

Green Colloidal Composites from Local Agro-wastes for Inhibition of Mild Steel Corrosion in 1 M HCl

ABSTRACT

Aims: To investigate the corrosion inhibition efficiency of green colloidal water-soluble composites formulated from *Thaumatococcus daniellii* extract (TDE) and local agro-wastes as alternative oilfield chemicals using mild steel in 1 M HCl.

Study design: Corrosion was monitored by Weight Loss (WL), Electrochemical Impedance Spectroscopy (EIS) and Potentiodynamic Polarization (PDP) techniques.

Place and Duration of Study: Materials and Oilfield Chemistry (MOC) laboratory, Department of Chemistry, Faculty of Science, University of Uyo, Nigeria, between December 2017 and March 2018.

Methodology: The standard procedures for thermo-gravimetric analyses (TGA), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) were exactly followed to evaluate corrosion efficiency.

Results: Inhibition efficiency of 91.7 % was obtained with TDE 30 °C but this efficiency decreased as temperature increased. Increase in TDE concentration increased charge transfer resistance and decreased double layer capacitance. Adsorption isotherms and kinetic models were also used to describe the adsorption and activation processes. The presence of TDE increases the activation energy and reduces the rate of corrosive attack of the acid on the steel specimens. The adsorption of *Thaumatococcus daniellii* extract (TDE) on the mild steel surface was characteristic of inhibition by physisorption. Composites from TDE were up to 99 % and 85 % efficient at 30 °C and 80 °C respectively.

Conclusion: Adsorption of TDE molecules is by spontaneous physical adsorption mechanism and is best approximated by the Langmuir adsorption isotherm. TDE formulations and composites could be exploited to produce an effective alternative eco-friendly oilfield corrosion inhibitor.

Keywords: adsorption; charge transfer resistance; corrosion inhibitor formulation; double layer capacitance; local materials, *Thaumatococcus daniellii*.

1. INTRODUCTION

When the natural pressure of existing wells depletes, production of hydrocarbons could decline except some chemical techniques are used to enhance production [1]. Such techniques include well acidizing and fracturing, commonly referred to as well stimulation. This involves forcing acid under high pressure through the well bore into the formation rock. On reaching the formation, the acid reacts chemically with rocks (like calcite, limestone, and dolomite), dissolves them, enlarge existing flow channels and open new ones [2, 3]. On the other hand, before reaching the formation, the live acid comes in contact with well construction materials which results in corrosion. Also, during production and transport, the spent acid also causes significant corrosion problems to associated materials.

The rate of corrosion usually depends on the type and concentration of the acid used. Hydrochloric acid (HCl) is usually deployed for well stimulation because it is economical and reacts fast with the formation rocks but HCl is very corrosive. To reduce the rate of HCl corrosion, small amounts of corrosion inhibitors are usually added to the well stimulation fluid [4]. Various corrosion inhibitors have been designed for use in various acidizing recipes [5-10]. The use of plant extracts is a promising adventure but limited by realities that plant extracts undergo microbial or biochemical degradation on storage and thermal degradation when applied at high temperature. To upgrade plant extracts for high temperature operations, small amounts of some synergistic substances are added, and the resulting

mixture is referred to as corrosion inhibitor formulation (CIF) or corrosion inhibitor package (CIP) or inhibitor cocktail (IC) according to Barmatov and co-workers [11]. Careful selection of additives should be made to ensure that these additives do not neutralize the acid, but only emulsify it while maintaining it in the reactive state [2].

Many plant extracts reported in literature are blended with potassium iodide to improve their inhibition efficiency [12, 13]. This paper reports preparation of a CIF using local precursors. A local water-soluble surface-active material is synthesized from palm fruit bunch and coded PPA. It is obtained from oil palm fruit bunch (Fig. 1, left), an agricultural waste which is in sustainable supply. The PPA is famous for its surface activity and ability to emulsify water and palm oil used in preparing local delicacy called 'otong' by the Ibibio people of Southern Nigeria. This surface activity motivated its choice. The base inhibitor is obtained by extracting the leaves of *Thaumatococcus daniellii* (Fig. 1, right) in ethanol and was coded TDE.

The 'sweet prayers' plant (Katemfe), *Thaumatococcus daniellii* (Benn.) is a rhizomatous plant found in the tropical rain forests and coastal areas of West Africa, particularly Nigeria, Ghana and Cote d'Ivoire [14]. *Thaumatococcus daniellii*, whether cultivated or in the wild, contributes to the economy of the rural people in most parts of Southern Nigeria through its stalks, leaves, fruits and rhizomes [15, 16]. Its local uses include mat weaving (stalks), roof thatching (stalks and leaves), food wrapping (leaves), as potherbs (leaves and rhizomes) and for sweetening drinks and food (fruits). However, the most exciting use of *T. daniellii*, for which it has earned global interest, is its use as a sweetener or taste modifier. The arils contain thaumatin, a group of intensely sweet proteins, about 3000 times sweeter than sucrose on weight basis [17]. The plant leaves are therefore non-toxic.



