Kinetics and Thermodynamic Study of Inhibition Potentials by Ethoxyethane Extracts of *Cochlospermum tinctorium* for the Oxoacid Corrosion of Mild Steel

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Abstract   The corrosion inhibition efficiency of a Cochlospermum tinctorium (CTE) on mild steel in 0.5M H_2SO_4 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 reach 97%. 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, this thesis includes the thermometric study for the mild steel corrosion in 0.5M H_2SO_4 acid solution in absence and presence of different CTE concentrations as inhibitor. Thermometric measurements data show that adding CTE to 0.5M H_2SO_4 and acid solution leads to decrease in the reaction number RN and the percentage reduction in RN in the presence of CTE increases with increasing CTE concentrations, therefore the Inhibition efficiency increases with increasing CTE concentration and it reaches to the highest value 90% by using 500 mgL^{-1} of CTE. Surface morphology of the mild steel specimens in the presence and absence of the inhibitor was evaluated by SEM analysis. SEM analysis revealed that the addition of inhibitor retarded the corrosion processes, where the grain boundary attacks were completely hindered by the adsorbed inhibitor molecules. The micrograph in the presence of CTE showed a near smoother surface with pit morphology lower than in the absence of plant extract.

Keywords   Corrosion, Mild Steel, Inhibition, Cochlospermum tinctorium, 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 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].

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 is presence of different chemical constituents in *cochlospermum tinctorium* from phytochemical screening. 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 [21].

2. Research Experimental

2.1. Collection and Extraction of the Plant Sample

Samples of *Cochlespermum tinctorium* were collected from Abocho, Dekina Local Government Kogi State, identified in University of Calabar Herbarium with voucher number 029 and family name *Cochlospermacae* and it was sun dried and grounded to powdered form, 300 g 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 H_2SO_4 [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].

2.2. 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 2cm^2 rectangular specimens and polished with emery papers (silicon carbide paper, 100- 1200) grades.

These polished coupons were subjected to water test in agreement with ASTM 2000 to make sure the metal surfaces were free of pits.

Each coupon were degreased by washing with and dipped in acetone and allowed to dry and was preserved in a desiccators. 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 H_2SO_4 for use in the various analysis.

2.3. Gravimetric Method of Analysis

The research studies were carried out by experiment, a weighed metal (mild steel) coupon was completely immersed in 250 ml 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 303 K. The corrosion product was removed after some hours intervals by washing each coupon (withdrawn from the text 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 experiments 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]

$$IE\% = \left(1 - \frac{W1}{W2}\right) \times 100 \qquad (3)$$

$$CR = \frac{W2 - W1}{At} \qquad (4)$$

$$\theta = 1 - \frac{W1}{W2} \qquad (5)$$

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^{-2}h^{-1}, A is the area of the mild steel cm^2, t is the total period of immersion (in hours) and θ is the degree of surface coverage of the inhibitor.

2.4. Thermometric Method

Measurement of temperature was 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]

$$RN \, (°C \, Min^{-1}) = \frac{T_m - T_i}{t} \qquad (6)$$

Where T_m and T_1 are the maximum and initial temperature. The inhibition efficiency (%IE of the inhibitor were evaluated from percentage reduction in the reaction number below

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

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 behaviour 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].

2.5. Surface Morphological Studies

Surface analysis was performed using scanning electron microscope. SEM images were obtained from MS surface after the immersion in 0.5 H_2SO_4 in the absence and presence of *cochlospermum tinctorium* for two hours at 30°C.

2.5.1. Micro Structural 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 as an inhibitor. The process series of preparatory stages carried out before the actual microscopic examination are sectioning, mounting, rough grinding, smooth grinding, polishing and etching.

Micro structural examination was done by using the metallurgical microscope. The etched specimen was placed on the microscope and the microstructure of the various coupons was obtained accordingly.

3. 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, Table 1. From the Table, it was evident that there was a 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 1 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 is 0.0235 in the 0.5M H_2SO_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.

3.2. Inhibition Efficiency and Degree of Surface Coverage

Inhibition efficiency and surface coverage of *Cochlospermum tinctorium* in 0.5M H_2SO_4 at 303 K-333 K was determined at several intervals in the presence of various concentrations of CTE inhibitor. These results are shown in Table 1.

At the inhibitor concentration of 0.5g/dm^{-3}, the maximum IE% was 97.3141% for 0.5M H_2SO_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 agree 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 97.3141% 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].

3.3. Effect of Temperature

The effect of temperature on the inhibitive efficiency of CTE inhibitor in 0.5 M H_2SO_4 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 1.; 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 2. 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. 1. 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 H_2SO_4 was investigated using the logarithm form of the Arrhenius equation, which can be shown in Equation 8 [5].

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

Where CR_1 and CR_2 are the corrosion rates of mild steel at the temperatures, T_1 (303 K) and T_2 (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. The result values ranges from 24.5977 kJmol^{-1} to 35.0749 kJmol^{-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 as reviewed in the work of Eddy et.al., 2010 [2].

