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Research Article

INHIBITING ALUMINIUM ACID CORROSION USING LEAVES EXTRACT OF *GUIERA SENEGALENSIS*

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ABSTRACT

The effects of *Guiera senegalensis* leaves extract as a potential green corrosion inhibitor for Aluminum (Al) in HCl acid solution was investigated using weight loss, LPR, FT-IR, and scanning electron microscope techniques at varying experimental conditions. The result indicates that the percentage inhibition efficiency increases with increase in concentration of the inhibitor and decreased with increase in temperature and immersion period. SEM images showed that the Al metal is protected by the inhibitor molecules, while FT-IR spectra indicates the mechanism of physical adsorption of inhibitors onto Al surface. LPR result showed that the inhibition efficiency of the inhibitor was moderate and act as mixed-type inhibitor. The data obtained from the thermodynamic parameters were fitted into various adsorption isotherms, Freundlich adsorption isotherm was observed to be the best fitted isotherm.

Keywords: Inhibition efficiency, Thermodynmaics, Weight loss, FT-IR, Asdorption isotherms

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1. INTRODUCTION

1.1 Corrosion of Aluminium

Corrosion is a naturally occurring phenomenon usually referred to as deterioration of metal which resulted from a chemical or electrochemical interaction with the environment [1]. Majority of metals corrode upon interactions with aggressive medium such as moisture in the air, oils, acids, bases, salts, aggressive metals polishes, and other liquid chemical substances [2]. Metals and their alloys will also corrode through exposure to gaseous materials such as acid vapour, formaldehyde, and sulphur containing gases [3]. Usually, metal corrode in the presence of chemicals such as acids, alkali, salts and sulphides. Though, acids such as phosphoric acid, HCl acid, nitric acid and hydrofluoric acid are used in pickling, etching and descaling of metals in many industries [4-6]. The corrosion inhibition of Aluminum and its alloys are the subject of great technological importance due to its increased industrial applications [7].

1.2 Plant as Green Inhibitor.

Green inhibitors include the alkaloids and flavonoids and other natural products obtained from natural sources like plant. The extraction is carried out by simple techniques with low cost and these plants consist of chemical compounds with negligible toxicity. Many corrosion control mechanisms have been employed using extracts obtained from various plants as corrosion inhibitors [8]. Plants as corrosion inhibitor had been accepted as sources of naturally occurring compounds, some of these plants extract contained complex molecular structures and having variety degrees of physical, chemical and biological properties [9,10]. As a result of these significant advantages, extracts of some plants and plant products have been study as corrosion inhibitors for metals and alloys under different environment and conditions [11]. The above qualities have made the naturally occurring plants to become an important source of a wide range of eco-friendly green inhibitors for corrosion control [12]. *Guiera senegalensis* (Gs) also called “moshi” which referred to as medicine, is one of the most essential medicinal plants in Africa which occurs naturally in Central and West Africa, comprising of Burkina Faso, Mauritania, Gambia, Senegal, Guinea-Bissau, Mali, Republic of Guinea, Niger, Nigeria, etc [13]. *Gs* is a green-grey-whitish plant that grows up to 3m high, the leaves have an elliptic oblong limb of about 3-5cm length and 15–25 mm with a mucronate and round apex, a very soft tomentose pubescence, conspicuous scales and a thin pubescent petiole of about 2-4 mm length

[14]. A bio-guided phytochemical study permits the identification of active compounds from *Gs* such as kaempferol, ethylgallate, gallic acid, 5-methylflavasperone, 5-methyldihydroflavasperone, guieranone A, quercitrin. β-sitosterol, 1,3,4-tri-*O*-galloilquinic acid, 3,4,5-tri-*O*-galloilquinic acid, miricitrin, rhamnetin, hyperoside, miricetin, quercetin, tiliroside, and isorhamnetin, in its leaves [13].

Fig.1. *Guiera senegalensis* leaves

It is required to use solution of acids in other to get rid of unwanted scales and corrosion products from metals and alloy. HCl and H_2SO_4 acids are universally employed for this purpose. However, these acids attack the material and initiate corrosion. This corrosion can cause severe damage to the metal and destroy its properties, thereby limiting its applications capacity [15]. The global problems arising from acid corrosion necessitate the development of several corrosion control techniques among which the use of chemical inhibitors has been broadly accepted as the most cost-effective method for preventing metals from acid corrosion. [16]. Although, synthetic organic compounds display good inhibitive properties, their application is still undesired because of their adverse effects on living organisms, environment, as well as their expense. In the latest years, there has been an effective increase in awareness of environmental and green chemistry [5]. Even though substantial research has been dedicated to corrosion inhibition by various plant extracts, information on the comprehensive mechanisms of the adsorption process and identification of the active constituents are still scarce [4]. This research work seeks to evaluate the efficiency of ethanol extract of *Guiera senegalensis* leaves as green corrosion inhibitor for aluminium in HCl solution through the use of weight loss, linear polarization resistance technique, Fourier transform infrared FT-IR and Scanning electron microscope SEM methods.

