml,

VEF for treated effluent=12/600*1000,

=20

$$\mathrm{BOD} = \frac{\{[7.3-6.35]-[7.4-6.9]\}*0.0115*1000}{20*0.0125}$$

=21mg/litre.

Table.6.Used for the BOD Values of Effluent Samples

DATE	BOD VALUES FOR INEFFLUENT (EFFLUENT) SAMPLE[mg/litre]	BOD VALUES FOR TREATED EFFLUENT SAMPLE[mg/litre]
04/NOV/2002	635	21
06/NOV/2002	800	18
08/NOV/2002	304	21
10/NOV/2002	690	16
13/NOV/2002	552	14

15/NOV/2002	469	12
18/NOV/2002	635	18
20/NOV/2002	607	16
22/NOV/2002	276	14
25/NOV/2002	1463	18
27/NOV/2002	717	21
29/NOV/2002	414	18
02/DEC/2002	221	16
04/DEC/2002	331	16
06/DEC/2002	276	18
09/DEC/2002	579	23
11/DEC/2002	635	12
14/DEC/2002	166	12
16/DEC/2002	193	14
18/DEC/2002	414	23
20/DEC/2002	304	9
23/DEC/2002	745	21
26/DEC/2002	690	14
28/DEC/2002	745	18
30/DEC/2002	800	25

Average BOD of effluent sample =546.44±279.359,

Average BOD of Treated effluent sample = 17.12±4.003,

3.2.COD Values of Effluent Samples

1ml N/8 $K_2Cr_2O_7$ =1mg O_2,

1ml N/16 $K_2Cr_2O_7$ = 0.5mg O_2,

But 1ml N/200 FAS = 0.08ml N/16 $K_2Cr_2O_7$, 1ml N/200 FAS = 0.04mg of O_2.

Amount of O_2 consumed by sample = blank titration (B)-sample titration (S),

So amount of O_2 consumed by Vml of sample =(B-S)*0.04mg,

Amount of O_2 consumed by 1litre of sample =[(B-S)*0.04*1000/V] mg,

But normality of FAS may not be exactly N/200 and is given by (2*0.0625)/T where T=Volume of FAS used in the standardization titration,

Thus B & S must be converted to exactly N/200 FAS.ie,B & S should be multiplied by N/0.025
Where
N is the actual normality of FAS.Thus substituting same in equation.
Amount of O2 consumed by 1litre of sample
= [(B-S)*N/0.005*0.04*1000/V] mg

C.O.D = [(B-S)*N/V*8000] mg/litre

Example -1.

COD for effluent sample,

B=24.45ml,

S=17.3ml,

T=12.55ml,

V=O.5ml,

N=[2*0.0625]/T

N=[2*0.0625]/12.55

N=0.00996.

So COD = [(B-S)*N/V*8000] mg/litre

= [(24.45-17.3)*0.00996/0.5*8000]

= 1139mg/litre,

Example- 2.COD for treated effluent sample

B=24.45ml,
S=21.95ml,
V=5.0ml,

N=0.00996,

COD = [(24.45-21.95)*0.00996/5.0*8000] mg/litre,
= 39.84mg/litre,
= 40mg/litre,

Table.7.Used for the COD Values of Effluent Samples

DATE	COD VALUES FOR INEFFLUENT (EFFLUENT) SAMPLE[mg/litre]	COD VALUES FOR TREATED EFFLUENT SAMPLE[mg/litre]
04/NOV/2002	1254	44
06/NOV/2002	1586	39
08/NOV/2002	606	45
10/NOV/2002	992	43
13/NOV/2002	802	37
15/NOV/2002	885	19

18/NOV/2002	1290	44
20/NOV/2002	937	33
22/NOV/2002	445	24
25/NOV/2002	3108	32
27/NOV/2002	1641	35
29/NOV/2002	656	34
02/DEC/2002	306	35
04/DEC/2002	656	30
06/DEC/2002	419	32
09/DEC/2002	1150	45
11/DEC/2002	1451	20
14/DEC/2002	540	27
16/DEC/2002	412	24
18/DEC/2002	992	48
20/DEC/2002	678	18
23/DEC/2002	1659	33
26/DEC/2002	1433	32
28/DEC/2002	835	50
30/DEC/2002	1392	71