Table 1. Weight loss, inhibition efficiencies, surface coverage and corrosion rate of mild steel in 0.5M H_2SO_4 in the presence and absence of extract of *Cochlospermum tinctorium* at varied temperature

| Time (h)/ Temp. (K)	Conc. (g/l)	Wt loss (g)	IE% (Inhibition efficiency)	Θ (Surface coverage)	Corrosion Rate (CR) g/cm²hr	Time (hrs)/ Temp. (K)	Conc. (g/l)	Wt loss (g)	IE% (Inhibition efficiency)	Θ (Surface coverage)	Corrosion Rate (CR) g/cm²hr
2h at 303K	Blank	0.1601			0.0181	2hrs at 333K	Blank	0.2001			0.0235
	0.1	0.0300	81.2617	0.8126	0.0035		0.1	0.0500	75.0124	0.7501	0.0058
	0.2	0.0258	83.8850	0.8388	0.0030		0.2	0.0422	78.9105	0.7891	0.0050
	0.3	0.0180	88.7570	0.8875	0.0018		0.3	0.0400	80.0099	0.8000	0.0048
	0.4	0.0110	93.1292	0.9312	0.0013		0.4	0.0322	83.9080	0.8390	0.0036
	0.5	0.0043	97.3141	0.9731	0.0005		0.5	0.0300	85.0000	0.8500	0.0031
4h at 303K	Blank	0.2101			0.0125	4hrs at 333K	Blank	0.2601			0.0158
	0.1	0.1000	52.4036	0.5240	0.0058		0.1	0.1111	57.2856	0.5728	0.0063
	0.2	0.0600	71.4421	0.7144	0.0036		0.2	0.1000	61.5532	0.6155	0.0060
	0.3	0.0456	78.2960	0.7829	0.0025		0.3	0.0811	68.8196	0.6881	0.0048
	0.4	0.0350	83.3412	0.8334	0.0018		0.4	0.0600	76.9319	0.7693	0.0031
	0.5	0.0150	92.8605	0.9286	0.0008		0.5	0.0455	82.5067	0.8250	0.0027
6h at 303K	Blank	0.2583			0.0090	6hrs at 333K	Blank	0.2983			0.0104
	0.1	0.1400	45.7994	0.4579	0.0056		0.1	0.1850	37.9818	0.3798	0.0064
	0.2	0.1100	57.4133	0.5741	0.0039		0.2	0.1600	46.3627	0.4636	0.0062
	0.3	0.0800	69.0282	0.6902	0.0032		0.3	0.1212	59.3697	0.5936	0.0047
	0.4	0.0612	76.3066	0.7630	0.0023		0.4	0.1011	66.1079	0.6610	0.0038
	0.5	0.0502	80.5652	0.8056	0.0019		0.5	0.0844	71.7063	0.7170	0.0033
8h at 303K	Blank	0.2713			0.0079	8hrs at 333K	Blank	0.3213			0.0095
	0.1	0.2000	26.2808	0.2628	0.0059		0.1	0.2700	15.9663	0.1596	0.0080
	0.2	0.1820	32.9153	0.3291	0.0048		0.2	0.2501	22.1599	0.2215	0.0065
	0.3	0.1630	39.9189	0.3991	0.0048		0.3	0.2201	31.4970	0.3149	0.0057
	0.4	0.1411	47.9911	0.4799	0.0041		0.4	0.2000	37.7528	0.3775	0.0056
	0.5	0.1300	52.0825	0.5208	0.0034		0.5	0.1800	43.9775	0.4397	0.0051
10h at 303K	Blank	0.3613			0.0082	10h at 333K	Blank	0.4213			0.0095
	0.1	0.3000	16.9665	0.1696	0.0070		0.1	0.3711	11.9154	0.1191	0.0090
	0.2	0.2802	22.4467	0.2244	0.0068		0.2	0.3433	18.5141	0.1851	0.0078
	0.3	0.2612	27.7055	0.2770	0.0058		0.3	0.3214	23.7123	0.2371	0.0073
	0.4	0.2400	33.5732	0.3357	0.0050		0.4	0.3020	28.3171	0.2831	0.0071
	0.5	0.2300	36.3409	0.3634	0.0050		0.5	0.3000	28.7918	0.2879	0.0068

Table 2. Some thermodynamic parameters of the studied CTE inhibitor for 0.5M H_2SO_4

Conc. (g/l)	E_a(Activation energy) kJmol^{-1}	Q_{ads}(Thermodynamic heat of adsorption) kJmol^{-1},	S(Entropy) Jmol^{-1}K
0.1	14.1417	-10.2906	-6.80
0.2	14.3021	-9.2216	-42.50
0.3	27.4613	-18.9971	283.30
0.4	28.5180	-26.6926	538.80
0.5	51.0839	-51.8461	1378.3

