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Adsorptive studies of the inhibitive properties of ethanolic extracts of *Parinari polyandra* on Mild steel in acidic media

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Abstract *Corrosion inhibition effectiveness of ethanol extracts of Parinari polyandra for mild steel was investigated using gravimetric and polarization methods. The influence of extract concentrations (0.1g/l to 0.5g/l) and temperatures (303K to 323K) on corrosion and corrosion inhibition were assessed. The results obtained showed that the plant extracts decreased the corrosion rate of mild steel in the acid medium. The corrosion rate decreased with increasing extract concentration for mild steel at 303 K. Inhibition efficiency in all the systems decreased with a rise in temperature, suggesting physical adsorption of the extract constituents on the metal surfaces. Linear polarization studies showed that the plant extract suppressed both the anodic and cathodic half reactions of the corrosion processes, thereby acting as mixed-type inhibitors. Langmuir isotherm was found to be the best isotherm that described the adsorption behaviour of the extract on the surfaces of mild steel at room temperature, whereas the adsorption property at elevated temperature was best described by the Freundlich and Temkin adsorption isotherms. Calculated values of free energy of adsorption, ΔG^{o}_{ads}, on mild steel in the presence of the inhibitor was found to be within the range expected for physical adsorption mechanism. Corrosion activation energy (E_a) values for mild steel in the acid solutions increased in the presence of the inhibitor and were found to be less than 80 kJmol^{-1}.*

Key Words: *Corrosion inhibition, mild steel, Parinari polyandra, adsorption, thermodynamics*

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List of symbols

CR	Corrosion rate
%IE	Inhibition efficiency
ΔW	Weight loss
i_{corr} c	Corrosion currents in the absence of the inhibitor
i_{inh}	Corrosion current in the presence of inhibitor
R_{ct}	Charge transfer uninhibited system
$R_{ct(inh)}$	Charge transfer for inhibited system
E_a	Activation energy
R	Gas constant
T	Temperature
A	Arrhenius constant
N	Avogadro's number
h	Plank constant
ΔS^0_{ads}	Standard entropy change
ΔH^0_{ads}	Standard enthalpy change
ΔG^0_{ads}	Standard free energy change
'a'	Temkin interaction parameter
θ	Surface coverage
C	Concentration of the inhibitor
1/n	Freundlich constant
K_{ads}	Equilibrium constant of adsorption

1.0 Introduction

Corrosion is one of the major challenges in the metallurgical industries (Tian and Zheng, 2019; Es'haghi *et al*., 2018). It is an electrochemical process that returns metals to their natural states through deterioration (Eddy *et al*., 2010a). Industrial development is vital in the history of any developed country. Most industries use various types of metals including their alloy for the construction or fabrication of their plants and other installations. In most cases, contact between the metal and aggressive medium (such as acid, base and salt) is unavoidable (Eddy *et al.*, 2009a, 2009b). Practically there has been no method established to completely eliminate the corrosion process. However, different approaches aim at slowing down the rate of corrosion are available. Consequently, industrial facilities exposed to aggressive medium are often protected from corrosion by adopting several options including painting, oiling, cathodic and anodic protections, etc. The use of inhibitors has been found to be one of the best options available for the protection of metals against corrosion (Eddy *et al*., 2015).

Inhibitors are compounds that tend to retard the rate of corrosion of metals through adsorption on the surface of the metal either by charge transfer from charged inhibitor molecule to charged metal surface (physical adsorption) or by electron transfer from the inhibitor's molecule to the vacant d-orbital of the metal (Eddy *et al.,* 2015). Available literature revealed that popular corrosion inhibitors are basically heterocyclic compounds that are rich in hetero atom or conjugated systems and those with suitable functional groups. However, some well-known corrosion inhibitors (including some organic compounds) have some disadvantages (such as low efficiency, high cost and high toxicity) which restrict their optimum usage. Progresses in search or design of new corrosion inhibitors has been directed to those that are less toxic, less expensive, biodegradable and eco-friendly (Awe *et al*., 2016). Therefore, the use of plant materials has given hope of meeting environmental requirements for corrosion inhibitors. Most plant -based materials are rich in phytochemicals (such as tannins, organic acids, alkaloids, saponins, terpenoids and flavonoids) that can enhanced their functions as green corrosion inhibitors (Sin *et al.,* 2017; *Rashid and Khadom, 2018;* Ma *et al.,* 2016*;* Büyüksagis *et al.,* 2015*;* Awe *et al.,* 2015*;* Umoren *et al., 2013*). Also, many researchers have investigated the inhibitory activity of bark, stem and leaf isolates of various plants as green corrosion inhibitors. The present work seek to investigate the effectiveness of ethanolic extract of *Parinari polyandra* as an environmentally friendly corrosion inhibitor for mild steel in 1.0 M HCl using gravimetric technique and potentiodynamic polarization.

