INHIBITION OF MILD STEEL CORROSION IN ACIDIC MEDIUM USING THEOBROMA CACAO POD

Izionworu, Vincent Onuegbu, Ukpaka, Chukwuemeka Peter and Oguzie, Emeka Emmanuel

Abstract— Corrosion inhibition effect of cold water extract of Theobroma cacao pods - Cocoa pod (TCP-CP) on mild steel corrosion in 1 M HCl base stock solution has been studied. The study was conducted using weight loss measurement narrowed down to the effect of immersion time, inhibitor concentration and temperature on the corrosion behavior of mild steel in 1 M HCl in the absence and presence of TCP-CP. The study also investigated the thermodynamic properties of the inhibitor in the corrodent and revealed that the adsorption of the cold extracts of TCP-CP on mild steel surface was concentration dependent and obeyed Langmuir adsorption isotherm. The equilibrium constant of adsorption process (K_{ads}) for TCP-CP inhibitor evaluated mathematically is 0.00266, 0.0271, 0.1795, 0.0253 and 0.0147 (mg/L) with a free energy of adsorption (ΔG^o_{ads}) value of -0.978, -1.060, -6.173, -0.942 and 0.737 kJ/mol at 303, 313, 323, 333 and 343 K respectively. The small values of K_{ads} suggest weak absorption which is corroborated by the low negative values of the free energy of adsorption, ΔG^o_{ads}, values obtained from thermodynamic measurements. The negative value of ΔG^o_{ads} suggests that the adsorption of TCP-CP inhibiting particles on the mild steel surface was favourable from thermodynamic point of view and provided proof that TCP-CP extracted with cold water is an efficient inhibitor and the thermodynamic properties of the examined concentrations determined.

Index Terms — Mild Steel; Corrosion inhibition; Theobroma cacao pods Husks; Thermodynamic properties; Weight Loss, Aqueous Extract, Plant Extract

◆

1 INTRODUCTION

THE growth in the demand of oil and gas around the world has led to the development of new techniques to reach new reservoirs in the offshore and onshore arena [1] putting pressure on most of the facilities with the attendant cost of maintenance soaring [2], [1]. The extensive continuous utilization and the ageing of facilities have further resulted in record failures in oil and gas plants. Research shows that between 1980 and 2006, 50% of European, major hazards of loss containment events arising from technical plants failures were primarily due to ageing plants mechanism caused by corrosion, erosion, and fatigue [3], [4].

World over, the issue of corrosion control challenge has continuously been capital intensive. A recent two-year global study on the cost of corrosion published by National Association of Corrosion Engineers (NACE) in 2016, puts the global cost of corrosion at US$2.5 trillion. This figure represents the catastrophe caused by corrosion.

In Nigeria, the cost of corrosion to the oil and gas industry is quite enormous. A research conducted in 2012 by Akinyemi et al using OML 124 an onshore oil production platform at South-Eastern part of Nigeria [30] revealed that the total cost of corrosion incurred by a single producing company was above $2.5 within a period of five years spanning from 2004 to 2008. This age long problem of metals and the resulting increased cost of pipeline corrosion management in the oil and gas industries [2], [1] has been confronted with different solutions ranging from use of Inhibitors , corrosion management planning at all phases of production such that corrosion information from existing field data is being incorporated into design information for new oil and gas field [6] and [7] in a bid to develop appropriate corrosion management methodologies that will enhance the design life of the pipelines and optimize production. On the other hand, other forms of corrosion control measures have been explored amongst which is the isolation of a metal from corrosive agents. This method has proved to be the most effective way to prevent electrochemical corrosion. Metal isolation can be in the form of quarantining of the metal which is almost practically impossible. This can however be achieved through coating or use of corrosion inhibitors., [8], [9], [10], [11]. Nowadays, researchers have fo-

---

- *Author: Izionworu, Vincent Onuegbu is currently pursuing PhD degree program in Chemical Engineering in Rivers State University, Nigeria, PH- +234 8068774599. E-mail: vincent.izionworu@ust.edu.ng*
- *Co-Author 1: Ukpaka Chukwuemeka, Peter is a Professor in the department of Chemical/Petrochemical Engineering department, in Rivers State University, Nigeria. PH- +234 8055136398.*
  E-mail: chukwuemeka24@yahoo.com
- *Author 2: Oguzie, Emeka Emmanuel is a professor and Centre Leader Africa Center of Excellence in Future Energies & Electrochemical Systems, Federal University of Technology, FUTO. PH- +234 8037026581*
  E-mail: Emeka.ugozie@futo.edu.ng

cused attention identifying naturally occurring molecules that exhibit strong affinity for metal surfaces in a bid to identify or develop compounds that show good inhibition efficiency with little or no environmental risk. Among these type of inhibitors referred to as "green corrosion inhibitors" are organic compounds that act by adsorption on the metal surface, such as ascorbic acid, phytic acid etc., [12] and extracts of natural substances [13], [14], [15], [16], [17], [18].

This study is focused on examining the efficacy of extract of Theobroma cacao pods also known as Cocoa pod represented by the acronym TCP-CP as organic corrosion inhibitors. Of mild steel corrosion in acidic environment of base stock of 1 M HCl using weight loss measurement. This report also presents a study of the effect of temperature on the inhibitor efficiency. The activation and adsorption parameters of TCP-CP as an inhibitor of corrosion of mild steel corrosion HCl environment was also examined.

2 Materials and Methods

2.1 Materials

The materials used in this research for the formulation and performance evaluation of the inhibitors are: plants extract of Theobroma cacao pod also known as Cocoa pod represented by the acronym TCP-CP and Mild Steel metal. Double distilled water.

Fig. 1. Theobroma cacao pods (dried and and wet)

The Mild Steel specimen used for the corrosion study is composed of C = 0.05 wt%, Si = 0.03 wt%, Mn = 0.6 wt%, P = 0.035 wt% and the remaining Fe. The Mild Steel density is 7.86g/cm^3. Hydrochloric acid, Ethanol and Acetone of analar grade acquired from Sinopharm Chemical Reagent Co., Ltd. were used without further purification. Distilled water obtained from Food Science Laboratory Department, Rivers State University, Nkolu-Oroworukwo, Port Harcourt, Nigeria were used for all solution preparations.