2. EXPERIMENTAL

2.1 Materials preparation

The sheets of Aluminium of composition presented in table 1 were determined using Energy Disperse X-Ray Fluorescence ED-XRF (S2-Ranger) and were mechanically pressed cut into a dimension of 4 by 3 by 0.11 cm coupons. These coupons were used as cut without further polishing. Though, they were degreased in ethanol, dried with acetone and stored in desiccators free from moisture before their use for corrosion studies. Coupons of the same dimension were used for both weight loss and other characterizations methods [17,18].

Table 1. Percentage composition of the Aluminium sheet sample

Elements/ Compounds	Al_2O_3	SiO_2	Fe_2O_3	SO_3	K_2O	Cl	CuO	TiO_2	Ga_2O_3	MnO
Composition (%)	99.36	0.27	0.20	0.04	0.03	0.03	0.02	0.01	0.01	0.01

Fresh and clean leaves of *Guiera senegalensis* (Family: *Combretaceae*) were collected from Dawakin Tofa L.G, Kano, Nigeria, and authenticated (voucher specimen no. 798) at the herbarium Research laboratory, Plant Science Department, Bayero University Kano, Nigeria. The leaves were washed with distilled H_2O, dried at room temperature for 14 days and powdered into 400g using mortar and pestle. The extraction was carried out with 1500 mL of 98% ethanol (Merck) for 14 days with regular shaking and repeated twice with another fresh solvent. The solution was pooled, passed via Whatmann filter paper and the crude were dried under reduced pressure with the aid of rotary evaporator (BUCHI Labortechnik AG/9230 Flawil/Switzerland) and the crude extract were dried in air for further usage [19]. All the reagents used for this research work are of analytical grade and were used without further purification.

2.2 Preparation of Test Solutions

The corrodent solutions (blank) were prepared at various concentrations of (0.20 M, 0.40 M, and 0.60 M) HCl acid from which the inhibitor solutions where prepared at various concentrations (0.20 g/L, 0.40 g/L and 0.60 g/L) from each of the prepared HCl solution. All preparations were done according to the standard procedures.

2.3 Phytochemical Screening

Phytochemical screening was conducted on the ethanol crude extract of leaves of *Guirea senegalensis* for identification of secondary metabolites including flavonoids, alkaloids, saponins, saponins, tanins, steroids, terpinoids and phenols based on the procedure reported by [20-23].

2.4 Weight Loss Measurement

Eah pre-weighed sample (coupon) of the aluminium metal under consideration was completely immersed into four different beakers containing 60 cm^3 of 0.00 g/L, 0.20 g/L, 0.40 g/L and 0.60 g/L of the inhibitor each in different concentrations of HCl (0.20 M, 0.40 M, 0.60 M) respectively. The beakers were covered and then immersed into water bath at 303K. After each hour (for four hours) the samples were removed, cleaned from all corrosion product, dried in ethanol and reweighed. This procedure was repeated at 313 K and 323 K temperatures. The corrosion rate C_R in ($mgcm^{-2}$ h^{-1}), the degree of surface coverage (θ) and the percentage inhibition efficiency (η) of the inhibitor were calculated from the result of weight loss using equations 1, 2 and 3 respectively [24].

$$C_R = (W_i - W_f)/At \qquad (1)$$

$$\theta = (W_i - W_f)/W_i \qquad (2)$$

$$\eta = ((W_i - W_f)/W_i)X100\% \qquad (3)$$

Where W_i and W_f are the weight losses of Al coupons before and after treatment, C_R is the corrosion rate ($mgcm^{-2}h^{-1}$), θ is the degree of surface coverage by the inhibitor, η is the percentage inhibition efficiency (% IE), A is the area of the Al coupon (cm^2), t is the immersion time (in hours) respectively.

2.5 Linear Polarisation Resistance (LPR) Analysis

Linear polarization resistance (LPR) using VERSASTAT 4 potentiostat was used to study the inhibition of Aluminium of dimension 1.0 cm x 1.0 cm in 0.2 M HCl at various inhibitor concentration (0.2 g/L, 0.4 g/L and 0.6 g/L) and at temperature of 298 K by scanning the current–potential (i–E) domain. A very small voltage usually less than 30 mV were applied to the Al metal above and below its corrosion potential. Over this constricted range in the vicinity of the corrosion potential, the current response found is linear. Thus, the polarization resistance (*Rp*) for the slope of this current–potential curve is constant [25]. As the working electrode is changed, a current is made to flow between the working and counter electrodes. Consequently, the material's resistance to polarization was established by taking the slope of potential against current curve [26]. After computing R_t from Nyquist plot and substituting Tafel slope values for anodic β_a and cathodic β_c in the equation.

$$I_{corr} = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)} x \frac{1}{R_t} \quad (4)$$

$$\%IE = \frac{(I_{corr\,(o)} - I_{corr\,(inh)})}{I_{corr\,(o)}} 100 \quad (5)$$

Where $I_{corr(o)}$ and $I_{corr(inh)}$ are corrosion current density values with and without inhibitors respectively [27].