Average COD of effluent sample =1045±,597.27,

Average COD of Treated effluent sample 35.76±11.652,

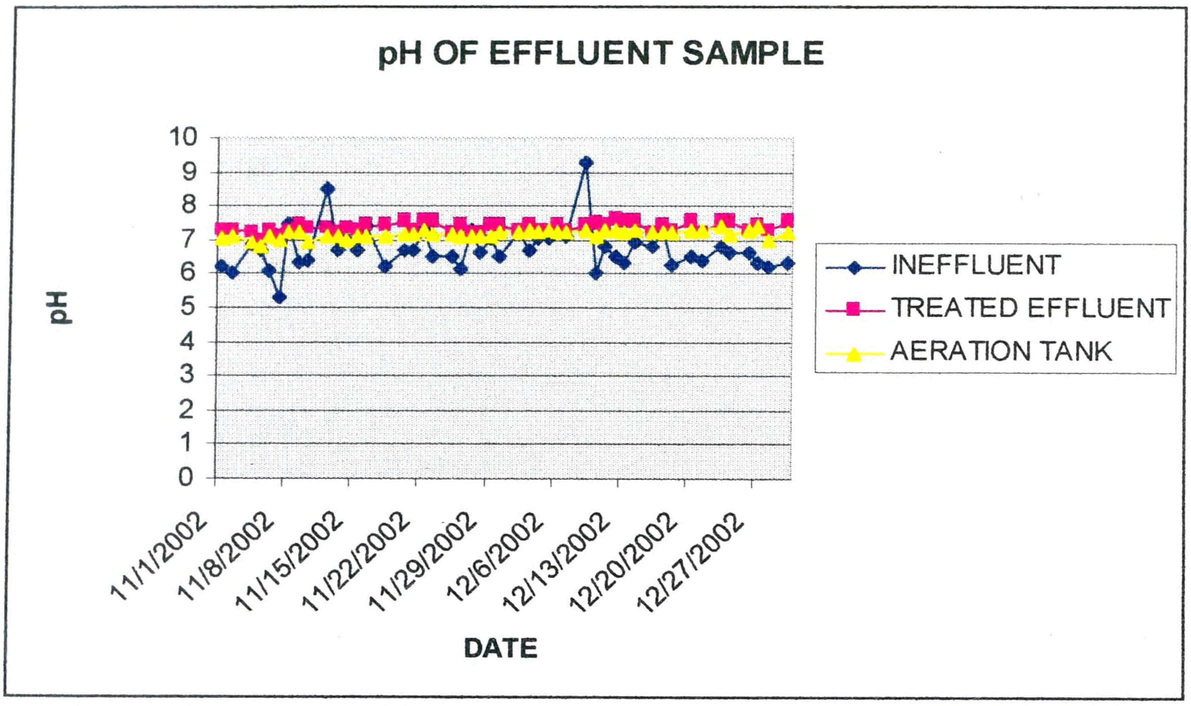


Fig.4.Variation of pH for effluent sample

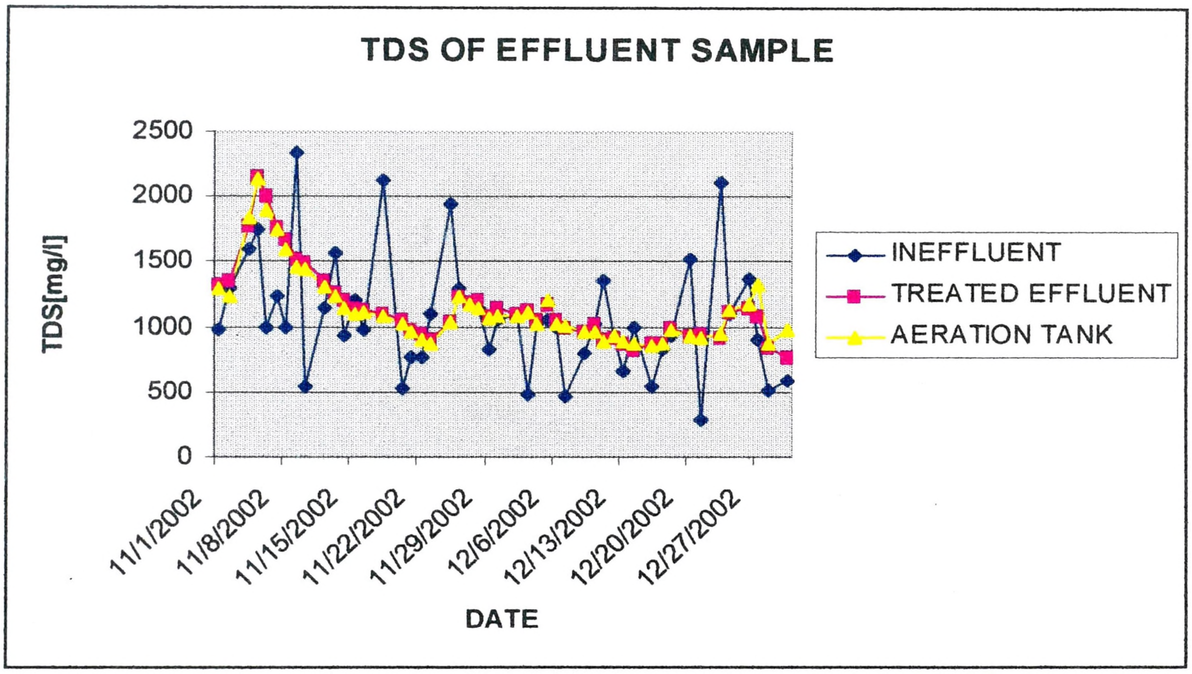