2.1.1 Material Preparation

A base stock aggressive solution of I M HCl was employed as corrodent. It was prepared by diluting analytical grade HCl (33%) with distilled water. Ethanol and acetone were used in their pure state to degrease and dry the coupons before they were used. The pods were air dried in a shade to conserve their active ingredients. The pods were then ground and 40g of the ground pod were added into 2000 ml of the distilled water. The resulting solution was allowed to stand for 48 hours with intermittent shaking within the period and then filtered. The resulting filtrate was made up to 2000ml with double distilled water. The residue obtained case was dried to constant weight and weighed. The concentration of the plant extract in the filtrate was determined using (1):

$$P_{ex}=W_{p1}-(W_{p3}-W_{p2}) \qquad (1)$$

Where P_{ex} is the weight of the extract in the distilled water, W_{p1}, original weight of the plant dissolved in the distilled water, W_{p3} was the weight of the plant residue plus the weight of Whatman filter paper of 110 mm diameter and W_{p2} was weight of filter paper alone. The inhibitor stock solution was concentrated to P_{ex}/2000ml. The volume concentrations of the extract used were 16, 33, 50, 67 and 83% of the volume of corrodent. All experiments were carried out at 30±1 ^{o}C and in aerated static solutions.

For Weight Loss analysis, the sheets of metal were mechanically press-cut to form coupons, each of a dimension of 3cm x 3cm x 0.14cm. Each coupon was first scrubbed with emery papers of variable grades (#200 to #1000) and degreased by washing with ethanol. The washed sample was then dipped in acetone, removed and further dried with warm air and stored in a desiccator before use.

2.2 Weight loss Experiment

The gravimetric measurement was carried out as reported by [19], [20], [21] and [22].

Initial test was carried out to study the inhibitory properties of the crude plant extracts using five concentrations as expressed above. The study was carried out at ambient temperature of 30^{o}C (303 K). The coupons were weighed and then totally immersed in 200ml of the test solutions at ambient temperature of 30±1^{o}C. The already cleaned coupons were weighed and suspended in 500 ml capacity bottles containing the test solutions using plastic thread loosely tied through 2 mm hole drilled at one end of the coupon. The study was monitored at 24 hours' interval for a period of 120 hours (5 days). At the end of each set of test the coupons were removed from the test solution and washed first with double distilled water, then degreased in absolute ethanol, dried using acetone and reweighed using analytical balance. Three measurements were performed to establish reliability and the mean value of the measurements were taken as the weight loss. The weight loss was calculated using the expression of (2a), (2b) and (2c). All experiments were carried out in unstirred solutions in a batch-like reactor system [23].

$$\Delta W_{L(A)} = W_{i(A)} - W_{f(A)} \quad (2a)$$

$$\Delta W_{L(B)} = W_{i(B)} - W_{f(B)} \quad (2b)$$

Where:

$\Delta W_{L(A)}$ is Weight Loss of Coupon A, $\Delta W_{i(A)}$ is Initial weight of Coupon A and $\Delta W_{f(A)}$ is Final Weight of Coupon A. also $\Delta W_{L(B)}$) is Weight Loss of Coupon B, $\Delta W_{i(B)}$is Initial weight of Coupon B and $\Delta W_{f(B)}$ is Final Weight of Coupon B. Coupon C is computed as weight loss for coupons A and B.

Weight Loss (ΔW) = Average of the replications

$$\Delta W = (W_{L(A)} + W_{L(B)} + W_{L(C)})/2 \quad (2c)$$

The corrosion rate (C_r) in mm/y of the metals in the test solution were calculated using the expression:

$$C_r = 87{,}600\Delta W/\rho At \quad (3)$$

Where:- ΔW is the change in weight or weight loss (g), ρ is the density of the Mild Steel metal (g/cm^3), A is the surface area and t is the exposure time. 87,600 is the conversion constant from cm h^{-1} to mm y^{-1} (mmpy). The surface coverage (θ) and the percentage inhibition efficiency, IE% were calculated for each exposure time using equations 4 and 5 respectively:

$$\theta = (1 - (C_r^{inh}/C_r^{blk}) \quad (4)$$

$$IE\% = (1 - (C_r^{inh}/C_r^{blk}) \, x \, 100\% \quad (5)$$

3.0 Results and Discussion

3.1 Weight Loss Studies

3.1.1 Effect of Concentration

The corrosion rate (C_r) values effect of Tables 1 gives the calculated results for corrosion rate of mild steel in the absence and presence of TCP-CP as an inhibitor and the inhibition efficiency of TCP-CP in mild steel corrosion in 1 M HCL corrodent respectively. It can be observed from Table 1 that the corrosion rate reduced and increased slightly over an immersion period of five days. An initial reduction in corrosion rate is observed from 3.083 to 2.2297 mmpy after the first three days and then an increase on the fouth and fifth day to 2.953 and 2.860 for a concentration of 81.30mg/L. The same trend is observed in all other systems as the concentration of TCP-CP is increased. It is therefore safe to conclude that increase in concentration of TCP-CP resulted in significant decrease in corrosion rate

Again, the calculated result of Table 2 shows that increase in concentration leads to increase in inhibition efficiency. A look at the table shows that at a concentration of 81.30 mg/L the inhibition efficiency was 93.70% and this figure increased to 98.87% when the coupons where immersed in a corrodent with 406.65 mg/L of TCP-CP. Also observed is the fact that increase in immersion time from one to five days resulted in reduced inhibition of efficceincy of about 1.4% less than the IE% as at the first day. This suggests that the inhibiting system lost some strength over time although an effective inhibitive.

