Int. J. Electrochem. Sci., 7 **(2012)** 7425 - 7439

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Corrosion Inhibition Potential of *Daniella Oliverri* Gum Exudate for Mild Steel in Acidic Medium

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Received: 9 June 2012 / *Accepted:* 16 July 2012 / *Published:* 1 August 2012

Physicochemical parameters of *Daniella olliverri* (DO) gum exudates were analyzed and the results indicated that the gum is acidic, brownish in colour, ionic and highly soluble in water but insoluble in acetone, chloroform and ethanol. GCMS spectrum of the gum indicated the presence of sucrose, dihex-5-en-2-yl phthalate, stearic acid, 2,6-dimethyl-4-nitrophenol and (E)-hexadec-9-enoic acid. Corrosion inhibition potential of the gum was investigated using weight loss and FTIR methods. *Daniella olliverri* gum has been found to be a good inhibitor for the corrosion of mild steel in HCl solution. Corrosion inhibition properties of the gum is attributed to the presence of aromatic, suitable functional groups and heteroatoms in its chemical constituents, which facilitated its adsorption. The adsorption of the gum on the surface of the metal was found to be endothermic, spontaneous and supported the mechanism of physical adsorption. The results obtained obeyed the Langmuir adsorption isotherm model.

Keywords: *Daniella olliverri* gum, physiochemical parameters, corrosion inhibition

1. INTRODUCTION

Gums are needed as recipient in pharmaceutical, food and cosmetic industries [1]. Gums are usually considered as any sticky substance that exudes form certain plants. It hardens on exposure to air and dissolves or forms viscous masses in water. In terms of solvent loving characteristics, gums are either hydrophobic or hydrophilic. They are high molecular weight molecules usually with colloidal properties [2].

Several studies have been carried out and reported for some plant gums and it is generally accepted that industrial utilization of a given gum depends on its physiochemical and rheological properties. For example, Mothe and Roa [3] stated that chemical and rheological parameters of gum solutions are useful in quality control, correlation with sensory assessment, handling applications and characterization of the size and shape of gum molecules. In their study, de Paula [2] found that *Albezia lebbeck* gum exudates are useful in the food industries because of their galactose, albinose and uronic acid content. Guar gum has a number of applications in the mining and mineral processing industry [4].

In the froth flotation of base metal and platinum group metal ores, guar gum is used as a depressant of naturally hydrophobic waste minerals, such as talc. The role of the polysaccharide is to adsorb on the talc surface, render it hydrophilic, and prevent its flotation. A wide variety of modified guar gums are available for this application. Natural guar gum is also employed as a binder of water-insoluble, ultrafine minerals in the froth flotation of potash ores [5]. Some gums have also been found to be good corrosion inhibitors for the corrosion of metals in acidic solutions. According to Eddy *et al*., [6], gums have been found to be good corrosion inhibitors due to the following reasons;

i. Through their functional groups, they form complexes with metal ions and on the metal surfaces.

ii. Gum-metal complexes occupy a large surface area, thereby blanketing the surface and protecting the metals from corrosive agents present in the solution.

iii. the presence of arabinogalactan, sucrose, oligosaccharides, polysaccharides and glucoproteins since these compounds contain oxygen and nitrogen atoms which are the centers of adsorption

iv. Most gums have COOH functional groups, which can enhance the donation of electron or charge transfer and hence facilitate inhibition through adsorption.

v. Most gums are less toxic, green and eco-friendly.

In view of the numerous advantages offered by some gums for corrosion inhibition systems, some researches have been carried out. For example, Umoren *et al* [7] reported the potential of *Gum Arabic* as corrosion inhibitor for aluminium in alkaline medium. The inhibition of aluminium corrosion by *Gum Arabic* was attributed to the presence of arabinogalactan, oligosaccharides, polysaccharides and glucoproteins The inhibitive effect of exudate gum from *Dacroydes edulis* in the corrosion of aluminium in HCl solutions was studied using weight loss and thermometric methods at 30-60^{o}C by Umoren *et al* [8] The results revealed that the exudate gum acted as an inhibitor for corrosion of aluminium in HCl solution. The inhibition efficiency of the gum was found to increase with increase in the concentration of the exudate gum but decreases with increase in temperature. The effect of naturally occurring exudate gum from *Raphia hookeri* (RH) on the corrosion of mild steel in H_2SO_4 in the temperature range 30-60 ^{o}C was also investigated by Umoren *et al* [9] using weight loss and hydrogen evolution techniques. Results obtained indicated that the exudate gum reduces the corrosion rate of mild steel. The adsorption of exudate gum from *Raphia hookeri* on the mild steel supported the Langmuir adsorption model. *Guar gum* has been shown to be an effective corrosion inhibitor for metal in aggressive acid environment by Abdallah [10]. Results obtained show that the gum acted as effective corrosion inhibitor in the different test media. Inhibition efficiency was found to increase with increase in the concentration of the tested material. Eddy et al. [6] found that *Anogessus leocarpus gum exudates* is a good corrosion inhibitor for the corrosion of mild steel in solutions of

HCl. They attributed the inhibition potential of the gum exudates to the presence of sucrose (10.03 %), phthalic acid (2.53 %), n-hexadecanoic acid (11.73 %), oleic acid (30.49 %), pentacenequinone (4.41 %) and 2,3- diphenylnaphthoquinone (21.43 %), which facilitated the adsorption of the inhibitor on the metal surface. This study therefore investigates the physicochemical properties and corrosion inhibition potential of *Daniella olliverri* (DO) gum exudates using weight loss method.