Fig.5.Variation of TDS for effluent sample

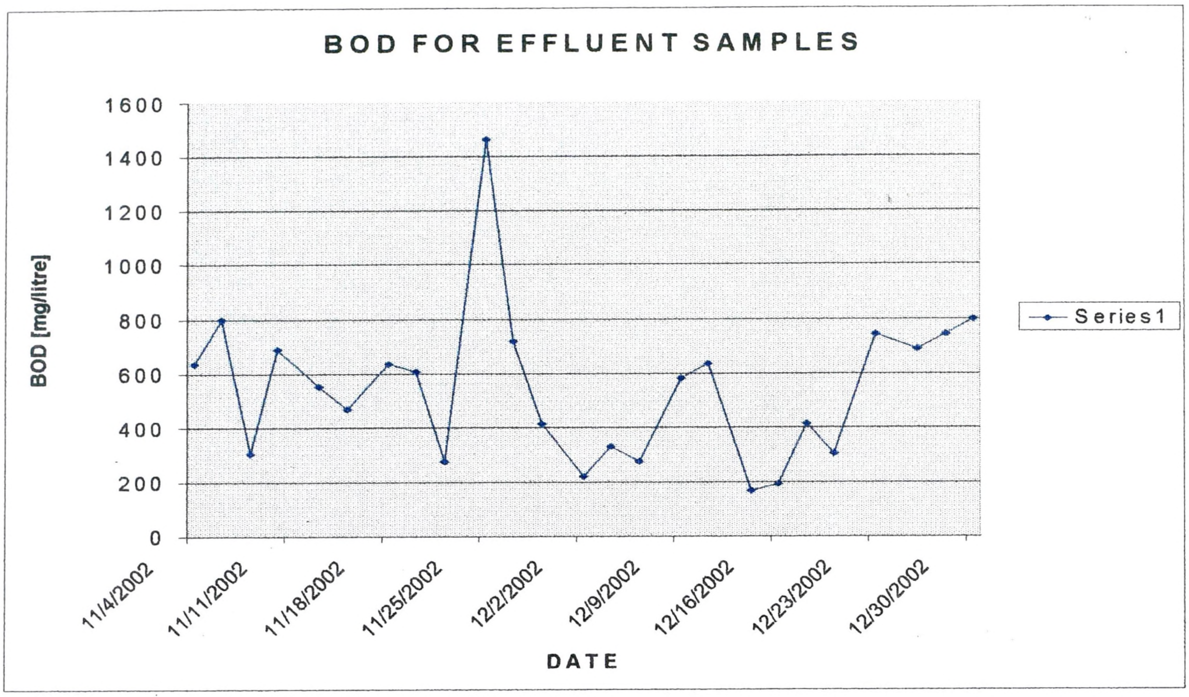


Fig.6.Variation of BOD for effluent sample

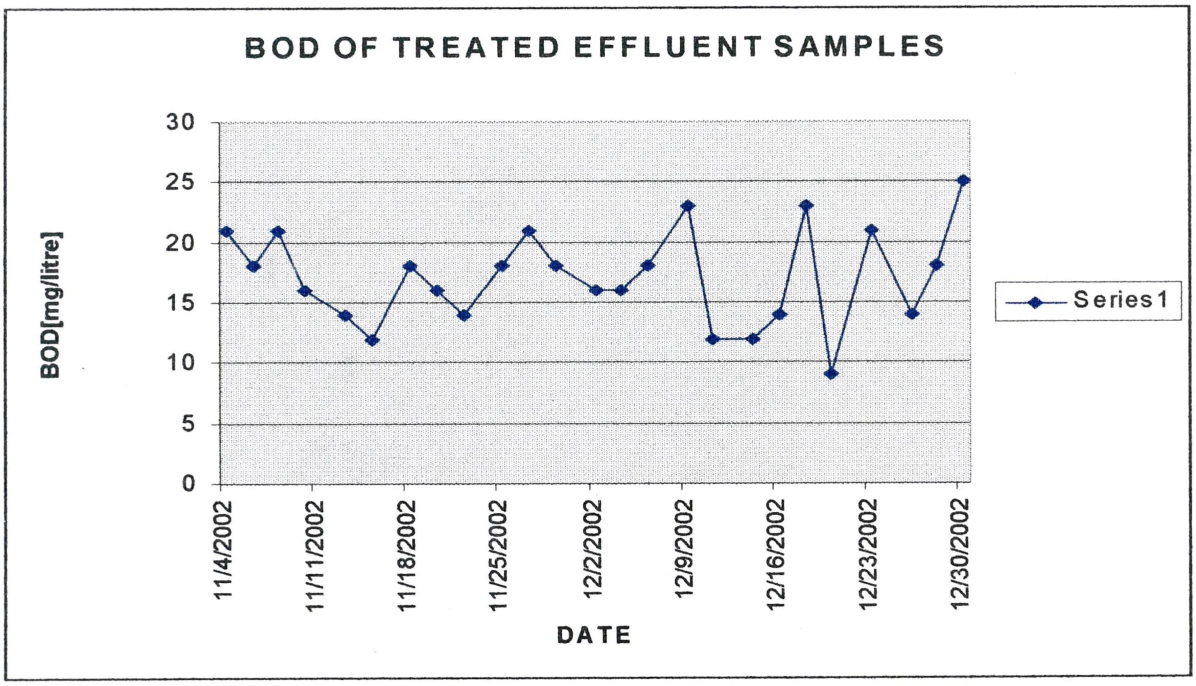


Fig.7.Variation of BOD for treated effluent sample

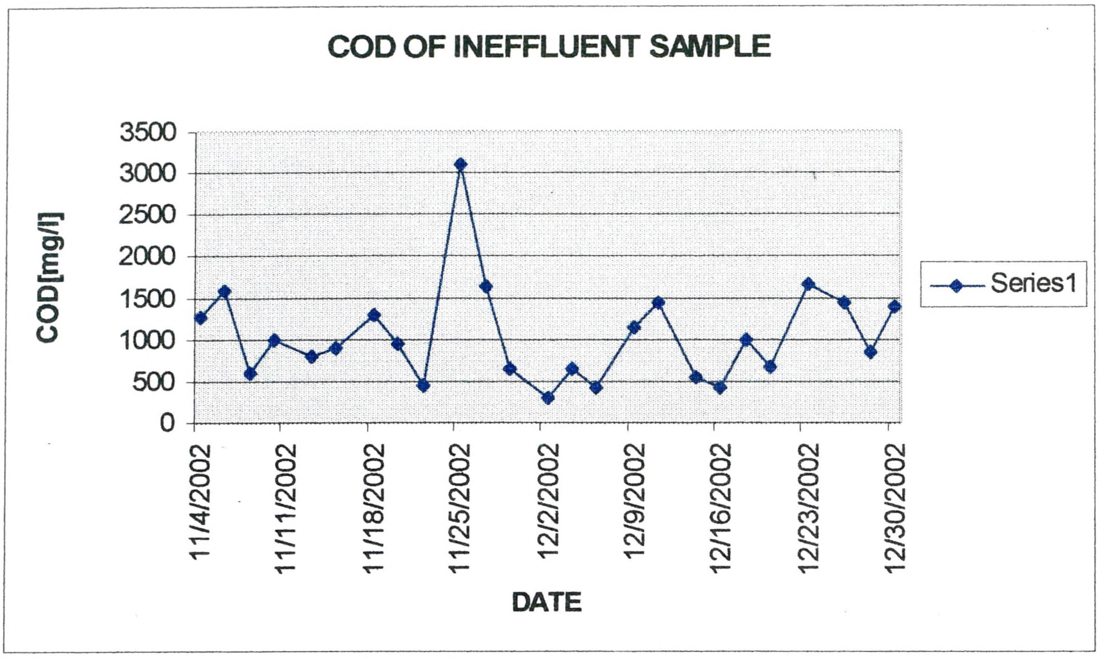