2.0 Experimental Procedure

The metal used for the study was mild steel of composition (% by weight); Mn (0.6), Si (0.03), P (0.36), C (0.15) and Fe (98.86). The metal was mechanically pressed cut into different coupons, each of dimension, 3 × 2 × 0.12 mm for weight loss measurement and 1 × 1 cm for electrochemical study. The coupons were polished with different grades of Silicon carbide (SiC) abrasive paper (#400 to #1200), degreased by washing with ethanol, cleaned with acetone and allowed to dry in the air before preservation in a desiccator. All reagents used for the study were analar grade and double distilled water was used for their preparation. Standardized solutions of 1.0 M HCl was used for weight loss and polarization studies, while the concentration range for the inhibitors was 0.1 to 0.5g/*l* respectively.

2.1 Extraction of plant

Samples of *Parinari polyandra* leaf was obtained from Zango- shanu in Sabon Gari Local Government Area, Kaduna State, Nigeria. 500g of the dried leaves were grounded and soaked in 5 L of ethanol solution for 48 hours. After 48 hours, the solution was filtered to obtained those fractions that are soluble in ethanol. Ethanol was driven out of the filtrate through evaporation at his boiling point. Stock solution of the extract obtained was used in preparing different concentrations of the extract in the acid solution through serial dilution (Awe *et al*., 2015).

2.2 Phytochemical analysis

Phytochemical analysis of the ethanol and aqueous extract of the sample was carried out according to the method reported by Qureshi and Eswar (2010). Frothing and Na_2CO_3 tests were used for the identification of saponin, bromine water and ferric chloride tests were used for the identification of tannin while Leberman's and Salkowski's tests (chloroform solution of the extracts with sulphuric acid and acetic acid) were used for the identification

of cardiac glycosides. The Dragendorf, Meyer and Hager's reagent tests (solution of potassium bismuth iodide, potassium mercuric iodide and saturated solutions of picric acid) were used for the identification of alkaloid.

2.3 Gravimetric method

A previously weighed metal (mild steel) coupon was completely immersed in 250 ml of the test solution in an open beaker. The beaker was covered with aluminum foil and inserted into a water bath maintained at 303 K. After every 24 hours, the corrosion product was removed by washing each coupon (withdrawn from the test solution) with solution containing 50 % NaOH and 100 g/*l* of zinc dust. The washed coupon was rinsed in acetone and air dried before re-weighing. The experiment was repeated at 313 K, 323 K and 333 K respectively. In each case, the difference in weight for a period of 168 hours was taken as the total weight loss. From the average weight loss (mean of three replicate analysis) results, the inhibition efficiency (%I) of the inhibitor, the degree of surface coverage (θ) and the corrosion rate of the mild steel CR) were calculated using equations 1, 2 and 3 respectively (Awe *et al*., 2015);

$$\%\, I = \frac{W_2 - W_1}{W_2} \times 100 \qquad (1)$$

$$\theta = {\%\, I}/{100} \qquad (2)$$

$$CR = \Delta W / At \qquad (3)$$

where W_2 and W_1 are the weight losses (g) for mild steel in the absence and presence of the inhibitor respectively, θ is the degree of surface coverage of the inhibitor, A is the surface area of the mild steel coupon (in cm^2), t is the period of immersion (in hours) and ΔW is the weight loss of mild steel after time, t.