Figure 1. Image of palm fruit branches (PFB) and *T. daniellii*

2. MATERIAL AND METHODS

2.1 Steel specimen

Mild steel (MS) sheets were purchased from Building and Construction Materials Market in Uyo, Akwa Ibom state and cut into coupons of dimension 2 cm x 2 cm, degreased in absolute ethanol and used without polishing. NACE Recommended Practice RP-0775 and ASTM G-1 & G-4 for surface finishing and cleaning of weight-loss coupons were followed. The steel was of chemical composition C (0.13), Si (0.18), Mn (0.39), P (0.40), S (0.04), Cu (0.025), Fe (balance).

2.2 Test solutions

Mature leaves of *T. daniellii* (TDLs) were harvested from a local bush in Ikot Ambon Ibesikpo in Ibesikpo Asutan Local Government Area of Akwa Ibom State, Nigeria, while the palm fruit bunches (PFBs) were obtained from a local oil palm processing mill. Both were transported to the laboratory,

washed convincingly in distilled water and air-dried. The TDLs were macerated and extracted using the procedures earlier reported [6]. Before washing, the PFBs were cut into small pieces using a knife. The dry PFBs were dried and ashed in the oven at 100 °C as earlier reported [18] to obtain the surface-active material coded PPA.

The acid solution (1 M HCl) was prepared by diluting appropriate volume of stock analytical grade hydrochloric acid in distilled water. Different concentrations (100 ppm, 200 ppm, 500 ppm, 700 ppm and 1000 ppm) of the TDE were prepared in the 1 M HCl. The compositions of the colloidal formulations are shown in Table 1. The resulting corrosion inhibitor formulations were stored at 4 °C in a refrigerator prior to use.

Table 1. Composition of formulations of TDE in 1 M HCl

Formulation code	Composition
TDE-PPA	1000 ppm TDE + 500 ppm PPA
TDECIFA	1000 ppm TDE + 500 ppm + 1.0 wt. % KI
TDECIFB	1000 ppm TDE + 500 ppm + 1.0 wt. % KI + 1.0 wt. % MgCl ₂
TDECIFC	1000 ppm TDE + 500 ppm + 1.0 wt. % KI + 1.0 wt. % MgCl ₂ + 500 ppm PPA

2.3 Corrosion measurements

The standard procedures reported earlier for thermo-gravimetric analyses (TGA), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) earlier reported in literature were exactly followed [19]. In addition, at least three gravimetric measurements were taken per test solution and the average value of weight losses are used in further calculations reported. Corrosion rate (CR) and inhibition efficiency ($E_{\%}$) for TGA were calculated using Eq. 1 and 2 respectively.

$$CR = \frac{WF \times A}{\rho \Delta t} \quad (1)$$

$$E_{\%} = 100 \left(\frac{CR_0 - CR_i}{CR_0} \right) \quad (2)$$

where CR_0 and CR_i are the corrosion rates (cmh^{-1}) in the absence and presence of the inhibitor, ρ is the density of iron, A is the average surface area (cm^2) of the metal specimens and t is the immersion time (h). This procedure was repeated at 60 and 90 °C. The inhibition efficiency (%) for EIS and PDP measurements were calculated using Eqs. 3 and 4 respectively.

$$\%E_{\text{EIS}} = 100 \left(\frac{R_{\text{ctI}} - R_{\text{ctR}}}{R_{\text{ctI}}} \right) \quad (3)$$

where R_{ctR} and R_{ctI} are charge transfer resistances in the absence and presence of inhibitor respectively.

$$\%E_{\text{RRP}} = 100 \left(1 - \frac{I_{\text{corrI}}}{I_{\text{corrR}}} \right) \quad (4)$$

where I_{corrR} and I_{corrI} are the corrosion current densities in the absence and presence of the inhibitor respectively. The magnitude of the double layer capacitance (C_{dl}) of the adsorbed film was calculated from constant phase element (CPE) constant (Y_0) and charge transfer resistance (R_{ct}) using Eq. 5

$$C_{\text{dl}} = (Y_0 R_{\text{ct}}^{n-1})^{\frac{1}{n}} \quad (5)$$

where n is a constant showing degree of roughness of the metal surface obtained from the phase angle given that $\phi^{\circ} = -1/\alpha$ and $n = 2\alpha(\pi)$ is the CPE exponent.

3. RESULTS AND DISCUSSION

3.1 Weight loss measurement

A direct and quantitative correlation between the amounts of the metal dissolved out by the acid due to corrosion is provided by the weight loss method. The corrosion rates of the metal coupons were estimated from experimental weight loss data and the corresponding inhibition efficiency computed and presented in Table 2. It can be observed from the table that corrosion rate increases with increase temperature. In the inhibited solutions, corrosion rate decreases as TDE concentration increases. This implies that TDE inhibits corrosion of the steel at all temperatures studied. Inhibition efficiency increases with increase in TDE concentration but decreased as temperature is raised. Similar observations have been reported by other authors [20-22].

Table 2: Corrosion rate and inhibition efficiency for mild steel corrosion in 1 M HCl containing different concentrations of TDE upto this certain range.

