

EXPERIMENTAL AND SURFACE MORPHOLOGICAL STUDIES ON THE INHIBITION POTENTIALS OF DIETHYL ETHER EXTRACT OF *cochlospermum tinctorium* FOR SUPER ACID CORROSION OF MILD STEEL

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ABSTRACT

The corrosion inhibition efficiency of cochlospermum tinctorium (CTE) on mild steel in 0.5M HClO₄ solution has been investigated using weight loss measurements, thermometric measurement and scanning electron microscopy studies. The weight loss measurement indicates increase corrosion inhibition efficiencies that reaches 92%. The weight loss and thermometric data established that the inhibition efficiency on mild steel increases with increase in the concentration of inhibitor, CTE. The adsorption of CTE obeys Langmuir adsorption isotherm. Thermodynamic parameters (K_{ads} , ΔG_{ads}^0) were calculated using the adsorption isotherm. Activation parameters of the corrosion process (ΔE_a , ΔQ_{ads} and ΔS_{ads}) were also calculated from the corrosion rates obtained from temperature studies. The adsorption isotherm indicates that the adsorption of CTE inhibitor on the surface of mild steel is physisorption and the thermodynamic values obtained indicates spontaneous and exothermic corrosion processes. Furthermore, the results of thermometric studies showed that the presence of CTE decreased in the reaction number (RN) and the percentage reduction of RN in the presence of CTE increases with increasing concentration of CTE. Inhibition efficiency is concentration dependent and reaches highest value of 89 % - 90 % respectively at 500mgL⁻¹ of CTE in both acids. Surface morphology of the mild steel specimens in the presence and absence of the inhibitor was evaluated by Scanning Electron Microscopy (SEM). SEM analysis revealed that the addition of inhibitor retarded the corrosion processes, where the grain boundary attack were completely hindered by the adsorbed inhibitor molecules. The micrograph in the presence of CTE showed a near smoother surface with a pit morphology lower than in the absence of plant mextract.

KEY WORDS: Corrosion, *Cochlospermum tinctorium*, Inhibition, Mild Steel, Surface morphology.

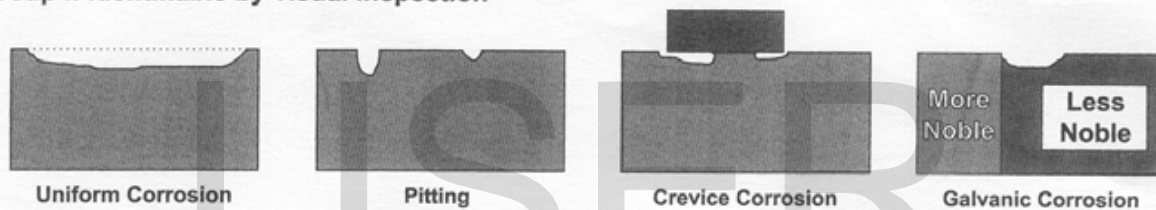
1. INTRODUCTION

Corrosion is the deterioration of materials by chemical interaction with their environment. It is the destruction or

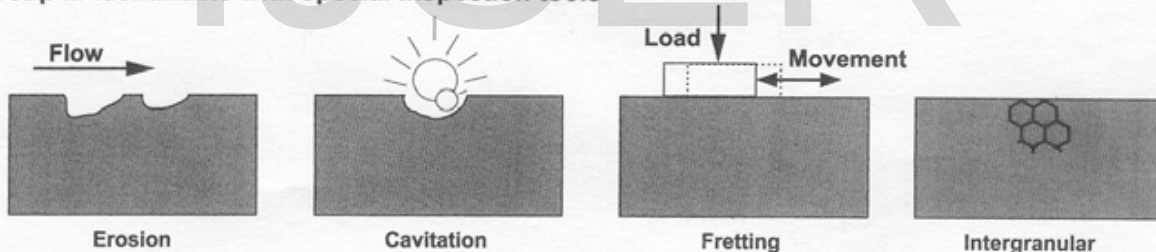
deterioration of a material because of its reaction with its environment [11]. The term corrosion is sometimes also applied

to the degradation of plastics, concrete, and wood, but generally refers to metals. The most widely used metal is iron (usually as steel). Corrosion can cause disastrous damage to metal and alloy structures causing economic consequences in terms of repair, replacement, product losses, safety and environmental pollution. Due to these harmful effects, corrosion is an undesirable phenomenon that ought to be prevented [20]. Corrosion control of metals is technically, economically, environmentally and aesthetically important. The best option is to use inhibitors for protecting metals and alloys against corrosion. As inorganic corrosion Fig.1.0[10]

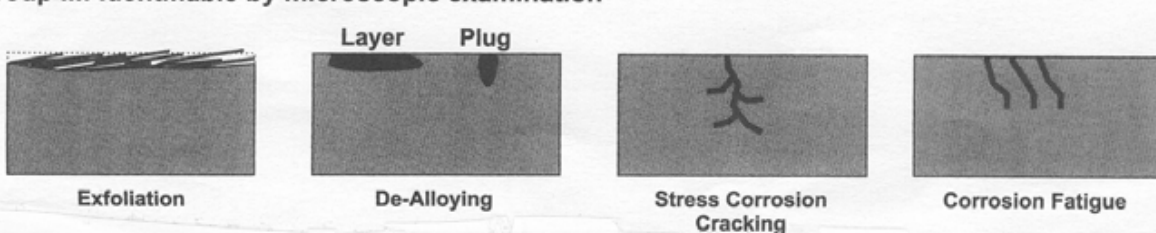
Group I: identifiable by visual inspection



Group II: identifiable with special inspection tools



Group III: identifiable by microscopic examination



This study is therefore focused at evaluating the anti-corrosive activities of its diethyl ether extract in acidic medium, H_2SO_4 . This is because there are presence of different chemical constituents in *cochlospermum tinctorium* from phytochemical screening. Organic amino

inhibitors are toxic in nature, so green inhibitors which are biodegradable without any heavy metals and other toxic compounds are promoted. Also plant products are inexpensive, renewable, and readily available. Tannins, organic amino acids, alkaloids and organic dyes of plant origin have good corrosion-inhibiting abilities. Plant extracts contain many organic compounds, having polar atoms such as O,P,S and N. These are adsorbed on the metal surface by these polar atoms and protective films are formed and various adsorption isotherms are obeyed [26].

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various adsorption isotherms are obeyed [21];

2.0 RESEARCH EXPERIMENTAL

2.10 COLLECTION AND EXTRACTION OF THE PLANT SAMPLE

Samples of *cochlospermum tinctorium* were collected from Abocho, Dekina Local Government Kogi State, identified in NDA botany session of the Biological sciences and it was sun dried and grounded to powdered form, 300g of the pulverized sample was weighed and soaked in diethyl ether for 48 hours. After 48 hours, the filtrate was distilled in a water bath that was maintained at 35° C in order to leave the extract free of diethyl ether.

The diethyl ether free extract was used in the preparation of the test solutions by

dissolving 0.1g, 0.2g, 0.3g, 0.4g, 0.5g of the extract in 1L of 0.5M HClO₄ [15] and then used to test for corrosion inhibition properties. This is because the inspection of *cochlospermum tinctorium* by Ahmad 2011 and Etuk *et al.*, 2009 was believed to contain phytochemicals that show the presence of heterotatoms which could serve as a source of bonding to metal surface to reduce corrosion processes in metals [17,18].

2.20 MATERIALS PREPARATION

Materials used were collected from Naval dock Yard Apapa, Lagos. The metals were subjected to elemental analysis. The sheet were mechanically press cut into different coupons, each of dimension 4.0 x 2.0 x 2cm² rectangular specimens and polished with emery papers (silicon cabide paper, 100- 1200) grades.

These polished coupons were subjected to water test [ASTM 2000] to make sure the metal surface were free of pits.