2. MATERIALS AND METHODS

2.1. Collection of Gum Sample

Samples of *Daniella oliverra* gum (DO-gum) were collected from mature stem of the plant during dry season. The gum was collected by tapping. A small axe was used to break the outer bark. Tapping was carried out by driving an area underneath the bark which was pulled back until the bark broke horizontally to give two broken edges. The cut was extended to about 4.0 cm wide and the bark was carefully pealed in two directions (both upward and downward) to form a (0.5-10m) wound. Gums formed slowly were collected along the length of the wounded trunk.

2.2. Purification of Gum

The gum was dissolved in cold distilled water and the clear solution was strained through muslin and was then centrifuged, depositing a small quality of dense gel. The clear straw-coloured supernatant liquor was separated and acidified to acidic pH with dilute hydrochloric acid. 80% of ethyl alcohol was slowly added and the gum precipitated was removed by centrifugation, washed with alcohol followed by ether and then dried.

2.3. Physicochemical analysis

In order to obtain the percentage yield of the gum; dried, precipitated and purified samples of DO-gum were obtained and weighed. The percentage yield was estimated with reference to the weight of the crude gum.

The solubility of the gums was determined in cold water, hot water, acetone, chloroform and ethanol. 1.0 g of the gum was added to 50 ml of the respective solvents and left overnight. 25 ml of the clear supernatants were taken in small pre- weighted evaporating dishes and heated to dryness over a digital thermostatic water bath. The weights of the residue with reference to the volume of the solutions were determined using a digital top loading balance (Model.XP-3000) and expressed as the percentage solubility of the gums in the solvents.

This was done by shaking 1% w/v dispersion of each of the sample in water for 5 minutes and the pH was determined using a pre-calibrated Oaklon pH meter (Model 1100). The electrode of the pH meter was immersed into the gum and the pH value was read directly through the meter's read out system.

2.4. Corrosion Inhibition Studies

Materials used for the study were mild steel of composition Mn (0.6), P (0.36), C (0.15) and Si (0.03) and the rest Fe. The sheet was mechanically pressed cut into different coupons each of dimension 5 x 4 cm. Each coupon was 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. Concentration of HCl used for the study was 0.1 M.

2.4.1. Gravimetric Method

In the gravimetric experiment, a previously weighed coupon was completely immersed in 250 ml of the test solution in an open beaker. The beaker was covered with aluminium foil and inserted into a water bath maintained at 303 K. After 24 hours, the corrosion product was removed by washing each coupon (withdrawn from the test solution) in a solution containing 50 % NaOH and 100 gl^{-1} of zinc dust. The washed coupon was rinsed in acetone and dried in the air before reweighing. 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 mild steel (CR) were calculated using the following equations,

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

$$\theta = (1 - \frac{W_1}{W_2}) \qquad 2$$

$$CR = \frac{W_2 - W_2}{At} \qquad 3$$

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

2.5. Chemical analysis of samples

2.5.1. FTIR analysis

FTIR analyses of purified sample of *Daniella oliverra* gum and that of the corrosion products (in the absence and presence of *Daniella oliverra* gum) were carried out using Shimadzu FTIR-8400S Fourier transform infra-red spectrophotometer The sample was prepared using KBr and the analysis was done by scanning the sample through a wave number range of 400 to 4000 cm^{-1}.

2.5.2. GC-MS analysis

GC-MS analysis was carried out on a GC clarus 500 Perkin Elmer system comprising a AOC-20i auto sampler and gas chromatograph interfaced to a mass spectrometer (GC-MS) instrument employing the following conditions: column

Elite-1 fused silica capillary column (30 x 0.25 mm ID x 1μM df, composed of 100% Dimethyl poly diloxane), operating in electron impact mode at 70 eV; helium (99.999%) was used as carrier gas at a constant flow of 1 ml /min and an injection volume of 0.5 μI was employed (split ratio of 10:1) injector temperature 250 ºC; ion-source temperature 280 ºC. The oven temperature was programmed from 110 ºC (isothermal for 2 min), with an increase of 10 ºC/min, to 200 ºC, then 5 ºC/min to 280 ºC, ending with a 9 min isothermal at 280 ºC. Mass spectra were taken at 70 eV; a scan interval of 0.5 seconds and fragments from 40 to 450 Da. Total GC running time was 36min.

Interpretation on mass spectrum GC-MS was conducted using the database of National Institute Standard and Technology (NIST) having more than 62,000 patterns. The spectrum of the unknown component was compared with the spectrum of the known components stored in the NIST library. The name, molecular weight and structure of the components of the test materials were ascertained. Concentrations of the identified compounds were determined through area and height normalization.

