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Corrosion Inhibition of Aluminum using Guava Leaf Extract as an Inhibitor

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Abstract: This study presents the inhibition against corrosion for aluminum metal using extract from guava leaf as an inhibitor. The aluminum metal was placed in a 0.5M H_2SO_4 solution at 32 ± 1°C. Thermometric, gravimetric, potentiodynamic, polarization and material simulation techniques were used for the investigation. The efficiency of the inhibitor was optimized using response surface methodology (RSM). The inhibitor (guava leaf extract) was characterized using a gas chromatography-mass spectrometer. The results obtained from gravimetric and thermometric techniques show that extract from guava leaf inhibits the corrosion of aluminum in an acidic environment. An increase in the efficiency of the inhibition of the guava leaf extract examined was found to be concentration-dependent. At room temperature of 32 ± 1^0C, an increase in the inhibitor and halide led to an increase in the efficiency of the inhibition. The inhibitor showed maximum inhibition efficiency and surface coverage of 98.41% and 0.97 respectively and a minimum corrosion rate of 0.51mm/yr. validated at the optimum conditions of inhibitor concentration of 10g/lolo + 0.4g KI, medium concentration of 0.10g/l and temperature of 45ºC. A minimum efficiency of 81.61% was validated at the concentration of 2g/lolo + 0.4g KI. Guava leaf extract as an inhibitor is a mixed type inhibitor based on the results of the potentiodynamic polarization thus highly effective and efficient for inhibition of corrosion in aluminum metal.

Keywords: Corrosion, Aluminum, Guava leaf, Inhibitor, Inhibition efficiency, Extract.

1. Introduction

Aluminum and its alloys are used in numerous applications and that leads to their exposure to certain substances which negatively affect their stability in nature. In industry, acid solutions are usually used for cleaning, picking, descaling, and oil well acidizing of metallic structures (Elmsellem *et al*., 2014; Ahamad *et al*., 2010; Nataraja *et al*., 2011; Tebbji *et al*., 2005). These are usually accompanied by the dissolution of metal, thereby leading to the failure of the material. Metals and alloys deployed to the service in such harsh environments must be protected since acid enhances the rate of dissolution of metals (Obi-Egbedi *et al*., 2011; Singh 2012). This can be done by adding some

species into the solution with which the metallic surface is in contact to inhibit corrosion reaction which will help in the reduction of corrosion rate. Incorporation of organic compounds to inhibit corrosion of metals in acidic environments was instituted (Fu *et al*., 2012), (Machinikova *et al*., 2008). Organic inhibitors contain oxygen, nitrogen, sulfur, phosphorus, and polar functional groups (Tan *et al*., 2020), (Singh *et al*., 2020). Virtually all organic inhibitors are environmentally unfriendly, toxic, non-biodegradable, and very expensive, hence there is a need for a better alternative due to the increase in the adverse effects of these chemicals (Lgaz *et al*., 2020), (Venkatesan *et al*., 2016), (Prabakaran *et al*., 2016). It becomes imperative to source for environmentally friendly, cheap, non-toxic, and biodegradable inhibitors that can replace these organic ones. Natural inhibitors such as extracts from leaves and natural polymers are environmentally friendly, cheap, non-toxic, and bio-degradable and can serve as good corrosion inhibitors for metals (Zerga *et al*., 2009; Mayakrishnan *et al*., 2016; Habibiyan *et al*., 2020; Olasunkanmi and Ebenso, 2020; El Mouaden *et al.* 2018). Seed, heart bark, roots, fruit and leaves extracts obtained from the plant had been proven to inhibit metallic corrosion in an acidic environment (Bahlakeh *et al*., 2019; Dehghani *et al*., 2019), (Hsissou *et al*., 2020; Bammou *et al*., 2018). Several researchers reported the use of natural and synthetic polymers as materials for inhibiting the dissolution of metal in an acidic environment and confirmed that the inhibitive efficacy of polymers depends on their molecular and also their structural constituents (Nwanonenyi *et al*., 2016a & b), (Umorem 2008). Investigation of inhibitive action of leaves and seed extracts of *Azadirachata indica* on mild steel corrosion in H_2SO_4 media with the aid of weight loss and gasometric methods show that the extracts acted not only as a good inhibitor but as mixed-type inhibitors in H_2SO_4 environment (Nwanonenyi, 2017; Oukinin *et al*., 2018; Sanaei *et al*., 2019; Abubakar M.S., Usman B. 2019). An investigation was also carried out on the anticorrosion nature of papaya leaves extracts on copper in H_2SO_4 solution and the result shows that the corrosion inhibition performance of the extract can reach 92.5% (Tan *et al*., 2020). This is an indication that extracts from some natural leaves inhibit the corrosion of metal in an acid environment. It is interesting to know that only a few varieties of plant and leaves extract have been thoroughly studied despite their great availability.

A critical review of prior reports on the application of extracts from leaves as an inhibitor for corrosion control shows no report on the utilization of guava leaf extract as an inhibitor in the inhibition of corrosion on aluminum metal in an acidic environment. Therefore, this present study aims to study the application of extracts from guava leaves and halide (KI) as an inhibitor in the corrosion control of aluminum metal in H_2SO_4.

2. Methodology

2.1 Material preparation

The mechanical press aided in cutting the aluminum sheet used in this work to dimensions of 3x3x3 cm^3. A small hole was drilled on one side of the coupon to support the thread and the aluminum metals were made grease free with the aid of ethanol. They were washed with distilled water, dried using acetone, and stored in desiccators. HCl used in this work was of BDH grade. Preparation of 0.1 HCl blank solution was made. Guava leaves collected from Onitsha were sun-dried for two days and the leaves that were dehydrated were crushed to enhance the enlargement of the surface area. There was an immersion of crushed leaves by weight of 40g with a particle size of 0.85mm in 1000 ml of distilled water for 48 h before filtering. The filtrate from the mixture of guava leaves extract and distilled water was used to prepare five different concentrations ranging from 2-10

g/l. This was done by dissolving the appropriate amount of guava leaves extract in one liter (1 L) of blank HCl and is according to the method prescribed by Chike-Onyegbula *et al*., (2012).