Test solution	30 °C		40 °C		50 °C		60 °C	
	CR	%I	CR	%I	CR	%I	CR	%I
1 M HCl	26.74	-	34.28	-	46.87	-	68.13	-
100 ppm TDE	5.64	78.9	8.71	74.6	15.84	66.2	31.14	54.3
200 ppm TDE	4.97	81.4	7.95	76.8	13.45	71.3	26.30	61.4
500 ppm TDE	3.93	85.3	6.92	79.8	12.56	73.2	23.37	65.7
700 ppm TDE	3.10	88.4	5.31	84.5	9.89	78.9	20.85	69.4
1000 ppm TDE	2.22	91.7	3.81	88.9	7.73	83.5	19.01	72.1

3.2 Adsorption of TDE

Adsorption isotherms are an important tool for evaluating the performance of corrosion inhibitors. As earlier reported [23], the fractional surface coverage data obtained were fitted into adsorption isotherm models proposed by Langmuir, Temkin, Flory-Huggins, Frumkin, Freundlich and the so-called thermodynamic/kinetic (El-Awady *et al.*). The best fit was determined by comparing both Pearson's and adjusted R^2 values [23]. The best fit was obtained with Langmuir model followed by Temkin model. According to the scheme of adsorption described by Ituen and co-workers [23] depicted in Fig. 2, the inhibitor molecules (adsorbate) constitute the bulk phase and is in contact with the surface of the mild steel (adsorbent). Should the TDE molecules and steel surface are contacted for long enough, equilibrium could be established between the amounts of TDE molecules adsorbed and that amount remaining in the bulk phase. These adsorption models (Langmuir and Temkin) considers the equilibrium relationship by a plot of a function of the amount of adsorbate adsorbed (θ) to the equilibrium concentration of the inhibitor (C) at a given temperature using the general form shown in Eq. 6:

$$f(\theta, x) e^{(-2a\theta)} = KC \quad (6)$$

where $f(\theta, x)$ denotes the configuration factor, which depends on the physical model and assumptions underlying the derivation of the particular model; K is the adsorption-desorption equilibrium constant, which describes how strongly the molecules are held on the adsorbent surface; and a is the molecular interaction parameter used to predict the nature of interactions in the adsorbed layer. This general form is amended by Langmuir and Temkin models according to Eq. 7 and Eq. 8 respectively. Free energy change of adsorption (ΔG_{ads}) can be deduced from K_{ads} values using the relationship in Eq. 9.

$$\frac{\theta}{C} = 1/K_{ads} + C \quad (7)$$

$$\theta = -\frac{1}{2a} \ln C - \frac{1}{2a} \ln K_{ads} \quad (8)$$

$$\Delta G_{ads} = -RT \ln 55.5 K_{ads} \quad (9)$$

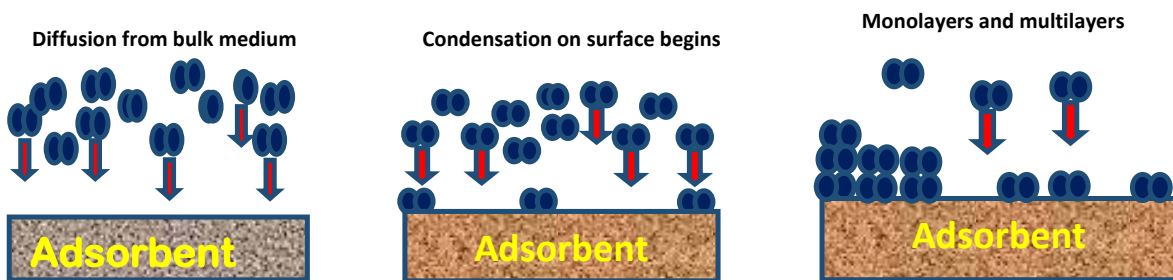


Figure 2. Schematic representation of adsorption of molecules on solid surfaces from bulk phase [23].

In both models, it is presumed that the corrosion inhibitor functions by initial diffusion from bulk medium to the metal surface and subsequent adsorption on the surface [23]. The adsorption may occur through four forms of adsorptive interactions as follows:

- electrostatic interaction between charged metal surface and charged inhibitor molecules;
- interaction of uncharged electron pair (which may come from non-bonding orbitals of hetero atoms) of the inhibitor molecules with the metal;
- interaction of pie-electrons with the metals; or
- a combination of two or more of the above [23]

The first case typifies physisorption mechanism; the next two are associated with chemisorption mechanism; and the last with mixed or physio-chemisorptions [24]. Quantitatively, physisorptions are also characterized by ΔG_{ads} values less negative than -20 kJmol^{-1} , chemisorptions are categorized by ΔG_{ads} values more negative than -40 kJmol^{-1} and physio-chemisorptions are associated with ΔG_{ads} values between -20 to -40 kJmol^{-1} . Results (Table 3) from analyses of both Langmuir plots (Fig. 3) and Temkin plots (Fig. 4) show that ΔG_{ads} for TDE at all the temperatures were in the range that is attributed to physisorption mechanism. Also K_{ads} decreases with increase in temperature, indicating that the strength of interaction of TDE with mild steel weakens as temperature increases, leading to desorption of some adsorbed TDE molecules. The negative values of lateral interaction parameter (α) indicate that repulsion takes place in the adsorbed medium.