3. RESULTS AND DISCUSSIONS

3.1. Physiochemical parameters

Table 1. Physicochemical properties of *Daniella oliverri* gum

Parameters	
Colour	Dark brown
Odour	Odourless
Taste	Bland
pH	4.4
%yield	48.0
Solubility in water	4.9
Solubility in ethanol	0.00
Solubility in acetone	0.00
Solubility in chlorofoam	0.00

Table 1 shows values of physiochemical parameters (colour, odour, taste, pH, and percentage yield, solubility in water, ethanol, acetone and chloroform) of *Daniella oliverra* gum. The colour of the crude gum was found to be dark brown (Fig. 1), the gum was found to be odourless with characteristic bland taste. The percentage yield for the gum was 48 % and its pH was 4.4. This indicates that the gum is mild acidic. DO-gum was found to be insoluble in acetone, ethanol and chloroform but soluble in water (solubility = 4.9 %) indicating that the gum is ionic. Ionic or polar compounds are soluble in solvents (such as water and other solvents) that have high dielectric constant. Ethanol, acetone and chloroform are organic solvent and are characterized with low values of dielectric constant. As a rule, polar compounds dissolve in polar solvents while non-polar compounds are soluble in non-polar solvents.

Figure 1. Photograph of crude sample of *Daniella oliverra*

3.2. GC-MS study of Daniella oliverra gum

The GC-MS spectrum of *Daniella oliverra* gum was presented six peaks with characteristics parameters presented in Table 2. Chemical structures of compounds suggested by reliable spectral library are presented in Fig. 2. Since the area (and height) under a chromatogram is proportional to the concentration of the active specie, data obtained from area normalization of the respective peaks were used in calculating the concentrations of the active constituents of the gum and the results obtained are also presented in Table 2.

Table 2. Characteristics of suggested compounds identified from GC-MS of *Daniella olliverri* gum

Line No	IUPAC Name	Molecular formula	Molar mass (g/mol)	RT(s)	Mass peak	% Conc.	Fragmentation peaks
1	Sucrose	$C_{12}H_{22}O_{11}$	342	14.642	20	26.89	40(10%), 42(20%),43(40%), 57(100%), 73(50%) , 86(10%).
2	dihex-5-en-2-yl phthalate	$C_{20}H_{26}O_4$	330	24.467	28	3.21	40(2%), 50(40%), 65(50%), 76(47%), 93(40%),104(50%),121(30%), 149(100%),177(50%).
3	hexadecanoic acid	$C_{16}H_{32}O_2$	256	27.942	58	16.59	40(2%), 41(90%), 65(100%), 69(70%), 83(60%), 97(50%) 98(40%), 112(20%), 127(5%) 207(2%), 220(2%), 264(5%).
4	(E)-hexadec-9-enoic acid	$C_{16}H_{30}O_2$	254	29.108	72	35.38	40(2%), 41(90%), 55(100%), 69(70%), 83(60%), 97(50%), 98(40%), 112(20%), 127(5%), 207(2%), 220(2%), 264(5%).
5	Stearic acid	$C_{18}H_{36}O_2$	284	29.250	60	14.54	40(2%), 41(70%), 43(100%), 57(60%), 73(80%), 85(30%), 98(20%), 116(10%), 129(20%), 171(5%), 185(20%), 199(10%), 213(2%), 227(10%), 241(20%), 284(40%).
6	2,6-dimethyl-4-nitrophenol	$C_8H_9NO_3$	167	31.117	49	3.40	40(2%), 51(20%), 66(30%), 77(40%), 91(2%), 107(70%), 122(30%), 167(100%), 168(30%), 274(50%), 281(2%).