Each coupon were degreased by washing with and dipped in acetone and allowed to dry and was preserved in a desicator. All

reagents that were used for the study were of analar grades and double distilled water. The prepared coupons were now subjected to corrosion testing using;

1. Gravimetric technique
2. Thermometric technique
3. Surface morphological studies

The concentrations of the inhibitors were within the range, 1 to 5mg/l. Each of these concentrations were used to prepare different test solutions by dissolving them in 0.5 HClO₄ for use in the various analysis

2.30 GRAVIMETRIC METHOD OF ANALYSIS

The research studies were carried out by experiment, a weighed metal (mild steel) coupon was completely immersed in

250ml of the test solution in an open beaker. The beaker was cover with aluminium foil and then inserted into a

water bath that was maintained at 303K. The corrosion product was removed after some hours intervals by washing each coupon (withdrawn from the test solution) in a solution containing 50 % NaOH (sodium hydroxide) and 100gl⁻¹ of zinc dust [13]. The washed coupon were rinsed in acetone and dried in the air before re-weighing.

The experiment were repeated at 330K [16]. In each case the difference in weight for a period of various hours were taken as the total weight loss from the average weight loss results (average of three replicator, the corrosion rate of mild steel and the degree of surface coverage were calculated using the Equation (3), (4) (5) respectively [19]

$$IE\% = \left(1 - \frac{W_1}{W_2}\right) \quad (3)$$

$$CR = \frac{W_2 - W_1}{At} \quad (4)$$

$$\theta = 1 - \frac{W_1}{W_2} \quad (5)$$

Where W_1 and W_2 are the weight losses (g) for mild steel in the presence and absence of the inhibitor respectively, CR is the corrosion rate of mild steel in gcm⁻²h⁻¹, A is the area of the mild steel cm², t is the total period of immersion (in hours) and θ is the degree of surface coverage of the inhibitor.

2.40 THERMOMETRIC METHOD

Measurement of temperature were carried out according to the method described by Ebenso and Eddy 2008. From the rise in temperature of the system per minute the reaction number (RN) and the inhibition efficiency were calculated using equation 6 and 7 [19]

$$RN (^{\circ}C Min^{-1}) = \frac{T_m - T_i}{t} \quad (6)$$

Where T_m and T_i are the maximum and initial temperature. The inhibition efficiency (%IE) of the inhibitor were evaluated from percentage reduction in the reaction number below

$$\%IE = \frac{RN_{aq} - RN_{wi}}{RN_{aq}} \quad (7)$$

Where RN_{aq} is the reaction number in the absence of inhibitors (blank solution) and RN_{wi} is the reaction number of the medium containing the inhibition.

This technique has proved to be of considerable value and help in studying corrosion behavior of a number of metals and alloys in various corroding environments. The technique is also useful in evaluating the inhibitor efficiency of a number of surface-active agents [27].

2.50 SURFACE MORPHOLOGICAL STUDIES

Surface analysis was performed using scanning electron microscope. SEM images were obtained from MS surface after the immersion in 0.5 HClO₄ in the

absence and presence of *cochlospermum tinctorium* for two hours at 30°C.

2.51 Microstructural Examination

The microstructure of the mild steel coupons were examined before and after the corrosion experiment to assess the effect of corrosion on the microstructure and the effect of the addition of the extract

2.52 Stages of Metallography

a. Sectioning

The mild steel metals to be metallographically examined were generally sectioned (cut) to a convenient size of 2.0 x 2.0 cm² before other steps to reveal its microstructures that were performed. The sectioning was carried out by lathe machine.

b. Mounting

The specimens were placed in a small mould and covered with a cold setting plastic for easier handling.

c. Grinding

(i). **Rough Grinding:** this stage involves the grinding of mild steel surface chosen for examination in order to obtain a flat, smooth surface using the grinding machine. The rough grinding machine removed the sharp corners or edges that were found on the surface of the metal after sectioning.

(ii). **Smooth Grinding:** this was done by using different grades of emery paper (silicon carbide) ranging from 120 to 1200 microns. The aim was to remove the

as an inhibitor. The process series of preparatory stages carried out before the actual microscopic examination are outlined below.

scratches created on the surface of the specimen from the rough grinding stage.

d. Polishing

This was conducted to remove scratches left from last grinding operation and a surface suitable for microscopic investigation after etching was obtained. At the end of this stage of operation, a mirror-like surface on the mild steel ready for etching operation were obtained.

e. Etching

This was done by immersing the polished coupons in a suitable chemical reagent (solution of nitric acid and ethanol, NITAL). The etching reagent gradually dissolved the surface layer of the mild steel sheets and preferentially attacked the grain boundaries.

f. Microscopic Examination

This was done by using the metallurgical microscope. The etched specimen was placed on the microscope and the microstructure of the various micrographs were obtained accordingly.

3.0 RESULTS AND DISCUSSION

3.1 WEIGHT LOSS MEASUREMENT

The loss in weight of mild steel in the presence and absence of *cochlospermum*

tinctorium at different temperatures and immersion time intervals was determined

in Table 3.10. From the tables, it was evident that there was metal dissolution in the presence and absence of plant extract. It is pertinent to note however that the weight loss was higher in the absence of the plant extract than its presence..

In general, weight loss was found to decrease steadily with increase in the concentration of the plant extract as the time of immersion increases.

The corrosion rate for mild steel in the absence and presence of the plant extract and at different time intervals are shown in Table 3.10 accordingly. The corrosion

rate is higher in the acid solutions in the absence of CTE than in the presence of CTE inhibitor. The maximum corrosion rate recorded was 0.0174 in the 0.5M HClO_4 acids.

The decrease in weight loss in the presence of plant extract and at all its concentrations may probably be due to interference of the plant extract with metal dissolutions. It is suggestive that since the plant contains some corrosion active ingredients [24], therefore the presence of these phytochemicals reduced the metal dissolution by blocking the sites on the metal surface.

3.20 INHIBITION EFFICIENCY AND DEGREE OF SURFACE COVERAGE

Inhibition efficiency and surface coverage of *cochlospermum tinctorium* in 0.5M HClO_4 at 303K-333K were determined at several intervals in the presence of various concentrations of CTE inhibitor. These results are shown in Table 3.10.

At the inhibitor concentration of 0.5g/L, the maximum IE% was 92.7007 % for 0.5M HClO_4 all which shows that CTE act as a good corrosion inhibitor for mild steel in acid corrodents.

This result suggests that the increase in efficiencies with increase in inhibitors concentration was due to increase of the number of molecules adsorbed onto mild

steel surface and reduces the surface area that is available for the direct acid attack on the metal surface, this agrees with the work of Afia *et. al.*, 2013 [25].

Adeyemi and Singh 1987 observed that some inhibitors are effective at short intervals and reduces inhibitive properties with time because of autocatalysis. The same observation was made in the present case. CTE exhibited higher inhibition at 92.7007% in immersion. The higher corrosion inhibition efficiency is due to the higher surface coverage. This is, so we assumed that the inhibitor molecules formed a protective blanket on the metal/solution interface [24].

Table 3.10 Weight loss, inhibition efficiencies, surface coverage and corrosion rate of mild steel in 0.5M HClO_4 in the presence and absence of extract of *cochlospermum tinctorium* at varied temperature.