Inspection of Table 2 showed that the value of Ea determined in 0.5M H_2SO_4, 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 2 present the values Ea and thermodynamic heat of adsorption of mild steel corrosion in the 0.5M H_2SO_4.
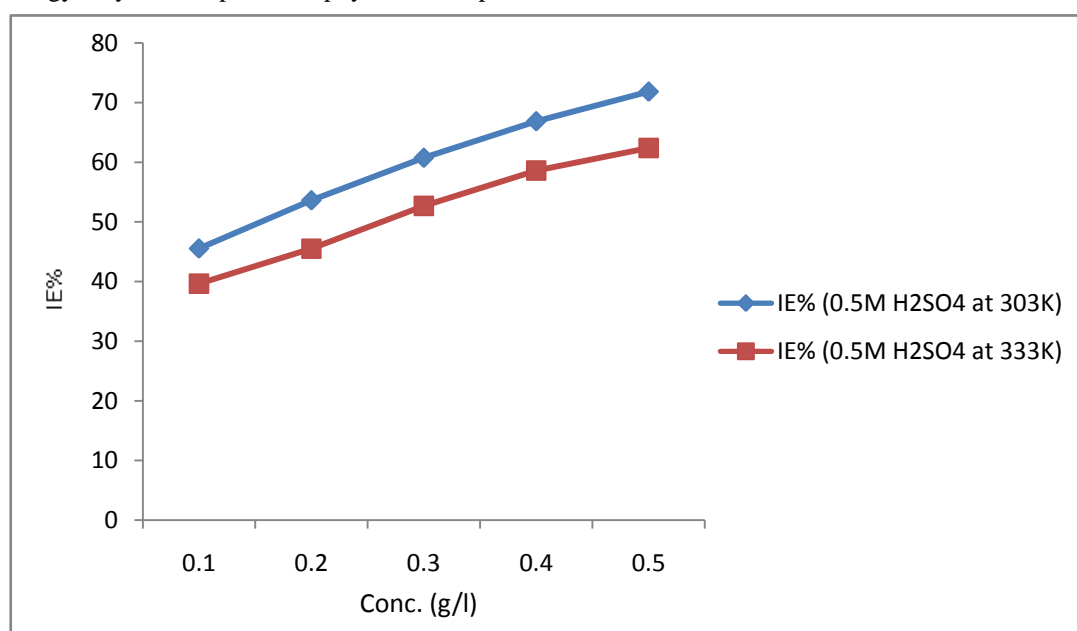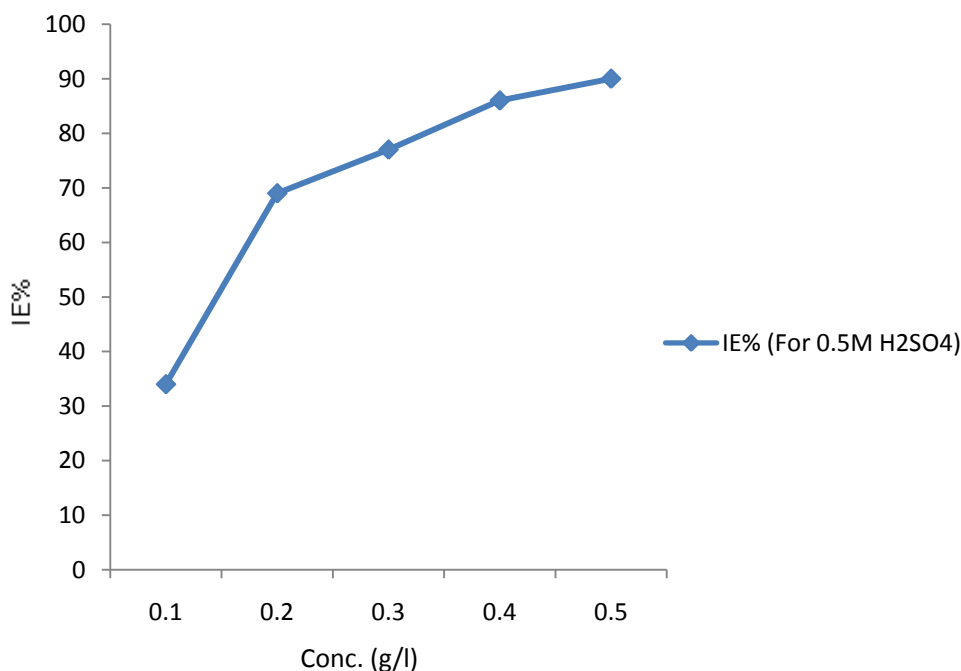