2.6 Surface Analysis

Surface morphologies of the Aluminium coupons for the fresh sample and for both before and after inhibition was studied using Scanning Electron Microscope machine (PRO X: phenonm World 800-07334) model, manufactured by phenonm World Eindhoven. Netherlands. Scanned images of fresh metal sample, unhibited and inhibited metal at 303 K in lowest HCl Concentration (0.20 M) were taken after 4hrs at an accelerating voltage of 15.00 kV and x 500 magnification.

FTIR analysis of the GS plant extract, fresh Aluminium and that of the corrosion product in 0.20 M HCl and 0.60 g/L inhibitor at 303 K after immersion time for 4hrs were carried out using Agilent Technology, FTIR (Cary 630) Fourier Transform Infrared Spectrophotometer, the analysis was done by scanning the sample through full scale wave number (in range of 650-4000 cm^{-1}).

3. RESULTS AND DISCUSSION

3.1 Phytochemical Screening

Previous studies indicated the presence in leaves *Guiera senegalensis* of two alkaloids, flavonoids, naphthyl butenone (guieranone A), naphthopyrans and tannins [28]. The phytochemical screening was conducted and the result revealed that Gs crude extract contains alkaloids, flavonoids, tannin, terpenoids, carbohydrates, proteins, saponins, steroids and phenols as presented in table 2.

Table 2. Phytochemical screening of leaves extract of *Guirera senegalensis*

Phytochemicals	Qualitative analysis
Flavonoids	+
Alkaloids	+
Saponins	+
Tannins	+
Steroids	+
Terpinoids	+
Phytosterols	-
phenols	+
Carbohydrates	+
Proteins	+

Key: + indicates the presence of phytochemicals, - indicates the absence of phytochemicals.

3.2 Weight Loss Analysis

The effect of (acid) corrodent concentration on weight loss of aluminium coupon has been studied at various HCl solutions (0.20 M, 0.40 M and 0.60 M) for the period of 4hrs immersion time in both the blank and inhibited solutions, all at various temperature (303 K, 313 K and 323 K). The results presented in table 3 of this study indicates that (the percentage inhibition efficiency (% IE) increased with increase in concentration of GS ethanolic extract to 65.71 % at 0.6 g/L, increase in temperature caused the decrease of the inhibitor efficiency (IE %) and decrease in the degree of surface coverage θ which can be seen in table 3. As the concentration of the corrodent HCl acid increases, the corrosion rate increases with increase in temperature to 1.5042 $mgcm^{-2}h^{-1}$ in blanked solution and decreases with increase in inhibitor. The above observation is due to the fact that the rate of chemical reaction increases as the concentration of active species increases [29]. The increase in corrosion rate as a result of increase in concentration of acid on inhibited aluminium may be attributed to the rupture of bond between inhibitor molecule and aluminium surface by acid molecules at higher concentrations to formation of hydrogen-aluminium bond. This results in higher accumulation of the active sites by acid molecules which prevents the penetration of extract molecules to the surface of the aluminium [30].

Table 3. Percentage inhibition efficiency (% IE) of the plant extract and Corrosion rate C_R obtained from weight loss experiment

Temp	**Inhibitor**	**Corrodent (HCl) Concentration**					
		0.20 M		**0.40 M**		**0.60 M**	
		%IE	**C_R**	**%IE**	**C_R**	**%IE**	**C_R**
303K	Blank	-	0.2188	-	0.3646	-	0.4729
	0.20g/L	45.71	0.1188	28.57	0.2604	37.65	0.3313
	0.40g/L	56.19	0.0953	47.43	0.1917	44.31	0.2958
	0.60g/L	65.71	0.0750	61.14	0.1417	58.82	0.2188
313K	Blank	-	0.3375	-	0.5583	-	0.7667
	0.20g/L	37.65	0.2104	25.00	0.4188	08.42	0.7021
	0.40g/L	53.09	0.1582	33.21	0.3729	13.86	0.6604
	0.60g/L	63.58	0.1229	40.67	0.3313	20.92	0.6063
323K	Blank	-	0.5975	-	0.9708	-	1.5042
	0.20g/L	37.28	0.4396	11.37	0.8604	05.00	1.3854
	0.40g/L	45.99	0.3229	14.59	0.8292	08.57	1.3333
	0.60g/L	57.49	0.2542	19.53	0.7813	11.43	1.2917

a) Effect of Immersion Time on Weight Loss

Weight loss for the corrosion process was studied at different time intervals (1 hr, 2 hrs, 3 hrs and 4 hrs) for the period of 4 hours and the result were presented figure 2. It was observed that the weight loss of Aluminium in HCl acid solution increases with increase in immersion time at all temperatures (303 K, 303 K and 303 K). The highest weight loss 0.0163 g was observed at highest immersion time of 4 hrs in the highest temperature of 323 K at 0.60 M HCl concentration, while the lowest weight loss 0.0012 g was observed in the lowest temperature at lowest corrodent concentration. Though, the weight loss is greatly reduced with the inhibitor compared to the blank solution. The decrease in weight loss with the inhibitor may owed to the adsorption of the phytochemical constituents in the extract on the Aluminium metal surface. This shows that metal is exposed to the corrosive environment, the more the contact time between the metal and the corrodent the more Al corrode. Increase in the weight loss of the metal in the acids solution indicates the instability of protective film for the longer contact time. Therefore, weight loss increase with increase in immersion time in all acidic environment.