Time (hrs)/ Temp. (K)	Conc. (g/l)	Wt loss (g)	IE% (Inhibi on efficienc y)	Θ (Surfa ce covera ge)	Corros ion Rate (CR) g/cm ² h r	Time (hrs)/ Temp. (K)	Conc. (g/l)	Wt loss (g)	IE% (Inhibi on efficienc y)	Θ (Surfa ce covera ge)	Corros ion Rate (CR) g/cm ² h r
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2hrs at 303K	Blank	0.1233			0.0145	2hrs at 333K	Blank	0.1533			0.0174
	0.1	0.0255	79.3187	0.7931	0.0027		0.1	0.0555	63.7964	0.6379	0.0065
	0.2	0.0222	81.9951	0.8199	0.0025		0.2	0.0455	70.3196	0.7031	0.0051
	0.3	0.0182	85.2392	0.8523	0.0021		0.3	0.0412	73.1245	0.7312	0.0048
	0.4	0.0122	90.1054	0.9010	0.0014		0.4	0.0328	78.6040	0.7860	0.0038
	0.5	0.0090	92.7007	0.9270	0.0010		0.5	0.0311	79.7129	0.7971	0.0035
4hrs at 303K	Blank	0.1600			0.0095	4hrs at 333K	Blank	0.2200			0.0129
	0.1	0.0800	50.0000	0.5000	0.0045		0.1	0.1299	40.9545	0.4095	0.0077
	0.2	0.0634	60.3750	0.6037	0.0037		0.2	0.1022	53.5454	0.5354	0.0053
	0.3	0.0417	73.9375	0.7393	0.0021		0.3	0.0811	63.1363	0.6313	0.0042
	0.4	0.0305	80.9375	0.8093	0.0017		0.4	0.0655	70.2272	0.7022	0.0037
	0.5	0.0184	88.5000	0.8850	0.0010		0.5	0.0600	72.7272	0.7272	0.0034
6hrs at 303K	Blank	0.1693			0.0068	6hrs at 333K	Blank	0.2193			0.0089
	0.1	0.0950	43.8865	0.4388	0.0033		0.1	0.1522	30.5973	0.3059	0.0061
	0.2	0.0745	55.9952	0.5599	0.0026		0.2	0.1200	45.2804	0.4528	0.0047
	0.3	0.0589	65.2096	0.6520	0.0022		0.3	0.1000	54.4003	0.5440	0.0037
	0.4	0.0500	70.4666	0.7046	0.0017		0.4	0.0933	57.4555	0.5745	0.0035
	0.5	0.0400	76.3733	0.7637	0.0015		0.5	0.0800	63.5202	0.6352	0.0028
8hrs at 303K	Blank	0.1700			0.0050	8hrs at 333K	Blank	0.2300			0.0060
	0.1	0.1400	17.6470	0.1764	0.0036		0.1	0.2000	13.0424	0.1304	0.0056
	0.2	0.1300	23.5294	0.2352	0.0035		0.2	0.1899	17.4347	0.1743	0.0056
	0.3	0.1290	24.1176	0.2411	0.0033		0.3	0.1800	21.7379	0.2173	0.0054
	0.4	0.0989	41.8235	0.4182	0.0028		0.4	0.1511	34.3043	0.3430	0.0039
	0.5	0.0818	48.1176	0.4811	0.0024		0.5	0.1388	39.6521	0.3965	0.0038
10hrs at 303K	Blank	0.1799			0.0038	10hrs at 333K	Blank	0.2399			0.0057
	0.1	0.1600	11.0617	0.1106	0.0036		0.1	0.2255	6.0025	0.0600	0.0056
	0.2	0.1581	12.1178	0.1211	0.0036		0.2	0.1899	9.5039	0.0950	0.0051

	0.3	0.1522	15.3974	0.1539	0.0036		0.3	0.2100	12.4635	0.1246	0.0050
	0.4	0.1455	19.1217	0.1912	0.0035		0.4	0.1800	24.9687	0.2496	0.0046
	0.5	0.1400	22.1789	0.2217	0.0032		0.5	0.1799	25.0104	0.2501	0.0040

3.30 EFFECT OF TEMPERATURE

The effect of temperature on the inhibitive efficiency of CTE inhibitor in 0.5 M HClO₄ at temperature in the range (303 – 333) K was studied. Temperature has a great effect on the corrosion phenomenon. Generally the corrosion rate increases with rising of the temperature. For this purpose, the temperature was varied in the range of 303 to 333 K, in the absence and presence of CTE. The corresponding data are shown in Fig 3.11; it is clear that the increase of corrosion rate is more pronounced with the rising temperature for blank solution, this is to say that the higher the corrosion inhibition efficiency the lower the corrosion rate.

For each inhibitor that concentration was selected which showed higher efficiency at 303 K. The results which given in Table 3.11 show that in plain as well as in acid containing CTE the corrosion rate increases and as a result the inhibition efficiency decreases with a rise in temperature as shown in fig. 3.11. This may be attributed to desorption of the inhibitors molecules at higher temperatures, thus exposing the metal surface to further attack

The effect of temperature on the corrosion of mild steel in 0.5M HClO₄ was investigated using the logarithm form of the Arrhenius equation, which can be shown in Equation 8 [5].

$$\log \frac{CR_2}{CR_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (8)$$

where CR₁ and CR₂ are the corrosion rates of mild steel at the temperatures, T₁(303 K) and T₂ (333 K), R is the molar gas constant and Ea is the activation energy. The activation energies calculated from equation 8 are recorded in Table 3.13. The result values ranges from 24.5977kJmol⁻¹ to 35.0749kJmol⁻¹. The activation energies are less than the threshold value (80kJmol⁻¹) required for the mechanism of chemical adsorption. Therefore, the adsorption of the studied CTE inhibitor on mild steel surface is consistent with the mechanism of charge transfer from the charged inhibitor's molecule to the charged metal surface, which represents physiosorption. This is in agreement with the work of Eddy *et.al.*, 2010 [2].

Inspection of Table 3.11 showed that the value of Ea determined in 0.5M HClO₄, CTE inhibitor is higher than that for uninhibited solution. The increase in the apparent activation energy may be interpreted as physical adsorption that occurs in the first stage. This present result is consistent with Martinez and Stem 2002 [4]. Szauer and Brand 1981 also explained the increase in activation energy due to an appreciable decrease in the adsorption of the inhibitor on the zinc surface with increase in temperature [6]. As adsorption

decreases more desorption of inhibitor molecules occurs because these two opposite processes are in equilibrium. Due to more desorption of inhibitor molecules at higher temperatures the greater surface area of mild steel comes in contact with

aggressive environment, resulting increased corrosion rates with increase in temperature and decrease efficiency of inhibitors. Table 3.11 present the values E_a and thermodynamic heat of adsorption of mild steel corrosion in the 0.5M HClO_4 .

Table 3.11; Some thermodynamic parameters of the studied CTE inhibitor for 0.5M HClO_4 .

Conc. (g/l)	E_a (Activation energy) kJmol^{-1}	Q_{ads} (Thermodynamic heat of adsorption) kJmol^{-1} ,	ΔS (Entropy) Jmol^{-1}K
0.1	24.5977	-21.7404	374.70
0.2	20.9612	-18.2758	259.20
0.3	23.1454	-21.0320	351.10
0.4	27.9569	-25.3724	495.80
0.5	35.0749	-32.8103	743.70