2.4 Linear polarisation resistance

Linear polarization measurement was used to determine the rate of corrosion of the metals in the presence of the inhibitor. All measurements were done in an Autolab frequency response analyzer (FRA) coupled to potentiostat that was connected to a computer system. The electrode system consisted of a glass corrosion cell kit with a platinum counter electrode, a saturated Ag/Ag reference electrode of mild steel which served as the working electrode. The working electrode was positioned in the glass corrosion cell kit, leaving 1 cm^2 surfaces in contact with the solution. Polarization tests were carried out in 1.0 M HCl solution at room temperature under static solution using a potentiostat (model: AuT71791 and PGSTAT 30), that was set at a scan rate of 0.003 V/sec. From the Tafel corrosion results, the inhibition efficiencies, corrosion rate and linear polarization resistance were obtained. The inhibition efficiencies were calculated using equation 4 and 5 respectively:

$$\%I = \left(1 - \frac{i_{inh}}{i_{corr}}\right) \times 100 \qquad (4)$$

$$\%I = \frac{R_{ct(Inh)} - R_{ct}}{R_{ct(Inh)}} \times \frac{100}{1} \qquad (5)$$

where i_{corr} and i_{inh} are the corrosion currents in the absence and presence of the inhibitor respectively and R_{ct} and $R_{ct(inh)}$ are the uninhibited and inhibited charge transfer resistance respectively (Awe *et al*., 2015).

3.0 Results and Discussion

3.1 Phytochemical screening

Table 1 presents results obtained for phytochemical screening of ethanol extract of *Parinari polyandra*. The results indicated the presence of all the tested phytochemicals (as recorded in Table 1) except phlobatanins. Ameh and Eddy (2018) has stated that the chemical structures of these phytochemicals are favourable to corrosion inhibition and that plant extracts often inhibit corrosion through synergistic interaction of its various phytochemical constituents with the surface of the metals. Consequently, preliminary investigation provides a background for the effectiveness of this extract as a corrosion inhibition

Table 1: Phytochemical screening results for ethanol extract of *Parinari polyandra*

Phytochemicals	Indicator
Tannins	+
Phlobatanins	-
Alkaloids	+
Cardiac Glycosides	+
Anthraquinones	+
Saponins	+
Flavonoids	+
Terpenes	+

**** + = Present - = Not present**

3.2 Gravimetric analysis

Plots for variation of weight loss with time (Fig.1) reveal two major information. The first is that weight loss increases with increase in the period of contact while the second information is that weight loss decreases with increase in the concentration of

the inhibitor. Therefore, the corrosion rate of the metal is decreased by the presence of ethanol extract of *Parinari polyandra* while inhibition efficiency increases with increase in the concentration of the extract. The extract thus acted as an adsorption inhibitor in that the extent of coverage increases with concentration (Eddy *et al*., 2010).

Weight loss was also found to decreased with increase in temperature (graphs not presented) which agrees with the mechanism of physiosorption, since the extent of adsorption decreases with temperature, contrary to chemisorption (in which the extent of adsorption/inhibition efficiency increases with increase in temperature (Awe, 2015).

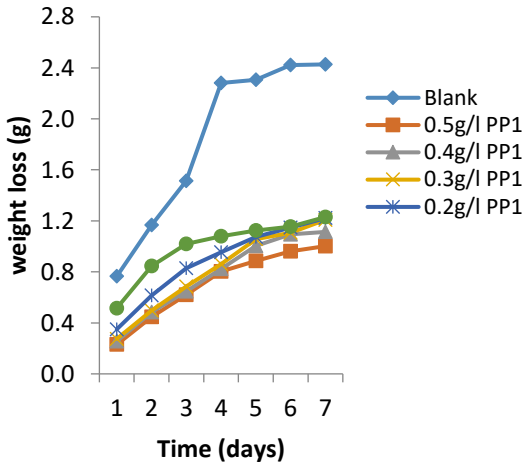

Fig. 1:Variation of weight loss with time for the corrosion of mild steel in solution of HCl containing various concentration of *Parinari polyandra* at 303K

It is worth remarking that weight loss is inversly proportional to corrosion rate (equation 2). Decrease in weight loss, with reference to that of the blank correspond to increase in inhibition efficiency. Calculated values of inhibition efficiency and weight loss for the inhibited and uninhibited (blank) corrosion of mild steel in 1 M HCl is presented in Table 2. The results showed dependency of corrosion rate with temperature and concentration. The rate increases with temperature but deceased as the concentration of the inhibitor increases.