b) Effect of Inhibitor Concentration

The effect of inhibitor (*Guirea senegslensis*) leave extract was studied at different concentrations (0.20 g/L, 0.40 g/L and 0.60 g/L), at various HCl concentration (0.20 M, 0.40 M and 0.60 M) and at various temperature (303 K, 313 K, and 323 K) for the corrosion inhibition of aluminium metal. The result in figure 2 shows the variation of weight loss with immersion time in various HCl concentrations containing different inhibitor concentrations at various temperatures (303 K, 313 K and 323 K). It is indicated that the weight loss of aluminum metal decreases with increase in inhibitor concentration and increases with increase in contact time, also it was observed that the weight loss increases with temperature and inhibitor concentration. Table 3 showed that the corrosion rate C_R decreases with increase in concentrations of inhibitor. Moreover, percentage inhibition efficiency (% IE) increased with increasing concentrations of inhibitor. Therefore, Gs extract inhibit the corrosion of Al metal in HCl solution.

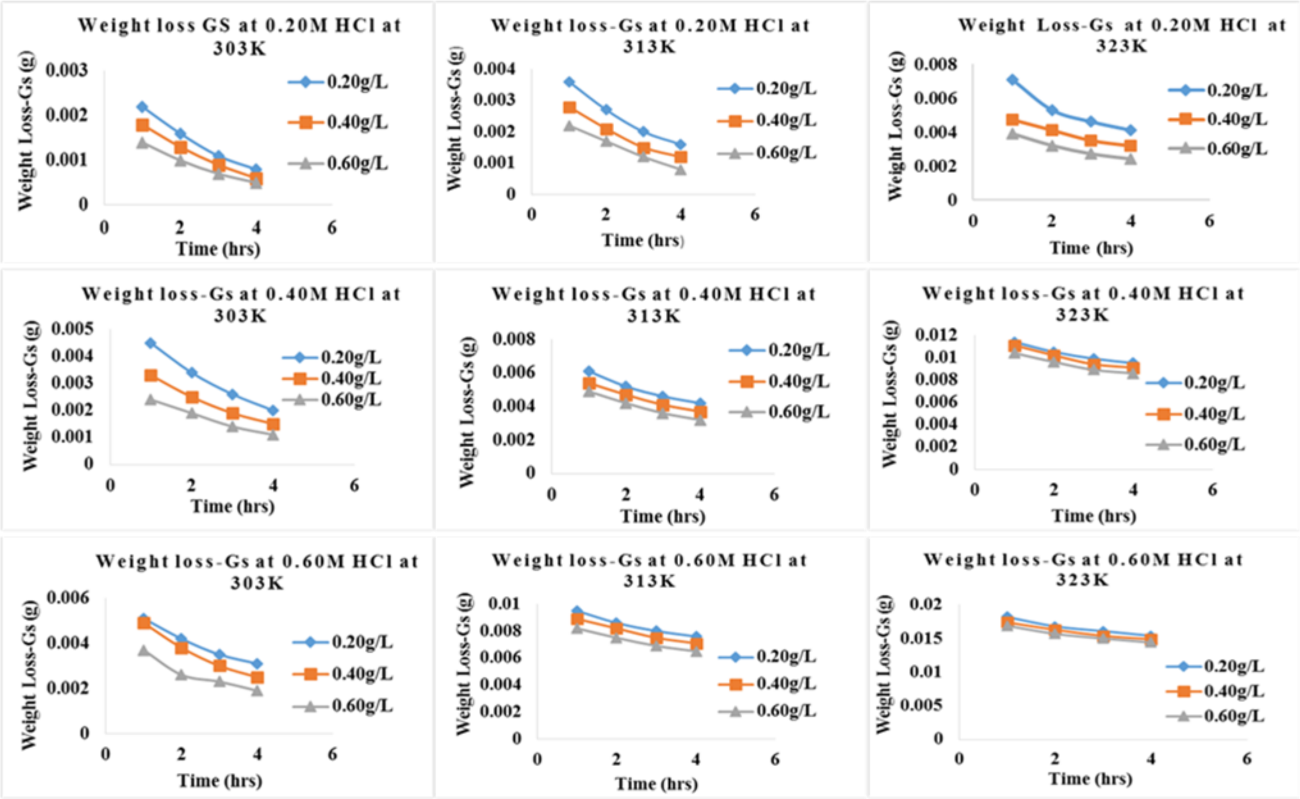

Fig.2. Weight loss at various acid and inhibitor concentrations and at different temperatures