2.2 Product Characterization

A gas chromatography-mass spectrometer (GCMS-QP2010 PLUS, SHIMADZU) was used to analyze the compounds or constituents of the guava leaf extract. The analysis is according to the method of (El Ouariachi *et al*., 2010; Rosaline *et al*., 2012; Oguzie *et al*., 2010). This method is the combination of gas chromatography (GC) and mass spectrometry (MS) features to spot the varied substances in guava leaves extract. Guava leaves extracts were separated into individual substances when heating the extract in GC and the heated substances will be carried by a column with an inert gas. Separated materials when surfaced from the open column will flow in the mass spectrometry and the compounds will be identified by mass spectrometry.

2.3 Potentiodynamic polarization measurement

PARC-263 (Advanced electrical system, electrolytic cell, and computer display unit) was used for the experiment. This method had been used by Oguzie *et al*., (2010) and Ihebrodike *et al*., (2011). The counter and reference electrodes were the saturated calomel electrode (SCE) with the graphite rod. The specimen (metal) was fixed in epoxy resin which exposes its surface area of 1 cm^2 to the test solution and served as the working electrode. With the help of a lugging capillary of the electrochemical workstation, electrodes were fixed to the electrolytic cell. While maintaining a room temperature of 30°C, the measurements in an aerated and unstirred solution were taken. At the end of 30 mins of immersion, the steady values of an open potential circuit (OPC) were obtained before each experiment. The potentiodynamic polarization study was conducted at the potential range of ± 250 mV verse corrosion potential at a 0.33 mV/s scan rate (Nadia *et al*., 2011). Power suit software was used to extrapolate the data and every test was conducted in triplicates for verification of the reproducibility of the system.

2.4 Gravimetric measurements

At different temperatures and days, the weight loss technique was employed with varied concentrations of guava leaf extract. The metal coupon was prepared carefully, weighed, cleaned, and immersed in 250 ml beakers with 200 ml of 0.1 M H_2SO_4 (blank). Other coupons were immersed in 250 ml beakers with 200 ml of guava leaf extract and KI with concentrations of 2, 4, 6, 8, and 10 g/l and 0.4g of guava extracts and KI respectively for up to five days with the aid of beakers and were kept at room temperature of (28 ± 1 ^{0}C). At temperatures of 30°, 40°, 50°, and 60° C, the experiments were also carried out with 2, 4, 6, 8, and 10 g/l concentrations of guava leaf extracts. The weight loss variations were carefully monitored on various days and temperatures. Coupons were retrieved at the appropriate day and time, dried, and weighed. Calculations of weight losses were in grams and the readings were tabulated after the experiments. The weight loss (Δw), corrosion rate (CR), and inhibition efficiency (IE) were calculated using Eqns. 1, 2, and 3 respectively. The surface coverage (θ) was obtained using Eqn. 4 as done by Nagm *et al*., (2012):

$$\Delta w = w_i - w_f \qquad \textbf{Eqn. 1}$$

$$CR = w_i - w_f / At \qquad \textbf{Eqn. 2}$$

$$IE\% = w_o - w_1 / w_o \times 100 \qquad \textbf{Eqn. 3}$$

$$\theta = w_o - w_i / w_o \quad \textbf{Eqn. 4}$$

w_i and w_f are the initial and final weights of metal samples respectively, whereas w_1 and w_o are the weight loss values in the presence and absence of inhibitors and halides respectively. A is the total area of the specimen and t is the immersion time.

2.5 Thermometric measurements

This method of thermometric measurements was employed to monitor the dissolution of metal in acid described by Mabrouk *et al*., (2011) and Eddy *et al*., (2012). Experiments were conducted using a thermostat set at a temperature of 30ºC and 100 ml for aluminum metal. The aluminum did not corrode in the media at a temperature of 30ºC. The temperature of the system containing the metal and the test solution respectively were regularly recorded until a steady temperature was achieved. The reaction number (RN) was obtained using Eqn.5 (Mabrouk *et al*., 2011, Eddy *et al*., 2012).

$$RN = T_m - T_i / t \quad \textbf{Eqn. 5}$$

T_m and T_i are the maximum and initial temperatures (in ºC) respectively, and t is the time in minutes elapsed to reach T_m. The percentage inhibition efficiency (% IE) was obtained using Eqn. 6 (Mabrouk *et al*., 2011)

$$\% IE = (1 - RN_{add} / RN_{free}) \times 100 \quad \textbf{Eqn.6}$$

Where RN_{free} and RN_{add} are the reaction numbers for the dissolution in free and inhibited medium respectively.

2.6 Weight loss method using response surface methodology

The weight loss method experiment was designed using the response surface methodology (RSM) of design expert software. Here, time (days), inhibitor concentration, and medium concentrations are the considered factors while corrosion rate, inhibition efficiency, and surface coverage are the expected responses of the study. The design matrix for the experiment is shown in Table 1. The responses are analyzed using the RSM. The ANOVA and graphical analyses of the inhibition efficiencies were carried out.

Table 1. Design matrix for the corrosion inhibition of Al in H_2SO_4 using guava leaves extract

Std	Run	Block	Factor 1; A: Time (days)	Factor 2; B: Inhibitor conc.(g/l)	Factor 3; C : Medium conc. (M)	Response 1; Corrosion rate (mm/yr)	Response 2; Inhibitor efficiency (%)	Response 3; Surface coverage (K)
2	3	Block 1	3	2.00	0.30			
11	4	Block 1	3	2.00	0.50			
10	5	Block 1	1	10.00	0.10			
16	6	Block 1	3	6.00	0.30			
5	7	Block 1	1	6.00	0.10			
8	8	Block 1	5	6.00	0.50			
4	9	Block 1	5	10.00	0.30			
15	10	Block 1	3	6.00	0.30			
3	11	Block 1	2	10.00	0.30			
1	12	Block 1	2	2.00	0.30			
9	13	Block 1	3	2.00	0.10			
14	14	Block 1	3	6.00	0.30			
7	15	Block 1	2	6.00	0.50			
17	16	Block 1	3	6.00	0.30			
12	17	Block 1	3	10.00	0.50			

A mathematical model in terms of the coded factors was obtained. Models were used to make predictions on the response for the given level of the factor. The high level of the factor was coded as +1 and the low level of the factor was coded as - 1. The values of the optimum inhibition parameters were also determined.