3.3 Kinetic study

The Arrhenius equation was applied to investigate the effect of temperature on the inhibition of the corrosion of mild steel by ethanol extract of *Parinari polyandra*. The mathematical expression of the Arrhenius equation can be written according to equation 6 (Awe *et al*., 2015)

$$k = Aexp\left(\frac{-E_a}{RT}\right) \quad (6)$$

CR denote corrosion rate of mild steel, A is the Arrhenius or pre-exponential factor, R is the gas constant and T is the temperature. Widely applied form of the Arrhenius equation engages the plotting of ln(CR) versus 1/T to obtained slope equal to E_a/R and intercept equal to lnA. The Arrhenius plots for the corrosion of mild steel in the presence of ethanol extract of *Parinari polyandra* are shown in Fig. 2 while Arrhenius parameters obtained from the plots are recorded in Table 2

Table 2. Corrosion rate of mild steel and inhibition efficiencies of the various inhibitors in 1.0 M HCl at 303 K, 313 K, 323 K and 333 K

System	CR ($gh^{-1}cm^{-2}$)	%IE
Blank at 303 K	0.00580	
0.1 g/*l* at 303 K	0.00342	40.90
0.2 g/*l* at 303 K	0.00285	50.86
0.3 g/*l* at 303 K	0.00210	63.69
0.4 g/*l* at 303 K	0.00202	65.03
0.5 g/*l* at 303 K	0.00182	68.58
Blank at 313 K	0.01190	
0.1 g/*l* at 313 K	0.00746	17.40
0.2 g/*l* at 313 K	0.00625	18.61
0.3 g/*l* at 313 K	0.00446	41.99
0.4 g/*l* at 313 K	0.00425	55.34
0.5 g/*l* at 313 K	0.00413	61.03
Blank at 323 K	0.01764	
0.1 g/*l* at 323 K	0.01533	5.76
0.2 g/*l* at 323 K	0.01284	12.21
0.3 g/*l* at 323 K	0.01142	16.82
0.4 g/*l* at 323 K	0.01046	23.17
0.5 g/*l* at 323 K	0.00976	30.38
Blank at 333 K	0.02563	
0.1 g/*l* at 333 K	0.02560	4.76
0.2 g/*l* at 333 K	0.02527	5.26
0.3 g/*l* at 333 K	0.02369	15.73
0.4 g/*l* at 333 K	0.02360	21.65
0.5 g/*l* at 333 K	0.02306	23.28

The plots displayed high level of fitness to the Arrhenius model as indicated by calculated R^2 values (Table 2). The activation energies are observed to increase with increase in the concentration of the extract indicating a progressive increase in the strength of adsorption with

concentration. The activation energy for the blank is also lower than tose obtained for the presence of the inhibitor This also indicate that the corrosion of mild steel in solution of HCl is retarded by various concentrations of ethanol extract of *Parinari polyandra* (Eddy and and Ita, 2011).

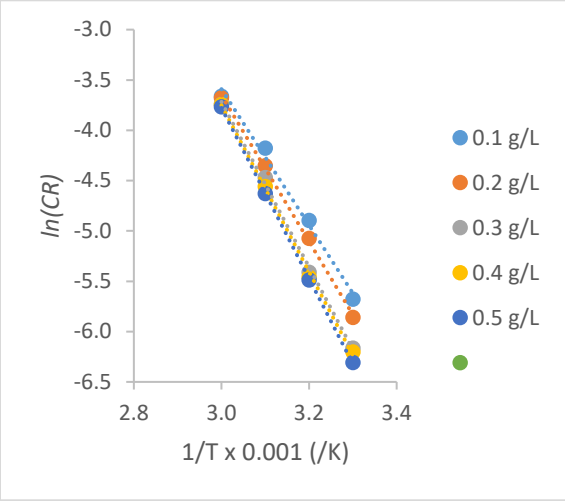

Fig. 2: Arrhenius plots for the corrosion of mild steel in 1M HCl in the presence of *Parinari polyandra*

Table 2: Arrhenius parameters for the adsorption of *Parinari polyandra* on mild steel surface

System	Slope	lnA	E_a (J/mol)	A	R^2
Blank	-4.8513	10.961	40.33	57584	0.9716
0.1 g/*l*	-6.7591	16.686	56.20	17645653	0.9918
0.2 g/*l*	-7.2669	18.148	60.42	76133581	0.9989
0.3 g/*l*	-8.2096	20.912	68.25	1.21E+09	0.9976
0.4 g/*l*	-8.2751	21.073	68.80	1.42E+09	0.9988
0.5 g/*l*	-8.4778	21.656	70.48	2.54E+09	0.9999