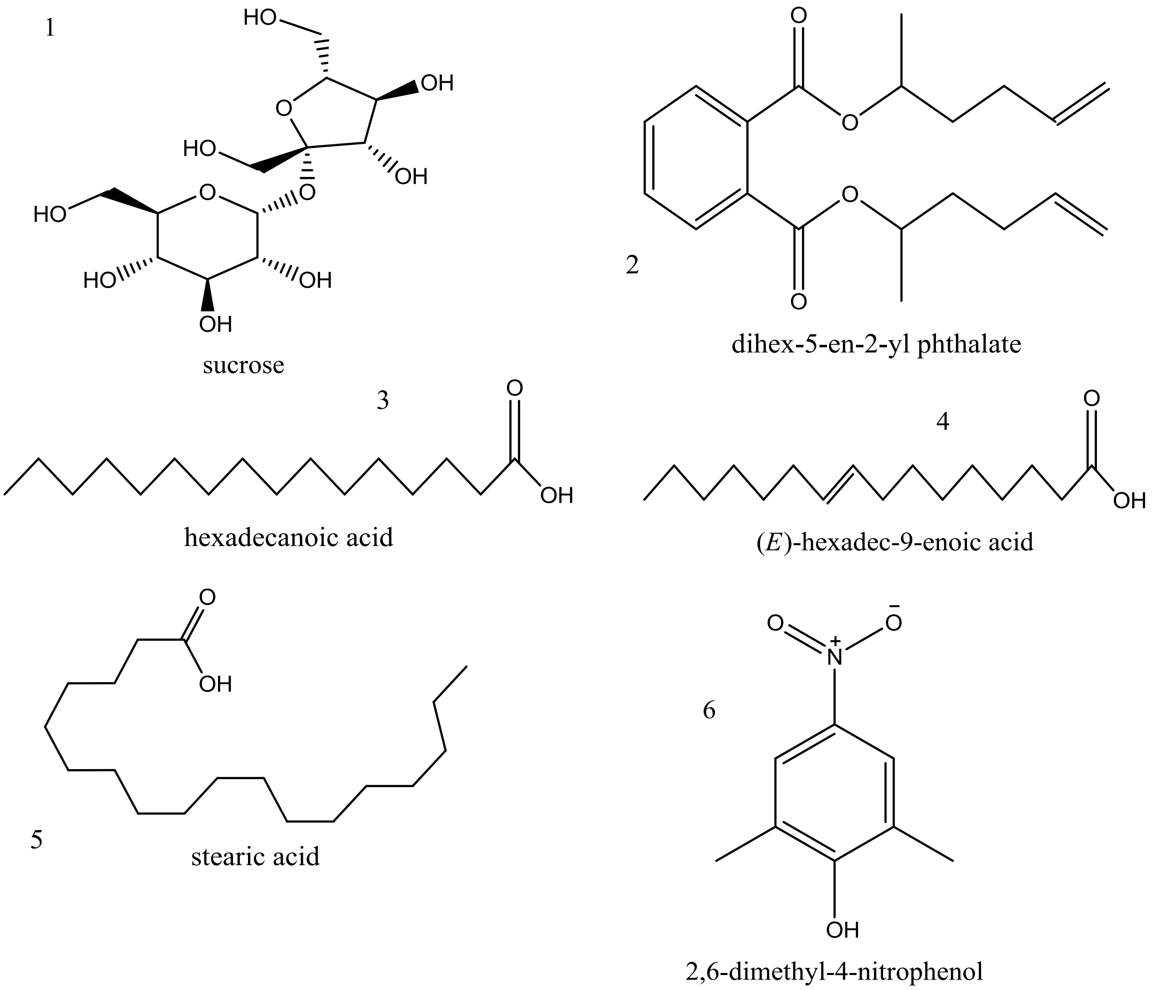

Figure 2. Chemical structures of compounds identified in the GCMS spectrum of Daniella olliverri gum (Numbering on the structures correspond to the line number in the GC-MS spectrum)

Also presented in Table 2 are the chemical names of the compounds, the retention time for each peak (RT), mass peak and fragmentation peaks. Line 1 of the GCMS spectrum of *Daniella oliverra* gum revealed the presence of 26.89 % of sucrose (second most abundant constituents) with a characteristics retention time of 14.642 minutes. Six fragmentation peaks, base peak value of 57 and mass peak value of 20 were also components of this line. In line 2, 3.21 % of an ester, dihex-5-en-2-yl phthalate was identified. This was found to be the least abundant constituents of *Daniella oliverra* gum. The compound was characterized by a retention time value of 24.467 minutes and eight fragmentation peaks. Line 3, 4 and 5 indicated the presence of 16.59, 35.38 and 14.54 % of hexadecanoic acid, (E)-hexadec-9-enoic acid and stearic acid. These acids are carboxylic acid and were characterized with retention time values of 27.942, 29.108 and 29.250 minutes respectively. Their mass peak values were 58, 72 and 60 respectively. In line 6, 3.40 % of phenol derivative (2,6-dimethyl-4-nitrophenol) was identified under the RT and mass peak values of 31.117 minutes and 49 respectively.

3.3. FTIR study on Daniella olliverri gum

FTIR spectrum of *Daniella olliverri* gum indicated nine prominent peaks. Frequencies and peaks of IR adsorption as well as associated functional group deduced from the FTIR spectrum of the gum are presented in Table 3.

Table 3. Peaks and intensity of adsorption of FTIR by *Daniella olliverri* gum

Peak (cm-1)	Intensity	Assignment (functional group)
1052.20	15.598	C-O stretch, alcohol, carboxylic acid, ester, ether
1247.02	34.587	C-O stretch, alcohol, carboxylic acid, ester, ether
1385.90	34.415	C-H scissoring and bending, alkanes
1423.51	32.998	Aromatic C=C stretch
1614.47	32.572	N-H bend, amine
1731.17	47.844	C=O stretch, alcohol, phenol, carboxylic acid
2139.13	62.839	C≡C stretch, alkyne
2933.83	32.959	OH aliphatic stretch
3380.36	15.635	OH stretch

The results obtained indicated the presence of C-O stretch at 1052.20 and 1247.02 cm^{-1}, C-H scissoring and bending vibrations due to alkene (1385.90 cm^{-1}), aromatic C=C stretch at 1423.51 cm^{-1}, N-H bending vibration due to amine (at 1614.47 cm^{-1}) C=O stretch due to phenol at 1731.17 cm^{-1}, C≡C due to alkynes' at 2139.13 cm^{-1}, OH aliphatic stretch at 2933.83 and OH stretch at 3380.36 cm^{-1}.

3.4. Corrosion inhibition study

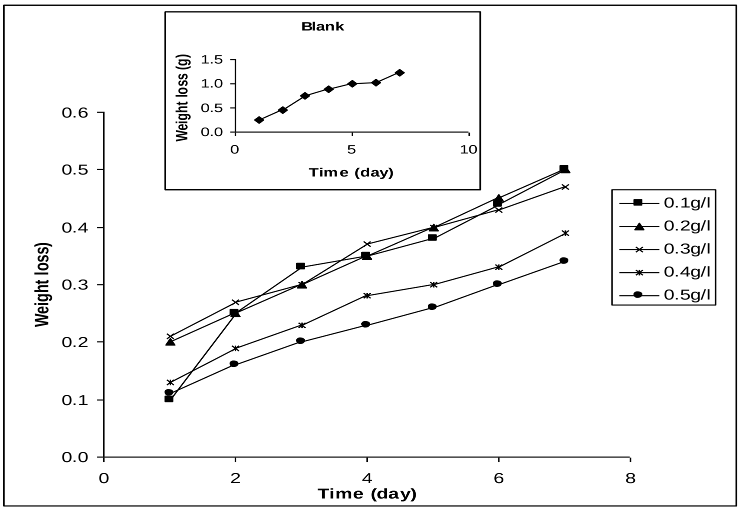

Figure 3. Variation of weight loss with time for the corrosion of mild steel in solutions of HCl containing various concentrations of *Daniella olliverri* gum (insert is the plot for the blank) at 303 K