2.7 Scanning electron microscopy

After immersion of aluminum metals in 0.1 M H_2SO_4 in the presence and absence of guava leaf extracts, an XL-30FEG scanning electron microscope was used to study the surface morphology of the metals. Metals (specimen) when retrieved from the acid medium were cleaned with double distilled water and dried in warm air before they were sent for SEM analysis.

3. Results and Discussion

3.1 The GC MS of the guava leaf extract

In Figure 1, the GC MS Chromatogram of guava leaves extracts shows various levels of peaks. Each of the peaks represents compound as determined by the GC MS. The analysis shows the presence of $C_{11}H_{22}O_2$ (186 Mol Weight: Decanoic acid, methyl ester, Capric acid methyl ester, Metholene 2095, Methyl caprinate, Methyl decanote, Methyl-n-): $C_{16}H_{32}O_2$ (256 Mol Weight: n-Hexadecanoic acid, n-Hexadecoic acid, Palmitic acid, Pentadecanecarboxylic acid, 1-Pentadecanecaxylic acid): $C_{10}H_{18}O_2$ (170 Mol Weight: Allyl heptanoate, Heptanoic acid, 2-propenly ester, Allyl enanthate, Allyl heptoate, Allyl heptylate, Heptanoic acid, allyl ester, 2-Propenyl): $C_{19}H_{36}O_2$ (296 Mol Weight: 11-Octadecenoic acid, methyl ester, Methyl 11-octadecenoate, Octadec-11-enoic, methyl ester, Methyl (11E)-11-octadecenoate): $C_{18}H_{36}O_2$ (284 Mol Weight: Hexadecanoic acid, 15-methyl ester $$ Methyl isoheptadecanoate, Methylhexadecanoate): $C_{18}H_{34}O_2$ (282 Mol Weight: Oleic Acid $$ 9-Octadenoic acid (Z)-$. delta (Sup9)-Octadecenoic acid, cis- Oleic Acid, cis-9-Octadecenoic Acid): $C_{18}H_{36}O_2$ (284 Mol Weight: Octadecanoic acid, Steanic acid, n-Octadecanoic acid $$ Hummko Industrene R, Hydrofol Acid 150, Hystrene S-97, Hystrene T-70, Hystrene 80): $C_{11}H_{18}O_2$ (182 Mol Weight: Cyclopropanecarboxylic acid, cyclohexylmethyl ester, Cyclohexylmethyl cyclopropanecarboxylate): $C_{21}H_{37}F_5O_2$ (416 Mol Weight: Pentafluoropropionic acid, octadecyl ester): $C_{18}H_{34}O$ (266 Mol Weight: 9-Octadecenal, Octadecenyl aldehyde, (9E)-9-Octadecenal.

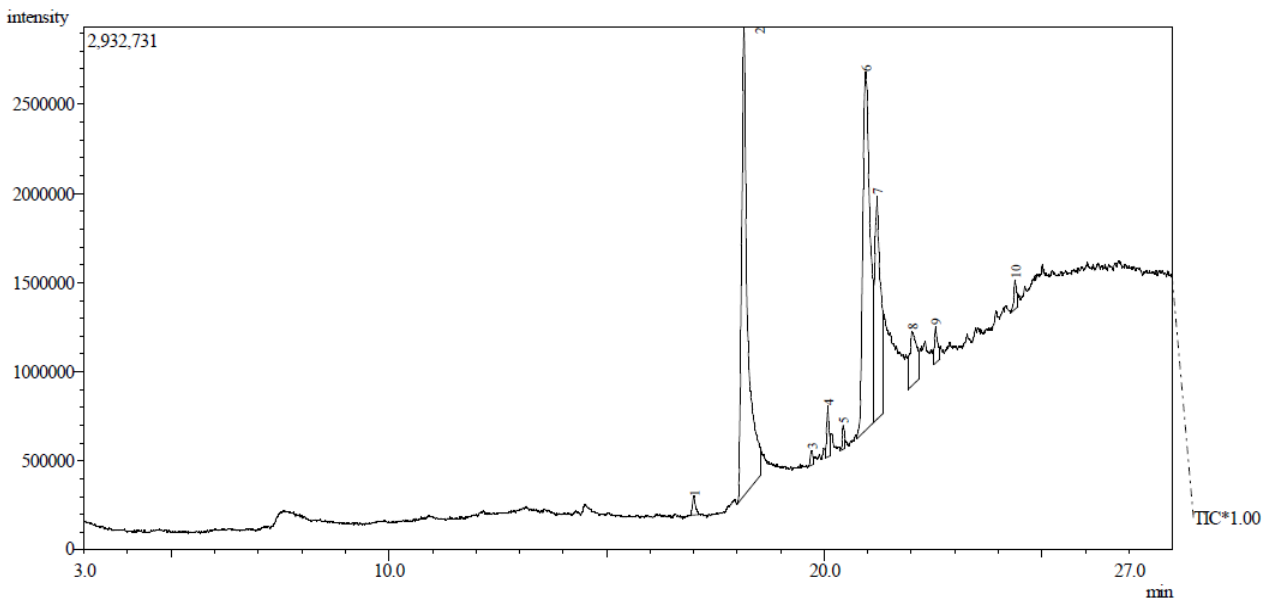

Figure 1. The GC MS chromatogram of the guava leaves extract

3.2 Potentiodynamic polarization study of aluminum corrosion on guava leaf

The inhibitive efficacy of guava leaf on the anodic and cathodic polarization curves of an aluminum electrode in 0.5 M H_2SO_4 solution was studied. The polarization curve obtained was shown in Figure 2. The corrosion parameters of Al such as $E_{corr.}$, and i_{corr} were calculated and listed in Table 2. A steady state potential was readily attained which is in line with the free corrosion potential, E_{corr} of the metal. It was shown after the Table was inspected and the values of E_{corr} were altered while the concentration of guava leaf was increased. It is evident that the incorporation of guava leaf into the system aids in positive potential shifting of the values of $E_{corr.}$ This is an indication that guava leaf extract proved to be an anodic inhibitor for Al. There was a significant decrease in the i_{corr} values on the increase of the additive concentration, indicating the increase in the resistance of aluminum to corrosion leads to the enhanced efficiencies of inhibition.