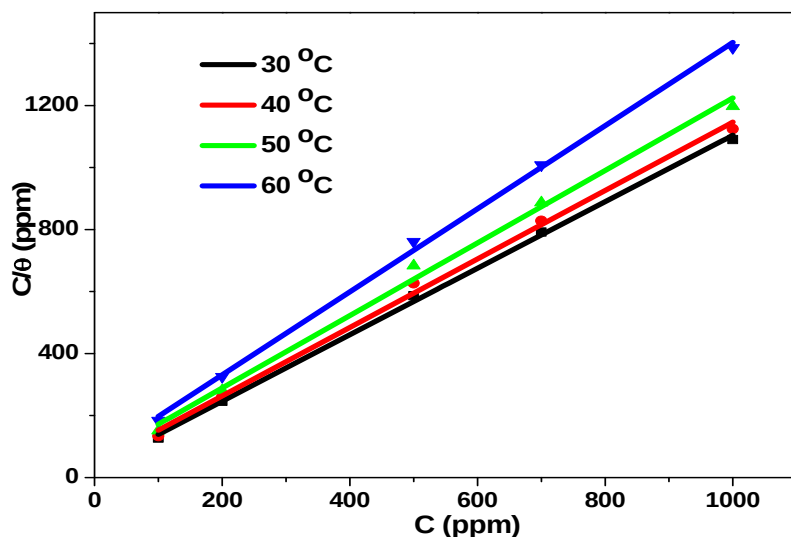


Figure 3. Langmuir adsorption isotherm for adsorption of TDE on steel in 1 M HCl

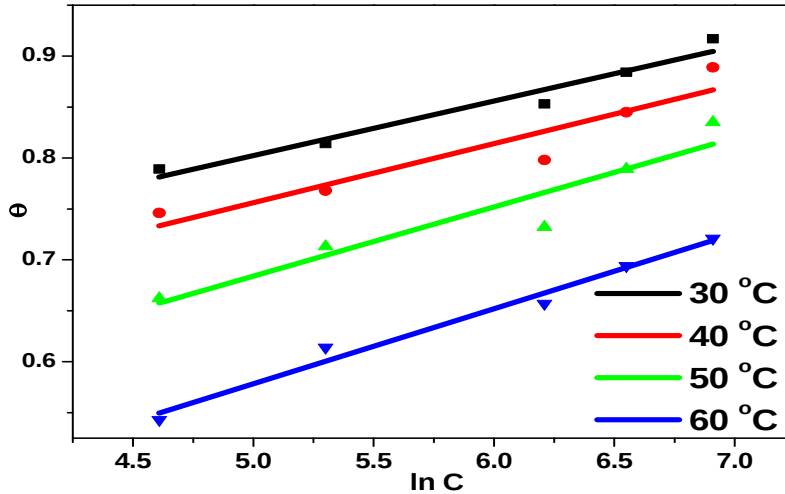


Figure 4. Temkin adsorption isotherm for adsorption of TDE on steel in 1 M HCl

Table 3. Parameters deduced from Langmuir and Temkin adsorption isotherms

T (°C)	Langmuir				Temkin				
	Pearson's R^2	Adjusted R^2	K_{ads}	ΔG_{ads} kJmol ⁻¹	Pearson's R^2	Adjusted R^2	α	K_{ads}	ΔG_{ads} kJmol ⁻¹
30	0.9994	0.9984	2.88	-12.78	0.9796	0.9461	-2.08	3.04	-12.92
40	0.9988	0.9988	2.01	-12.27	0.9435	0.8537	-2.70	2.12	-12.40
50	0.9978	0.9941	1.12	-11.09	0.9515	0.8737	-3.61	1.63	-12.09
60	0.9993	0.9982	0.91	-10.86	0.9912	0.9767	-5.75	1.02	-11.17

3.3 Kinetic and thermodynamic studies

Corrosion rate was found to increase with temperature increase for both the uninhibited and inhibited solutions. The corrosion rate data were then fitted into Arrhenius kinetic model (Eq.10) and activation energy was determined from linear plots of $\log CR$ against reciprocal of temperature (Fig. 5). The activation energy obtained was higher in the presence of TDE than the free acid solution, depending on TDE concentration. Based on the concept of activation and collision theory, it can be considered that before the acid solution corrodes the metal surface, molecules of the acid must collide with the metal surface molecules. The acid molecules should possess energy up to a minimum threshold called the activation energy.

$$\log R = \log A - \frac{E_a}{2.303RT} \quad (10)$$

where E_a is the activation energy, A the Arrhenius frequency factor, R is the universal gas constant and T is absolute temperature. In the presence of the inhibitors, the activation energy was found to increase (Table 4). This implies that the acid molecules must acquire extra (higher) energy in the

inhibited solution for corrosion to occur, hence corrosion inhibition. Therefore, addition of TDE deepens the energy barrier well and increases the activation energy.