Figure 1. Variation of inhibition efficiency for mild steel with different concentration of CTE inhibitor in 0.5 M H_2SO_4 at 303 K and 333 K
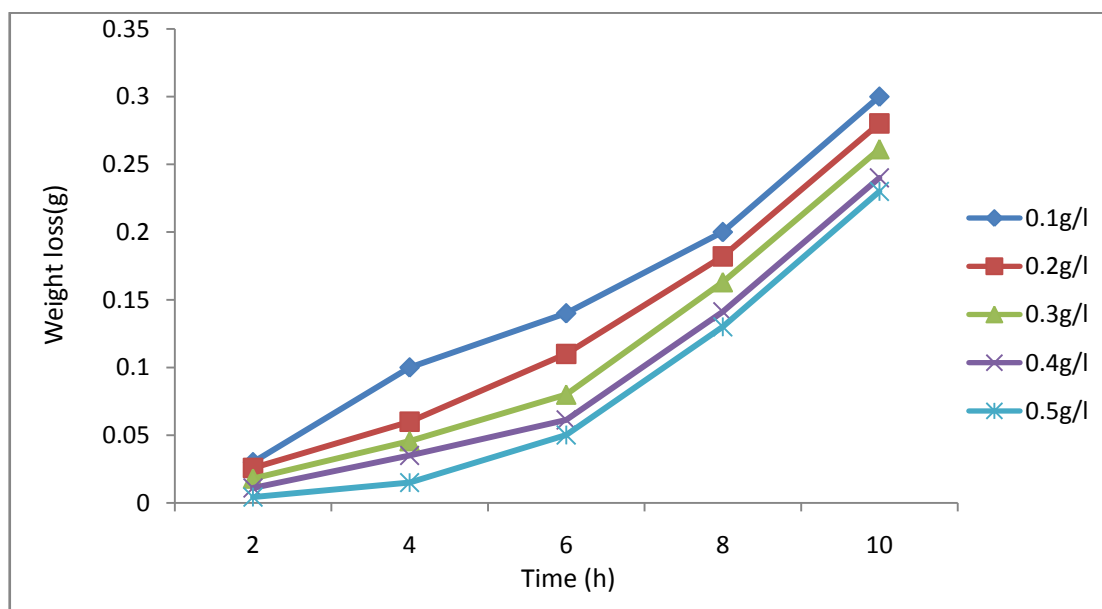
Figure 2. Variation of weight loss with time for the corrosion of mild steel in 0.5M H_2SO_4 containing the various concentrations of CTE at 303 K
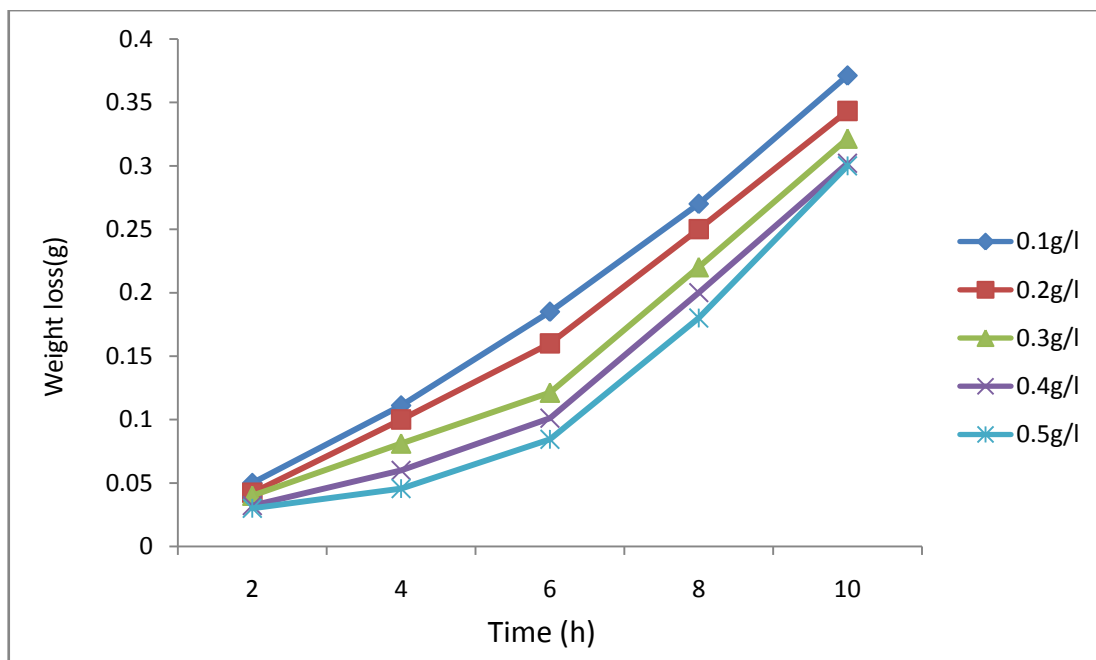
Figure 3. Variation of weight loss with time for the corrosion of mild steel in 0.5M H_2SO_4 containing the various concentrations of CTE at 333 K
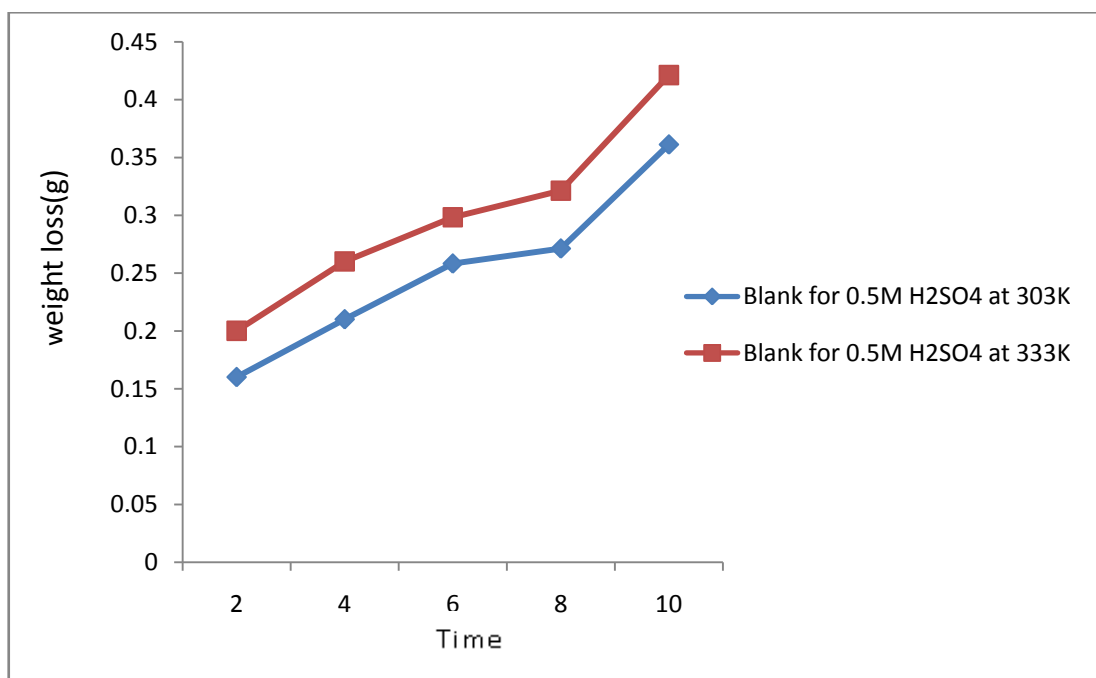
Figure 4. variation of weight loss with time for the corrosion of mild steel in 0.5M H_2SO_4 in the absence of CTE inhibitor at 303K and 333K

Figure 5. Variation of inhibition efficiency with concentration for the corrosion of mild steel in 0.5M H_2SO_4 in the presence of CTE inhibitor for thermometric measurement

3.4. 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 Awardy *et. al.,* and Frumkin) were tested and the Langmuir adsorption isotherm was found to provide the best description of the adsorption behaviour of these inhibitors. The Langmuir isotherm is given by equation 9 [29]:

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

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/θ versus log C in fig 6. 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].