Table 1 Calculated Values of Corrosion Rate (mmpy) for Mild Steel Corrosion 1 M HCL in the Absence and Presence of Different Concentrations of TCP-CP Extract

TCP-CP System Conc (mg/L) or (vol. in mls)	Corrosion Rate (mmpy)				
	Day 1	Day 2	Day 3	Day 4	Day 5
Blank	48.945	44.358	40.731	35.520	32.680
81.30	3.083	2.621	2.297	2.953	2.860
162.65	1.829	1.754	1.475	1.893	1.766
243.98	1.468	1.401	1.194	1.433	1.398
325.30	0.944	1.018	0.888	1.075	1.112
406.65	0.5521	0.7120	0.6037	0.8294	0.8235

Table 2 Calculated Values of Inhibition Efficiency (IE%) for Mild Steel Corrosion 1 M HCL in the Absence and Presence of Different Concentrations of TCP-CP Extract

TCP-CP System Conc. (mg/L) or (vol. in mls)	Inhibition Efficiency (IE%)				
	Day 1	Day 2	Day 3	Day 4	Day 5
Blank	-	-	-	-	-
81.30	93.70	94.09	94.36	91.69	91.25
162.65	96.26	96.05	96.38	94.67	94.60
243.98	97.00	96.84	97.07	95.97	95.72
325.30	98.07	97.71	97.82	96.97	96.60
406.65	98.87	98.37	98.52	97.66	97.48

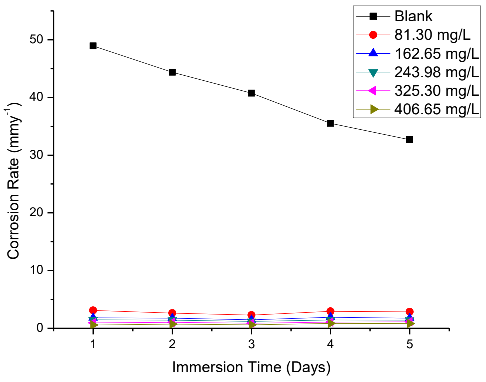

Fig. 1. Variation of Rate of Mild Steel Corrosion with Time in the Absence and Presence of Different Concentrations of TCP-CP in 1 M HCL

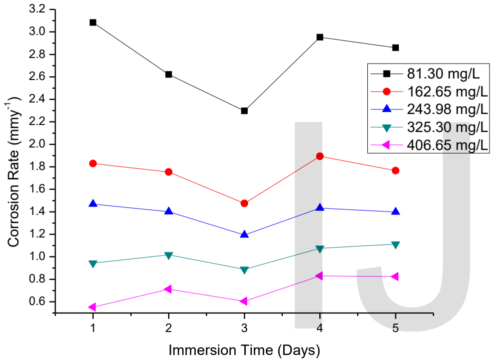

Fig. 2. Variation of Rate of Mild Steel Corrosion with Time in the Presence of Different Concentrations of TCP-CP in 1 M HCl

Figure 1 and Fig2. the effect of time and concentration of TCP-CP on the corrosion rate of mild steel in HCL environment. It is observed that in the absence of TCP-CP the corrosion rate of mild steel was very high when compared with corrosion rates of mild steel in corrodents with the different concentrations of TCP-CP. The plots also indicate that there is not much variation in the corrosion rate within the period of test. The rise in rate of corrosion after the third day of immersion can be attributed to the loss of some covered active sites likely because of particle displacement.

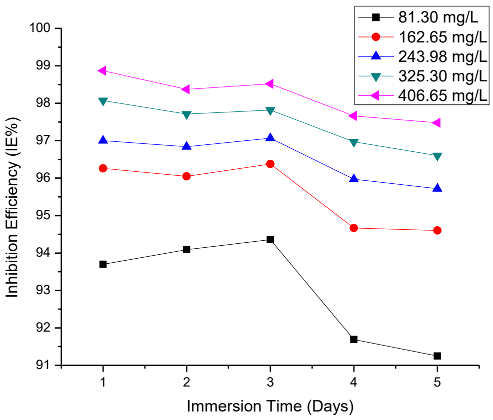

Fig. 3. Variation of Inhibition Efficiency of Different Concentrations of TCP-CP with Time for Mild Steel Corrosion in 1 M HCL

The inhibition efficiency plot against time of Fig3. shows that apart from the least concentration where there was a steep drop in inhibition efficiency between day 3 and 5, increase in concentration resulted to a slight reduction in IE% over the five-day period of immersion.

3.2 Temperature Effect on the Effectiveness of Theobroma Cacao Pods (TCP-CP) as an Inhibitor

The results of corrosion rates and inhibition efficiency of mild steel corrosion in 1 M HCL at different temperatures of 303, 313, 323, 333 and 343K and in the presence of different concentrations of TCP-CP calculated from the gravimetric test seen in Tables 3 and 4. The corrosion rate tabulated in Table 3 shows that corrosion rate increased with increase in concentration and temperature. Although a slight decrease is noticed at temperature of 323 K it can be concluded that increase in temperature of the corroding environment affects the performance of the inhibitor TCP-CP.

Table 3 Calculated Values of Corrosion Rate (mmpy) of Mild Steel Corrosion in 1M HCL Solution in the Absence and Presence of Different Concentrations of TCP-CP at 303K, 313K, 323K, 333K and 343K

TCP-CP System Conc. (mg/L)	Corrosion rate (mmpy) 303K	313K	323K	333K	343K
Blank	23.8174	43.672	295.591	520.68	735.531
81.30	7.5539	14.7981	12.8787	128.2299	307.8920
162.65	4.7470	10.4640	8.7922	115.8465	155.5146
243.98	4.2929	15.8507	19.2768	31.0616	76.5086
325.30	3.7357	8.5033	6.6664	28.3579	36.7167
406.65	2.3116	8.9573	4.5406	19.2561	19.8547

Table 4 Calculated Values of Inhibition Efficiency (IE%) of Mild Steel Corrosion in 1M HCL Solution in the Presence of Different Concentrations of TCP-CP at 303K, 313K, 323K, 333K and 343K

TCP-CP System Conc. (mg/L)	Inhibition Efficiency (IE%) 303K	313K	323K	333K	343K
Blank					
81.30	68.28	66.12	95.64	75.37	58.14
162.65	80.07	76.04	97.03	77.75	78.86
243.98	81.98	63.71	93.48	94.03	89.60
325.30	84.32	80.53	97.74	94.55	95.01
406.65	90.30	79.49	98.46	96.30	97.30