The other activation parameters given in Table 4 were derived from the transition state equation (Eq. 11). Linear plots of $\log\left(\frac{CR}{T}\right)$ against reciprocal of temperature (Fig. 6).

$$\log\left(\frac{CR}{T}\right) = \left[\left(\log\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S^\ddagger}{2.303R}\right)\right)\right] - \left(\frac{\Delta H^\ddagger}{2.303RT}\right) \quad (11)$$

where $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are the enthalpy and entropy change of activation respectively. The values of $\Delta S^\ddagger$ are all negative which implies that a decrease in disorderliness of the system takes place on moving from reactants to activated complex [25]. It also indicates that the activated complex in the rate determining step involves an association of inhibitor on metal surface instead of dissolution of the metal. The negative sign of $\Delta H^\ddagger$ reflects the exothermic nature of mild steel corrosion in HCl. Thermodynamically, it is consistent for an exothermic process with decreasing entropy to be spontaneous at temperatures that are not too high like those studied.

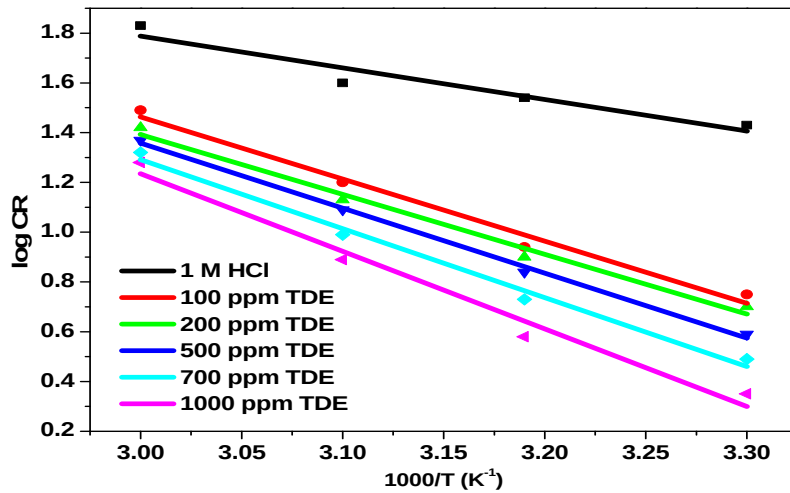


Figure 5. Arrhenius kinetic plot for TDE adsorption on mild steel in 1 M HCl solution

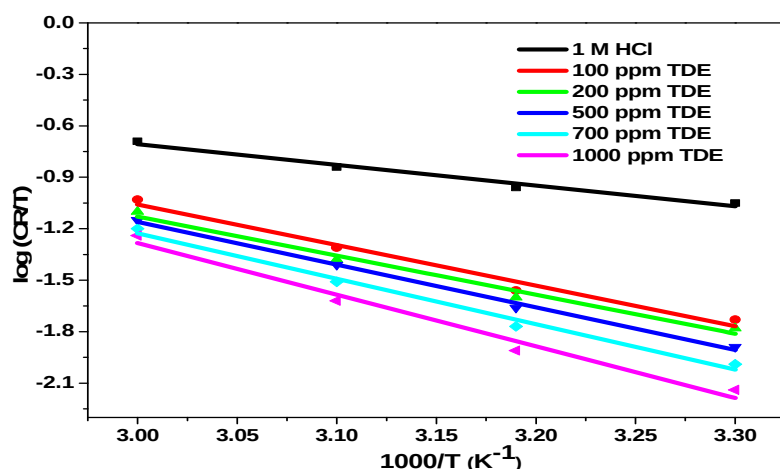


Figure 6. Transition state plot for TDE adsorption on mild steel in 1 M HCl solution

Table 4. Kinetic and Thermodynamic parameters for inhibition of mild steel corrosion in 1 M HCl by TDE

Solution	E_a (kJmol ⁻¹)	$\Delta H^\ddagger$ (kJmol ⁻¹)	$\Delta S^\ddagger$ (kJmol ⁻¹)
1 M HCl	16.51	-14.28	-0.18
100 ppm TDE	18.23	-19.44	-0.17
200 ppm TDE	21.46	-24.01	-0.17
500 ppm TDE	30.09	-28.97	-0.15
700 ppm TDE	36.77	-33.72	-0.13
1000 ppm TDE	41.38	-35.65	-0.12

3.4 Electrochemical studies

Many researchers have used electrochemical techniques especially EIS and PDP to explain corrosion of metals and their inhibition by different extracts [26, 27]. In EIS, emphasis is laid on measurement of the complex – impedance of the system under steady state as a function of frequency (f) or angular frequency (ω) of a sinusoidal perturbation of small amplitude. In this study, the data for the various frequencies were plotted as a set of points in the complex-impedance plane, with Z' and Z'' as x- and y-axes, called Nyquist plot or complex plane plots shown in Fig. 7 [28]. Analyses of the plot using electrical equivalent circuit model shown in Fig.8 yields some EIS parameters shown in Table 5 used to describe the corrosion process.