3.4 Thermodynamic and adsorption study

In corrosion study, thermodynamic parameters can be useful in predicting the nature of adsorption, the feasibility of the adsorption and the heat content of the adsorption process. Entropy and enthalpy data for the inhibition of the corrosion of mild steel in 1 M HCl were obtained through the slope and intercept of the Transition state plots respectively. The Transition state equation relates the corrosion rate to standard entropy and enthalpy of adsorption as follows (Eddy and Ebenso, 2010),

$$\ln\left(\frac{CR}{T}\right) = ln\left(\frac{R}{Nh}\right) + \frac{\Delta S^0_{ads}}{R} - \frac{\Delta H^0_{ads}}{RT} \qquad (7)$$

A high degree of linearity was observed for plots of $\ln\left(\frac{CR}{T}\right)$ versus $\frac{1}{T}$. Transition state plots for various concentrations of the inhibitor (and that of the blank) are presented in Fig. 3 while calculated values of ΔH^0_{ads} and ΔS^0_{ads} are recorded in Table 3. Standard enthalpies of adsorption of the inhibitors were positive while standard values of entropy change were negative. Therefore, the adsorption of the inhibitor is endothermic and is facilitated in the direction of increasing order.

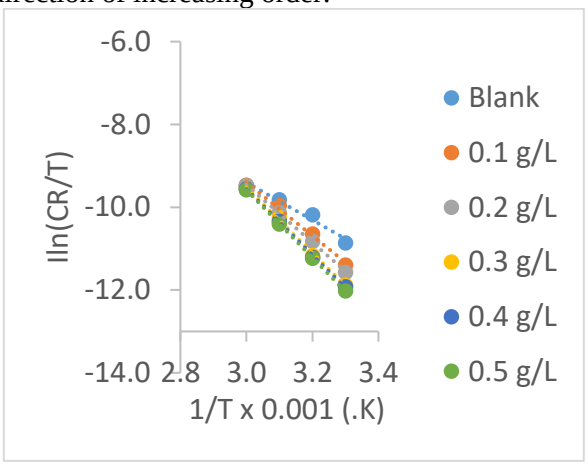

Fig. 3: Transition state plots for the adsorption of *Parinari polyandra* on mild steel surface

Table 3: Thermodynamic parameters for the adsorption of *Parinari polyandra* on mild steel surface

System	Slope	Intercept	ΔH^0_{ads} (J/mol)	ΔS^0_{ads} (J/mol)	R^2
Blank	-4.5367	4.2084	37.72	-105.10	0.9679
0.1 g/*l*	-6.4444	9.9337	53.58	-57.50	0.9911
0.2 g/*l*	-6.9522	11.396	57.80	-45.34	0.9988
0.3 g/*l*	-7.8949	14.159	65.64	-22.37	0.9974
0.4 g/*l*	-7.8604	14.321	65.35	-21.03	0.9987
0.5 g/*l*	-8.1631	14.903	67.87	-16.19	0.9998

Adsorption isotherms can provide information on the inter and intra molecular interactions within the molecule and with the adsorbent respectively (Sabirneeza, 2016; Biswas *et al*., 2015). Adsorption isotherm studies give the descriptive mechanism on how the organic inhibitor is adsorbed on the metal

surface (Adejoro et al., 2015; Obi-Egbedi *et al*., 2012).

Adsorption of organic molecules occurs when the interaction energy between the metal surface and organic molecule is higher than that of metal surface and water molecule. It is evident in Figs. 4 and 5 that Freundlich and Temkin adsorption isotherm gave best fitted isotherms for the adsorption of the plant extract on the surface of mild steel (with R^2 values above 0.9).

The Temkin adsorption model can be written as

$$Exp(-2a\theta) = k_{ads}C \quad (8)$$

where 'a' is the interaction parameter, θ is the surface coverage of the inhibitor, k_{ads} is the Temkin adsorption equilibrium constant and C is the concentration of the inhibitor in the bulk electrolyte. Simplification of equation 8 yielded equation 9,

$$\theta = -\frac{1}{2a}lnk_{ads} + \left(-\frac{1}{2a}\right)lnC \quad (9)$$

On the other hand, the Freundlich adsorption equation can be written according to equation 10, which is transformed to equation 11

$$\theta = k_{ads}C^{1/n} \quad (10)$$

$$ln\theta = lnk_{ads} + \frac{1}{n}lnC \quad (11)$$

Based on equations 9 and 11, Temkin and Freundlich adsorption isotherms were plotted and are shown in Figs. 4 and 5 respectively. Slope, intercept, Temkin and Freundlich parameters are presented in Table 4.