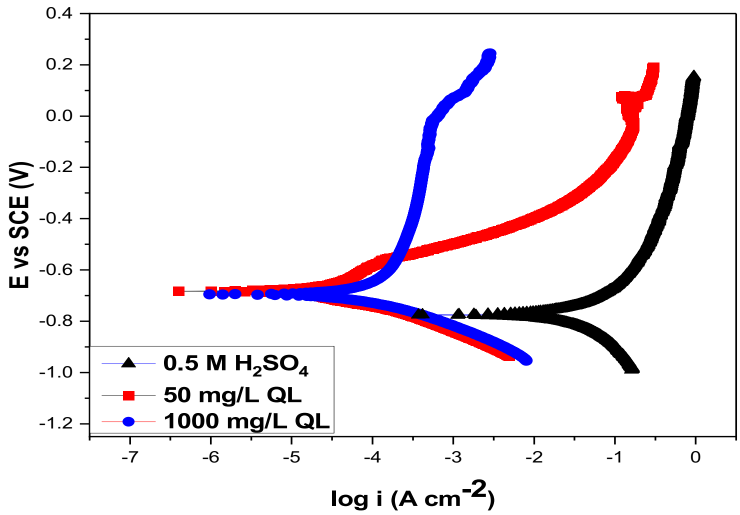

Figure 2. Potentiodynamic polarization for aluminum in: 0.5 M H_2SO_4 in the presence and absence of different concentrations of guava leaf extracts

Table 2. Potentiodynamic polarization parameters for aluminum in 0.5 M H_2SO_4 in the absence and presence of guava leaf

System	I_{corr} (µA/cm^2)	E_{corr} (mV vs SCE)	IE%
0.5 M H_2SO_4	258.9	-784.8	
50 mg /L GL	20.3	-711.6	92.2
100 mg/L GL	12.8	-698.9	95.1

3.3. Electrochemical impedance spectroscopy considerations on guava leaf

In the presence of guava leaf, the Nyquist plots showed a pronounced capacitive loop followed by an inductive loop for the Al samples immersed in 0.5 M H_2SO_4 solution as shown in Figure 3. The circumference of the Nyquist plots can be related to charge transfer resistance as mentioned earlier. Accordingly, the size of the capacitive loops was greater in the presence of guava leaf extract compared to that in the blank solution confirming the higher corrosion resistance of the aluminum metal in the presence of the inhibitor. Furthermore, the result obtained showed that the Q_{po} value was far lower in the inhibited environment compared to the blank solution, while the R_{po} was greater for the inhibited than for the uninhibited Al. Also, the value of inductance was greater for the inhibited Al sample than for the uninhibited, showing that the addition of guava leaf modified the electrochemistry of the Al sample by reducing the corrosive attack of the aggressive species. Further

evidence was provided via the higher value of R_{ct}, for Al in the presence of the inhibitor than the value obtained in the absence of guava leaf. The electrochemical impedance parameters of Al were calculated and it is given in Table 3. It is obvious that the adsorption of guava leaf species serves as a barrier blocking the contact between the Al substrate and the electrolyte solutions.

3.4 Scanning electron microscopy result

Plate 1a shows the SEM micrographs of aluminum specimens dipped in 0.1 M H_2SO_4 in the presence and absence of an optimum concentration of guava leaf extract + KI. The micrograph received specimen shown in Plate 1a appears smooth. However, the uninhibited solution as shown in Plate 1b, shows a rough surface due to the effective dissolution of aluminum in an aggressive environment but in the presence of guava leaf extract + KI, the roughness is reduced significantly Plate 1c. It shows the evidence of adsorbed species on the aluminum surface, and also confirms the adsorption of the inhibitors (guava leaf extract + KI) constituents on the surface of the metal.

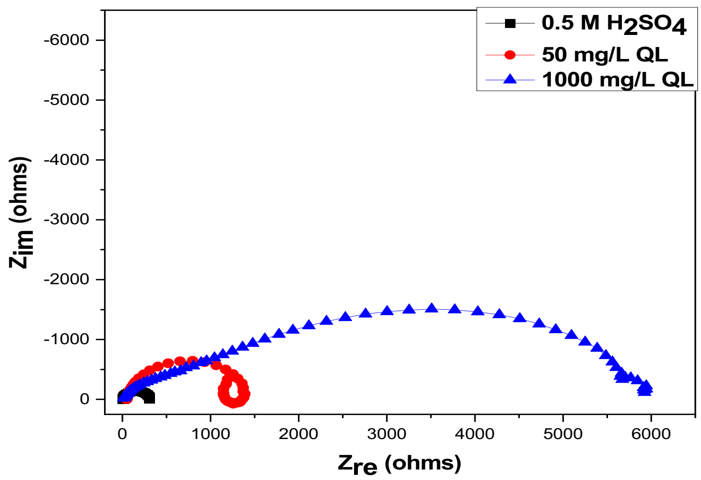

Figure 3. Electrochemical impedance spectroscopy for mild steel in: 0.5 M H_2SO_4 in the presence and absence of different concentrations of guava leaf extract.

Table 3. Electrochemical impedance parameters for aluminum in 0.5 M H_2SO_4 in the absence and presence of guava leaf

System	R_s (Ωcm^2)	R_{L1} (Ωcm^2)	R_{ct} (Ωcm^2)	Q_{dl} ($\Omega^{-1}s^n$ cm^2)	L
0.5 M H_2SO_4	1.96	7.74	257	3.48	5.77
200 mg /L GL	3.79	1247	1418	3.19	1392
100 mg/L GL	4.07	5323	5404	2.69	5358