Fig.8.Variation of COD for effluent sample

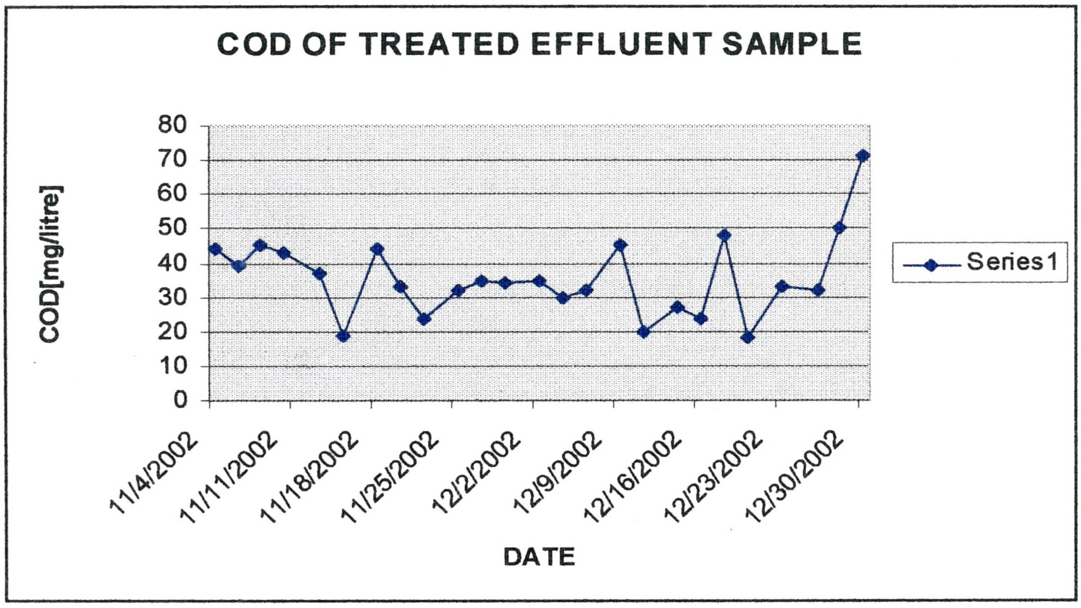


Fig.9.Variation of COD for Treated effluent sample

CHAPTER.4

4.DISCUSSION

Before measure the p^H and TDS, the p^H meter & conductivity meter should be calibrated.

The BOD of the sample under investigation is the amount of free oxygen expressed in mg/litre, required for the biochemical oxidization of the organic matter in the sample under the conditions of the test.