The results indicated that there is a repulsive behaviour of the inhibitor's molecules since the interaction parameters were negative. Also from the Fruendlich parameter (n), it is observed that the factor decreases with increase in temperature, indicating that the number of inhibitor's molecules that is adsorbed on the surface of the metals decreases with increasing temperature.

The Fruendlich and Temkin adsorption parameters were also used to calculate the standard free energy of adsorption of the inhibitor on the surface of the metal. These constants are related to the free energy of adsorption according to equation 12,

$$\Delta G^0_{ads} - RTln(55.5k_{ads}) \quad (12)$$

The free energy changes as recorded in Table 4 indicate that the adsorption of the inhibitor is spontaneous (since values of ΔG^*_{ads} are negative) and followed the mechanism of physical adsorption (because the ΔG^*_{ads} are less than the threshold value of -40 kJ/mol).

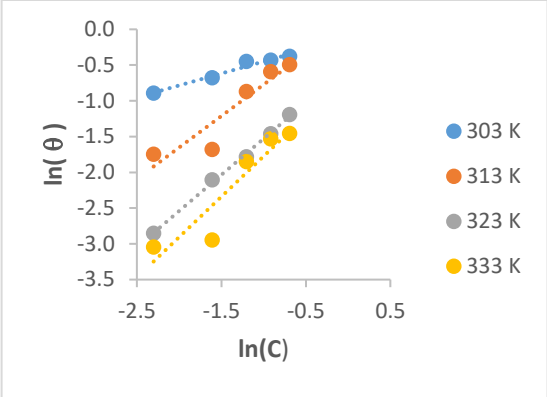

Fig. 4. Freundlich isotherm for PP1 adsorption on mild steel surface in 1.0 M HCl solutions at various temperature

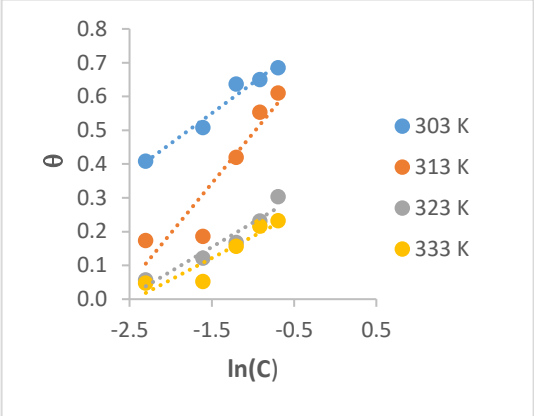

Fig. 5. Temkin isotherm for PP1 adsorption on mild steel surface in 1.0 M HCl solutions at various temperature

Table 4: Temkin and Freundlich parameters for the adsorption of *Parinari polyandra* on mild steel surface

T (K)	lnk_{ads}	a/n	ΔG^*_{ads} (kJ/mol)	R^2
303	4.5674	-0.09	-21.62	0.9679
313	2.6571	-0.15	-17.36	0.8628
323	2.5660	-0.07	-17.67	0.9285
333	2.4474	-0.06	-17.89	0.8602
303	-0.1156	2.99	-9.83	0.9678
313	-0.1064	1.14	-9.85	0.8702
323	-0.5186	0.99	-8.81	0.9969
333	-0.6446	0.88	-8.49	0.8658

3.5 Electrochemical measurement

Polarization measurements are suitable for monitoring the progress and mechanism of the anodic and cathodic partial reactions as well as identifying the effect of the additive on either partial reaction. Potentiondynamic and Linear polarization experiments were conducted to investigate the effect of adsorbed extracts on the kinetics of the anodic and cathodic processes. The corrosion current is a function of the reactivity of a metal in an aqueous environment. The higher the values of i_{corr}, the higher the dissolution of the metal and vice versa. Potentiodynamic polarization curves (Tafel plots) for mild steel in 1.0 M solutions of HCl in the absence and presence of various concentration of the inhibitors are shown in Fig. 6 while the electrochemical parameters derived from the polarization curves and inhibition efficiencies are summarized on Tables 4 The Tafel plots show Tafel region, plateau region and high polarization region. The plots revealed high dominance of the Tafel region and thus a wide potential range. Addition of the inhibitor seems to affects the anodic as well as the cathodic partial reactions by, shifting the corrosion potential (E_{corr}) slightly toward more positive (anodic) values and reducing the anodic and cathodic current densities (i_{corr}). This is an indication of a mixed-type corrosion inhibition mechanism. From the polarization curves however, it is obvious that the plant extracts exerted more significant inhibiting effect on the cathodic hydrogen ion reduction reaction in 1.0 M HCl. The %IE data obtained (Tables 4) follows the same trend with those calculated from gravimetric measurement. This confirm that the extract actually inhibited the corrosion of mild steel (Awe *et al*., 2015)