Results show that the shapes (depressed semicircles) of the plots for the different test solutions are similar, which indicates that the mechanism of corrosion is the same for the free acid solution and for the inhibited solutions. However, each depressed semicircle increases in radius according to the trend 1000 pm TDE > 500 ppm TDE > 100 ppm TDE > 1 M HCl as may be observed in Fig. 7. This trend is similar to the trend of increase in charge transfer resistance (Table 5) which implies that addition of TDE reduces conduction of charges to and fro the double layer between the metal and electrolyte.

This reduced conduction of charge can be attributed to corrosion inhibition resulting from thin surface insulating film of TDE formed on the steel surface through adsorption from solution. This thin film induces a double layer which capacitance as calculated decreases with increase in charge transfer resistance and TDE concentration. Inhibition efficiency increases with increase in TDE concentration, similar to trends observed with weight loss experiment.

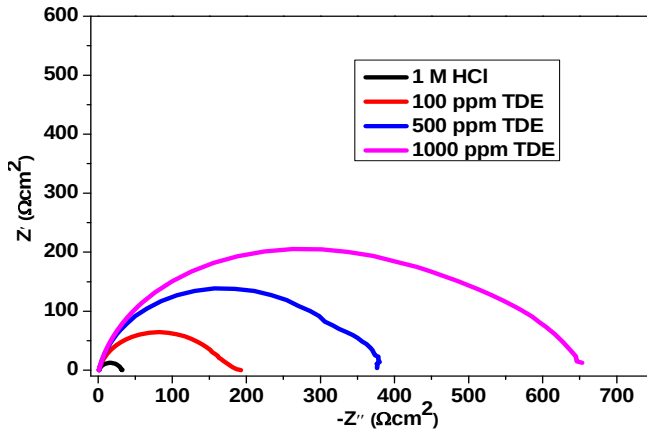


Figure 7. Nyquist plots for the inhibition of steel corrosion in 1 M HCl with and without different concentrations of TDE.

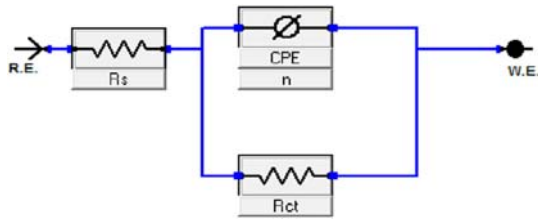


Figure 8. Equivalent circuit used for fitting of EIS data.

Table 5. Some EIS parameters obtained for inhibition of steel corrosion in 1 M HCl without and with different concentrations of TDE.

Parameters	1 M HCl	100 ppm TDE	500 ppm TDE	1000 ppm TDE
$R_s (\Omega\text{cm}^2)$	1.03 ± 0.06	1.12 ± 0.03	1.16 ± 0.04	1.21 ± 0.08
$R_{ct} (\Omega\text{cm}^2)$	32.44 ± 1.21	189.02 ± 3.15	374.76 ± 8.95	651.09 ± 7.06
$Y_o (\Omega^{-1}\text{s}^n\text{cm}^{-2})$	205.1	142.3	153.6	168.7
$\alpha (\times 10^{-3})$	857.4	889.1	881.7	872.4
Fit ($\times 10^{-3}$)	23.1	64.7	87.4	43.2
n	0.88	0.86	0.85	0.82
$C_{dl} (\mu\text{Fcm}^{-2})$	140.42	122.43	92.84	64.13
$\eta_{EIS} (\%)$	-	82.84	91.34	95.02

Data obtained from PDP were used to construct the Tafel plot shown in Fig. 9 and analyses of the plots by data fitting of the anodic and cathodic branches yield some parameters presented in Table 6.

It can be inferred from the results that the inhibited and non-inhibited solutions yielded similar shapes, confirming that the mechanism of corrosion is the same for all the test solutions. The obtained corrosion current densities decreased on addition of TDE and as TDE concentration decreases, implying that TDE addition leads to reduced current due to inhibitive effect of its adsorbed molecules on the steel surface. E_{corr} values shift to more positive values on addition of TDE but the shift is not up to -80 mV. From literature reports, such an inhibitor can be said to act as mixed type inhibitor with anodic predominance [29, 30]. The trend of inhibition efficiency obtained is similar to that of weight loss and EIS results.

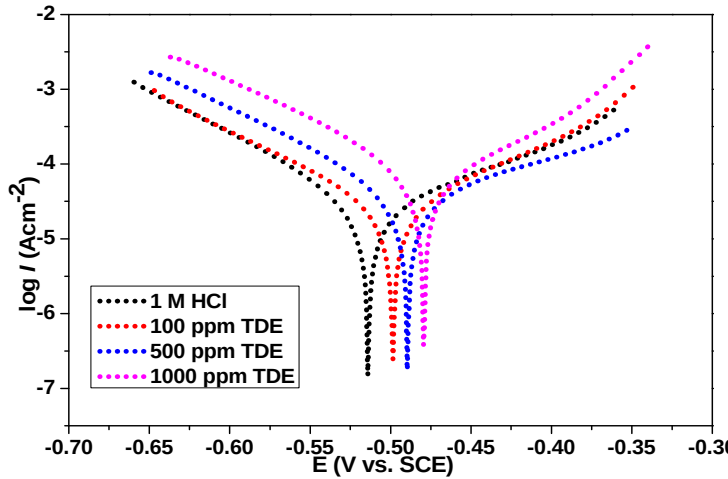


Figure 9. Tafel plots for the inhibition of steel corrosion in 1 M HCl with and without different concentrations of TDE.

