Optimization of *Chrysophyllum albidum* leaf extract as corrosion inhibitor for aluminium in 0.5 M H$_2$SO$_4$

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**ABSTRACT**

Inhibition of *Chrysophyllum albidum* leaf (CAL) extract toward 0.5 M H$_2$SO$_4$ corrosion of aluminium was optimized applying response surface methodology. Corrosion analysis was carried out using weight loss and electrochemical techniques. The results of the various analyses of the leaf extracts acted as a good corrosion inhibitor for aluminium in 0.5 M H$_2$SO$_4$. Inhibition efficiency increases as the extract concentration increased. Results of molecular dynamic simulations of the active constituents of the extracts confirmed the adsorption potentials of the ethanol extracts of CAL. Optimal inhibition efficiency of 78.43(%) was obtained at optimum inhibitor concentration of 1.00 g/l, 11.71hs and temperature of 303.60k

**Keywords**: Aluminium, corrosion, optimal, electrochemical, *Chrysophyllum albidum*

1. **INTRODUCTION**

Aluminum is characterized with natural resistance due to the formation of a thin and protective film oxide on its surface [1]. However, when aluminium is exposed to H$_2$SO$_4$
endowed environment, such as acid pickling solutions, chemical etching, industrial cleaning or scale dissolving, these processes result in great weight loss of aluminium [2]. In order to minimize and/or prevent aluminium dissolution, various types of corrosion preventive materials are used, most of them are organic compounds, which contain atoms of nitrogen, sulphur, oxygen and phosphor in their structure [3-5].

Although most of the synthetic compounds applied as inhibitors have commendable inhibitive ability, their exorbitant cost and toxic nature tends to be the main setbacks in the use of these compounds as corrosion inhibitors [6, 7]. In compliance with global call for clean solution to world energy demand and healthy environment, scientist have in recent times beamed their research network on the development of green revolution (eco-friendly) in the name of organic compounds in response to accruable gains of using plant extracts which are naturally conformed to such terms that includes formulations that are not toxic to humans, have great environmental effect, high level of biodegradability, and maintenance of commendable efficiency and very low cost [8].

Extraction and effective use of natural plant extracts that commands presence of organic complex with great number of empty adsorption sites ready to accept lonely \(\text{sp}^2\) electron pairs that are always present on the nitrogen, sulphur, and oxygen atoms of the heterocyclic rings are inevitable [9-12].

Chrysophyllum albidum (CA) is a dominant canopy tree of low land and mixed forest zone from the family of sapotaceae. It is commonly distributed from West Africa to Sudan and frequently found in villages in Anambra, Nigeria [13-19]. African star apple as it is commonly called grows up to a height of 25-37m with a major girth varying from 1.5 to 2 m [24]. The root, bark and leaves of CA have been employed as rich sources of antioxidants which acts against oxidative stress related disease such as diabetes, coronary heart diseases [26].

CAL extract contains many organic compounds, such as phenolics, terpenoids and tannins as their major phytocompounds [27] and also saponins, flavornoids and alkaloids in moderate amount to scavenge free radicals induce detoxification [28-30]. Thorough assessment of various research work carried out by scientists showed that little or no reported work on inhibitive effects of CAL extract on sulphuric acid corrosion of aluminium have been done by any researcher.

Hence, the main objective of this onerous task is to investigate the CAL extract as potential inhibitor of the aluminium corrosion in 0.5 M H\(_2\)SO\(_4\). The investigation was carried out by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy methods. The shifting mechanisms of plant extracts and corrosion products were analyzed with the aid of FT-IR. The effects of temperature on the inhibitive ability of the extract molecules of the extract were adequately studied. Some thermodynamic and kinetics parameters (isotherm properties) were calculated in order to validate the results of the various process variables involved.

This study embraced central composite design in the investigation of independent variables, such as concentrations of the acid, concentrations of the inhibitor, temperature and time variations (input) and dependent variables, referred within the context of this studies as expected responses; weight loss, corrosion rate and inhibition efficiency (output). Effects of critical parameter of corrosion process of aluminium inhibition by CAL extract were listed on Table 2 [18, 19].
2. EXPERIMENTAL METHODS

2.1. Gravimetric Method

Gravimetric (weight loss) method was carried out on aluminium alloy (AA3003) specimen with the composition: 1.22% Mn, 0.55% Fe, 0.363% Si, 0.017% Cu, 0.064% Pb, 0.026% Ti, 0.009% V, 0.19% others 97.672% Al. Each metal coupon, which was 0.04 cm thickness was mechanically pressed cut into coupons of dimensions 2.6 × 2.6 × 0.04 cm. The coupons were used unpolished, but were degreased in absolute ethanol, dried in acetone, weighed and stored in moisture free desiccators prior to use.