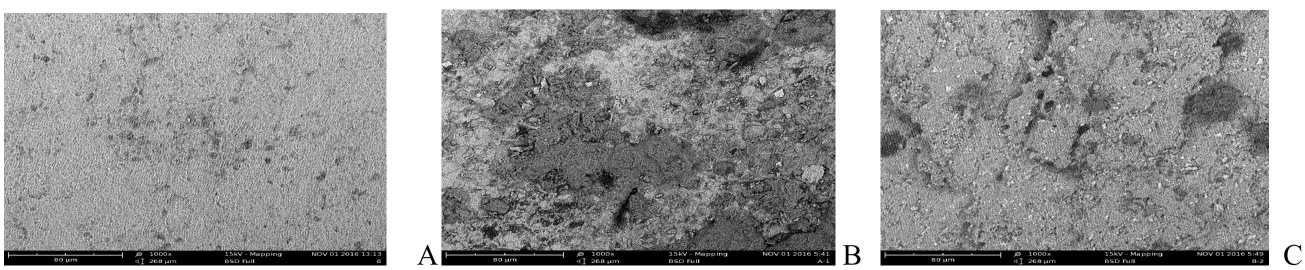

Plate 1. SEM images of the aluminum surface after immersion at 27 °C in 0.1 M H_2SO_4 (A) As received, (B) without inhibitors, and (C) with 2 g/l of guava leaf extract + KI

3.5 Gravimetric measurement results

3.5.1 Weight loss

At room temperature of (27 ± 1°C), there was a dissolution of aluminum metal coupon in 0.5M H_2SO_4 in the presence and absence of varying concentrations of guava leaf extracts + KI on different days (days 1 to 5). This was revealed in the plot of weight loss of aluminum coupons versus time Figure 4 in the presence and absence of guava leaf extract + KI at 27 ± 1°C. The dissolution of aluminum coupon in acid decreases with days but was highly controlled on the incorporation of guava leaf extract + KI into acid media. This is a strong indication that guava leaf extract + KI acted as a good inhibitor for aluminum in a 0.5 M H_2SO_4 solution.

3.5.2 Corrosion rate

Table 4 indicated the control of corrosion rate was achieved when different concentrations of guava leaf extracts + KI were incorporated in the H_2SO_4 solution after 5 days. In Table 4, there was an indication from the recorded data that the aluminum corrosion reduces with time (days) in 0.5M H_2SO_4. It signifies that the potency of diluted acid solution reduces with time or it could be that the corroded surface formed a stable surface which might lead to preventing the diffusion of diluted acid solution at the surface of the metal. Figure 5 depicts the variation of corrosion rate with different concentrations of guava leaf extract + KI on different days. There was a reduction in corrosion rate with guava leaf extracts + KI, and the corrosion rate of aluminum was reduced at each of the studied concentrations. The reduction process of the metal dissolution was also shown in Table 4. The obtained data in Table 4 is in line with the traditional method. The dependence of the inhibitory action on the quantities of inhibitory species obtained in the system was shown when the concentration of guava leaf extract + KI was increased.

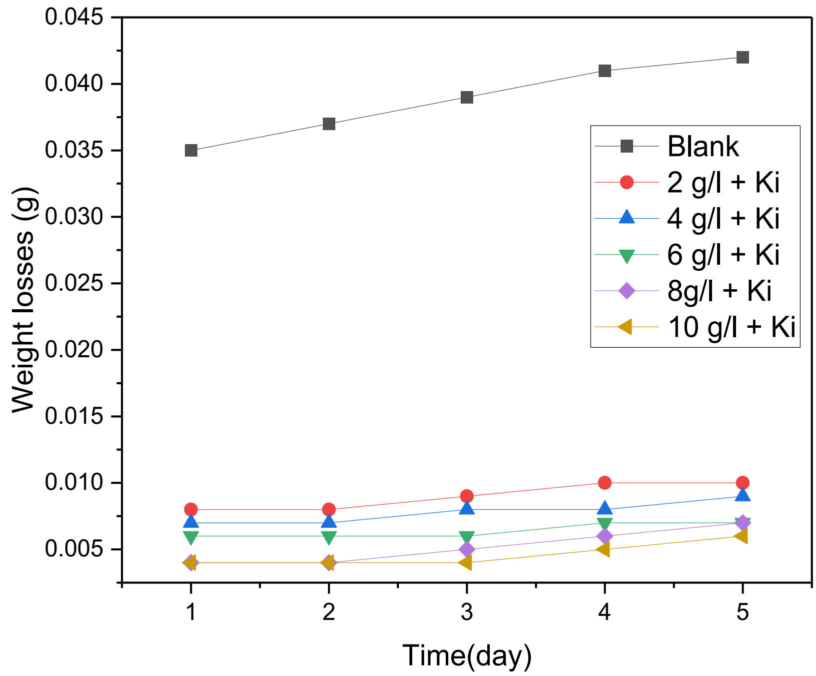

Figure 4. Weight loss against time for aluminum corrosion in 0.5 M H_2SO_4 in the absence and presence of different concentrations of guava leaf extract + 0.4 g KI

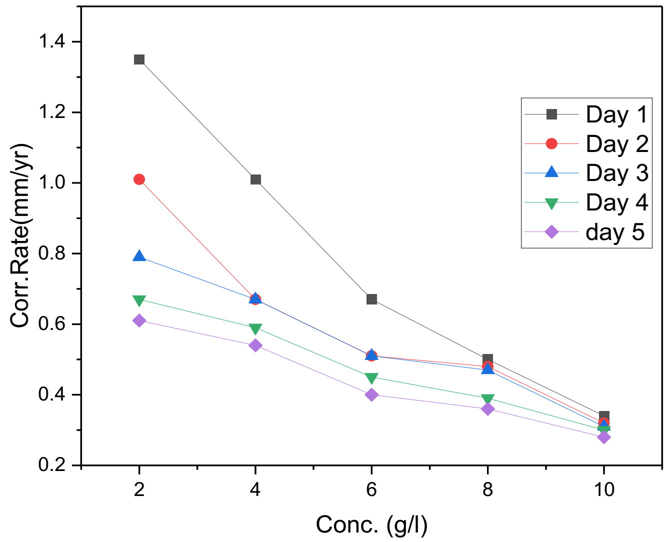

Figure 5. Variation of corrosion rate with different concentrations of guava leaf extract + KI on different days

3.5.3 Inhibition efficiency

By comparing the corrosion rates of aluminum in 0.5M H_2SO_4 in the blank and inhibited solutions, the effectiveness of guava leaf extracts + KI in retarding the dissolution of aluminum in H_2SO_4 was observed. This was expressed as a function of the inhibition efficiency (% IE). Figure 6 shows the relationship between the inhibition efficiency and different concentrations of guava leaf extract + KI in 0.5 M H_2SO_4 at 27 ± 1°C. An increase in the inhibition efficiency was observed as the inhibitor concentration increased. The maximum inhibition efficiency value of 98.41% was obtained at the highest concentration of (10 g/l) of guava leaf extract + (0.4 KI) shown in Table 5. Also, the efficiency of inhibition was seen to decrease with time (days) which is an indication that guava leaf extract + KI as an inhibitor for corrosion is time-dependent.