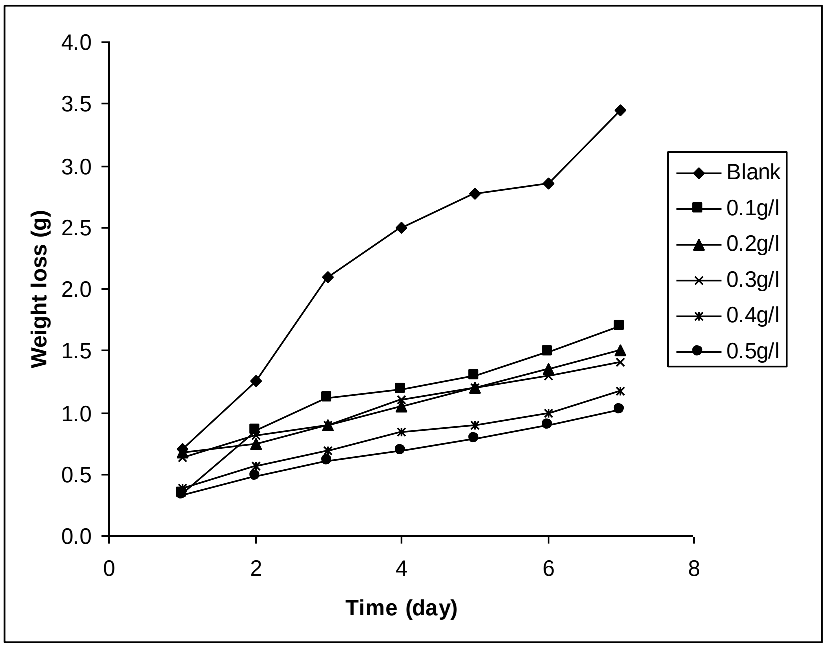

Figure 4. Variation of weight loss with time for the corrosion of mild steel in solutions of HCl containing various concentrations of *Daniella olliverri* gum.

Figs. 3 and 4 show plots for the variation of weight loss with time for the corrosion of mild steel in 0.1 M HCl containing various concentrations of *Daniella olliverri* gum at 303 and 333 K respectively. From the plots, it is evident that weight loss of mild steel decreases with increase in the concentration of *Daniella olliverri* gum but increase with increasing temperature and with the period of contact. These indicate that the rate of corrosion of mild steel increases with increase in temperature and with the period of contact and that *Daniella olliverri* gum inhibited the corrosion of mild steel in solutions of HCl.

Table 4. Corrosion rates (CR) and inhibition efficiencies (%I) of *Daniella olliverri* gum

C (g/l)	CR x 104 at 303 K	CR x 104 at 333 K	% I (303 K)	%I (333 K)
Blank	3.66	10.25		
0.1	1.49	5.06	59.35	50.639
0.2	1.49	4.46	59.35	56.446
0.3	1.40	4.20	61.79	59.059
0.4	1.16	3.48	68.29	66.028
0.5	1.01	3.04	72.36	70.383

Table 4 presents corrosion rates of mild steel and inhibition efficiencies of various concentrations of *Daniella olliverri* gum in various media. From the results obtained, it is evident that the corrosion rate of mild steel increases with temperature but decreases with increase in the concentration of *Daniella olliverri* gum. However, inhibition efficiency of *Daniella olliverri* gum increases with increase in concentration but decreases with increasing temperature. These indicate that *Daniella olliverri* gum is an adsorption inhibitor for the corrosion of mild steel in solution of HCl and that the adsorption of the inhibitor favours the mechanism of physical adsorption. For a physical adsorption mechanism, the inhibition efficiency, hence the extent of adsorption tends to decrease with increase in temperature but for a chemical adsorption mechanism, the reverse is the expected [11].

3.4.1. Kinetic of inhibition of mild steel corrosion by Daniella olliverri gum

The kinetic of the corrosion of mild steel in solution of HCl, in the presence and absence of *Daniella olliverri* gum was studied by fitting data obtained from weight loss measurements to expected plots for different reactions order. The results obtained indicated that the plot of – log(weight loss) versus time were linear for all concentrations of *Daniella olliverri* gum. This indicate that the corrosion of mild steel and its inhibition by *Daniella olliverri* gum is consistent with a first order kinetic, which can be written as follows [12],

$$-\log(\text{weight loss}) = k_1 t/2.303 \qquad 4$$

where k_1 is the first order rate constant and t is the time in day. Fig. 5 show kinetic plots for the corrosion of mild steel in 0.1 M HCl and its inhibition by *Daniella olliverri* gum.