Considering one factor at a time, the weight loss method was carried out at different temperatures and with various concentrations of the CA extracts. According to this method, weighed aluminium alloy coupons were independently immersed in 250 ml open beakers containing 200 ml of 0.5 M H$_2$SO$_4$. More so, Al coupons were separately immersed in 250 ml open beakers containing 200 ml of 0.5 M H$_2$SO$_4$ with various concentrations of the extract. The variation of weight loss was monitored periodically at various temperatures in the absence and presence of various concentrations of the extract.

At the stipulated time, the aluminium coupons were removed, rinsed with deionize water, dried in acetone and reweighed. The weight loss was calculated as the difference between the initial and the final weight after the removal of the corrosion product.

Weight loss measurements were undertaken using a FAJA digital weighing balance of the range 0.0001 to 2000g. All the weighed results are presented in duplicate form with standard deviation range of 0.001 to 0.2g.

2.2. Electrochemical Techniques

For potentiodynamic polarization and electrochemical impedance spectroscopy, test metal samples of aluminum for electrochemical experiment were shaped into cylindrical specimens and fixed in polytetrafluoroethylene (PTFE) rods using epoxy resin in a manner that exposed only one surface area of 1 cm$^2$. The electrodes used were polished with silicon carbide (from 800 to 1200 grit), rinsed with double distilled water, degreased by ethanol and dried in acetone.

The electrochemical experiment were conducted in a three electrode corrosion cell applying a VERSASTAT 400 complete dc voltametry and corrosion system with V3 studio software for electrochemical impedance spectroscopy and potentiodynamic/Galvanostat corrosion system with E-chem. software for potentiodynamic polarization experiments. An application of platinum sheet as counter electrode and a saturated. Calomel electrode (SCE) as reference electrode complimented the potentiodynamic studies. The calomel electrode was connected through a lugging capillary.

Impedance measurements were carried out in an unhindered and aerated solutions at the end of 1800s at 32 ± 1 °C. The measurements were performed when the corrosion potentials ($E_{corr}$) was maintained at a frequency range of 100 kHZ-0.1HZ and a signal amplitude perturbation of 10 mV [18]. Potentiodynamic polarization studies were carried out between the potential range of -250 to 250 mV versus corrosion potential ($E_{corr}$) at a scan rate of – 250 to 400 mVs$^{-1}$. Every single test was performed in triplicate to authenticate the reproducibility of the results obtained. All tests were carried out using fresh solutions steadily maintained at a temperature of 32 ± 1°C in a digital thermostat [19].
3. RESULTS AND DISCUSSION

3.1. Weight loss measurements

Figure 1, represents the relation between time and inhibition efficiency of aluminium coupons in solution of 0.5 M H$_2$SO$_4$ devoid of and in the presence of different concentrations of inhibitor extracts. Close examination of the Figure 1. IE (%) vs time for CAL graph in various concentrations) reveals that the loss of weight of aluminium increases proportionately with increasing time in all tested solutions. It is of note that the slopes of the plotted lines, which represent the rate of weight loss of aluminium, are affected by the addition of the inhibitive extract. The corrosion inhibition increases with increase in extracts concentration and the tabulated (Table 1) values of inhibition efficiency of aluminium in 0.5 M H$_2$SO$_4$, time and different concentrations of CAL extracts revealed strong inhibitive ability of the extract molecules for the H$_2$SO$_4$ corrosion of aluminium.