$$\Delta G_{ads}^0 = -2.303RTlog(55.5K_{ads}) \qquad (10)$$

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 4. from the results obtained, the free energies ranges from ranged from -9.8994 kJmol[-1] to -11.0948 kJmol[-1] for 0.5M H_2SO_4 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 showed in the figure 6a, b, c, d and e below) are adsorbed on the active sites of the metal surface forming (Metal-Inhibitor)$_{ads}$ complex. This complex protects the metal surface from
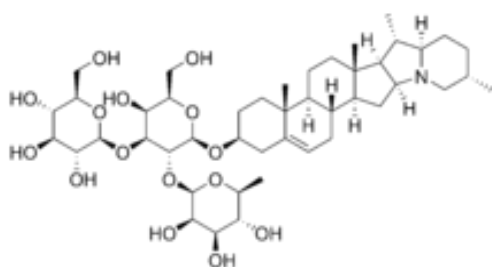
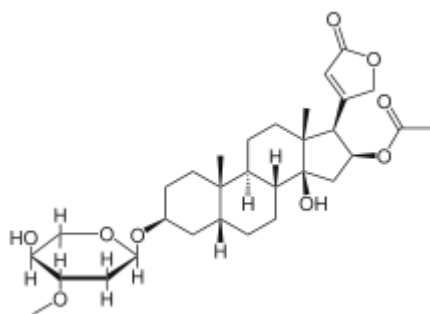further attack by the aggressive acid solution, consequently corrosion processes are arrested.
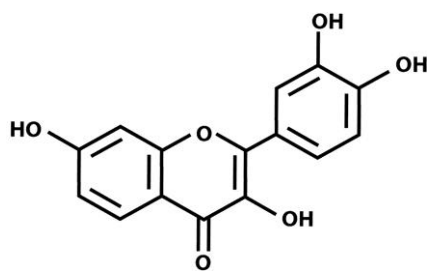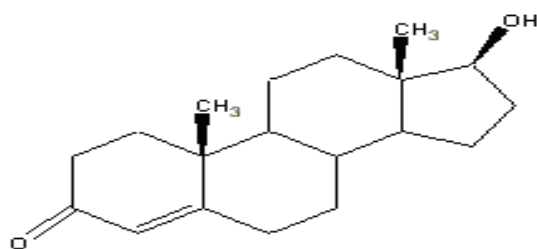

a. flavonoids
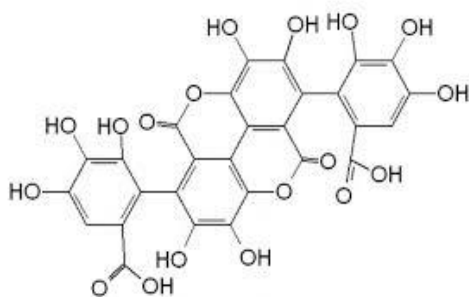
b. Tannin

c. Saponin

d. Cardiac glycoside

e. Steroid

Figure 6.

Table 3. 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_{ads}	R^2	$\Delta G^0_{ads}\ (kJmol^{-1})$
0.5M H₂SO₄ + CTE	303K	0.7157	-0.0379	0.9990	-9.8994
	333K	0.7108	-0.0041	0.9970	-11.0948

Table 4. Table for the plot of log C/θ against log C

Log C(mg/l)	0.5M H_2SO_4	
	Log C/θ (303K)	Log C/θ (333K)
2.0000	2.3416	2.4019
2.3010	2.5717	2.6430
2.4771	2.6936	2.7554
2.6020	2.7768	2.8341
2.6989	2.8426	2.9038

3.5. Thermodynamics/Adsorption Study

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

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

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, are negative indicating that the adsorption of the studied amino acids on mild steel surface is exothermic [Sharma and Sharma1999].

Since the reactions were carried out at constant pressure, the value of Q_{ads} will be approximate of H$_{ads}$ [Ulicks 1960]. The value of entropy, Sads will be determined using equation 12.

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

Activation energy of dissolution of metal increased with the inhibitor concentrations. Negative signs of enthalpies of adsorption in Table 3 reflect the exothermic nature of dissolution and the increasing difficulty of corrosion with the inhibitor. It is also evident from the table 3 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 3, it can be said that the adsorption of CTE inhibitor is spontaneous at any temperature [26].

3.6. Thermometric Measurements

The dissolution reaction of mild steel in 0.5M H₂SO₄ 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 behaviour 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 5 shows the result for the dissolution of mild steel in 0.5M acid corrodents in the absence and presence of different concentration of CTE.

CTE in 0.5M H_2SO_4(303K)

y = 0.715x + 0.916
R^2 = 0.999
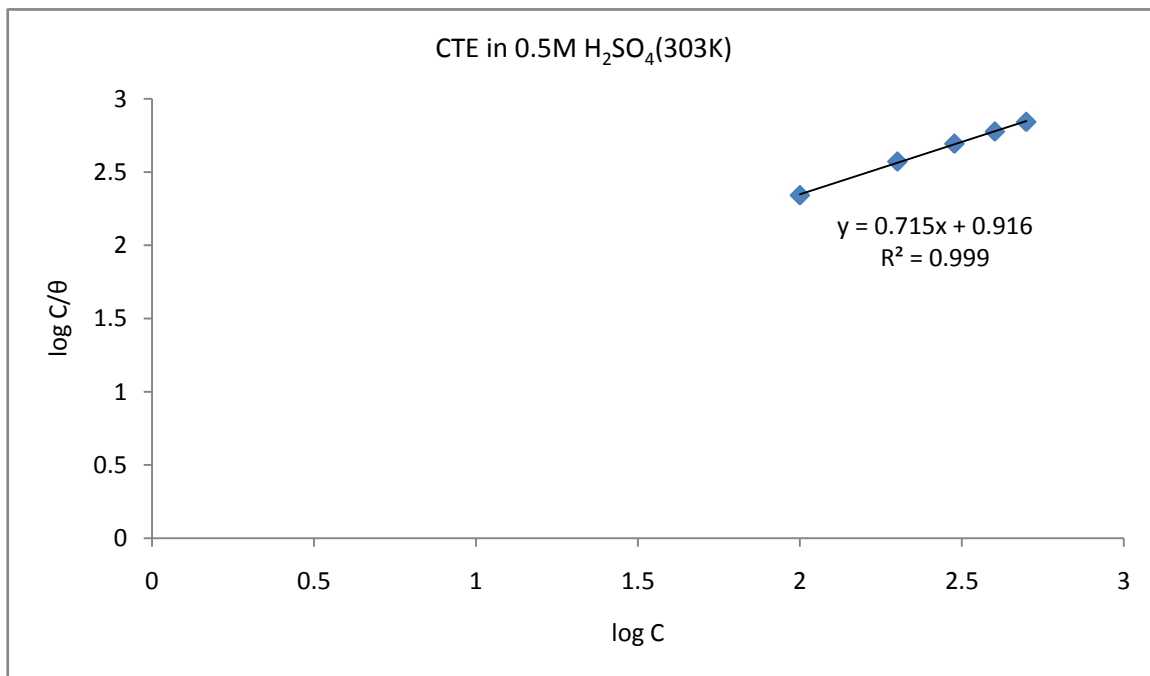
Figure 7.   Langmuir isotherm for the adsorption of CTE inhibitor on the surface of mild steel