c) Effect of Temperature

Temperature effect on weight loss of aluminum metal was studied for both the inhibited and uninhibited metal at various HCl concentration (0.20 M, 0.40 M and 0.60 M) for the period of 4hrs at different temperature (303 K, 313 K and 323 K). The results are presented in figure 2. From the plots, it is clear that the weight loss increases with increase in temperature at various acid concentrations. It is also observed from table 3 that the corrosion rate increases with increasing temperature and decreases with increase in inhibitor concentration. The corrosion rates at 0.00 g/L and 0.6 g/L inhibitor in 0.2 M HCl at 303 K are 0.2188 $mgcm^{-2}h^{-1}$ and 0.0750 $mgcm^{-2}h^{-1}$ respectively, while at 323 K and 0.60 M HCl, the corrosion rates raised to 1.5042$mgcm^{-2}h^{-1}$ for the blank and 1.2917 $mgcm^{-2}h^{-1}$ for 0.6 g/L inhibitor respectively. This shows that increase in temperature increases the reactivity of active constituents of the corrosion medium which in turns decreases the performance of the plant extract in inhibiting the corrosion of metal. Rise in temperature generally increases the rate of hydrogen gas evolution on the cathode, consequently leads to a higher rate of metal dissolution. It is also supported by the fact that chemical reactions increase with increasing temperature. Moreover, increase in temperature increases the kinetic energy of molecules of the corrosion medium which leads to overcoming of energy barrier for corrosion to occur in high speed [31]. This may be attributed to the higher dissolution rates of metal at an elevated temperature and a possible desorption of adsorbed inhibitor molecules because of increased solution agitation as a result of high rates of H_2 gas evolution, which may also decrease the capability of the inhibitor molecule to be adsorbed on Al metal surface. Thus, such behaviour which was observed in both corrodents, suggests physical adsorption of the extracts on the corroding aluminium metal surface [32]. Hence, the plant extract inhibits the corrosion of Al predominantly in the lowest temperature.

3.2.1 Kinetic Study

The kinetic for corrosion of Aluminium in hydrochloric acid solution was investigated. The data obtained from weight loss measurements were used to plot $\log C_R$ against reciprocal of absolute temperature 1/T which gives a straight line with a slope equals to $-E_a/2.303R$ from which the activation energies were calculated using the Arrhenius equation and the resulted are given in table 4. The results indicate that addition of plant extracts up to 0.60 g/L in various HCl solution increases the activation energy from 40.84 to 72.33 $KJmol^{-1}$. The maximum activation energy of 72.33 $KJmol^{-1}$ was noticed for 0.60 g/L plant extract in the highest HCl concentration. This is due to the fact that the amount of extract is more and hence, hindering the reaction process to occur. Furthermore, calculated values of E_a for the blank solution ranges between 39.78 to 40.95 $KJmol^{-1}$, while the values of E_a for the inhibitor concentration ranges from 46.76 $KJmol^{-1}$ to 72.33 $KJmol^{-1}$ at various concentrations, result shows that E_a were found to be greater in inhibited solution at 0.6 g/L (72.33 $KJmol^{-1}$) than those found in blank, which suggests the formation of adsorption film of physical electrostatic reaction [33,34].

$$\log C_R = \log A - (Ea/2.303RT) \qquad (6)$$

Where C_R is the corrosion rate, A is the Arrhenius pre-exponential factor, E_a is the activation energy, R is the molar gas constant and T is the absolute temperature of the system.

Values of other kinetic parameters (rate constant and half-life) were deduced at various acid concentration (0.20 M, 0.40 M and 0.60 M), different inhibitor concentration (0.00 g/L, 0.20 g/L, 0.40 g/L and 0.60 g/L) at all temperatures (303 K, 313 K and 323 K). The results were presented in table 5 below. The results obtained show that as the concentration of HCl increases, rate constant increases from 1.18 $x10^{-3}$ h^{-1} to 7.85 $x10^{-3}$ h^{-1} at all temperatures, increase in inhibitor concentration decreases the rate constant. On the other hand, half-life decreases from $5.87x10^2$h to $0.81x10^2$ h with increase in acid concentration and increase with inhibitor concentration. Moreover, increase in temperature leads to increase in rate constant and decrease in half-life of the corrosion process. Thus, the leave extract of *Guirea senegalensis* increases the half-life of aluminium in HCl solutions thereby reducing the inhibition of Al metal from acid corrosion.

Table 4. Activation energy Ea, at various inhibitor and HCl Concentrations

Inhibitor Concentration (g/L)	Activation Energy Ea $KJmol^{-1}$ 0.20 M	0.40 M	0.60 M
0.00	40.84	39.78	40.95
0.20	46.76	48.50	58.23
0.40	49.31	59.51	60.55
0.60	49.54	69.44	72.33

Table 5. Rate Constant K and Half-life $t_{1/2}$ at various inhibitor concentration, HCl Concentration and at different temperature

Tempt K	Inhibitor Conc. (g/L)	Rate Constant K x10^{-3} h^{-1}			Half-life $t_{1/2}$ x10^{2} h		
		0.20 M	0.40 M	0.60 M	0.20 M	0.40 M	0.60 M
303	0.00	1.18	2.04	2.63	5.87	3.40	2.64
	0.20	0.64	1.40	1.61	10.83	4.69	4.30
	0.40	0.51	0.99	1.60	13.58	7.00	4.34
	0.60	0.39	0.78	1.19	17.77	8.88	5.81
313	0.00	1.76	2.70	4.72	3.94	2.57	1.47
	0.20	1.19	2.25	4.21	5.82	3.07	1.64
	0.40	0.86	2.08	4.10	8.10	3.33	1.70
	0.60	0.70	1.89	3.64	9.90	3.67	1.90
323	0.00	3.28	5.69	9.58	2.11	1.22	0.72
	0.20	2.39	5.22	8.59	2.91	1.33	0.81
	0.40	1.86	4.50	8.26	3.73	1.54	0.84
	0.60	1.50	4.38	7.85	4.63	1.58	0.88