**Table 1.** Results of IE (%) of Al in H$_2$SO$_4$ versus time at various concentrations of CAL extract.

<table>
<thead>
<tr>
<th>Concentration (g/l)</th>
<th>Time (h) / IE(%) of Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>0.2</td>
<td>28.33</td>
</tr>
<tr>
<td>0.45</td>
<td>30.05</td>
</tr>
<tr>
<td>0.7</td>
<td>32.87</td>
</tr>
<tr>
<td>0.95</td>
<td>34.00</td>
</tr>
<tr>
<td>1.2</td>
<td>35.65</td>
</tr>
</tbody>
</table>

3.2. Adsorption Studies

Adsorption isotherms are usually used to describe the adsorption process. The most frequently used isotherms include Langmuir, Temkin, Frumkin, Flory-Huggins, etc. the establishment of adsorption isotherms that describe the adsorption of a corrosion inhibitor can provide important clue to the nature of the metal – inhibitor interaction. In order to obtain the adsorption isotherm, the degree of surface coverage ($\theta$) for various concentrations of the inhibitor has been calculated according to equation (1).

$$\theta = (1 - \frac{\text{inh}}{\text{uninh}}) \quad \text{------------------------ (1)}$$

where: inh and uninh indicate inhibited and uninhibited corrosion respectively.

In this study, Langmuir is tested for the CAL extract at three temperature ranges of: 303K, and 323K. Straight lines Fig. (1) indicate that the plant extracts obey Langmuir adsorption isotherms and is given by equations (2).
Langmuir: \( \log C/\theta = \log c – \log k \)  \hspace{1cm} (2)

where: \( \theta \) is the degree of surface coverage, \( K \) is the equilibrium constant of the adsorption isotherm, \( C \) is the concentration of the inhibitor in the bulk solution. The linear correlation coefficient is close to unity, Table 2, hence, adsorption of inhibitor follows Langmuir, adsorption isotherms. \( R^2 \) values are in the range as listed in Fig (1). The four adsorption isotherms are strictly based on the assumption that each active site of the metal surface holds one adsorbed species. Therefore, one adsorbed water molecule is replaced by one molecule of the inhibitor adsorbed CAL extract) on the aluminum surface.

The apparent free energy of adsorption \( (\Delta G^0_{ads}) \) is calculated from the relation;

\[
\Delta G^0_{ads} = -2.303 \, RT \log 55.5 \, K_{ads} \hspace{1cm} (3)
\]

where: \( k_{ads} = \theta/c \, (1 - \theta) \)

Figure 1. Plot of Langmuir isotherm for aluminum in H\(_2\)SO\(_4\) CAL extract

The values of \( K_{ads} \), \( \Delta G^0_{ads} \) and other adsorption isotherm properties of Langmuir are shown on In respect to the fitted data to the Langmuir isotherm, the correlation coefficient, \( R^2 \) value is close to unity, indicating excellent adherence to Langmuir adsorption isotherm [22]. The negative values of \( \Delta G^0_{ads} \) indicate the spontaneous adsorption of the inhibitor as the value of the free energy of adsorption is not only negative but ran short of the specified range of \(-40 \, \text{kJ} \, \text{mol}^{-1}\) required for chemical adsorption. This is in compliance to the previous studies [23,
From the Frumkin adsorption parameter, the lateral interaction term ($\alpha$) gave positive values indicating attractive behavior of the inhibitor on the aluminium surface. From Temkin adsorption parameter, the attractive value (a) is negative, signifying that repulsion exists in the metal/electrolyte interface [25]. The value of the size parameter (x) is positive; the positivity of the value clearly indicates that the adsorbed molecules of the extract are bulky [26]. The values of $k_{ads}$ are relatively small indicating that the interaction between the adsorbed extract molecules and aluminium surface is physically adsorbed. This is also supported by lower negative ($\Delta G_{ads}$) values for CAL extract [27, 28]. Generally, close examination of isotherm studies of corrosion inhibition of aluminium in CAL extract listed in table 2 showed that the process of film formation which acted as a barrier concealing the surface of aluminium, influenced that of destruction of the metal surface and occurred according to the mechanism of physical adsorption in a stronger ter.

Table 2 Adsorption parameters for the corrosion inhibition of aluminium in H$_2$SO$_4$ by CAL extract.