CTE in 0.5M H_2SO_4(333K)

y = 0.710x + 0.990
R^2 = 0.997
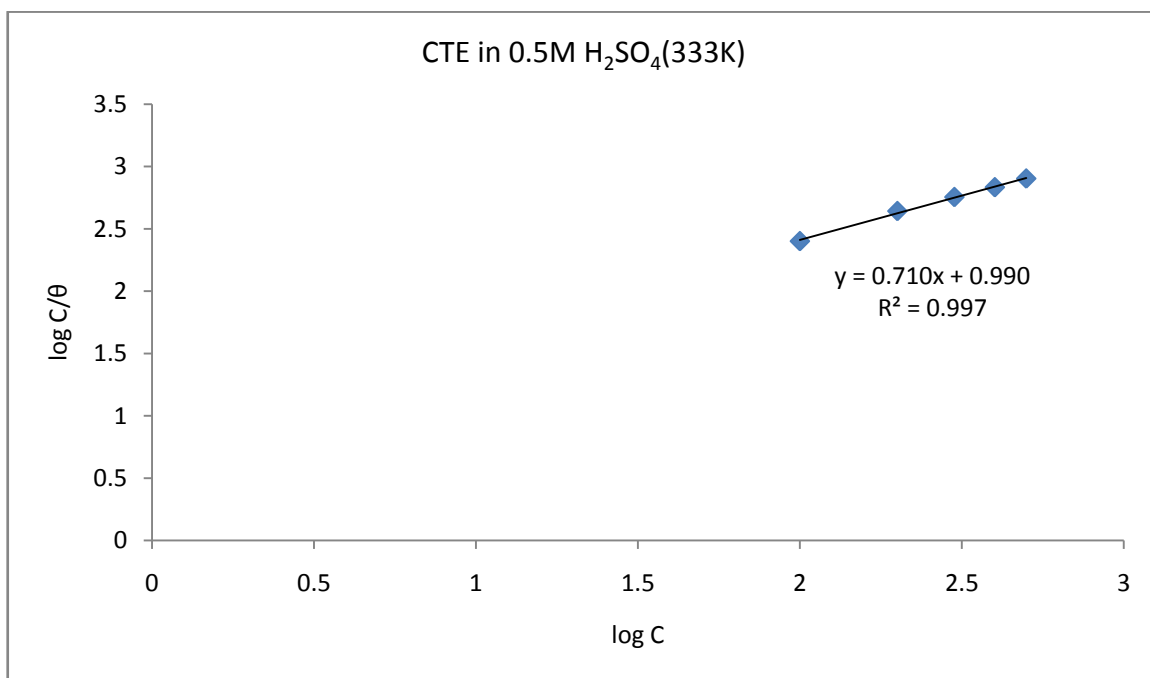
Figure 8.   Langmuir isotherm for the adsorption of CTE inhibitor on the surface of mild steel

Table 5. Reaction number, inhibition efficiencies, surface coverage for the inhibition of mild steel in 0.5M H_2SO_4 in the presence and absence of CTE inhibitor for thermometric measurement

Conc.(g/) + H_2SO_4	Reaction number	IE% (Inhibition efficiency)	Θ(Surface coverage)
Blank	1.00	-	-
0.1g/l	0.66	34.00	0.34
0.2g/l	0.31	69.00	0.69
0.3g/l	0.23	77.00	0.77
0.4g/l	0.14	86.00	0.86
0.5g/l	0.10	90.00	0.90

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 show end in Fig. 5.

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 5 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 H_2SO_4 and the IE% increased to about 90% at $0.5g/dm^{-3}$. The 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.

3.7. Metallographic Examination of Micrographs

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 H_2SO_4.