The computed data for the IE using gravmetric (GM), linear polarization resistance (LPR) and Potentiodynamic polarization (PDP) shows that the %IE increases with an increase in inhibitor concentration as a result, the surface area covered by the inhibitor increased. It was also found that there was good agreement between the experimental techniques employed as the regression coefficient gave values great than 0.9 (Tian and Zheng, 2019; Awe *et al*., 2015).

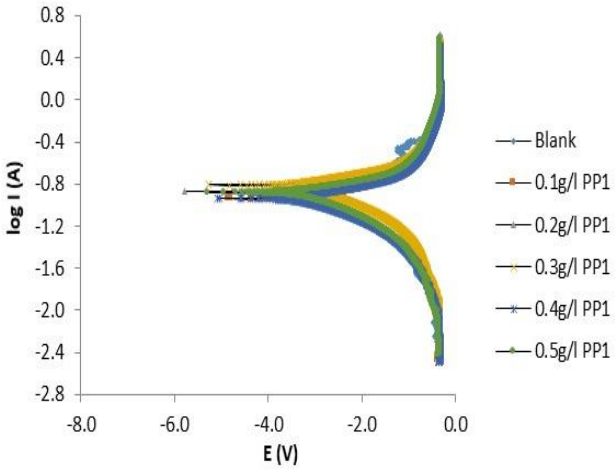

Fig. 6: Polarization curve for the corrosion of mild steel in 1.0 M HCl in the presence and absence of various concentrations of PP1 at 303 K

Table 4. Tafel polarization parameters and linear Polarization Resistant obtained at various concentration of inhibitors on mild steel in acidic media

C (g/L)	Potentiodynamic polarization			Linear polarization	
	E_{corr} (mV)	Icorr (µA)	IE %	R_p (Ω/cm^2)	%IE
Blank	-864.95	1179.0	-	17.105	-
0.1	-940.20	654.25	44.50	35.223	51.44
0.2	-869.38	516.46	56.19	41.87	59.15
0.3	-808.70	372.83	68.37	58.157	70.59
0.4	-932.58	331.41	71.89	61.59	72.23
0.5	-882.40	286.53	75.69	66.049	74.10

4.0 Conclusions

The results and findings obtained from this study indicated that ethanol extract of *Parinari polyandra* is a good adsorption inhibitor for the corrosion of mild steel in acidic medium. The adsorption of the inhibitor agreed with physisorption mechanism and submit the the adsorption models of Freundlich and Temkin. Thermodynamics of the inhibitor's adsorption is in accordance with spontaneous adsorption that supports physiosorption mechanism while the heat of the reaction supports exothermic process with increasing degree of association.

5.0 References:

Adejoro, A., Ojo, F. K., & Obafemi, S. K. (2015). Corrosion inhibition potentials of ampicillin for mild steel in hydrochloric acid solution. *Journal of Taibah University for Science*, 9, 2, pp. 196–202.

Ameh, P. O. & Eddy, N. O. (2018). Experimental and Computational Chemistry studies on the inhibition efficiency of phthalic acid (PHA) for the corrosion of aluminum in hydrochloric and tetraoxosulphate (VI) acids. *Protection of metals and physical chemistry of surfaces*, 54, 6, pp.1169-1181.

Awe, F. E., Idris, S. O. & Abdulwahab, M. (2016). Studies on the inhibitive properties of *Boscia senegalensis* in aluminium-HCl environment. *Moroccan Journal of Chemistry*, 4, pp. 629-638.

Awe, F. E., Idris, S. O., Abdulwahab, M. & Oguzie, E. E.. (2015). Inhibitive and adsorptive effect of *Parinari polyandra* on mild steel corrosion in aqueous sulphuric acid. *African Journal of Pure and Applied Chemistry*, 9,6, pp. 125-134,.

Biswas, A., Pal, S. & Udayabhanu, G. (2015). Experimental and theoretical studies of xanthan gum and its graft co-polymer as corrosion inhibitor for mild steel in 15% HCl. *Applied Surface Science*, 353, pp. 173–183.