<table>
<thead>
<tr>
<th>Adsorption isotherm</th>
<th>Temperature (k)</th>
<th>$R^2$</th>
<th>Log K</th>
<th>K</th>
<th>$\Delta G_{ads}$ (KJ/mol)</th>
<th>Isotherm property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir isotherm</td>
<td>303</td>
<td>0.994</td>
<td>-0.233</td>
<td>0.5848</td>
<td>-8.767</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.998</td>
<td>-0.135</td>
<td>0.7328</td>
<td>-9.952</td>
<td>-</td>
</tr>
<tr>
<td>Frumkin isotherm</td>
<td>303</td>
<td>0.996</td>
<td>-1.1815</td>
<td>0.0658</td>
<td>-3.263</td>
<td>$\alpha$</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.959</td>
<td>-1.2905</td>
<td>0.0512</td>
<td>-2.805</td>
<td>2.1595</td>
</tr>
<tr>
<td>Temkin isotherm</td>
<td>303</td>
<td>0.977</td>
<td>-1.7892</td>
<td>0.0162</td>
<td>0.267</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.913</td>
<td>-2.2724</td>
<td>0.0053</td>
<td>3.286</td>
<td>-2.8223</td>
</tr>
<tr>
<td>Flory-Huggins isotherm</td>
<td>303</td>
<td>0.905</td>
<td>0.637</td>
<td>4.3351</td>
<td>-13.815</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.837</td>
<td>0.893</td>
<td>3.8163</td>
<td>-16.310</td>
<td>1.323</td>
</tr>
</tbody>
</table>

3.3. FT–IR analysis of Chrysophyllum albidum extract and corrosion product

Fig. 2 presents the analysis of pure CAL extract and corrosion product of Aluminum in H$_2$SO$_4$ with the inhibitor. The results revealed that the stretch bands 3543.24 cm$^{-1}$ to 3852 cm$^{-1}$ represent strong and broad stretch bond of aliphatic and aromatic 3261.46 to 3477.62 cm$^{-1}$ for medium and often broad stretch of amines and amides. Wave band of 3053.02 cm$^{-1}$ and 3142.8 cm$^{-1}$ are variable stretch of alky and aldehyde bond group. The wave band of 2971.96 cm$^{-1}$ stands for strong and very broad stretch of carboxylic acid (free bond of alcohol). Wave bands of 2751.94 cm$^{-1}$, 2829.14 cm$^{-1}$ are two-peaked medium stretched bond of aldehyde. 2458.58 cm$^{-1}$ waveband range of 2674.74 cm$^{-1}$ are strong and very sharp stretch bond of carboxylic acid (alcohol). Wave band of 2404.54 cm$^{-1}$ to 2030.12 cm$^{-1}$ represent variable and sharp stretch bond of alkyne and nitrite/ Waveband 1837.48 cm$^{-1}$ to 1658.56 cm$^{-1}$ are strong representative of stretch bond of acids, esters, anhydride and aldehydes. Wave bands 1597.8 cm$^{-1}$, 1439.54 cm$^{-1}$ are multiple sharp, medium peaks stretch of aromatic bond.
Figure 2. *Chrysophyllum albidum* leaf (Pure) extract
3. 4. Potentiodynamic polarization

The potentiodynamic polarization curves of Al in the absence and presence of CAL extracts in 0.5 M H₂SO₄ solution are shown in Figure 3. The values of the polarization parameters are provided in table (3), where E_{corr} and I_{corr} are respectively the corrosion potential and current density. Both were obtained from the extrapolation of the anodic and cathodic Tafel slopes with respect to the E_{corr} values. The values of polarization parameters revealed that in the presence of extract molecules, especially at higher concentrations of 1000 mg/l Al displayed lower Icorr value of 11.6mA² and more positive Ecorr values of -458 mV in studied environment. The results showed that the introduction of CAL extract reduces both the cathodic and the anodic corrosion current densities, this implied that the corrosion rate of Al sample in the presence of the inhibitor was drastically reduced when compared to the uninhibited Al [23-28]. “Also, the E_{corr} of the inhibited Al is more positive (anodic) than the uninhibited Al. This showed that in the absence of CA extract, Al have a higher susceptibility to corrosion in acidic environment than the inhibited Al sample”.

The corresponding current densities have been given in table 3. It is evident that the extract shifts both the anodic and cathodic curves to lower values of current densities. The polarization curves for the Al samples in 0.5M H₂SO₄ environment exhibited passivation behavior and do not differ in nature of transition from active to passive states. The similarities of the polarization curves of both the uninhibited and inhibited Al samples indicate that the mechanism of the corrosion of Al in the absence of the inhibitor did not change even when CAL extract was introduced into the aggressive solution.