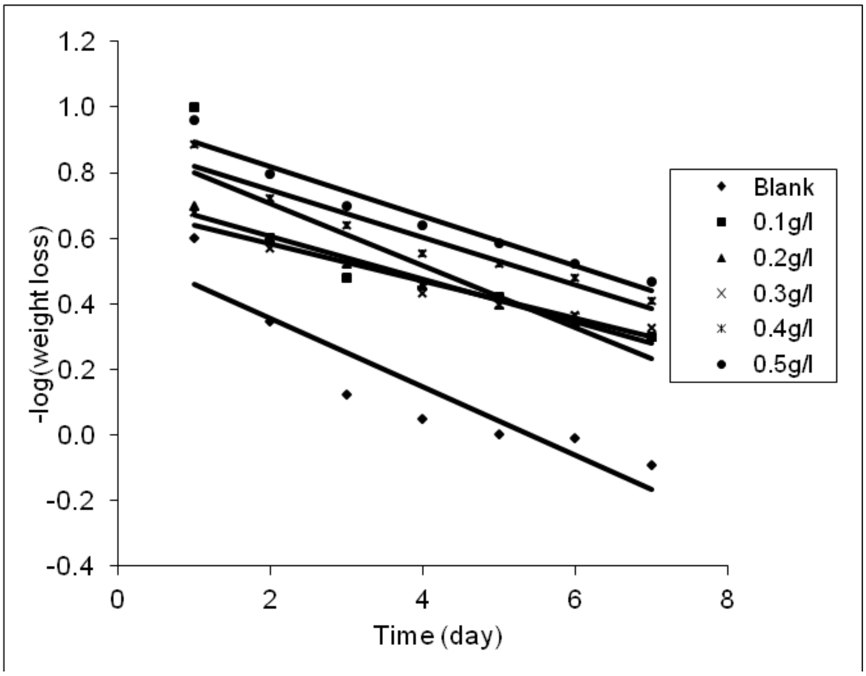

Figure 5. Variation of –log(weight loss) versus time for the corrosion of mild steel in solutions of HCl containing various concentrations of *Daniella olliverri* gum at 303 K

Table 5. Kinetic parameters for the corrosion of mild steel in 0.1 M HCl containing various concentrations of *Daniella olliverri* gum at 303 and 333 K

C (g/l)	k_1		$t_{1/2}$ (day)		R^2	
	303 K	333 K	303 K	333 K	303 K	333 K
Blank	0.2391	0.2386	2	2	0.8445	0.8445
0.1	0.2179	0.2179	3	3	0.7659	0.7658
0.2	0.1504	0.1370	5	5	0.9828	0.9936
0.3	0.1299	0.1322	5	5	0.9547	0.9547
0.4	0.1667	0.1660	4	4	0.9358	0.9458
0.5	0.1753	0.1683	4	4	0.9512	0.9623

Values of kinetic parameters deduced from the plots are presented in Table 5. Also for a first order reaction, the rate constant is related to the half-life according to the following equation,

$$t_{1/2} = 0.683/k_1 \qquad 5$$

Calculated values of $t_{1/2}$ are also presented in Table 5. From the results, it is evident that *Daniella olliverri* gum increases the half-life of mild steel in solutions of HCl.

3.4.2. Effect of temperature

The effect temperature on the corrosion of mild steel in the absence and presence of *Daniella olliverri* gum, was studied using the Arrhenius equation, which can be written as follows [13],

$$\log \frac{CR_2}{CR_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad 6$$

where E_a is the activation energy, CR_1 and CR_2 are the corrosion rates of mild steel at the temperatures T_1 (303 K) and T_2 (333 K) respectively. Calculated values of E_a, which ranged from 30.72 to 34.23 kJ/mol are presented in Table 6.

Table 6. Heat of adsorption and activation energy for the inhibition of the corrosion of mild steel in solutions of HCl by *Daniella olliverri* gum

Concentration of Daniella olliverri gum (g/l)	E_a (kJ/mol)	Q_{ads} (kJ/mol)
0.0	28.83	
0.1	34.23	-7.40
0.2	30.72	-2.50
0.3	30.74	-2.40
0.4	30.78	-2.15
0.5	30.81	-2.03

The results revealed that the activation energies for the inhibited systems are higher than that of the blank. Therefore *Daniella olliverri* gum retarded the rate of corrosion of mild steel by increasing the activation energy. Also, the activation energies are within the range of values expected for the mechanism of physical adsorption. Therefore, the adsorption of *Daniella olliverri* gum on mild steel surface is consistent with the mechanism of physical adsorption.

3.4.3. Thermodynamics/adsorption study

Since the corrosion inhibition was carried out at constant pressure, the heat adsorbed should approximate the enthalpy change. In this study, the heat of adsorption of *Daniella olliverri* gum was calculated using the following equation [14],

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right]x\left(\frac{T_1 x T_2}{T_2 - T_1}\right)kJmol^{-1} \qquad 7$$

where θ_1 and θ_2 are the degrees of surface coverage of the inhibitor at temperatures, T_1 (303 K) and T_2 (333 K) respectively and R is the gas constant. Calculated values of Q_{ads} are also recorded in Table 6. These values are positive indicating that the adsorption of *Daniella olliverri* gum on mild steel surface is endothermic.

The adsorption characteristics of *Daniella olliverri* gum was also investigated by fitting data obtained for the degree of surface coverage of the inhibitor into various adsorption isotherms namely Langmuir, Freundlich, Temkin, El- Awardy, Frumkin and Flory Huggins adsorption isotherms. The tests indicated that Langmuir isotherm best described the adsorption characteristics of the inhibitor. The assumptions establishing the Langmuir adsorption model can be written as follows [15],

$$C/\theta = C + 1/K_{ads} \qquad 8$$

$$\log(C/\theta) = \log C - \log K_{ads} \qquad 9$$

where C is the concentration of the inhibitor in the bulk electrolyte, K is the adsorption equilibrium constant and θ is the degree of surface coverage of the inhibitor.