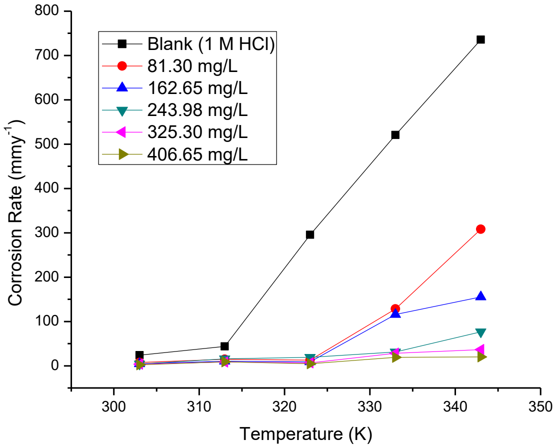

Fig. 4. Plots of Corrosion Rate Against Temperature for Mild Steel Corrosion in 1 M HCL Solution in the Absence and Presence of Different Concentrations of TCP -CP

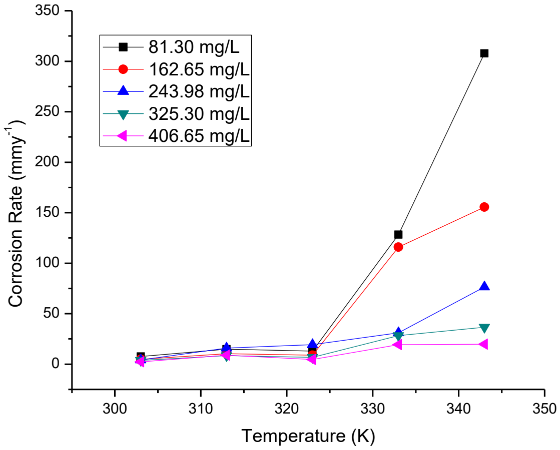

Fig. 5. Plots of Corrosion Rate Against Temperature for Mild Steel Corrosion in 1 M HCL Solution in the Presence of Different Concentrations of TCP -CP

As expected, following the calculated result of Table 3 discussed above the plots of Figure 4 show a wide gap between the plot for corrosion rate for blank corrodent compared to corrosion rate for corrodents with different concentrations of TCP-CP. While the plots of Fig.5 give a graphical representation of the corrosion rate in the presence of the inhibitor TCP-CP. The increase in corrosion rate after 323 K indicates that the inhibitor performance is affected by increase in temperature although this is minimal for corrodents with higher concentrations of TCP-CP. This effect of temperature can be attributed to H^+ diffusion to the metal surface which normally increases with increase in temperature. At higher temperature a typical hydrogen atom that blocks the cathodic area by adsorption in lower temperature is disrupted reducing its adsorption and hence opens up corrosion active sites leading to increase in rate of corrosion. This understanding is in agreement with the report of [24].

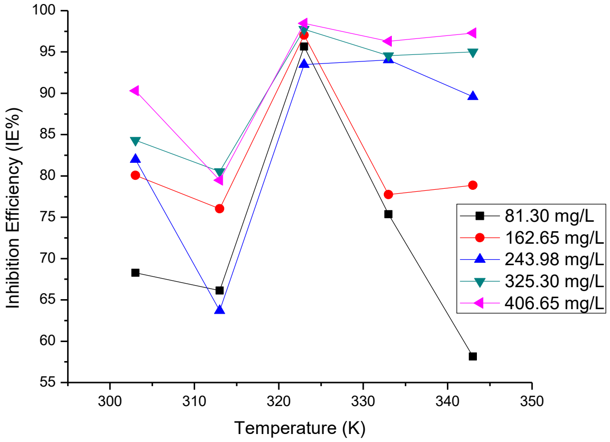

Fig. 6. Plots of Inhibition Efficiency of Different Concentration of TCP-CP Against Temperature for Mild Steel Corrosion in 1 M HCL Solution

The calculated inhibition efficiency of different concentrations of TCP-CP plotted against temperature for mild steel corrosion in 1 M HCL corrodent is presented in Table 4 above. It is observed that the inhibition efficiency at 303, 313, 323, 333 and 343 K increased with increase in concentration. The increase in IE% with increase in concentration is due to the increase in the surface area of the mild steel covered by the particles of the inhibitor TCP-CP. Also, the IE% of TCP-CP in mild steel corrosion in 1 M HCl increased as the temperature increased from 313 to 323 K but it reduced as the temperature was increased beyond 323K. This behavior graphically presented in Fig6. is as a result of a shift of the equilibrium constant towards desorption of the particles of TCP-CP on the surface of the Mild Steel [22].

3.3 Adsorption Consideration for TCP-LP Inhibitor

An understanding of the nature of the interaction between Mild Steel surface and the inhibitor - TCP-CP explored through adsorption Isotherm investigation using inhibitor concentration and surface coverage (θ) values seen in Tables 5, 6, 8 and 9calculated from gravimetric measurement
gives the calculated values of Concentration (mg/L) and Surface coverage (θ), Concentration (mg/L)/Surface Coverage (θ) for Langmuir plots, Natural logarithm of concentration and values of surface coverage (θ) and Logarithm of concentration and logarithm of values of surface coverage (θ) for TCP-CP inhibitor adsorption on Mild Steel in 1 M HCl solution at 303, 313, 323, 333 and 343 K respectively. The values of Tables 6, 8 and 9 were fitted to (6), (7) and (8) Langmuir, Temkin and Freudlich isotherms models respectively and plotted as seen in Fig7., Fig8. and Fig9. showing plots of Langmuir, Temkin and Freudlich isotherms respectively. From the values of the linear correlation coefficient (R^2) tabulated in Tables 10, it is observed that TCP-CP best fit is the Langmuir isotherm model at temperatures of 303 to 343 K with R^2 values of 0.99511, 0.94555 and 0.99791, 0.99009 and 0.99892 respectively. This indicates that single particles of the extract of TCP-CP covered active sites of the mild steel metal at temperatures above ambient temperature [21].