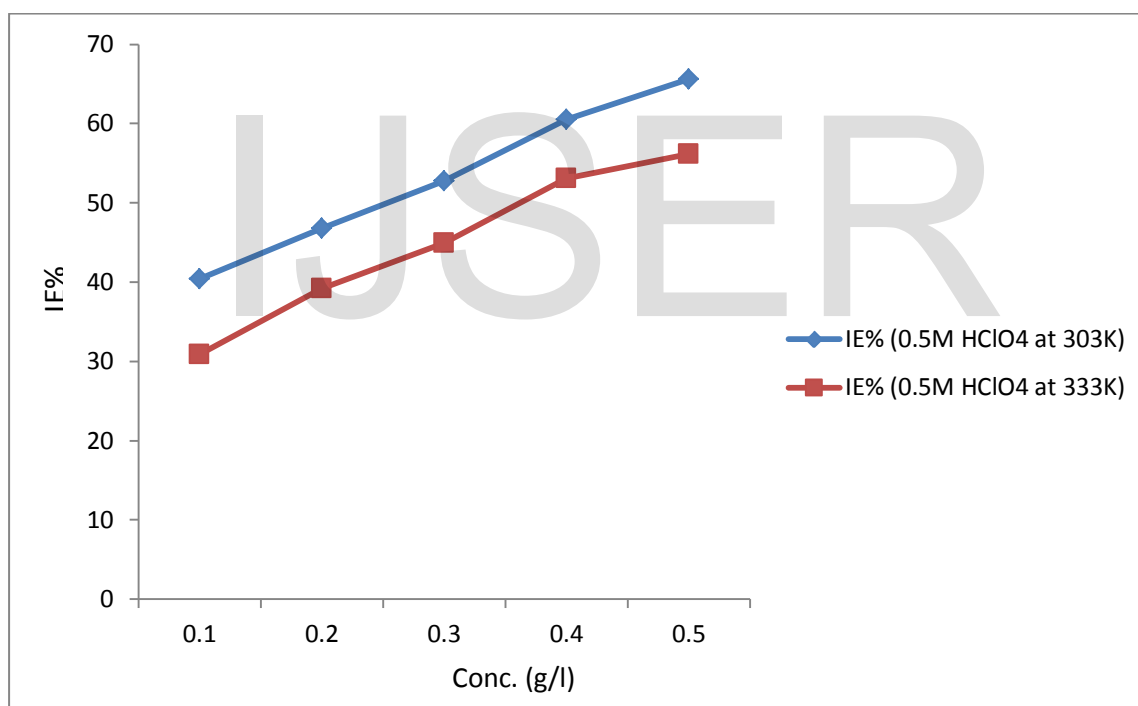


Fig 3.11: Variation of inhibition efficiency for mild steel with different concentration of CTE inhibitor in 0.5M HClO_4 at 303K and 333K.

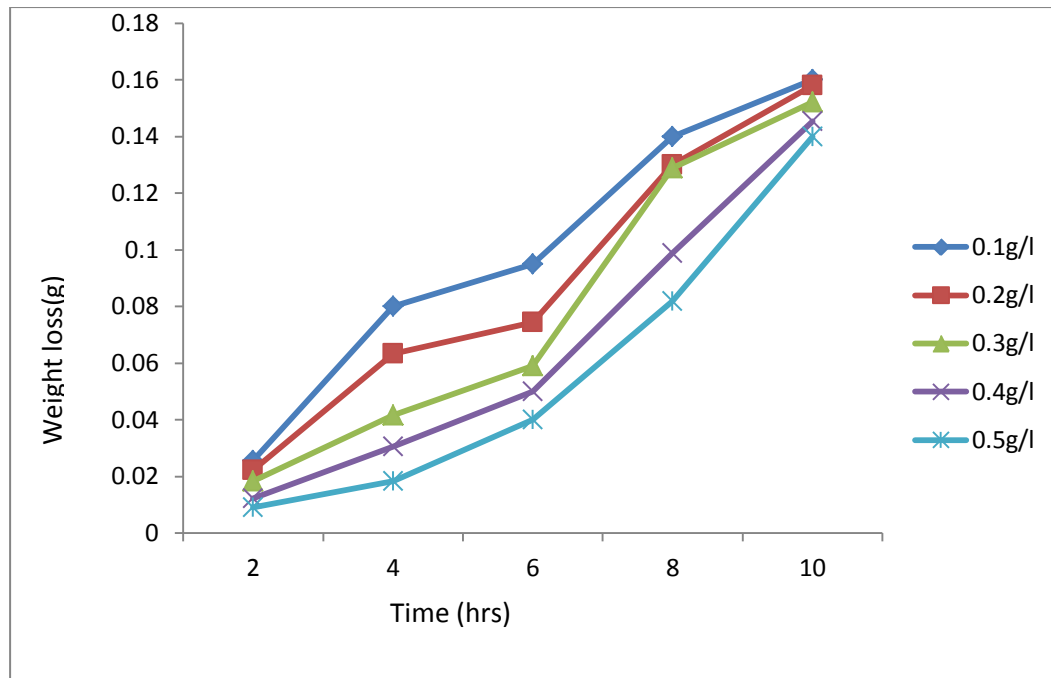


Fig 3.12: variation of weight loss with time for the corrosion of mild steel in 0.5M HClO₄ containing the various concentrations of CTE at 303K

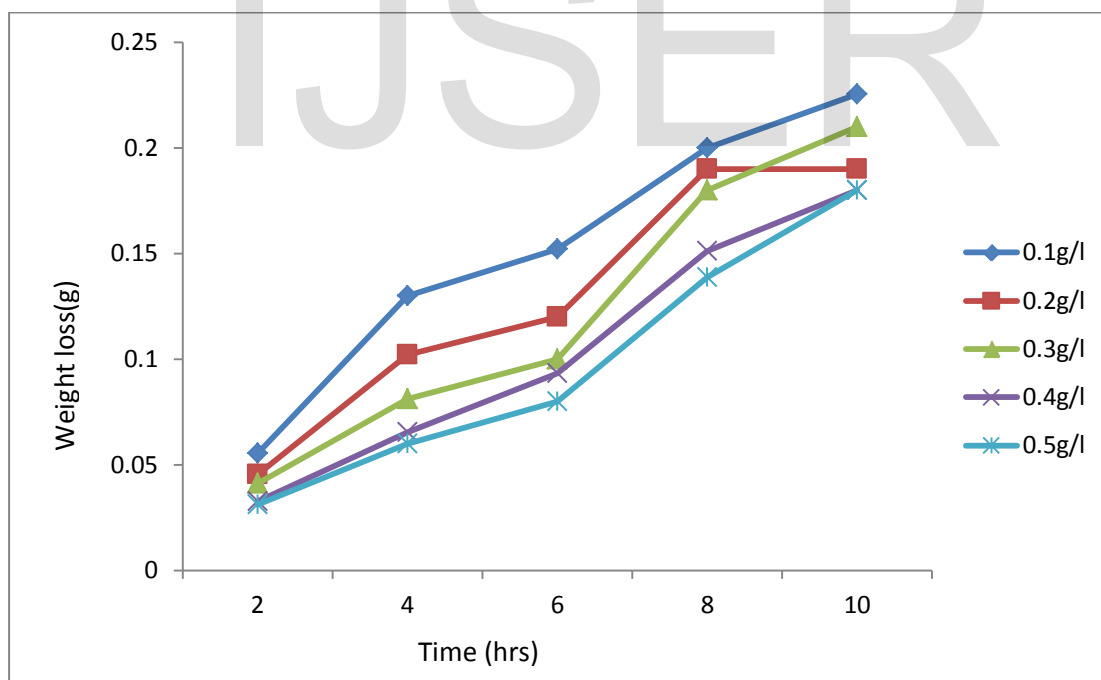


Fig 3.16: variation of weight loss with time for the corrosion of mild steel in 0.5M HClO₄ containing the various concentrations of CTE at 333K

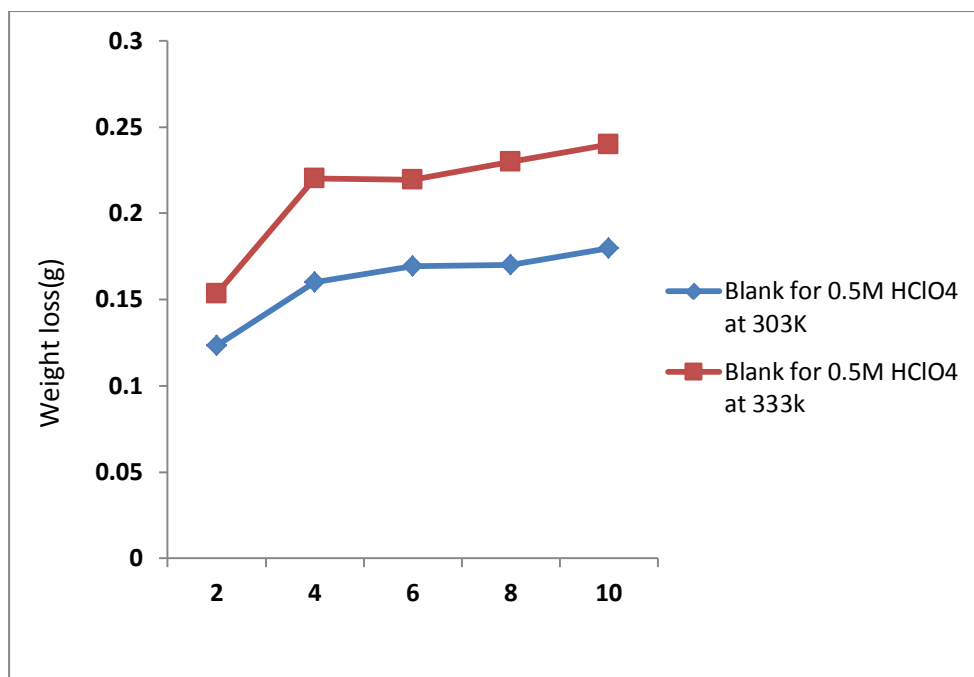


Fig 3.18: variation of weight loss with time for the corrosion of mild steel in 0.5M HClO₄ in the absence of CTE inhibitor at 303K and 333K.