Fig. 6 presents the Langmuir isotherms for the adsorption of *Daniella olliverri* gum on mild steel surface. Values of adsorption parameters deduced from the plots are presented in Table 7.

The equilibrium constant of adsorption calculated from the intercept of the Langmuir plot is related to the standard free energy of adsorption according to the following equation [16 - 17],

$$\Delta G^0_{ads} = -2.303RT\log(55.5*K_{ads}) \qquad 10$$

where ΔG^0_{ads} is the standard free energy of adsorption of ethanol extract of *Daniella olliverri* on mild steel surface, R is the universal gas constant and K_{ads} is the equilibrium constant of adsorption.

Calculated values of free energy of adsorption are also presented in Table 7. The free energies are negatively less than the threshold value of -40 kJ/mol, thereby supporting the mechanism of physical adsorption.

Table 7. Langmuir parameters for the adsorption of *Daniella olliverri* gum on mild steel surface

T (K)	Slope	$\log K_{ads}$	ΔG^0_{ads} (kJ/mol)	R^2
303	0.8793	0.1231	-10.8	0.9934
333	0.8010	0.1048	-10.7	0.9967

Therefore, the adsorption of *Daniella olliverri* on mild steel surface is spontaneous and supports the mechanism of charged transfer from the charged inhibitor to the charged metal surface.

3.4. 4. Mechanism of inhibition of the corrosion of mild steel by Daniella olliverri gum

Corrosion inhibitors are compounds whose chemical structures have aromatic systems with hetero atoms (such as N, O, S, P) that can facilitate the adsorption of the inhibitors on the surface of the metal. Also, the presence of functional groups such as C=O and –OH have been found to facilitate or enhance the adsorption of an inhibitor. A careful examination of the chemical structures of compounds in *Daniella olliverri* gum reveals that they could be potential corrosion inhibitors because they have met at least one of the expected requirements.

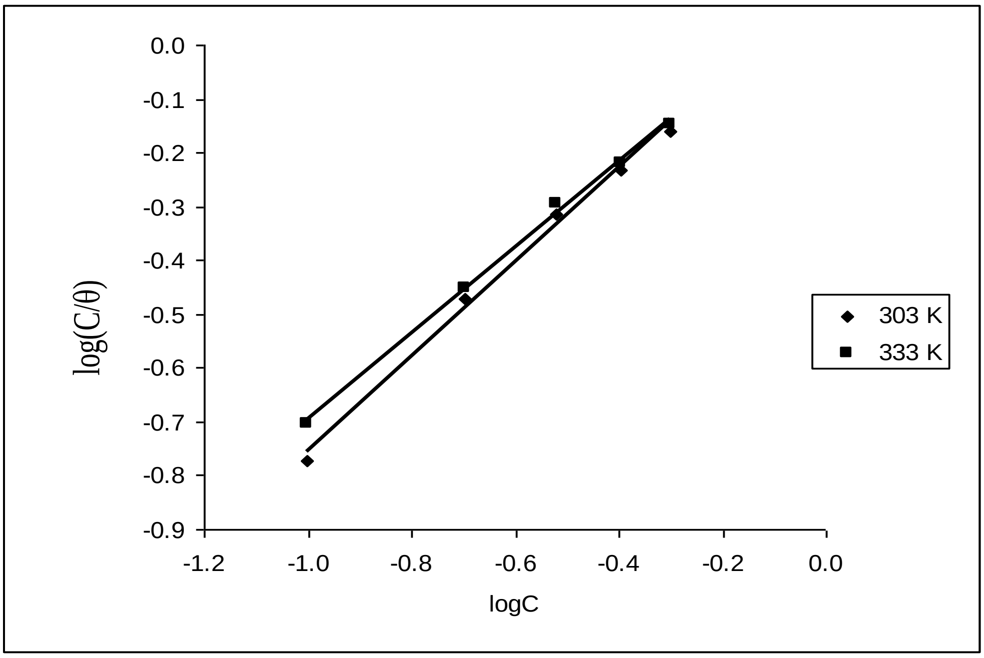

Figure 6. Langmuir adsorption isotherm of *Daniella olliverri* gum on mild steel surface

Table 8. Peaks and intensity of adsorption of FTIR by corrosion product

Peak (cm^{-1})	Intensity	Assignment (functional group)
870.89	55.3994	C-H bend, phenyl ring substitution band
1017.48	58.5721	C-O stretch, alcohol, carboxylic acid, ester, ether
1392.65	53.1186	C-H scissoring and bending, alkanes
1640.51	44.6424	N-H bend, amine
3169.15	23.3405	OH aliphatic stretch
3305.14	23.6597	OH stretch

Having established that the mechanism of inhibition is through the adsorption of the inhibitor, it was necessary to study the functional groups that are involved in the adsorption of the inhibitor. The study was carried out by comparing functional groups in the FTIR of pure sample of *Daniella olliverri* gum and that of the corrosion product of mild steel when *Daniella olliverri* gum was used as an inhibitor (Fig. 8). In the light of this, it was found that C-O stretch at 1247.02 cm^{-1} was shifted to 1017.48 cm^{-1}, N-H bend at 1614.47 cm^{-1} was shifted to 1640.51 cm^{-1}, OH aliphatic stretch at 2933.83 cm^{-1} was shifted to 2933.83 cm^{-1} and the OH stretch at 3380.36 cm^{-1} was shifted to 3305.14 cm^{-1}. The shifts in frequencies indicate that there is an interaction between mild steel and the inhibitor [18]. New bond, due to phenyl substitution ring, was found at 870.89 cm^{-1}. On the other hand, C=C aromatic stretch at 1423.51 cm^{-1}, C≡C stretch due to alkyne at 2133.83 cm^{-1} and C-O stretch at 1247.02 cm^{-1} were absence in the spectrum of the corrosion product suggesting that these bonds have been used for adsorption of the inhibitor on mild steel surface [19].