$$C/\theta = 1/K_{ads} + C \quad \text{(Langmuir isotherm)} \quad (6)$$

$$\mathrm{Exp}(-2a\Theta) = K_{ads}C_{inh} \quad \text{(Temkin isotherm)} \quad (7)$$

$$\Theta = K_{ads}C_{inh} \quad \text{(Freundlich)} \quad (8)$$

$$K_{ads} = 1/55 \exp\left(-\Delta G^{o}_{ads}/RT\right) \quad (9)$$

The equilibrium constant of adsorption process (K_{ads}) for TCP-CP inhibitor evaluated mathematically from intercept values resulting from the plot of Fig7. using values and presented in Table 7 is 0.00266, 0.0271, 0.1795, 0.0253 and 0.0147 (mg/L) with a free energy of adsorption (ΔG^o_{ads}) value of -0.978, -1.060, -6.173, -0.942 and 0.737 kJ/mol at 303, 313, 323, 333 and 343 K calculated from the mathematical relationship of (9). The small value of K_{ads} suggest weak absorption which is corroborated by the low negative values of the free energy of adsorption, ΔG^o_{ads}, values obtained from thermodynamic measurements. The negative value of ΔG^o_{ads} suggests that the adsorption of TCP-CP inhibiting particles on the mild steel surface was favourable from thermodynamic point of view [21] and supports a physiosorption adsorption process [25], [26].
The standard enthalpy (ΔH^O_{ads}) and entropy (ΔS^O_{ads}) changes of adsorption presented in Table 7 is calculated from the linear plot of ΔG^O_{ads} against Temperature (K) using the fundamental thermodynamic equation expressed as (10).

$$\Delta G^0_{ads} = \Delta H^0_{ads} - T\Delta S^0_{ads} \quad (10)$$

Where ΔG^0_{ads} is the free energy of adsorption, ΔH^0_{ads} is the standard enthalpy change of adsorption and ΔS^0_{ads} is the standard entropy change of adsorption while T retains its usual meaning as temperature in K. ΔG^0_{ads} is plotted against T and the intercept and slope of the resulting linear plot gave the values of ΔH^0_{ads} and ΔS^0_{ads}.

Table 7 Calculated Values of Surface Coverage(θ) for TCP-CP at 303, 313, 323, 333 and 343 K

Conc. (mg/L)	Surface Coverage (θ) 303 K	313 K	323 K	333 K	343 K
81.3	0.6828	0.6612	0.9564	0.7537	0.5814
162.65	0.8007	0.7604	0.9703	0.7775	0.7886
243.98	0.8198	0.6371	0.9348	0.9403	0.8960
325.3	0.8432	0.8053	0.9774	0.9455	0.9501
406.65	0.9029	0.7949	0.9846	0.9630	0.9730

Table 6 Calculated Values of Concentration. (mg/L)/Surface Coverage(θ) for Langmuir Plots for Extract of TCP-CP at 303, 313, 323, 333 and 343 K

Conc. (mg/L)	Conc. (mg/L)/Surface Coverage(θ) 303 K	313 K	323 K	333 K	343 K
81.3	119.0612	122.967	85.00352	107.8641	139.8344
162.65	203.1365	213.9014	167.6362	209.1937	206.26
243.98	297.6248	382.9835	261.0009	259.4582	272.3046
325.3	385.8133	403.9524	332.8058	344.0373	342.3919
406.65	450.3592	511.5764	412.994	422.2667	417.9316

Table 7 Adsorption Parameters for TCP-CP Adsorption on Mild Steel in 1 M HCL Solution at a Temperature Range of 303 - 343 K.

Temp. (K)	Intercept	Slope	R^2	K_{ads}	ΔG^o_{ads} (kJ/mol)	ΔH^o_{ads} (kJ/mol)	ΔS^o_{ads} (J/mol/K)
303	37.6479	1.0393	0.9951	0.0266	-0.978		
313	36.9285	1.1893	0.9456	0.0271	-1.060		
323	5.5721	1.0096	0.9979	0.1795	-6.173	-13.140	35.47
333	39.496	0.9389	0.9901	0.0253	-0.942		
343	68.0712	0.8512	0.9989	0.0147	0.737		

Table 8 Calculated Values for Temkin Plots for Extract of TCP-CP Adsorption on Mild Steel in 1 M HCL solution at 303, 313, 323, 333 and 343 K

Conc. (mg/L)	In Conc	Surface Coverage (θ) 303 K	313 K	323 K	333 K	343 K
81.3	4.3981	0.6828	0.6612	0.9564	0.7537	0.5814
162.65	5.0916	0.8007	0.7604	0.9703	0.7775	0.7886
243.98	5.4971	0.8198	0.6371	0.9348	0.9403	0.8960
325.3	5.7847	0.8432	0.8053	0.9774	0.9455	0.9501
406.65	6.0080	0.9029	0.7949	0.9846	0.9630	0.9730

Table 9 Calculated Values for Freundlich Plots for Extract of TCP-CP Adsorption on Mild Steel in 1 M HCL Solution at 303, 313, 323, 333 and 343 K

Conc. (mg/L)	Log Conc	Surface Coverage (θ) 303 K	313 K	323 K	333 K	343 K
81.3	1.9101	0.6828	0.6612	0.9564	0.7537	0.5814
162.65	2.2113	0.8007	0.7604	0.9703	0.7775	0.7886
243.98	2.3874	0.8198	0.6371	0.9348	0.9403	0.8960
325.3	2.5123	0.8432	0.8053	0.9774	0.9455	0.9501
406.65	2.6092	0.9029	0.7949	0.9846	0.9630	0.9730

Table 10 Calculated values of Correlation Corfficient (R^2) for Langmuir, Temkin and Freundlich isotherm for TCP-CP adsorption on Mild Steel in 1 M HCL solution

Temperature	Langmuir R^2	Temkin R^2	Freundlich R^2
302	0.99511	0.93723	0.93456
313	0.94555	0.1532	0.13122
323	0.99791	-0.10597	-0.11292
333	0.99009	0.80844	0.81163
343	0.99892	0.97535	0.95

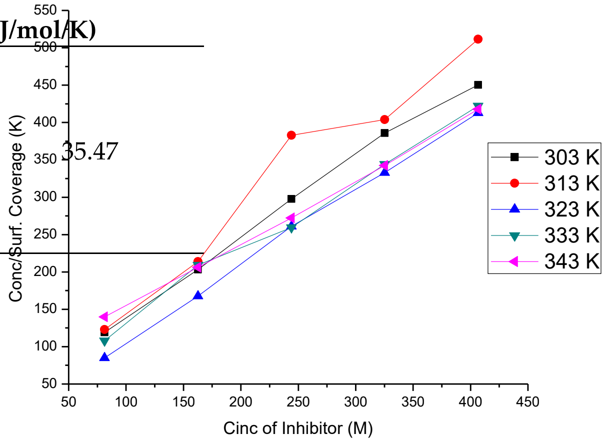

Fig. 7. Langmuir Adsorption Isotherm of TCP-CP Extract on Mild Steel Surface in 1 M HCL Solution at Different Temperature.