3.2.2 Thermodynamic Studies

The free energy of adsorption ΔG_{ads} at different temperatures was calculated using equation 7 below [35].

$$\Delta G_{ads} = -2.303RTlog(55.5K_{ads}) \qquad (7)$$

Where ΔG_{ads} is the Gibbs free energy, K_{ads} is the adsorption equilibrium constant obtained from the intercept of each adsorption isotherm, R is the molar gas constant, T is the absolute temperature of the system, 55.5 is constant value which represent the concentration of water in a solution. The calculated values of ΔG_{ads} for the tested isotherm in table 6 ranges between -6.95 KJmol^{-1} and -0.92 KJmol^{-1} which are negatively less than -40 KJmol^{-1} which is necessary for the mechanism of chemical adsorption to occur. Moreover, the negative values of ΔG_{ads} shows the stability of the adsorbed layer and the spontaneity of adsorption. Consequently, the adsorption process of GS leaves extract on Aluminium surface is spontaneous. Also, the mechanism of physical adsorption is said to be the nature of metal-inhibitor interaction [36,37].

Table 6. Change in Gibbs free energy, k_{ads} correlation coefficient and slope at various temperature and HCl concentration

HCl	ΔG			K_{ads}			R^2		
Conc.	303 K	313 K	323 K	303 K	313 K	323 K	303 K	313 K	323 K
0.2M	-9.43	-9.92	-9.76	0.7598	0.8164	0.6817	0.9891	0.9992	0.9722
0.4M	-9.31	-8.67	-6.95	0.7269	0.5042	0.2399	0.9569	0.9971	0.9626
0.6M	-9.06	-7.39	-9.08	0.6564	0.3078	0.1850	0.9204	0.9910	1.0000

Activation enthalpy ΔH_a and entropy ΔS_a of corrosion process were calculated using the transition state equation 8:

$$log(CR/T) = \left\{log \frac{R}{N_A h + \frac{\Delta S_a}{2.303R}}\right\} - \frac{\Delta H_a}{2.303RT} \qquad (8)$$

Where ΔH_a is the activation enthalpy, ΔS_a is the activation entropy for the corrosion process, N_A is Avogadro's number and h is plank's constant. A of Plot CR/T Vs recipeocal of absolute temperature 1/T which gives a straight line with a slope equals to $\frac{-\Delta H_a}{2.303R}$ and intercept equals to $\left\{log \frac{R}{N_A h + \frac{\Delta S_a}{2.303R}}\right\}$ from which activation enthalpy and entropy values for the corrosion process were computed at various HCl and inhibitor concentration and the result are presented in table 7. The values of activation enthalpy which is positive in the presence and absence of inhibitor reflects that the dissolution process is endothermic [38]. While the negative values of entropies of adsorption indicate that the activated complex in the rate determining step represents association rather than dissociation, which means that there is reduction in disorderliness on going from reactant to activated complex [39]. The negative value of ΔH_{ads} and the positive value of ΔS_{ads} indicate the feasibility of the reaction. Furthermore, all the ΔG_{ads}, ΔH_{ads} and ΔS_{ads} values indicate that the adsorption process GS extract is spontaneous and exothermic in nature [30].

Table 7. Activation Enthalpy (in $KJmol^{-1}$) and Entropy (in $Jmol^{-1}$) values at various HCl concentrations and extract concentrations

Inhibitor Concentration	Thermodynamic Parameter	Acid concentration		
		0.20 M	0.40 M	0.60 M
Blank	ΔH	38.24	37.18	38.35
	ΔS	-189.15	-188.38	-181.58
0.20g/L	ΔH	44.16	45.90	55.63
	ΔS	-174.49	-162.55	-128.04
0.40g/L	ΔH	46.71	56.91	57.95
	ΔS	-168.13	-128.63	-122.77
0.60g/L	ΔH	46.94	66.84	69.73
	ΔS	-169.47	-98.22	-84.69

3.2.3 Adsorption Isotherm

Five selected models of adsorption isotherms: Langmuir, Freundlich, Temkin, El-Awady and Forry-Huggins were used for this study to describe the mode of adsorption in terms of the adsorption characteristics of the inhibitor and to establish the best adsorption isotherm(s). The result of this investigation were presented in Table 8 and 9. Their correlation coefficients (R^2) values were used to determine the best fit isotherm. Freundlich adsorption isotherm which has the correlation coefficients (R^2) extractly equal to unity (1) is suggested to be the best fitted adsorption isotherm for inhibitor/metal surface interaction. Freundlich equation is an ideal isotherm for physical adsorption which describes the formation of multi-layer adsorbate on the outer surface of the adsorbent. The Freundlich equation is presented by equation 9 [36-40].

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

Where θ the degree of surface coverage, K_{ads} is is the equilibrium constant of adsorption process and C is the inhibitor concentration.