The test measures the oxygen utilized during a specific incubation period for the biochemical degradation of organic material (carbonaceous demand) and the oxygen used to oxidize inorganic material such as sulfides and ferrous iron.[1]

The BOD concentration in most wastewater exceeds the concentration of dissolved oxygen (D.O) available in an air-saturated sample. Therefore, it is necessary to dilute the sample before incubation to bring the oxygen demand and supply into appropriate balance. Because bacterial growth requires nutrients such as nitrogen, phosphorus and trace metals. These are added to the dilution water which is buffered to ensure that the p^H of the incubated sample remains in a range suitable for bacterial growth.[1]

The sample is diluted with aerated water containing neutrients and microbiological seed and its oxygen content is determined. It is then incubated (or) 30°c for 3 days and the oxygen content is again determined the same procedure is for a blank (distilled water).[1]

When determine the BOD, the sample consists of filling with sample, to overflowing, an airtight bottle of the specified size and incubating it at the 30^{0}C for 3 days. Dissolved oxygen is measured initially and after incubation, and the BOD is computed from the difference between initial and final DO. Because the initial DO is determined immediately after the dilution is made, all oxygen uptake.[1]

Determination of D.O [Winkler Method][6]

The dissolved oxygen content of the sample under investigation is the amount of free atmospheric oxygen expressed in mg/litre at the time of determination under conditions of the test.

Manganous sulphate is added to the effluent sample under alkaline conditions. Here the precipitation of Manganous (II) hydroxide occurs and with the O_2 present higher hydroxides such as Manganous (111) hydroxide forms on acidification in the presence of iodine irons, I_2 is liberated & estimated by $Na_2S_2O_3$ titration.

$4Mn(OH)_2 + O_2 + 2H_2O \rightarrow 4Mn(OH)_3 \downarrow_{(Brown)}$ — (1)

When titrate with acid

$2I \rightarrow I_2 + 2e$

$2Mn(OH)_3 + e + 3H^+ \rightarrow Mn^{2+} + 3H_2O$

$2Mn(OH)_3 + 2I^- + 6H^+ \rightarrow I_2 + Mn^{2+} + 6H_2O$ — (2)

Liberated I_2 is determined by a titration with $Na_2S_2O_3$

$I_2 + 2e \rightarrow 2I^-$

$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e$

$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$ — (3)

By equations (1),(2) & (3)

1 mole of O_2=4 moles of $Na_2S_2O_3$

Standardization of the sodium thiosulphate solution is very important in this method.Here the strength is obtained to four decimals. If the strength is varies slightly, the DO value also changed.

COD is the Amount of chemically oxidizable matter of organic. as well as inorganic present in wastewater expressed in mg/litre of the sample.

The chemical oxygen demand (C.O.D) is used as a measure of the oxygen equivalent of the organic matter content of a sample, that is susceptible to oxidation by a strong chemical oxidant.[1]

$Cr_2O_7^{2-} + 6e + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$

$6(Fe2+ \rightarrow Fe^{3+} + e)$

$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

Ag^+ catalyses the reaction under strong acidic media and Hg^+ prevents the chloride interference. If not
$2Cl \rightarrow Cl_2 + 2e$

Determination of COD, 20%w/v Hg_2SO_4 solution in 10%v/v sulphuric acid is used to prevent the chloride interference. Hg_2SO_4 is toxic. Therefore after determination of COD, the solution should be replaced separately.

CHAPTER.5

CONCLUSION

According to our results, the parameters which measure the quality of water are maintain to the level, which specify by the Central Environmental Authority(CEA). Therefore the treated effluent can be reused for cleaning purposes (or) safe to be released to the environment.

REFERENCES

1.Arnold E.Greenberg, Lenore S-Clescerpi & Andrew D.Eaton, 18th edition 1992,Standard methods for the examination of water & waste water , 5010 pp 5-1,

2.COD- UMA/ISO 6060:1989,

3.McCraw-Hill,3rd edition, Chemical Engineering Series,CPI(Chemical Process Industries), PP-50,

4.Orion p^H meter,model 410A,Instruction manual,

5.Orion Conductivity meter,model 115,Instruction manual,pp 21-26,

6.UMA/ISO 5815:1989,

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