Figure 3. Plot of polarization curves of Al in H₂SO₄ in the absence and presence of various concentrations of CA extracts.
Table 3. Electrochemical kinetic parameters obtained from polarization curves of Al in the absence and presence of different concentrations of CA extracts in 0.5 M H$_2$SO$_4$

<table>
<thead>
<tr>
<th>Concentration (gl$^{-1}$)</th>
<th>$-E_{\text{corr}}$ (mv)</th>
<th>$I_{\text{corr}}$ (uAcm$^{-2}$)</th>
<th>$\theta$</th>
<th>IE(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 M H$_2$SO$_4$</td>
<td>528</td>
<td>258.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>200</td>
<td>516</td>
<td>96.2</td>
<td>0.623</td>
<td>62.3</td>
</tr>
<tr>
<td>1000</td>
<td>458</td>
<td>11.6</td>
<td>0.955</td>
<td>95.5</td>
</tr>
</tbody>
</table>

3. 5. Impedance spectroscopy

Results obtained by impedance spectroscopy are shown in Fig 6. The Nyquist plots showed a capacitive loop followed by an inductive loop for Al samples in 0.5 M H$_2$SO$_4$ solution. The diameter of the semi circles are related to charge transfer resistance. The size of the capacitive loops was greater in the presence of CAL extract, compared to that in inhibitor-free environment, an indication of a higher corrosion resistance for Al in the presence of the inhibitor. The emergence of an inductive loop for the electrolyte may indicate some non-faradic processes, such as adsorption and desorption of corrosion products which occurred at the aluminum/electrolyte interface.

The equivalent circuit model shown in figure 5 was used to model the impedance results gotten for Al in H$_2$SO$_4$ solutions, on application of Zsimpwin software. The $R_s$ is the solution resistance, $Q_{dl}$ and $R_{lo}$, respectively, indicated the values of capacitance of charge and the resistance of the charge layer to penetration of the electrolyte solution on to Al sample. On the other hand, the inductance, L, and charge transfer resistance, ($R_{ct}$) projected the processes within the store of charges. The result showed that the $Q_{dl}$ value was lower in the inhibited environment compares to the inhibitor-free Al. Similarly; the value of inductance was greater for the inhibited Al sample than for the uninhibited. The obtained result indicated that the introduction inhibitory extracts obviously modified the electrochemistry of the Al sample by minimizing the penetration of electrolyte into the substrate electrolyte interface, thus, reducing the rate of the corrosion in the acid solutions. This can also be evidenced by the higher value of $R_{ct}$ (3,507 $\Omega$cm$^2$) for Al in the presence of the inhibitor than the value (253$\Omega$cm$^2$) obtained in the absence of CAL. It was obvious that Al surfaces can form a protective layer of Al$_2$O$_3$ when in contact with aqueous solutions [1, 2, 38-45]. This layer can characteristically reduce the rate of the electrochemical corrosion on the Al surface. Inevitably, in the presence of the extract, the extract molecules were adsorbed on the surface of Al.

This creates a strong barrier between the Al surface and the electrolyte solutions. In this way, the corrosion potential of the Al sample shifts to more positive regions implying a decreased surface area available for the electrochemical processes. More so, introduction of the inhibitor also slowed down the rate of penetration of the electrolyte. Hence, the rate of the electrochemical processes in the Al/electrolyte interface is drastically reduced. From the present result, the introduction of the CAL extract in the 0.5 M H$_2$SO$_4$ solution seem to reduce the susceptibility of the Al substrate to dissolution and to the electrochemical processes occurring at the substrate/electrolyte interface. This manifested in the shift of $E_{\text{corr}}$ to greater noble potentials, the reduction of current densities in the inhibited environment and the increased size
of the diameter of the Nyquist plots. It can be deduced that the adsorption of CAL extract acts as an impedance preventing the contact between the Al substrate and the electrolyte solutions.

![Figure 4](image)

**Figure 4.** (a) Impedance spectra obtained at various concentrations of CAL extract. (b) Equivalent electrical circuit used to fit impedance data.

**Table 4.** Impedance parameters for aluminum in H$_2$SO$_4$ in absence and presence of different concentrations of CAL extract.