Table 8. Correlation coefficient R^2 values for all the tested isotherms at various HCl concentration and temperature

Isotherms	Tempt. K	R^2		
		0.20 M	0.40 M	0.60 M
Langmuir	303	0.9902	0.9485	0.8294
	313	0.9980	0.9871	0.7227
	323	0.9860	0.9246	0.9923
Freundlich	303	0.9891	0.9569	0.9204
	313	0.9992	0.9971	0.9910
	323	0.9722	0.9626	1.0000
Temkin	303	0.9766	0.9271	0.8752
	313	0.9984	0.9851	0.9503
	323	0.9482	0.9285	0.9927
El-awady	303	0.9720	0.9283	0.8906
	313	0.9980	0.9924	0.9866
	323	0.9514	0.9573	0.9998
Flory-Huggins	303	0.9322	0.7894	0.5816
	313	0.9918	0.9611	0.6367
	323	0.8568	0.8013	0.9896

3.3 Linear Polarization Resistance (LPR) Study

The result for the LPR curves are presented in figure 3 and the calculated parameters are shown in table 9 as presented. It was observed that log of current density against potentials for the overlaid Tafel plot for linear polarization resistance study changes in acid solution as the extract concentration increases for both cathodic and anodic slopes which obeys the Tafel's law. This also indicated that the the inhibitor is a mixed-type inhibitor, protecting both the anodic and cathodic electrochemical reactions. Parameters such as percentage inhibition efficiency (%IE), corrosion rate (C_R), corrosion potential (E_{corr}**)**, cathodic (βc) and anodic (βa) Tafel slopes and corrosion current density **(**$í_{corr}$**)** were obtained by extrapolating Tafel lines. The inhibition efficiencies (% IE) presented in table 9 indicates that inhibition efficiency (%IE) increases with increase in concentration of extract thereby reducing the rate of corrosion of Al metal in HCl acid solution [41].

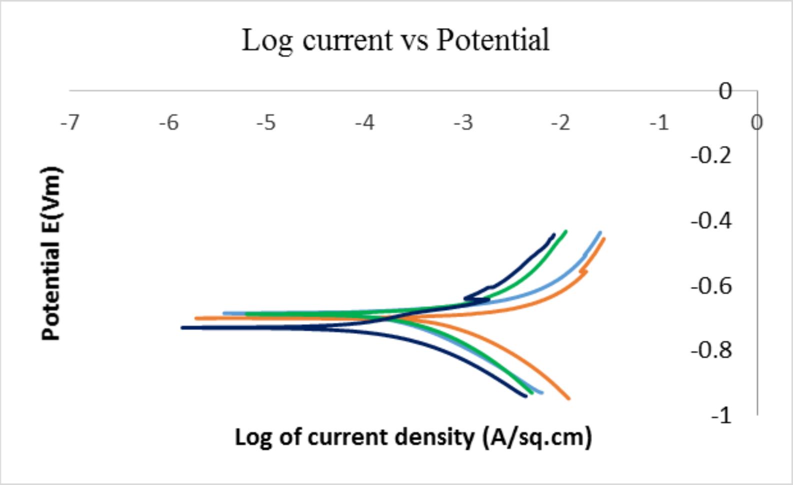

Fig.3. Overlaid Tafel plot for linear polarization resistance study for the inhibited and uninhibited Al corrosion systems. (Red = 0.00 g/L, Blue = 0.20 g/L, Green = 0.40 g/L, Purple = 0.6 g/L)

Table 9. Calculated parameters for linear polarization resistance for Al metal corrosion in HCl acid in the presence and absence of inhibitor at 303 K

Inhibitor	E_{cor} (mV)	I_{cor} (μA)	β_a (mV)	β_c (mV)	C_R (mmpy^{-1})	%IE
0.00g/L	-701.151	-389.197	29.996	102.270	4.2362	0
0.20g/L	-686.207	-174.422	29.482	120.184	1.8985	55
0.40g/L	-688.711	-148.647	34.705	107.143	1.6180	61
0.60g/L	-730.088	-133.295	99.898	90.255	1.4509	65

3.4 Surface Morphology Studies

a) Scanning Electron Microscopy (SEM) Analysis

Investigations for the surface morphologies of fresh Aluminium, corroded and inhibited aluminum specimens in 0.20 M HCl at 303 K were carried out by scanning electron microscopy (SEM) after immersion period of 4hrs, the SEM images were presented in figure 4 (a) for fresh sample, (b) for the corroded sample and (c) for inhibited samples (in 0.20 g/L inhibitor). The result in figure (b) shows that metal surface was severely corroded in the uninhibited solution which is uniformly damaged by cracks all over the metal surface. Figure (c) shows that the metal surface was inhibited by the plant extract of GS. This is the evident that application of GS leaves extract to acid solutions protects the Aluminium metal from corrosion by formation of protective layer on the surface through adsorption of the extract on the aluminium surface and hence GS leaves extract can be used in controlling the corrosion of Aluminium in acidic environment.