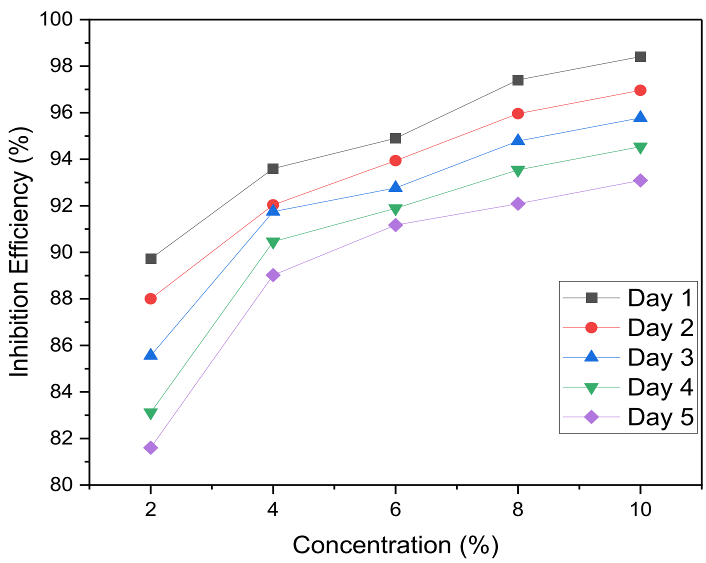

Figure 6. Variation of inhibition efficiency with different concentrations of guava leaf extract + KI on different days

Table 4. Calculated values of weight losses (g) for aluminum in 0.5 M H_2SO_4 at different concentrations of inhibitor (guava leaf extract) with constant halide (KI) at a constant temperature

SYSTEM	WEIGHT LOSSES WITH HALIDES 0.4gKI				
DAY /CONC.	1	2	3	4	5
BLANK	0.035	0.037	0.039	0.041	0.042
2 g/LOLE	0.008	0.008	0.009	0.010	0.010
4 g/LOLE	0.007	0.007	0.008	0.008	0.009
6g/LOLE	0.006	0.006	0.006	0.007	0.008
8g/LOLE	0.004	0.004	0.005	0.006	0.007
10g/LOLE	0.004	0.004	0.004	0.005	0.006

Table 5. Calculated values of corrosion rate (mm/year), inhibition efficiency (%), and surface coverage (θ) for Al in H_2SO_4 in the presence and absence of guava leaf extract + KI (weight loss measurement at 27± 1 °C)

System	Corrosion rate (mm/yr)					Inhibition efficiency (IE %)					Degree of Surface Coverage				
DAY/ CONC.	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
BLANK	11.7	6.23	4.38	3.45	2.83										
2g/LOLE+0.4gKI	1.35	1.01	0.79	0.67	0.61	89.72	88	85.56	83.12	81.6	0.90	0.88	0.86	0.83	0.82
4g/LOLE+0.4gKI	1.01	0.67	0.67	0.59	0.54	93.6	92.04	91.75	90.46	89.02	0.94	0.92	0.92	0.90	0.89
6g/LOLE+0.4gKI	0.67	0.51	0.51	0.45	0.4	94.9	93.94	92.77	91.89	91.17	0.95	0.94	0.93	0.92	0.91
8g/LOLE+0.4gKI	0.50	0.48	0.47	0.39	0.36	97.41	95.96	94.78	93.54	92.09	0.97	0.96	0.95	0.94	0.92
10g/LOLE+0.4gki	0.34	0.32	0.31	0.3	0.28	98.41	96.96	95.78	94.54	93.09	0.98	0.97	0.96	0.95	0.93

3.6 *Thermometric results*

The result from the thermometric method is of great importance in the measurement of corrosion because it has proved to be a sensitive method used to test corrosion studies. It has also helped in determining the corrosion behavior of metals and their alloys in aggressive environments when the reaction numbers (RN) are introduced. The calculated values of reaction number (RN) and percentage reduction in the reaction RN for aluminum dissolution in 0.5 M H_2SO_4 which contains different concentrations of guava leaf extract + KI obtained from thermometric measurement are presented in Table 6.

Table 6. Calculated values of reaction number (RN) and percentage reduction in RN for aluminum in 0.5 M H_2SO_4 containing different concentrations of guava leaf extract + KI.

System	Reaction number (RN) ($^{O}C\ min^{-1}$)	**%** Reduction in RN (> inhibition efficiency)
Blank	0.50	—
2 g/l + 0.4KI	0.26	52.00
4 g/l + 0.4 KI	0.20	70.50
6 g/l + 0.4 KI	0.14	81.00
8 g/l + 0.4 KI	0.11	86.33
10 g/l + 0.4 KI	0.07	92.10

3.7 *RSM results of the weight loss method*

For the corrosion inhibition of metal in the medium with guava leaf extract + KI, presented in Table 7, corrosion rate, inhibition efficiency, and surface coverage are the responses to the factors of time, inhibitor concentration, and medium concentration. The data below presents the variations of corrosion rate with time, inhibitor concentration, and medium concentration of aluminum in the H_2SO_4 acid environment. A decrease in corrosion rate with an increase in inhibitor concentration was

observed while there was an increase in corrosion rate with an increase in time and medium/acid concentration. The decrease in corrosion rate with an increase in the concentration of the inhibitor is evidence that guava leaf extract + KI (inhibitor) is a good inhibitor that inhibited the corrosion of aluminum in an acidic medium. It was observed also that an increase in the concentration of the guava leaf extract increases the inhibition efficiency and surface coverage while an increase in time decreases the efficiency of the inhibition. These observations are in agreement with previous studies (Ndibe *et al*., 2012, Abdulwahab *et al*., 2012).