Table 6. Some PDP parameters obtained for inhibition of steel corrosion in 1 M HCl without and with different concentrations of TDE.

Parameters	1 M HCl	100 ppm TDE	500 ppm TDE	1000 ppm TDE
β_a (mV/decade)	84.2	87.4	93.2	112.4
β_c (mV/decade)	94.6	86.4	80.3	81.7
I_{corr} (μAcm^{-2})	628.4	114.5	58.8	38.6
E_{corr} (mV)	-514	-498	-489	-478
η_{PDP} (%)	-	81.8	90.6	93.9

3.5 Sensitivity of TDE composites to geothermal gradient

It can be inferred from the inhibition efficiencies of TDE obtained that TDE alone can only inhibit the corrosion efficiently at surface conditions. In the field, where 1 M HCl can be used for descaling of tubular and casings, as the acid moves downhole, its temperature increases due to geothermal gradient. This results in increase in aggressiveness of the acid. Usually, many plant based corrosion

inhibitors are thermally degraded at downhole temperatures. To enhance the suitability of TDE, it was formulated with other green substances and tested under similar conditions as TDE. Results show that the composites show better inhibitive effects even at higher temperatures. For instance, the efficiency of TDE was 91.7 and 31.5 % efficient at 30 °C and 80 °C respectively. The efficiency increased to up to 99.8 and 85.9 % with TDECIFC which implies good performance at high temperature. However, since the composites were prepared in aqueous medium, evaporation of the bulk medium occurred above this temperature, so measurements at higher temperatures were difficult.

Table 7: Inhibition efficiency of TDE composites at different temperatures (in a broader range over 60°C, with higher ranges)

System	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C
1000 ppm TDE	91.7	88.9	83.5	72.1	52.6	31.5
TDE-PPA	93.7	92.1	87.5	78.9	67.6	51.6
TDECIFA	95.2	94.6	93.8	90.6	82.4	74.8
TDECIFB	97.3	97.0	95.2	92.4	85.8	78.2
TDECIFC	99.8	98.8	97.7	95.3	92.6	85.9

4. CONCLUSION

Green colloidal water-soluble corrosion inhibitor formulations from *Thaumatococcus daniellii* extract (TDE) and some local agro-wastes were investigated as alternative oilfield chemicals for inhibiting the corrosion of mild steel. These formulations effectively inhibit the corrosion of mild steel in 1M HCl at 30 to 60 °C. Adsorption of TDE molecules is by spontaneous physical adsorption mechanism and is best approximated by the Langmuir adsorption isotherm. TDE formulations could be exploited to produce an effective alternative eco-friendly oilfield corrosion inhibitor.

CONSENT

Not applicable

ETHICAL APPROVAL

Not applicable

REFERENCES

1. Ituen EB, Akaranta O, James AO, Sun S. Green anticorrosive oilfield chemicals from seeds and leaf extracts of *Griffonia simplicifolia* for mild steel. J. Chem. Mater. Res. 2016; 5: 45-57.
2. Brezinski MM, Desai B, inventors; Halliburton Energy Services, Inc., assignee. Method and composition for acidizing subterranean formations utilizing corrosion inhibitor intensifiers. United States patent US 1997; 5:697,443.
3. Walker ML, inventor; Halliburton Company, assignee. Method and composition for acidizing subterranean formations. United States patent US 1985; 4:552,672.
4. Finšgar M, Jackson J. Application of corrosion inhibitors for steels in acidic media for the oil and gas industry: a review. Corros. Sci. 2014; 86:17-41.
5. Yadav M, Sharma U. Non-toxic corrosion inhibitors for N80 steel in hydrochloric acid. Arabian Journal of Chem. 2016; 9:S1487-S1495.
6. Ituen E, Akaranta O, James A, Sun S. Green and sustainable local biomaterials for oilfield chemicals: *Griffonia simplicifolia* extract as steel corrosion inhibitor in hydrochloric acid. Sustainable Materials and Technologies 2017; 11:12-18
7. Brezinski MM. New environmental options for corrosion inhibitor intensifiers. InSPE/EPA exploration and production environmental conference 1999; 299-305.
- 8 Umoren SA, Solomon MM. Effect of halide ions on the corrosion inhibition efficiency of different organic species—a review. Journal of Industrial and Engineering Chemistry 2015; 21:81-100.
9. Walker ML, inventor; Halliburton Company, assignee. Method and composition for acidizing subterranean formations. United States patent US 1994; 5:366,643.
10. Ali S, Reyes JS, Samuel MM, Auzerais FM, inventors; Schlumberger Technology Corporation, assignee. Self-diverting acid treatment with formic-acid-free corrosion inhibitor. United States patent US 2011; 7: 902,124.
11. Barmatov E, Geddes J, Hughes T, Nagl M. Research on corrosion inhibitors for acid stimulation. In CORROSION 2012. NACE International.