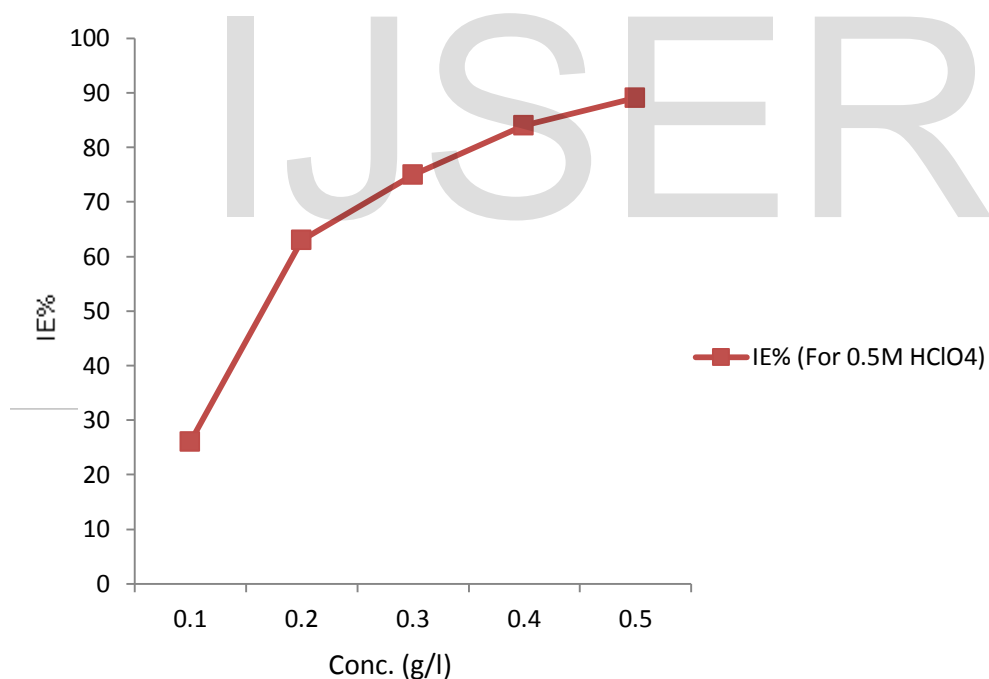


Fig 3.19: variation of inhibition efficiency with concentration for the corrosion of mild steel in 0.5M HClO₄ in the presence of CTE inhibitor for thermometric measurement.

3.40 ADSORPTION ISOTHERM

The adsorption isotherm can be determined by assuming that inhibition effect is due mainly to the adsorption at metal solution interface. Basic information on the adsorption of inhibitors on the metal surface can be provided by adsorption isotherm. In order to obtain the isotherm, the fractional surface coverage values θ as a function of inhibitor concentration must be obtained. The values of θ can be easily determined from the weight loss and electrochemical measurements by the ratio %IE/100, where %IE is inhibition efficiency obtained by weight loss and thermometric measurement. So it is necessary to determine empirically which isotherm fits best to the adsorption of inhibitors on the mild steel surface. Several adsorption isotherms (viz., Langmuir, Freundlich, Temkin, Flory-Huggins, Bockris-Swinkel, El Awdary *et. al.*, and Frumkin) were tested and the Langmuir adsorption isotherm was found to provide the best description of the adsorption behavior of these inhibitors. The Langmuir isotherm is given by equation 9 [29]:

$$\log\left(\frac{C}{\theta}\right) = \log C - \log K_{ads} \quad (9)$$

Where C is the concentration of inhibitor, K_{ads} is the equilibrium constant of the adsorption process, and θ is the surface coverage. Plot $\log C/\theta$ versus $\log C$ in Fig. 3.20 to Fig. 3.23 yields a straight line with slope and regression coefficient, R_2 , almost equal to unity. This suggests that CTE inhibitor in present study obeyed the Langmuir isotherm and there is negligible interaction between the adsorbed molecules. Free energy of adsorption was

calculated using the relation in equation 10 [30].

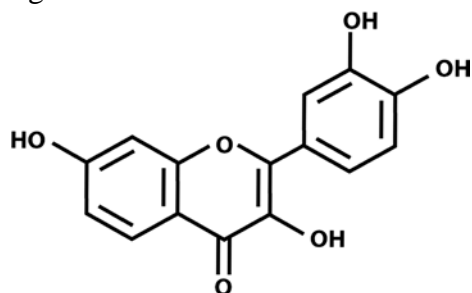
$$\Delta G_{ads}^0 = -2.303RT \log(55.5K_{ads}) \quad (10).$$

The equilibrium constant of adsorption (K_{ads}) obtained from the intercept of Langmuir plots is related to the free energy of adsorption. Calculated values of free energy of adsorption, ΔG_{ads}^0 are also presented in table 3.14. from the results obtained, the free energies ranges from ranged from 10.1457 kJmol⁻¹ to -11.790 kJmol⁻¹ for 0.5M HClO₄ and are negatively less than the threshold value of -40kJmol⁻¹ required for the mechanism of chemical adsorption. Therefore, the adsorption of the CTE inhibitor on mild steel surface in sulphuric is spontaneous and favours the mechanism of adsorption. Generally, values of ΔG_{ads}^0 around -20kJ/mol are consistent with the electrostatic interaction between the charged molecules and the charged metal (physical adsorption) whereas those more negative than -40kJ/mol involves charge sharing or transfer from the inhibitors molecule to the metal surface leading to the formation of a donor-acceptor bond (chemical adsorption). For the natural specie investigated in this study, ΔG_{ads}^0 values, indicate that the adsorption of the inhibitors is physical. This is in good agreement with the value obtained by other workers [16,19]. They observed in physical adsorption that the values of ΔG_{ads}^0 negative. Thus the process is a spontaneous one.