Büyüksagis A, Dilek M & Kargioğlu M (2015) Corrosion inhibition of st37 steel in geothermal fluid by Quercus robur and pomegranate peels extracts. *Protection of Metals and Physical Chemistry of Surfaces* 51, pp. 861–72

Eddy, N. O. & Ebenso, E. E. (2010). Adsorption and quantum chemical studies on cloxacillin and halides for the corrosion of mild steel in acidic medium. *International Journal of Electrochemical Science,* 5 , 6, pp. 731- 750.

Eddy, N. O. & Ita, B. I. (2011). Theoretical and experimental studies on the inhibition potentials of aromatic oxaldehydes for the corrosion of mild steel in 0.1 M HCl. *Journal of Molecular Modeling* 17, 633-647.

Eddy, N. O. & Odiongenyi, A. O. (2010). *Corrosion inhibition and adsorption properties of ethanol extract of Heinsia crinata on mild steel in H_2SO_4. Pigment and Resin Technology*, 38, 5, pp. 288-295.

Eddy, N. O., Ibok, U. J. & Ebenso, E. E. (2010). Adsorption andquantum chemical studies of the inhibitive properties of tetracycline for the corrosion of mild steel in 0.1 M H_2SO_4. *Anales des la Asociacion Quimica Argentina* (*The Journal of the Argentine Chemical Society*), 97, 2, pp. 178-194.

Eddy, N. O., Ibok, U. J., Ebenso, E. E., Ahmed El Nemr, & El Sayed H. El Ashry (2009). Quantum chemical study of the inhibition of the corrosion of mild steel in H_2SO_4 by some antibiotics. *Journal of Molecular Modeling* 15, 9, pp.1085-1092.

Eddy, N. O., Momoh-Yahaya, H. & Oguzie, E. E.(2015). Theoretical and experimental studies on the corrosion inhibition potentials of some purines for aluminum in 0.1 M HCl. *Journal of Advanced Research* 6, pp. 203-216.

Eddy, N. O., Odoemelam S. A. & Odiongenyi, A. O. (2009). Joint effect of halides and ethanol extract of *Lasianthera Africana* on the inhibition of the corrosion of mild steel in H_2SO_4. *Journal of Applied Electrochemistry*, 39, 6, pp. 849- 857.

Es'haghi M, Amjad A, Asghari S and Lotfi A 2018 Studying effect of plantain extract behavior as an eco-friendly corrosion inhibitor on the mild steel in 1 M HCl solution *Anti-Corrosion Methods and Materials* ***65*** *310–6*

Ma, X., Jiang, X., Xia, S., Shan, M., Li, X., Yu, L. & Tang, Q. (2016). New corrosion inhibitor acrylamide methyl ether for mild steel in 1 M HCl *Appl. Surf. Sci.* ***371*** *248–57*

Obi-Egbedi, N. O., Obot, I. B. and Umoren, S. A. (2012). *Spondias mombin L.* as a green corrosion inhibitor for aluminium in sulphuric acid: correlation between inhibitive effect and electronic properties of extracts major constituents using density functional theory. *Arabian Journal of Chemistry*, 5, 3, pp. 361–373.

Rashid, K. & Khadom, A. (2018). Evaluation of environmentally friendly inhibitor for corrosion of mild steel in phosphoric acid solution: unconventional approach. *Anti-Corrosion Methods and Materials*, 65, pp. 506-514.

Sabirneeza, A. A. F. (2016). A novel water-soluble, conducting polymer composite for mild steel acid corrosion inhibition," *Journal of Applied Polymer Science*, 127, 4, pp. 3084–3092.

Sin, H. L. Y., Rahim, A. A., Gan, C. Y., Saad, B., Salleh, M. I. & Umeda, M. (2017). *Aquilaria subintergra* leaves extracts as

sustainable mild steel corrosion inhibitors in HCl *Measurements*, 109, pp. 334-345.

Tian, Y. & Zheng, M. (2019). Inhibition effect of silicate and molybdate on the corrosion of SS 316 in neutral corrosive solution at high temperature *Materials. Research. Express*, 6, pp. -15.

Umoren, S. A., Gasem, Z. M. & Obot, I. B. (2013). Natural products for material protection: inhibition of mild steel corrosion by date palm seed extracts in acidic media *Industrial Engineering and Chemical Research*, 52, pp. 14855–14865