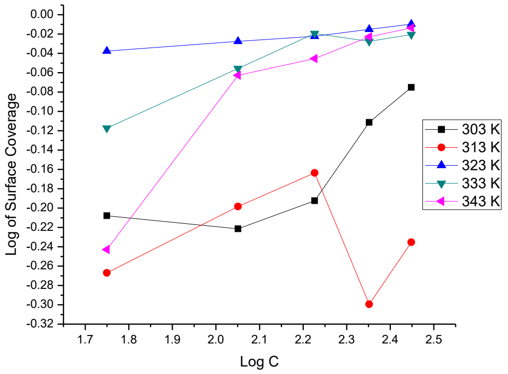

Fig. 8. Temkin Adsorption Isotherm of TCP-CP Extract on Mild Steel Surface in 1 M HCL Solution at Different Temperature.

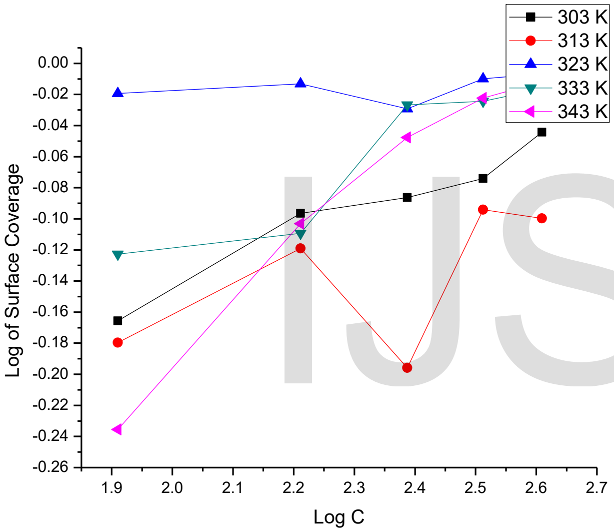

Fig. 9. Freudlich Adsorption Isotherm of TCP-CP Extract on Mild Steel Surface in 1 M HCL Solution at Different Temperature.

3.4 Thermodynamic and Activation Parameters of TCP-CP

The result of thermodynamic activation parameters namely – standard enthalpy of activation (ΔH^O) and standard entropy of activation (ΔS^O) of Mild Steel corrosion process in 1 M HCl solution were calculated using weight loss measurement in the absence and presence of TCP-CP as the base calculation. While the result of apparent activation energy (E_a) was calculated from Arrhenius equation expressed as (11), and the resulting Arrhenius plots of Fig10. at a temperature range of 303 – 343 K in 1 M HCl base stock corrodent solution in the absence and presence of TCP-CP at concentration of 81.3, 162.65, 243.98, 325.3 and 406.65 mg/L are reported in Table 11, the results of the thermodynamic activation parameters – **ΔH^O** and **ΔS^O** computed from the transition equation (13) and the transition state plots of Fig15. for Mild Steel in 1 M HCl Solution in the absence and presence of TCP-CP are presented in Table 12.

$$C_r = A\exp(-E_a/RT) \quad (11)$$

Where Cr is the corrosion rate of the blank or inhibited corrodent solution, A is the Arrhenius pre-exponential factor, R is the universal gas constant (8.314 JK^{-1} mol^{-1}) and T is the absolute temperature (K). From the Arrhenius plot of log C_r against 1/T for the corrosion of mild steel in 1 M HCl corrodent solution in the absence and presence of the inhibitor at concentrations ranging from 81.3 mg/L to 406.65 mg/L, the slope was determined while the activation energy was calculated using (12).

$$E_a = -\ (\text{slope}) \times 2.303R \quad (12)$$

To calculate the standard enthalpy of activation (ΔH^O) and the standard enthropy of activation (ΔS^O), the transition state equation was used (13):

$$C = RT/Nh\exp(\Delta S^o/R)\exp(-(\Delta H^o/RT)) \quad (13)$$

Where h is Plank's constant (6.62607004 x 10^{-34} m^2kgs^{-1}), N is the Avogadro number (6.022141 x 10^{23}) and all other terms retain their initial meaning.
The values of ΔH_a and ΔS_a were calculated respectively from the slope and intercept of the plot of $\log Cr/T$ against $1/T$ such that:

$$Intercept = \log(R/Nh) + \Delta S^o/(2.303R) \quad (14)$$

$$\text{Slope} = \Delta H^o/2.303R \quad (15)$$

The activation energy for the inhibited solution is lower than that for the blank, uninhibited solution indicating that a predominant chemisorption adsorption especially at higher temperature took place.
As expected from the concept of transition - state theory, the values of ΔH^O for concentrations of TCP-CP and the corresponding values of E_a are close to each other. The positive value of ΔS^o for the inhibitor indicates that the activated complex in the rate determining step represents a dissociation step, this means that there is increase in disorder during the course of transition from transition state to activated complex state, [22], [27] this is understandable as the inhibitor was extracted using water and used in that state.