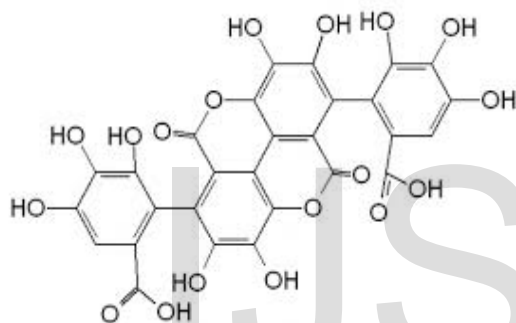
If adsorption is the key to corrosion inhibition mechanism and that the derivation of an adsorption isotherm is largely based on empirical deductions [27],

then the phytochemicals in *cochlospermum tinctorium* as investigated in the work of Ahmad 2011 [17] (the phytochemical structures are shown in the figure 3.20a, b, c, d and e below)

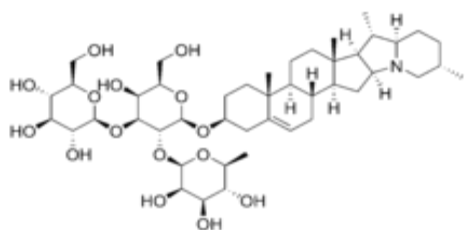
Fig 3.20. a. flavonoids



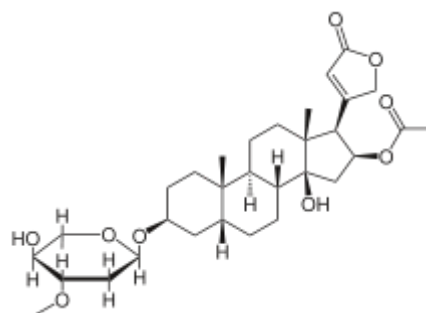
b. Tannin



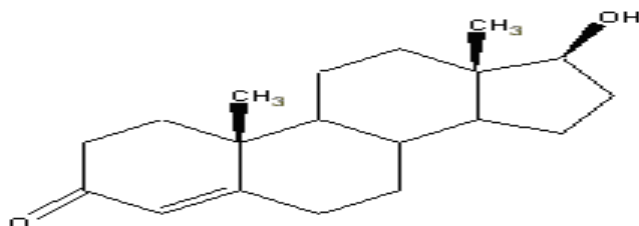
c. Saponin



d. Cardiac glycoside



e. Steroid



are adsorbed on the active sites of the metal surface forming $(\text{Metal-Inhibitor})_{\text{ads}}$ complex. This complex protects the metal surface from further attack by the aggressive acid solution, consequently corrosion processes are arrested.

Table 3.15 Langmuir parameters for the adsorption of the CTE studied inhibitor on mild steel surface in acid medium at different temperature.

	Temp. (K)	Slope	$\log K_{\text{ads}}$	R^2	$\Delta G_{\text{ads}}^0 (\text{kJmol}^{-1})$
0.5M HClO ₄	303K	0.6979	0.0044	0.9948	-10.1457
+ CTE	333K	0.6211	0.1049	0.9969	-11.7906

Table 3.16 Table for the plot of $\log C/\theta$ against $\log C$

Log C(mg/l)	0.5M HClO ₄	
	Log C/ θ (303K)	Log C/ θ (333K)
2.0000	2.3938	2.5104
2.3010	2.6307	2.7076
2.4771	2.7546	2.8241
2.6020	2.8203	2.8768
2.6989	2.8822	2.9498

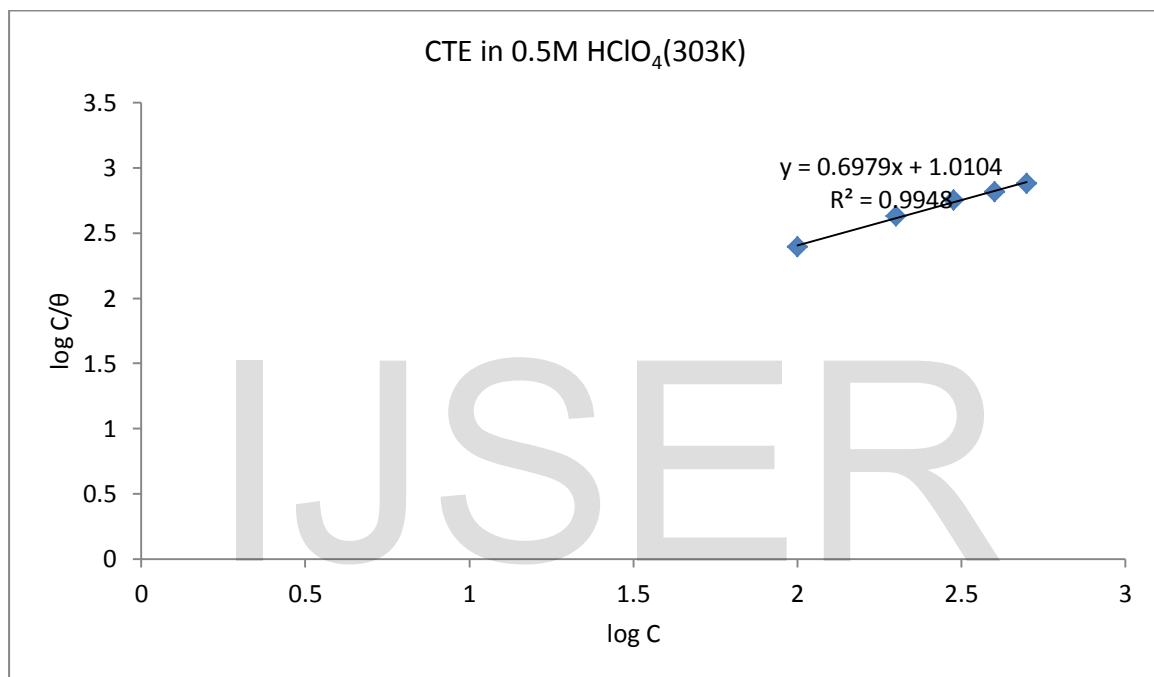


Fig. 3.30 Langmuir isotherm for the adsorption of CTE inhibitor on the surface of mild steel.

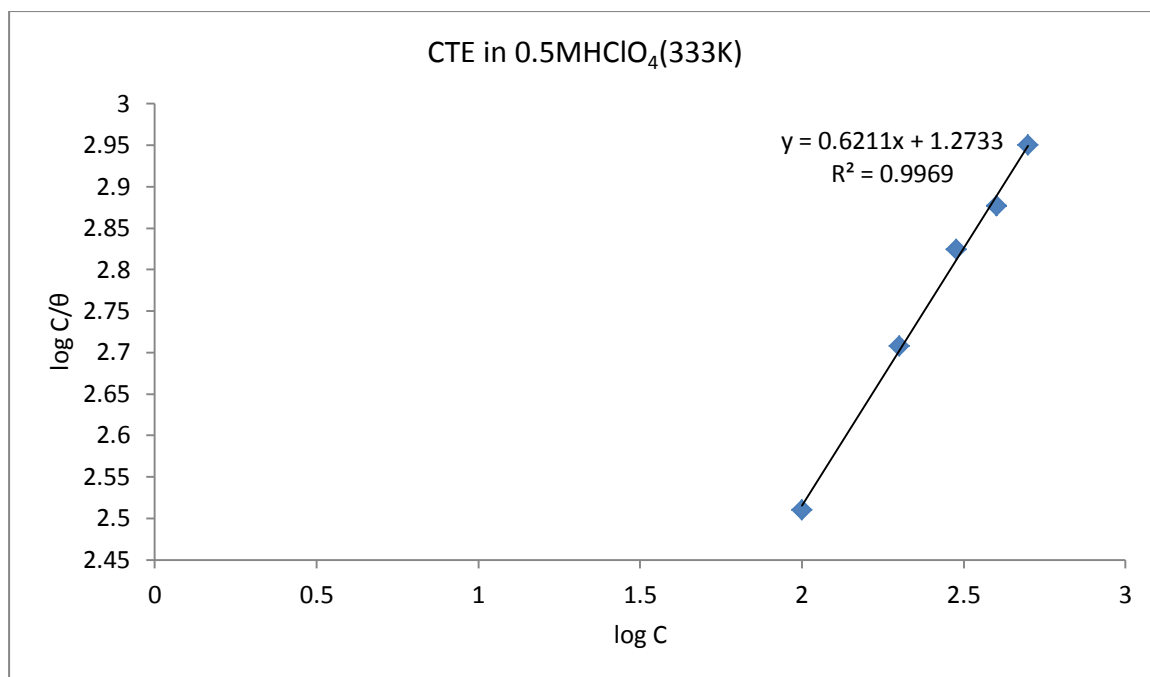


Fig. 3.31 Langmuir isotherm for the adsorption of CTE inhibitor on the surface of mild steel.