Table 7. The RSM result of the corrosion inhibition of Al in H_2SO_4 using guava leaf extract with Halide

Std	Run	Block	Factor 1; A: Time. (days)	Factor 2; B: Inhibitor conc.(g/l)	Factor 3; C : Medium conc. (g/l)	Response 1; Corrosion rate (mm/yr)	Response 2; Inhibitor efficiency (%)	Response 3; Surface coverage
2	3	Block 1	3	2.00	0.30	4.88	90.25	0.9
11	4	Block 1	3	2.00	0.50	4.63	78.77	0.79
10	5	Block 1	1	10.00	0.10	0.51	97.11	0.97
16	6	Block 1	2	6.00	0.30	2.02	90.84	0.91
5	7	Block 1	2	6.00	0.10	1.18	74.95	0.74
8	8	Block 1	3	6.00	0.50	4.04	95.24	0.95
4	9	Block 1	3	10.00	0.30	1.18	95.83	0.96
15	10	Block 1	3	6.00	0.30	2.02	90.84	0.91
3	11	Block 1	2	10.00	0.30	0.84	84.42	0.84
1	12	Block 1	5	2.00	0.30	2.69	50.09	0.5
9	13	Block 1	3	2.00	0.10	2.37	86.43	0.86
14	14	Block 1	3	6.00	0.30	2.02	90.84	0.91
7	15	Block 1	5	6.00	0.50	2.36	62.12	0.62
17	16	Block 1	3	6.00	0.30	2.02	90.84	0.91
12	17	Block 1	3	10.00	0.50	1.85	91.72	0.92

3.7.1. Graphical analysis of the inhibition efficiency IE (%) as determined using RSM

The graphical analyses of inhibition efficiency of the inhibitor of guava leaf extract + KI (aluminum in H_2SO4) are shown in Figure 7. The Normal plots of residuals against studentized residuals were utilized to test the significance of the model order. A linear graph was obtained for the plot residuals versus studentized residuals. The relationship between the factors and responses of the experimental design is shown in the 3-D surface plots. The factors include inhibitor concentration, medium concentration, and time of the metal (aluminum) immersion. The responses are the inhibition efficiency, corrosion rate, and surface coverage in an acidic medium. These observations are in agreement with previous studies (El Ouariachi *et al*., 2010). The graphs of the inhibition efficiency versus inhibition concentration, medium concentration, and time were presented in the 3-D surface plots. Further analysis of the data was addressed in terms of analysis of variance, mathematical model, and optimization. The analysis of variance aids in identifying the model's significance terms. The power of the variable was used to confirm the quadratic models. The model shows the inhibition efficiency of the inhibitor as a function of inhibitor concentration, medium concentration, and time. The interactive behavior of the inhibitor concentration, medium concentration, and time was also identified.

3.8 The ANOVA results of response surface methodology

The ANOVA of the corrosion rate of Al in H_2SO_4 with halide using guava leaves extracts indicated a model F- value of 7.73 which implies the model is significant (Table 8). Values of Prob >

F less than 0.05 indicate the model terms are significant. In this case, A, B, $A^{2,}$ and C^2 are significant model terms. The Pred R-Squared of 0.6626 is in reasonable agreement with the Adj R-Squared of 0.7911. Adequate precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 11.599 indicates an adequate signal. The source of noise may be attributed to non-controllable factors of oxygen content and flow rates of the inhibitor's functional group. The model is significant and can be used to navigate the design space.