328 12. Obot IB, Obi-Egbedi NO, Umoren SA, Ebenso EE. Synergistic and antagonistic effects of
 329 anions and *Ipomoea invulcrata* as green corrosion inhibitor for aluminium dissolution in
 330 acidic medium. Int. J. Electrochem. Sci. 2010; 5(7): 994-1007.

331 13. Eduok UM, Umoren SA, Udoh AP. Synergistic inhibition effects between leaves and
 332 stem extracts of *Sida acuta* and iodide ion for mild steel corrosion in 1M H₂SO₄ solutions.
 333 Arabian Journal of Chemistry, 2012; 5(3):325-337.

334 14. Yeboah SO, Hilger, TH, Kroschel, J. *Thaumatococcus daniellii* (Benn.) Benth. – A
 335 natural sweetener from the rain forest zone in West Africa with potential for income
 336 generation in small scale farming. J. Applied Sci. 2003; 6:854-859.

337 15. Arowosoge OGE, Popoola L. Economic analysis of *Thaumatococcus daniellii*
 338 (miraculous berry) in Ekiti State. Nig. J. Food Agric. Environ 2006; 41:264-269.

339 16. Osemeobo JG. Living on wild plants: Evaluation of the rural household economy in
 340 Nigeria. Cambridge Journal 2005; 7:246-256.

341 17. Van der Wel H, Loeve K. Isolation and characterization of thaumatin I and II, the sweet-
 342 tasting proteins from *Thaumatococcus daniellii* benth. Eur. J. Biochem., 1972; 31: 221-225.

343 18. Udoetok IA. Characterization of ash made from oil palm empty fruit bunches (oefb). Int.
 344 J. Environ. Sci. 2012; 3:518-24.

345 19. Ituen EB, Akaranta O, Umoren SA. N-acetyl cysteine based corrosion inhibitor
 346 formulations for steel protection in 15% HCl solution. Journal of Molecular Liquids 2017;
 347 246:112-118

348 20. Alvarez PE, Fiori-Bimbi MV, Neske A, Brandán SA, Gervasi CA. *Rollinia occidentalis*
 349 extract as green corrosion inhibitor for carbon steel in HCl solution. Journal of Industrial and
 350 Engineering Chemistry 2018; 58:92-99.

351 21. Hassannejad H, Nouri A. Sunflower seed hull extract as a novel green corrosion inhibitor
 352 for mild steel in HCl solution. Journal of Molecular Liquids 2018; 254(1):377-382.

353 22. Qiang Y, Zhang S, Tan B, Chen S. Evaluation of *Ginkgo* leaf extract as an eco-friendly
 354 corrosion inhibitor of X70 steel in HCl solution. Corrosion Science 2018; 133: 6-16

355 23 Ituen E, Akaranta O, James A. Evaluation of performance of corrosion inhibitors using
 356 adsorption isotherm models: an overview. Chem Sci Int J. 2016; 18: 1-34.

357 24. Amar H, Benzakour J, Derja A, Villemin D, Moreau B, Braisaz T. Piperidin-1-yl-
 358 phosphonic acid and (4-phosphono-piperazin-1-yl) phosphonic acid: a new class of iron
 359 corrosion inhibitors in sodium chloride 3% media. Applied surface science 2006; 252 (18):
 360 6162-6172.

- 361 25. El-Meligi AA. Hydrogen production by aluminum corrosion in hydrochloric acid and
362 using inhibitors to control hydrogen evolution. International Journal of Hydrogen Energy
363 2011; 36(17):10600-10607.
- 364 26. Srivastava M, Tiwari P, Srivastava SK, Kumar A, Ji G, Prakash R. Low cost aqueous
365 extract of *Pisum sativum* peels for inhibition of mild steel corrosion. Journal of Molecular
366 Liquids 2018; 254:357-368
- 367 27. Saxena A, Prasad D, Haldhar R, Singh G, Kumar A. Use of *Saraca ashoka* extract as
368 green corrosion inhibitor for mild steel in 0.5 M H₂SO₄. Journal of Molecular Liquids 2018;
369 258 (15): 89-97.
- 370 28. Bard AJ, Inzelt G, Scholz F. (Eds.). Electrochemical dictionary. Springer Science &
371 Business Media 2008.
- 372 29. Sin HLY, Rahim AA, Gan CY, Saad B, Salleh MI, Umeda M. *Aquilaria subintergra*
373 leaves extracts as sustainable mild steel corrosion inhibitors in HCl. Measurement 2017;109:
374 334-345.
- 375 30. Alibakhshi E, Ramezanzadeh M, Bahlakeh G, Ramezanzadeh B, Mahdavian M,
376 Motamedi M. *Glycyrrhiza glabra* leaves extract as a green corrosion inhibitor for mild steel
377 in 1 M hydrochloric acid solution: Experimental, molecular dynamics, Monte Carlo and
378 quantum mechanics study. Journal of Molecular Liquids 2018; 255:185-198.