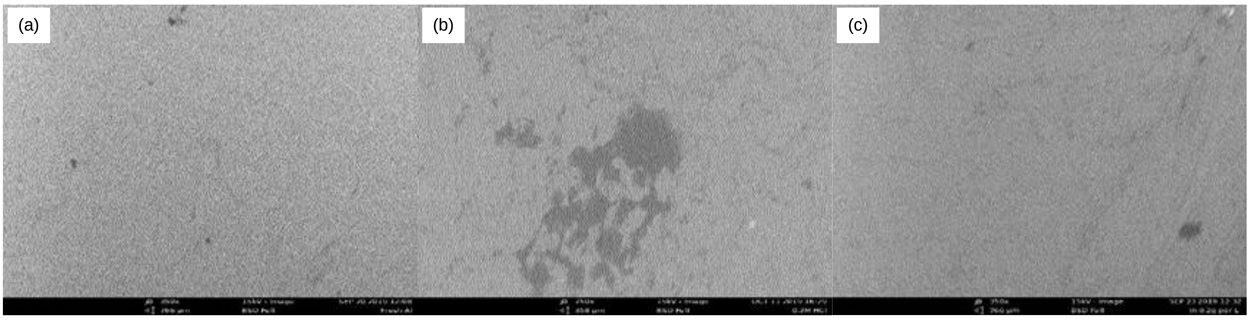

Fig.4. Scanning Electron Microscope (SEM) Images for a) fresh b) uninhibited and c) inhibited Aluminium samples

b) Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

The FT-IR spectra of the GS extract, corroded sample (corrosion product) with and without inhibitor and that of fresh Aluminium sample were carried out and the results are in figure 5 respectively. From the spectra of uncorroded and corroded aluminium without inhibitor, it can be observed that the spectra are IR in active. Comparing the spectrum of extract and corrosion product with inhibitor, the result indicates various chemical shift. Thus, the shift of bands in the frequencies clearly shows that there is an interaction between the metal surface and inhibitor molecule [42].

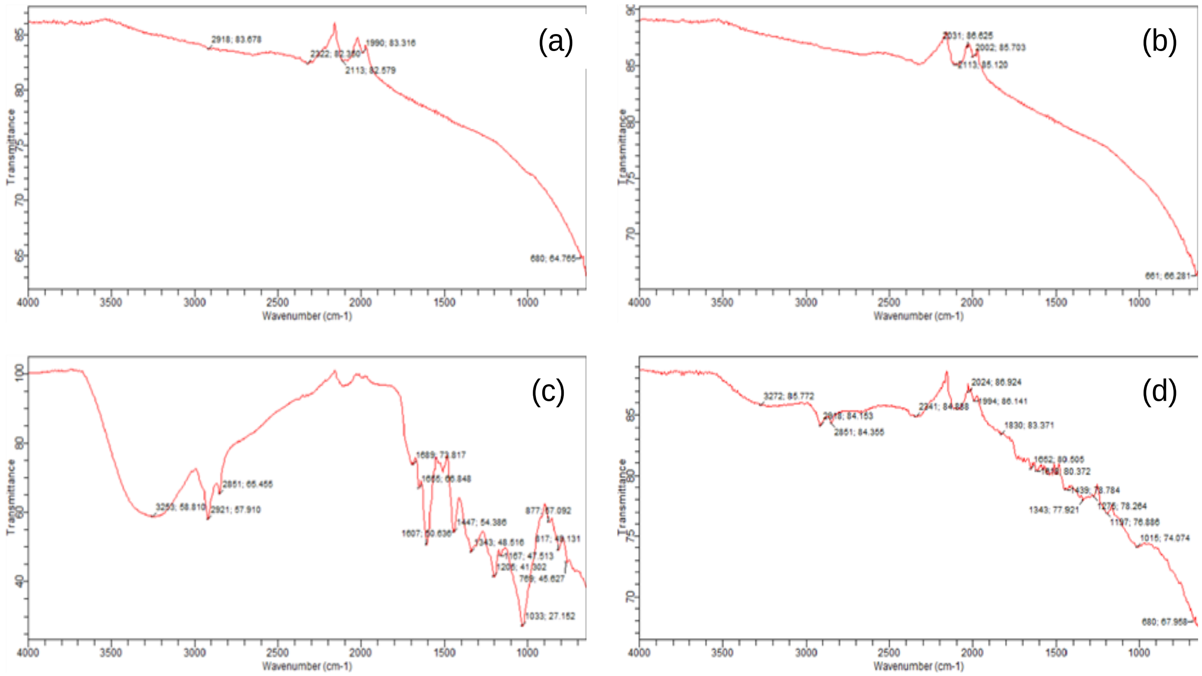

Fig.5. FT-IR Spectra for (a) fresh Al sample (b) corroded Al in HCl (c) ethanol plant extract (d) inhibited Al

4. CONCLUSION

The ethanolic extract of leaves of *Guiera senegalensis* was found to moderately inhibit aluminum metal in HCl solution through a mechanism of physical adsorption. From linear polarization resistance experiments, the inhibitor was found to be mixed type inhibitor and the phytochemical present in the plant that may be responsible for the inhibition include the detected alkaloids, flavonoids, terpenoids, tannin, carbohydrates, proteins, steroids, saponins and phenols.

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