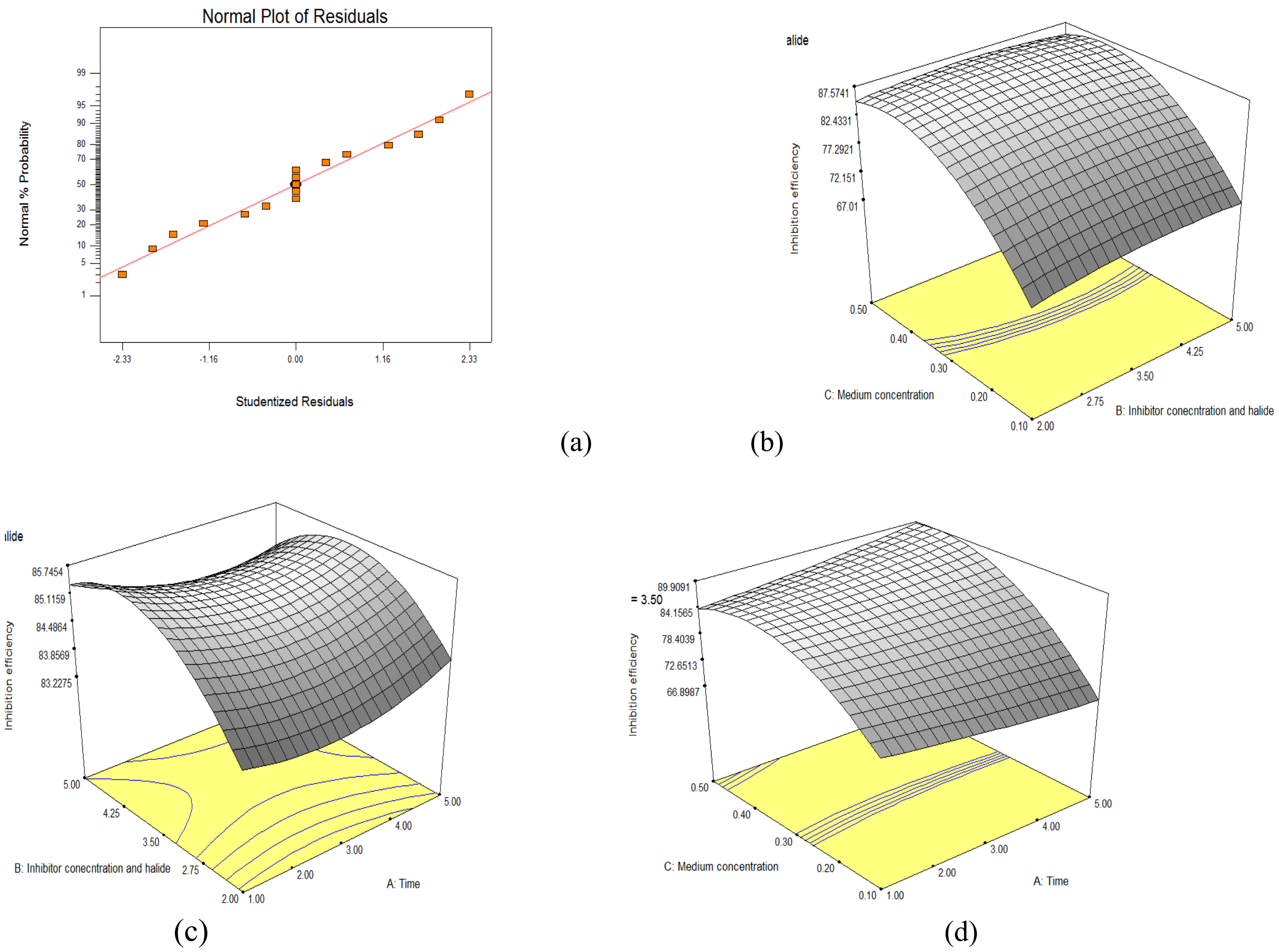

Figure 7. IE (%) of guava leaf extract with halide as corrosion inhibitor of Al. in H_2SO_4
(a) Normal plot of residuals against studentized residuals IE (%), (b) IE (%) against inhibitor concentration and medium concentration (c) IE (%) against Inhibitor concentration and time (d) IE (%) against medium concentration and time.

3.9 Mathematical models of the inhibition efficiency

The mathematical model of the inhibition efficiency of the guava leaf extracts as corrosion inhibitor of the metals in acid media are presented in Eqn. 7. The model was obtained using RSM tools of design expert software. The model explained the relationship between the inhibition efficiency (IE), time (A), inhibitor concentration (B), and medium concentration (C). The mathematical model in terms of coded factors was obtained with the CCD of RSM. The model in terms of the coded factors forecasted the response for given levels of each factor. The positive sign in the model signifies the synergistic effect, while the negative sign signifies an antagonistic effect. Time (A), inhibitor concentration (B), quadratic terms of time, and medium concentration (AC) are the significant terms of the model. Considering the significant terms, the model for the corrosion

inhibition efficiency of guava leaf extract for the aluminum metal in an acidic solution is presented in Eqn. 7. The model for the corrosion inhibition of Al in H_2SO_4 by guava leaves extract with halide is:

$$IE = + 92.04 + 2.80*B + 0.91*A^2 – 2.74*C^2 – 0.95*A*C + 1.38*B*C \quad \textbf{Eqn. 7}$$

Table 8. ANOVA for the corrosion inhibition efficiency of Al in H_2SO_4 with halide using guava leaves extract.

ANOVA for Response Surface Quadratic model; corrosion rate Analysis of variance table [Partial sum of squares – Type III]						
Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F	
Model	2.74	9	0.30	7.73	0.0067	Significant
A- Time	1.34	1	1.34	33.91	0.0006	
B- Inhibitor conc	0.44	1	0.44	11.09	0.0126	
C- Medium conc.	2.000E-004	1	2.000E-004	5.074E-003	0.9452	
A^2	0.32	1	0.32	8.00	0.0254	
B^2	0.13	1	0.13	3.22	0.1156	
C^2	0.48	1	0.48	12.26	0.0100	
AB	0.046	1	0.046	1.17	0.3147	
AC	0.040	1	0.040	1.01	0.3473	
BC	0.000	1	0.000	0.000	1.0000	
Residual	0.28	7	0.039			
Lack of Fit	0.28	3	0.092			
Pure Error	0.000	4	0.000			
Cor Total	3.02	16				
Std. Dev.	0.20		R-Squared			0.9086
Mean	0.72		Adj R-Squared			0.7911
C.V. %	27.53		Pred R-Squared			0.6626
PRESS	4.41		Adeq. Precision			11.599

3.10 Optimum parameters of the corrosion inhibition efficiency of guava leaf extract + KI for the aluminum metal in H_2SO_4

The optimization tool was activated via the numerical optimization function of the CCD of RSM. The optimum inhibition efficiency of the guava leaf extract with halide for the corrosion inhibition of Al in H_2SO_4 was obtained as 98.41%, with surface coverage of 0.97 and corrosion rate of 0.51mm/yr validated at the optimum conditions of time of 1 day, inhibitor concentration of 10g/l and medium concentration of 0.10g/l at temperature of 45^{o}C . The data in Table 9 shows the optimum inhibition concentration, optimum medium concentration, and optimum time, as well as the response optimum inhibition efficiency of aluminum metal in acid medium.

Table 9. Optimum parameters of the corrosion inhibition of guava leaf extract and halide for the corroded aluminum metal in H_2SO_4.

Medium	Inhibitor	Optimum inhibitor conc. (g/l)	Optimum time (days)	Optimum medium conc. (g/l)	Optimum inhibition efficiency (%)
H_2SO_4	Guava leaf extract + KI	10	1	0.10	98.41

On the basis of literature, the inhibitory action on natural extracts occurred via the intermolecular synergistic effect of the various components (Ezeh *et al*., 2023; Lrhoul *et al*., 2023).

Conclusion

Guava leaf extract + KI were found to be good inhibitors for aluminum corrosion in a 0.1 M H_2SO_4 environment. The protective layer formed by guava leaf extract promotes the passivation of aluminum, inhibiting the dissolution of the metal ions which further hinders the corrosion process. The optimum inhibition efficiency of the guava leaf extract with halide for the corrosion inhibition of Al in H_2SO_4 was obtained as 98.41%, with maximum surface coverage of 0.97 and minimum corrosion rate of 0.51mm/yr validated at the optimum conditions of time of 1 day, inhibitor concentration of 10g/l and medium concentration of 0.10g/l at temperature of 45°C. Inhibition efficiency (%) of the guava leaf extract + KI increased with an increase in the concentration of the extract and halide and decreased with time (days). The efficiency of the inhibition of guava leaf extract and halide was deduced to be concentration and time dependent. Thus, the guava leaf extract which is a natural extract possessing diverse phytochemicals is very effective in the corrosion inhibition of metals.

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Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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