The metallographic structural micrographs before and after immersion in plain acids and in presence of 0.5g/l plant extracts are shown as Figures 9 a, b, c, respectively. Fig. 9a 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.
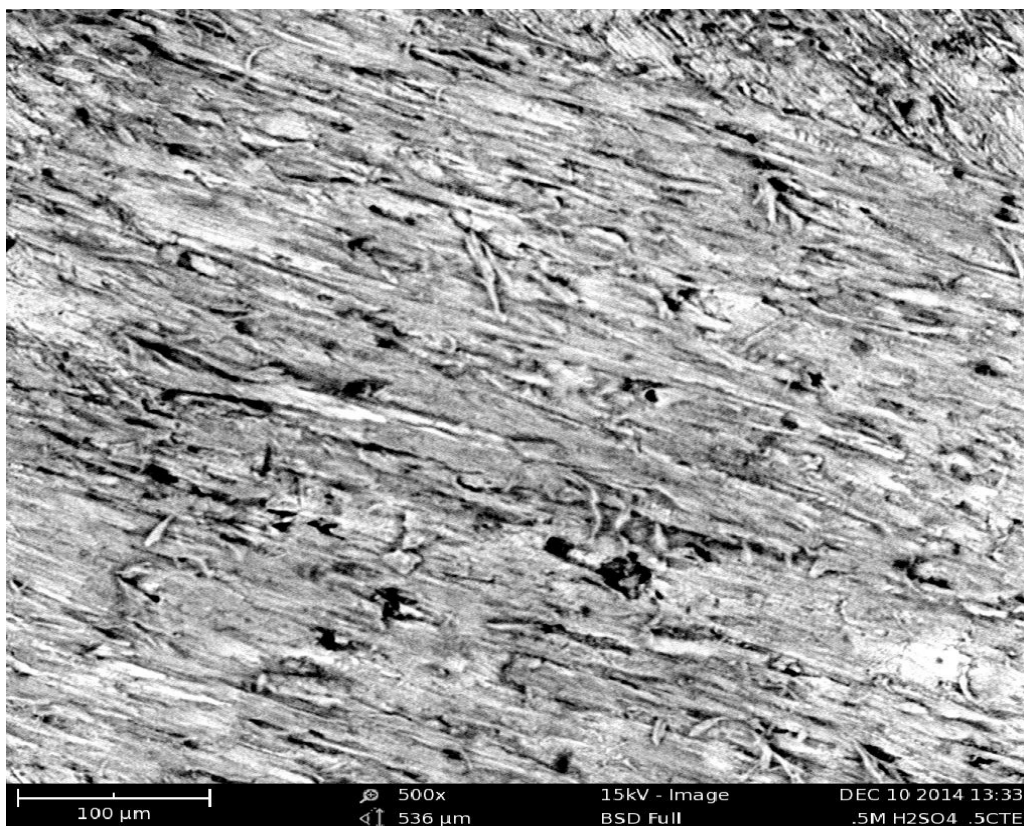
From Fig. 9b the micrograph in 0.5M H_2SO_4 without inhibitor is shown, it is evident that there is a form of grain boundary attack by the acids.
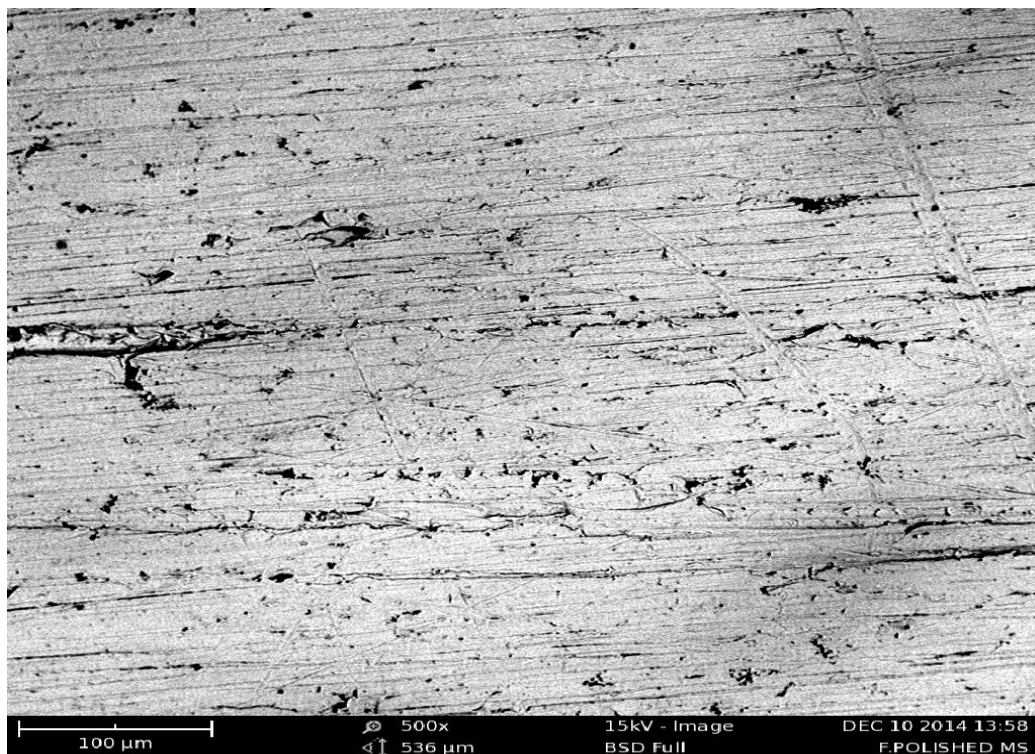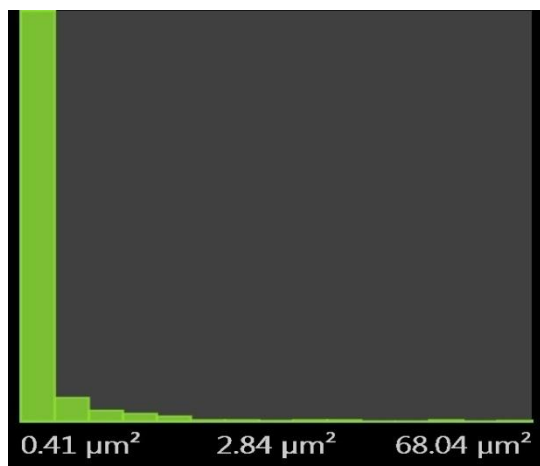