Table 11 Activation Parameters for Mild Steel in 1 M HCl Solution in the Absence and Presence of TCP-CP Inhibitor Obtained from Weight Loss Measurement

Inhibitor	Conc. (mg/L)	Log Cr/T ($mmy^{-1}K^{-1}$)					ΔS^o_{ads} (J/mol/K)	ΔH^o_{ads} (KJ/mol)
Blank	-	-1.3407	-1.0207	0.0898	0.1235	0.1917	423.42	78.45
TCP-CP	81.3	-1.6174	-1.3253	-1.3993	-0.4012	-0.0340	413.16	79.24
	162.65	-1.8191	-1.4758	-1.5651	-0.4453	-0.3307	405.61	77.86
	243.98	-1.8628	-1.2955	-1.2242	-1.0170	-0.6387	327.05	53.04
	325.3	-1.9232	-1.5660	-1.6853	-1.0565	-0.9576	304.05	47.04
	406.65	-2.1316	-1.5434	-1.8521	-1.2246	-1.2246	282.98	41.22

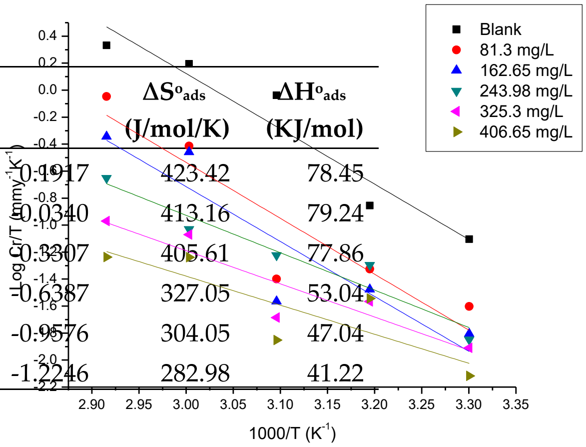

Fig. 11. Transition State Plot of Log Cr/T Versus 1000/T for Mild Steel in 1 M HCl Solution in the Absence and Presence of TCP-CP

Table 12 Calculated Values of Activation Energy for Mild Steel in 1 M HCl Solution in the Absence and Presence of TCP-CP Inhibitor Obtained from Weight Loss Measurement.

Inhibitor	Conc (mg/L)	Log Cr					Slope	Activation Energy (Ea) ($kJmol^{-1}$)
1 M HCl	Blank	1.3769	1.6402	2.4707	2.7166	2.8666	-4.2372	81.13
TCP-CP	81.3	0.8782	1.1702	1.1099	2.1080	2.4884	-4.2786	81.92
	162.65	0.6764	1.0197	0.9441	2.0639	2.1918	-4.2065	80.54
	243.98	0.6328	1.2000	1.2850	1.4922	1.8837	-2.9098	55.71
	325.3	0.5724	0.9296	0.8239	1.4527	1.5649	-2.5967	49.72
	406.65	0.3639	0.9522	0.6571	1.2846	1.2979	-2.2927	43.90

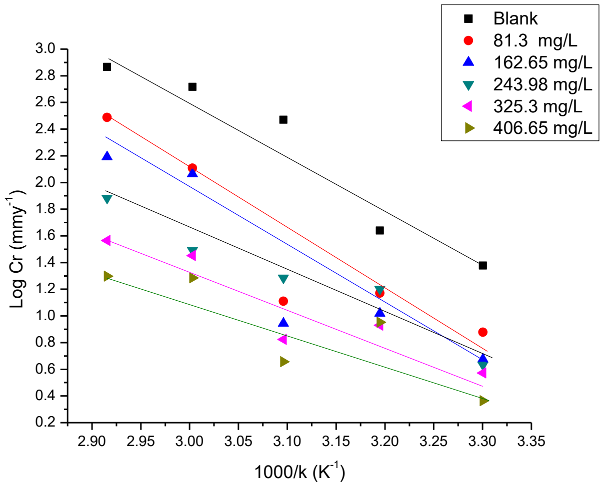

Fig. 10. Arrhenius Plots of log Cr Verses 1000/T for Mild Steel Corrosion in 1 M HCl Solution in the Absence and Presence of TCP-CP

4 Conclusion

From the forgoing, decrease in corrosion rate and high inhibition efficiency in all cases of experimental use of the crude extract of TCP-CP indicates that it is a good inhibitor of corrosion of Mild Steel in HCl environment. The results also show that the corrosion rate of mild steel in 1 M HCL decreased with increasing concentration of TCP-CP crude extract. This result when compared with the uninhibited solution here referred to as blank solution indicates that the inhibiting action of the tested crude extract is concentration dependent.

As a function of time of immersion, the inhibition efficiency did not show significant difference implying that under the experimental condition, particles of cold extracts of the crude extracts formed a stable film on the metal surface after the first day of immersion. It is likely that the noticeable drop in the IE% is due partly to degradation of the particles of the crude extracts. The inhibition mechanism has been suggested [28] indicating that molecules of the inhibitor get adsorbed on the surface of the metal via the heteroatoms (P, O, N) and functional groups inherent in the inhibitor TCP-CP. The study indicates that the waste [29] resulting from corrosion of metals can be reduced.

REFERENCE

[1] C.I. Ossai, "Advances in Asset Management Techniques: An Overview of Corrosion Mechanisms and Mitigation Strategies for Oil and Gas Pipelines," *International Scholarly Research Network ISRN Corrosion*, vol. 2012, Article ID 570143, 10 pages, 2012.

[2] R., Nicholson, J., Feblowitz, C. Madden, & R., Bigliani, "The Role of Predictive Analytics in Asset Optimization for the Oil and Gas Industry-White Paper,", http://www.tessella com/wpcontent/uploads/2008/02/IDCWP31SA4Web.pdf,(2010).

[3] P., Horrocks, D., Mansfield, K., Parker, J., Thomson, Atkinson, T. and J. Worsley, "Managing Ageing Plant," http://www.hse .gov.uk/research/rrpdf/rr823-summary-guide.pdf.

[4] http://www.hse .gov.uk/research/rrpdf/rr823-summary-guide.pdf

[5] National Association of Corrosion Engineers (NACE), "International Measures of Prevention, Application and Economics of Corrosion Technology," (IMPACT) International, 2016.

[6] B., Khajota, D. Sormaz, and S. Nesic, "Case-based reasoning model of CO_2 corrosion based on field data," *CORROSION*, paper no. 07553. (2007).

[7] K. U. Raju, "Successful scale mitigation strategies in Saudi Arabian oil fields," in International Symposium on Oilfield Chemistry, The Woodlands, Tex, USA, paper no.121679, 2009.

[8] I., Ali, and N., Foaud, Inhibition of aluminum corrosion in hydrochloric acid solution using black mulberry extract. *Journal of Material and Environmental Science, 3* (5), 917-924, 2012.

[9] H., Ashassi-Sorkhabi, B., Aligholipour, D., Seifzadeh, and B., Shaabani, The Effect of Some Schiff Bases on the Corrosion of Aluminium in HCl Solution. *Applied Surface Science*, vol. *252*, pp. 4039-4047, 2006.