3.50 THERMODYNAMICS/ADSORPTION STUDY

The heat of adsorption of the inhibitors was calculated using equation 11,

$$Q_{ads} = 2.303 \left[\left(\frac{\theta_2}{1-\theta_2} \right) - \left(\frac{\theta_1}{1-\theta_1} \right) \right] \times \left(\frac{T_2 T_1}{T_2 - T_1} \right) \text{ kJmol}^{-1} \quad (11)$$

where R is the molar gas constant, θ_1 and θ_2 are the degrees of surface coverage of the inhibitor at the temperatures T_1 (303 K) and T_2 (333 K). Calculated values of Q_{ads} recorded in Table 3.13, are negative indicating that the adsorption of the studied amino acids on mild steel surface is exothermic [9].

Since the reactions were carried out at constant pressure, the value of Q_{ads} will be approximate of ΔH_{ads} [1]. The value of entropy, ΔS_{ads} is determined using equation 12.

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S \quad (12)$$

Activation energy of dissolution of metal increased with the inhibitor concentrations. Negative signs of enthalpies of adsorption in Table 3.13 reflect the exothermic nature of dissolution and the increasing difficulty of corrosion with the inhibitor. It is also evident from the Table 3.13 that the entropy of activation increases with the inhibitor concentration. This implies that in the rate determining, a decrease in disordering takes place on going from reactants to the activated complex and the activated molecules were in higher order state than that at the initial state. But as the concentration of inhibitor rises, the disordering of activated complex rises and the entropy of activation acquires positive medium as recorded in table. Since the values of thermodynamic heat of adsorption are less than zero and that of thermodynamic entropy greater than zero for acid medium recorded in Table 4.13, it can be said that the adsorption of CTE

inhibitor is spontaneous at any temperature [9].

3.60 THERMOMETRIC MEASUREMENTS

The dissolution reaction of mild steel in 0.5M HClO₄ in the absence and presence of CTE inhibitor was also studied using thermometric method. This technique has proved to be of considerable value and help in studying corrosion behavior of a number of metals and alloys in various corroding environments. The technique is

also useful in evaluating the inhibitor efficiency of a number of surface-active agents [31]. Table 3.16 shows the result for the dissolution of mild steel in 0.5M acid corrodents in the absence and presence of different concentration of CTE.

Table 3.12. Reaction number, inhibition efficiencies, surface coverage for the inhibition of mild steel in 0.5M H₂SO₄ and 0.5M HClO₄ in the presence and absence of CTE inhibitor for thermometric measurement.

Conc.(g/l) + HClO ₄	Reaction number	IE% (Inhibition efficiency)	Θ (Surface coverage)
Blank	1.00	-	-
0.1g/l	0.74	26	0.26
0.2g/l	0.37	63	0.63
0.3g/l	0.25	75	0.75
0.4g/l	0.16	84	0.84
0.5g/l	0.11	89	0.89

It is seen that the dissolution of mild steel starts directly from the immersion of the mild steel coupons in the test solution as evident in the constant temperature with time. The temperature of the system rises gradually due to the exothermic corrosion reaction to reach a maximum value T_m . The experiment revealed that the maximum temperature T_m was attained at a very short time (t) by the free acid solution and the inhibition efficiency increased with increase in inhibitors concentration as showned in Fig. 3.15.

Further inspection of the thermometric measurement revealed that on addition of the inhibitor, the maximum temperature attained decreases while the time required

reaching it increases. This is an indication that CTE inhibits the corrosion of zinc in the acidic environments, probably by adsorption on the metal surface. The extent of inhibition depends on the degree of coverage of the metal by the adsorbed molecules which in turns depend on the concentration of the CTE [3]. The RN and %I was calculated by equation 6 and 7 respectively.

Table 3.16 shows the calculated values of RN and the percentage of inhibition efficiency for the various concentration of the inhibitor investigated. It is very clear from the table that RN decreased in the presence of the CTE compared to the blank solution. Also, the percentage

reduction in RN in the presence of CTE increases with increasing concentration of the CTE, therefore the Inhibition efficiency increase with increasing CTE concentration in 0.5M H₂SO₄ and the IE% increased to about 89 % at 0.5g/L. The

3.70 METALLOGRAPHIC EXAMINATION OF MICROGRAPHS

Metallography is useful in the study of corrosion because it helps to identify the type of corrosion on the material. The surface morphology of the metal was evaluated by scanning electron microscopy (SEM) to show the micrographs of the freshly polished mild steel surface, corrosion specimens with and without CTE inhibitor in 0.5M HClO₄.

The metallographic micrographs of the mild steel coupons before and after immersion in plain acids and in presence of 0.5g/L plant extracts are shown as Figures 3.30 (a), (b), (c) respectively. Fig. 3.50.(a) shows plain metal surface before immersion. The surface shows a more uniform distribution of ferrite and pearlite structure in the grain structures with distinct grain boundary pits at a magnification of x500.

From Fig. 3.30.(b) the micrograph in 0.5M HClO₄ without inhibitor is showned, it is evident that there is a form of grain boundary attack by the acids. Corrosion attacked and distorted the grain boundaries of the mild steel in the absence of plant extract. The micrographs in Fig 3.30 (b) showed that the attach is localized and affects basically the grain boundaries. This

result trend obtained in thermometric measurement is consistent with that obtained for weight loss measurement, indicating the good corrosion inhibition potentials of *cochlospermum tinctorium* in acid corrodent.

is suggestive that the type of corrosion is a galvanic corrosion.

From Fig.3.30 (c) the micrographs in 0.5M HClO₄ in the presence of inhibitor is showned. The addition of plant extract retards the corrosion process as evidenced in Fig.3.50.(c), where the grain boundary attack has been completely hindered by the adsorbed inhibitor molecules. The micrographs Fig.3.30.(c) showed a near smoother surface with a pit morphology lower than those in the absence of plant extract, the result of pores histogram before and after immersion in plain acid and in the presence of 0.5g/L CTE inhibitor as obtained in Fig.3.31 (a), (b), (c), are confirmatory evident.

Furthermore, the histogram revealed the pores diameter of the mildsteel coupons. Fig. 3.31 (a) indicates the pores diameter of freshly polished coupon which is less than that of pores diameter of mild steel coupon in acidic media as showned in Fig. 3.31 (b). Fig. 3.30 (c) which shows the mildsteel coupons in the presence of plant extract recorded a fewer pores. In this case, the grain boundaries are preserved indicating the effectiveness of the inhibitor.