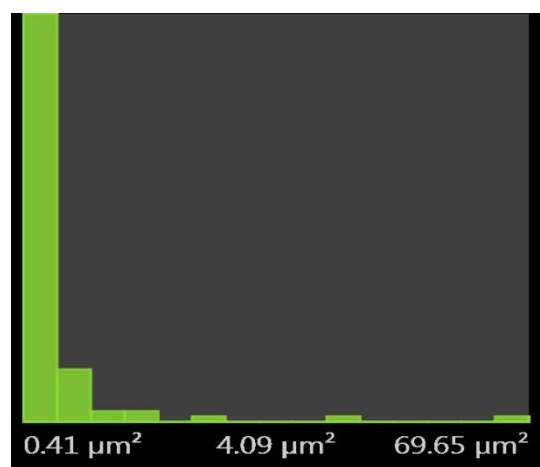**Figure 9a.** Micrograph for Freshly Polished MS before immersion
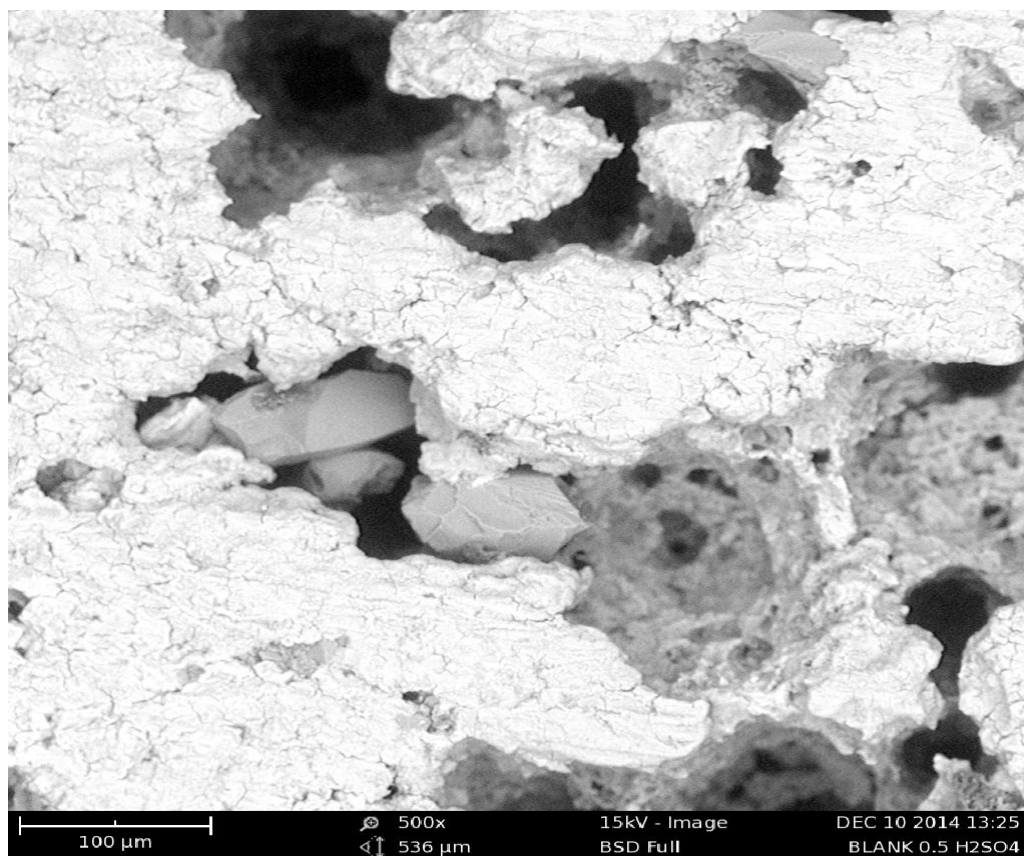
Figure 9b.   Micrograph for MS in 0.5M H_2SO_4 without CTE
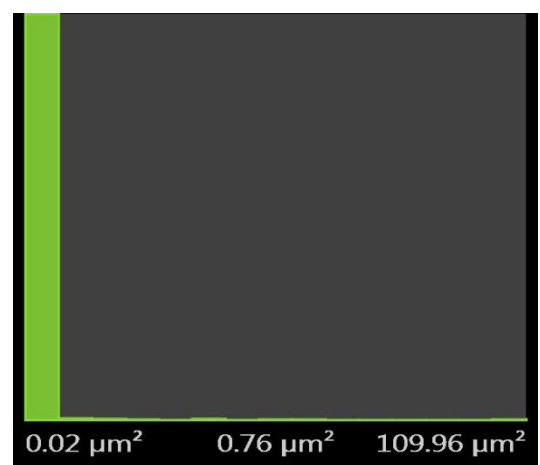

Figure 9c.   Micrograph for MS in 0.5M H_2SO_4 with CTE

Figure 10. Pores Histogram for a freshly polished mild steel before immersion

Figure 11. Pores Histogram for 0.5M H$_2$SO$_4$ mild steel without inhibitor

Figure 12. Pores Histogram for 0.5M H$_2$SO$_4$ mild steel with inhibitor

The addition of inhibitor retards the corrosion process as evidenced in Fig. 9c, where the grain boundary attack has been completely hindered by the adsorbed inhibitor molecules. The micrographs Fig. 9c 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 acids and in the presence of 0.5g/L CTE inhibitor as obtained in Fig. 10-12. are confirmatory evident.

4. Conclusions

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 conclusions were derived;

- CTE acts as inhibitor for mild steel in 0.5M H$_2$SO$_4$ 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 inhibitor in 0.5M H$_2$SO$_4$ 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 H$_2$SO$_4$ and protection efficiency reaches to 97.3141% by weight loss method and to 90% by thermometric method.
- Thermometric measurements data show that the reaction number decreased with CTE addition to 0.5M H$_2$SO$_4$ 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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