4. CONCLUSIONS

The study was designed to find out the physiochemical properties of *Daniella olliverri* gum, chemical structures of their active constituents, FTIR study and their application as corrosion inhibitors. From the findings of the study, the following conclusions are made,

i. *Daniella olliverri* gum is a dark brown, odourless and mildly acidic gum. The gum is ionic and is insoluble in ethanol, acetone and chloroform but is soluble in water.

ii. The chemical constituents of *Daniella olliverri* gum include sucrose (26.89 %), dihex-5-en-2-yl phthalate (3.21 %), hexadecanoic acid (16.59 %), (E)-hexadec-9-enoic acid (35.38%, stearic acid (14.54 %) and 2,6-dimethyl-4- and 2,6-dimethyl-4- nitrophenol (3.40 %)

iii. FTIR analysis of *Daniella olliverri* gum indicates the presence of the following vibrations, C-O stretch at 1052.20 and 1247.02 cm^{-1}, C-H scissoring and bending vibrations due to alkene (1385.90 cm^{-1}), aromatic C=C stretch at 1423.51 cm^{-1}, N-H bending vibration due to amine (at 1614.47 cm^{-1}) C=O stretch due to phenol at 1731.17 cm^{-1}, C≡C due to alkynes' at 2139.13 cm^{-1}, OH aliphatic stretch at 2933.83 and OH stretch at 3380.36 cm^{-1}

iv. *Daniella olliverri* gum has been found to be a good adsorption inhibitor. Its inhibition proceeded via the mechanism of physical adsorption; E_a and ΔG^0_{ads} values were lower than threshold values of 80 and -40 kJ/mol) and was best described by Langmuir adsorption model.

v. The mechanism of inhibition of mild steel corrosion by *Daniella olliverri* gum is by adsorption of the gum through C=C aromatic stretch at 1423.51 cm^{-1}, C≡C stretch (due to alkyne at 2133.83 cm^{-1}) and C-O stretch at 1247.02 cm^{-1}. The formation of phenyl ring at 870.89 cm^{-1} also enhanced the adsorption of the inhibitor on mild steel surface. Therefore, inhibition of mild steel corrosion by *Daniella olliverri* gum occurred through synergistic adsorption of the various components of the gum, hence the formation of multiple adsorption layers is proposed.

References

1. D.M.W. Anderson and N. A. Morrison, *Food Additives and Contaminants*, 7 (1990) 175.
2. R.C.M. De Paula, S.A. Santana and I. F. Rodrigues, *Carbohydrate Polymers* 44 (2001) 133.
3. C.G. Mothe and M.A. Roa, *Food hydrocolloids*, 13 (1999) 501.
4. G.S. Mhinzi, *Food Chem.*, 77 (2002) 301.
5. X. Ma and M. Pawlik. *Carbohydrate Polymers*, 70, (2007) 15.
6. N.O. Eddy, P. Ameh, C.E. Gimba, and E.E. Ebenso, *Int. J. Electrochem. Sci.* 6 (2011) 5815.
7. S.A. Umoren, I.B. Obot, E.E. Ebenso, P.C. Okafor, O. Ogbobe, and E.E. Oguzie, *Anti-Corrosion Methods and Materials*, 53(5) (2006) 277.
8. S.A. Umoren, I.B. Obot, E.E. Ebenso, N. Obi-Egbedi, *Port. Electrochimica Acta* 26 (2008) 1
9. S.A. Umoren, and E.E. Ebenso, *Pigment and Resin Technol*ogy, 37(3) (2008) 173.
10. M. Abdallah, *Portugaliae Electrochimica Acta*, 22 (2004)161.
11. K.N. Mohana and A.M. Badiea, *Corr. Sci.* 50 (2008) 2939.
12. M.A. Quraishi, M.Z.A. Rafiquee, S. Khan and N. Saxena, *J. Appl. Electrochem.* 37(2007) 1155.
13. N.O. Eddy and B.I. Ita, *Int. J. Quantum Chem.*, 111(14) (2011) 3456.
14. N.O. Eddy and B.I. Ita. *J. Mol. Modeling* 17(2) (2010) 359.
15. N.O. Eddy *Pigment and Resin Technology, 39(6)* (2010) *347*.
16. N.O. Eddy and E. E. Ebenso, *J. Mol. Modeling* 16 (2010) 1291.
17. X. *Li, S. Deng, H. Fu* and *T. Li, Port. Electrochimica Acta 54* (2009) *4089.*
18. A.O. Odiongenyi, S.A Odoemelam,N.O. Eddy *Port. Electrochimica Acta* 27(1) (2009) 33.
19. N.O. Eddy and A.O. Odiongenyi. *Pigment and ResinTechnology,*38(5) (2010) *288.*