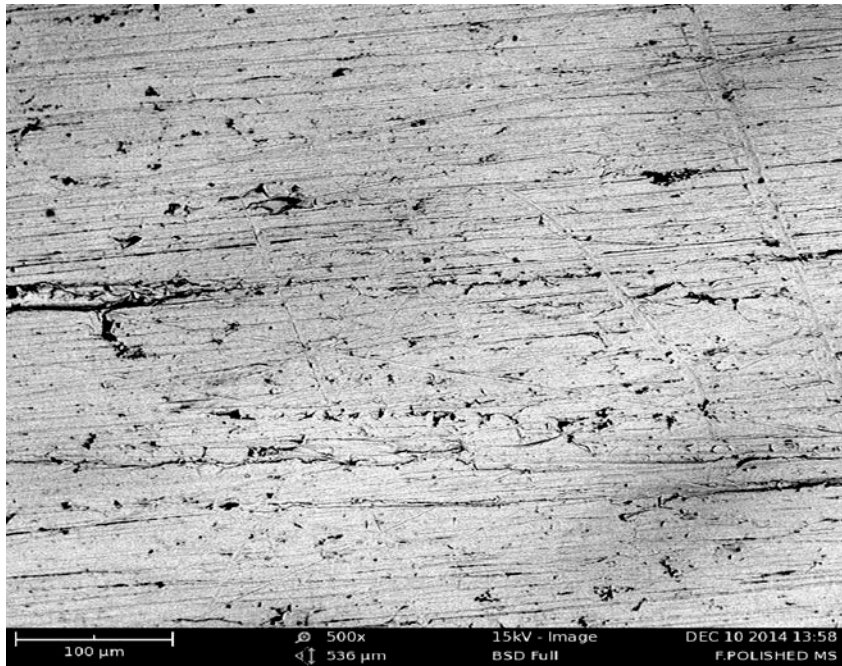


Fig.3.30.(a) Micrograph for Freshly Polished MS before immersion

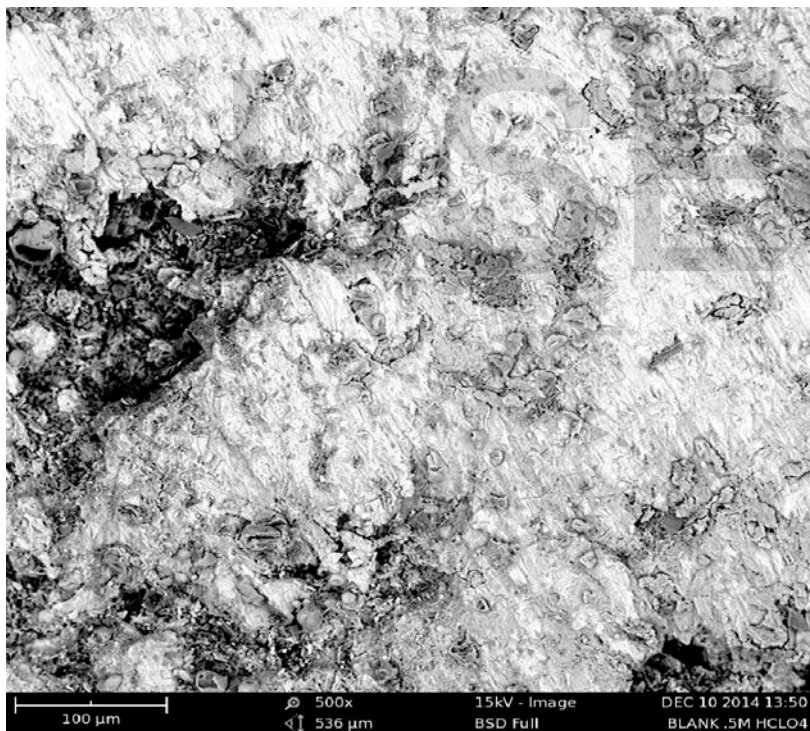


Fig.3.30.(b) Micrograph for MS in 0.5M HClO₄ without CTE

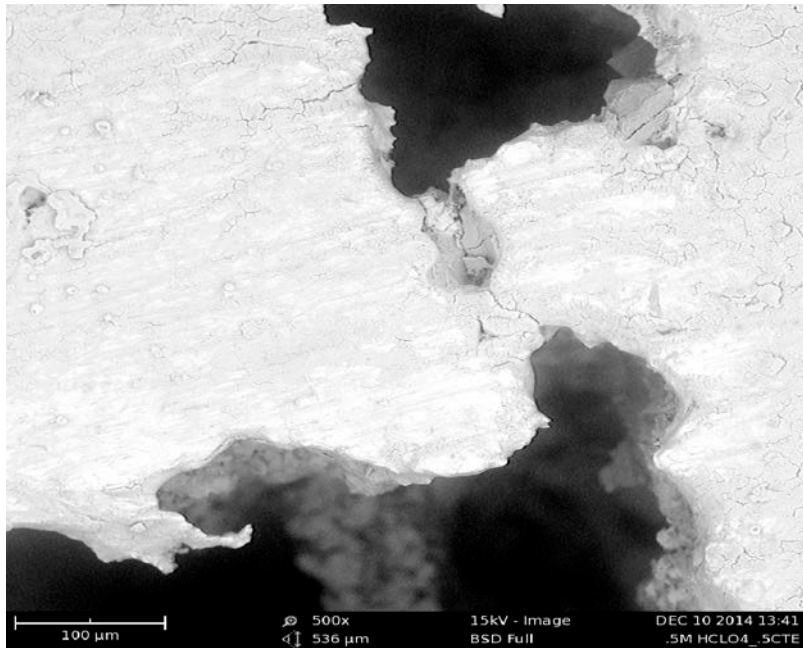


Fig.3.30.(c) Micrograph for MS in 0.5M HClO₄ with CTE



Fig 3.31 (a): Pores Histogram
for a freshly polished mild steel before immersion

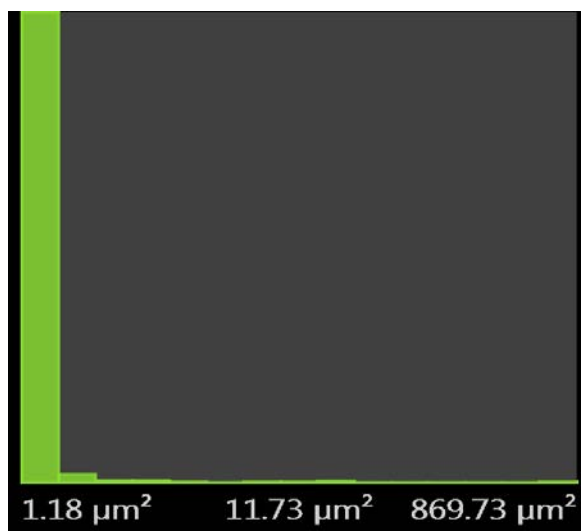


Fig 3.31 (b): Pores Histogram
for 0.5M H₂SO₄ mild steel without inhibitor

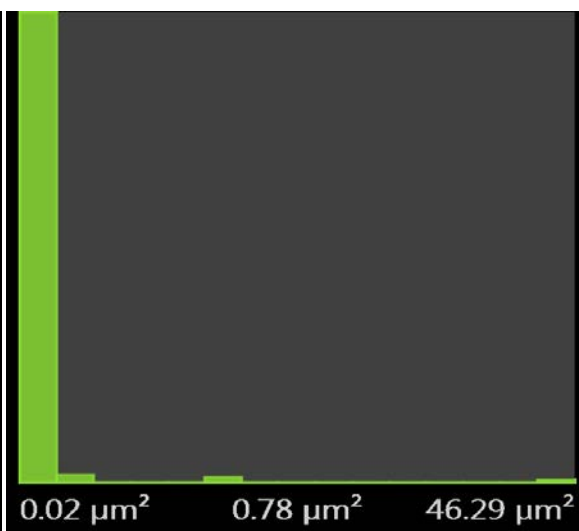


Fig 3.30 (c): Pores Histogram
for 0.5M H₂SO₄ mild steel with inhibitor

CONCLUSION

This research investigated the phenomenon of corrosion mild steel metal in acidic media. Weight loss, thermometric measurements and Scanning electron microscope were used in this study. From the result and discussions in this thesis, the following conclusion were derived;

- CTE acts as good inhibitor for mild steel in 0.5M HClO₄ media.
- Inhibition efficiency increases with increase in concentration of inhibitor.
- Compared to several inhibitors in literature, CTE exhibited higher inhibition efficiency for Mild Steel.
- The inhibition mechanism is explained by adsorption. The adsorption of CTE inhibitor in the acid corrodent obey Langmuir adsorption isotherm.
- The thermodynamic parameters calculated from the adsorption

isotherms showed that strong electrostatic interaction between the mild steel surface and CTE (physisorption) occurred in the inhibition process.

- Thermometric measurements data show that the CTE acted as good inhibitor in 0.5M HClO₄ for mild steel corrosion.
- The rates of mild steel corrosion generally are increased with increasing temperature.
- Corrosion rate decreased with CTE addition in 0.5M HClO₄ and protection efficiency reaches to 92.7007% by weight loss method and to 89% by thermometric method.
- Thermometric measurements data show that the reaction number decreased with CTE addition to

0.5M HClO_4 and protection efficiency increased with increase in CTE concentration.

- The metallographic micrographs showed that the morphology pits of

mild steel in the absence of CTE demonstrated a higher number than that in the presence of inhibitor.

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