[10] M., Bouklah, A., El Idrissi, B., Hammouti, and A., Ouassini, "Corrosion inhibition of steel in sulphuric acid by pyrrolidine derivatives," *Applied Surface Science*, vol 252, no. 6, pp. 2178–2185, 2006.

[11] E. E., Oguzie, "Inhibition of acid corrosion of mild steel by Telfaria occidentalis extract," *Pigment & Resin Technology*, vol. 34, pp. 321–326, 2005.

[12] M. A., Amin, R. S., Bayoumy, S. S. A., El-Rehim, and E. E. F., El-Sherbini, The inhibition of low carbon steel corrosion in hydrochloric acid solutions by succinic acid: Part I. Weight loss, polarization, EIS, PZC, EDX and SEM studies. *Electrochimica Acta*,52, pp. 3588, 2007.

[13] B. A., Abd-El-Nabey, A. M., Abdel-Gaber, A. M., El-Zayady, M., Saadawy, and I. M., Sidahmed, "Inhibitive action of some plant extracts on the corrosion of steel in acidic media," *Corrosion Science*, vol. *48*, pp. 2765–2779, 2006.

[14] A., Bouyanzer, B., Hammouti, and L. Majidi, "Pennyroyal Oil from *Mentha pulegium* as Corrosion Inhibitor for Steel in 1 M HCl," *Material Letters*, vol. ***60***, pp. 2840–2843, 2006.

[15] L. R., Chauhan, and G., Gunasekaran, "Eco friendly inhibitor for corrosion inhibition of mild steel in phosphoric acid medium," *Corrosion Science*, vol *49*, no. *25*, pp. 4387–4395, 2004.

[16] M.A., Chidiebere, C.E., Ogukwe, K.L., Oguzie, C.N., Eneh, E.E., Oguzie, "Corrosion inhibition and adsorption behavior of Punica granatum extract on mild steel in acidic environments: Experimental and theoretical studies," Industrial & Engineering Chemistry Research vol. 51, pp. 668-677, 2012.

[17] P. B., Raja, M. G., Sethuraman, "Inhibitive effect of black pepper extract on the sulphuric acid corrosion of mild steel," *Materials letters*, vol. *62*, pp. 2977–2979, 2008a.

[18] P. B., Raja, and M. G., Sethuraman, "Natural products as corrosion inhibitor for metals in corrosive media—a review," Materials Letters, vol. 62, no. 1, pp. 113–116, 2008-b.

[19] E. E., Oguzie, C. K., Enenebeaku, C. O., Akalezi, S. C., Okoro, A. A., Ayuk, and E. N., Ejike, "Adsorption and Corrosion inhibiting effect of Dacryodis edulis extract on low carbon steel corrosion in acidic media," *Journal of Colloid Interface Science*, vol. *349*, pp. 283. 2010.

[20] P. C., Okafor, M. E., Ikpi, I. E., Uwah, E. E., Ebenso, U. J., Ekpe, and S. A., Umoren, Inhibitory action of Phyllanthus amarus extracts on the corrosion of mild steel in acidic media, *Corrosion Science*, vol. 50, no. 8, pp. 2310–2317, 2008.

[21] I.O, Arukalam, O., Ogbobe, I.C., Madufor, and E., Oguzie, "Understanding the Influence of Molecular Weight on the Corrosion Inhibition Performance of Two Cellulosic Polymers," *American Chemical Science Journal*, 10(4); 1-14. (2016).

[22] M., Yadav, R.R., Sinha, T.K., Sarkar, I., Bahadur, and E. E., Ebenso, "Application of new isonicotinamides as a corrosion inhibitor on mild steel in acidic medium: Electrochenical, SEM, EDX, AFM and DFT investigations," *Journal of Molecular Liquids* vol. *212*, pp 686-698, 2015.

[23] A.K., Singh, E.E., Ebenso, and M.A., Quraishi, "Inhibition Effect of Cefradine on Corrosion of Mild Steel in HCl Solution," International Jpurnal of Electrochemical Science. Vol. 9, pp. 352-364. Res Chem Intermed 39: 3033. (2013). https://doi.org/10.1007/s11164-012-0815-3

[24] B., Amrita, P., Sagar, and G., Udayabhanu, "Experimental and theoretical studies of Xanthan gum and its graft co-polymer as corrosion inhibitor for mild steel in 15% HCl," *Applied Surface Science* Vol. 353, Pp 173-183. (2015).

[25] A.A., Farag, A.S., Ismail, and M.A., Migahed, "Inhibition of Carbon Steel Corrosion in acidic solution using some newly polyster derivative," Journal of Molecular Liquids vol. 211, pp. 915-923, 2015.

[26] S., Manimegalai and P., Manjula, "Thermodynamic and Adsorption Studies for Corrosion Inhibition of Mild Steel in Aqueous Media by Sargasam Swartzii (Brown Algae)" *Journal of Matrial and Environmental Science* vol. 6, no. 6, pp. 1629-1637, 2015.

[27] C.O., Akalezi, G.O. Onyedika, H.F., Chahul, and E.E., Oguzie, "Experimental and Theoritical Studies on the Corrosion inhibition of Mild Steel in Acidic Media by Pentaclethra Macrophylla Plant Extract," *Futo Journal Series*, vol 2. No. 1, pp-264-280, 2016.

[28] V. O., Izionworu, E.E., Oguzie, and C.P., Ukpaka, "Electrochemical, SEM, GC-MS and FTIR Study of Inhibitory Property of Cold Extract of Theobroma Cacao Pods for Mild Steel Corrosion In Hydrochloric Acid," *International Journal of Engineering Trends and Technology, submitted for publication*, 2020.

[29] V. O., Izionworu, J. G., Akpa, Characteristics and Composition Analysis of Municipal Solid Waste in Port Harcourt City, Nigeria – A Prelude to Methane Emission Estimation in the City's Dump Sites International Journal of Scientific & Engineering Research, vol. 9, no. 2, 2004-2009, 2018.

[30] O. O., Akinyemi, C. N., Nwaokocha, A. O., Adesanya, "Evaluation of Corrosion Cost of Crude oil Processing Industry," Journal of Engineering Science and Technology, vol. 7, no. 4, 517 – 528, 2012.