<table>
<thead>
<tr>
<th>Systems</th>
<th>$R_s$ (Ωcm$^2$)</th>
<th>$R_{L1}$ (Ωcm$^2$)</th>
<th>$R_{ct}$ (Ωcm$^2$)</th>
<th>$Q_{dl}$ (Fcm$^{-2}$)</th>
<th>L</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 M H$_2$SO$_4$</td>
<td>1.96</td>
<td>7.8</td>
<td>253</td>
<td>3.42</td>
<td>5.6</td>
</tr>
<tr>
<td>200 gl$^{-1}$</td>
<td>3.78</td>
<td>1189</td>
<td>1216</td>
<td>3.19</td>
<td>1202</td>
</tr>
<tr>
<td>1000 gl$^{-1}$</td>
<td>4.07</td>
<td>2314</td>
<td>2408</td>
<td>2.69</td>
<td>1202</td>
</tr>
</tbody>
</table>


The response of weight loss, corrosion rate and inhibition efficiency to the factors of acid concentration, inhibitor concentration, temperature and time for the corrosion inhibition of aluminum in H$_2$SO$_4$ solution using various concentrations of CAL extract are presented in Table 6.
3.6.1. Graphical analysis of the inhibition efficiency (IE (%)) as determined, using RSM.

Response surface methodology is a powerful statistical technique used in the analysis of inhibition efficiency of CAL extracts on aluminum in H₂SO₄ solutions. From Figure (5), it is obvious that increase in the extract concentrations increases inhibition efficiency of the corrosion process.

The ANOVA and graphical analyses of the inhibition efficiencies of extracts were carried out. The mathematical models for inhibition efficiency of CAL extract for corrosion inhibition of aluminum in the sulphuric acid solutions in terms of coded and actual factors are presented in equations (7) and (8). The model in terms of coded factors was used to make predictions about the response for given levels of each factor [29, 48].

The high levels of the factors were coded as +1 and the low levels of the factors were coded as -1 [48]. From the RSM graph, Figure 5 (a), predicted versus actual plot is used to test the significance of the model’s order. It shows linear graph while the graphs of 3-D surface plots show the relationship between the factors and responses (inhibition efficiency) of the designed experiment version 8.1.

Figure (b) however shows IE (%) versus inhibitor concentration and acid concentration, (c) IE (%) versus time and acid concentration (d) IE (%) versus temperature and acid concentration, (e) IE (%) versus temperature and inhibitor concentration, (f) IE (%) versus time and inhibitor concentration and (g) IE (%) versus time and temperature. Increase in concentration increases the inhibition efficiency of CAL extracts [46]. Also inhibition efficiency of the extract reduces as temperature rises [48-50].
Figure 5. Inhibition efficiency (%) of Al in H₂SO₄ Medium with CAL extract: (a) Predicted versus actual (b) IE (%) versus temperature and acid concentration (c) IE (%) versus inhibitor concentration and acid concentration (d) IE (%) versus time and acid concentration

Table 5. Response surface methodology results of the Inhibition of Al in H₂SO₄ Medium with CAL Extract.

<table>
<thead>
<tr>
<th>Std</th>
<th>Run</th>
<th>Factor 1, Acid Conc. (M)</th>
<th>Factor 2, Inhibitor Conc. (g/l)</th>
<th>Factor 3, T Temperature (K)</th>
<th>Factor 4, t Time (hr)</th>
<th>Response 1, Weight Loss (g)</th>
<th>Response 2, Corrosion Rate (mg/cm²/hr)</th>
<th>Response 3, Inhibition Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>1</td>
<td>1</td>
<td>0.7</td>
<td>313</td>
<td>4</td>
<td>0.054</td>
<td>1.502</td>
<td>61.89</td>
</tr>
<tr>
<td>21</td>
<td>2</td>
<td>1</td>
<td>0.7</td>
<td>303</td>
<td>8</td>
<td>0.041</td>
<td>0.563</td>
<td>71.4</td>
</tr>
<tr>
<td>13</td>
<td>3</td>
<td>0.5</td>
<td>0.2</td>
<td>323</td>
<td>12</td>
<td>0.162</td>
<td>1.502</td>
<td>42.19</td>
</tr>
<tr>
<td>27</td>
<td>4</td>
<td>1</td>
<td>0.7</td>
<td>313</td>
<td>8</td>
<td>0.054</td>
<td>0.751</td>
<td>69.62</td>
</tr>
<tr>
<td>29</td>
<td>5</td>
<td>1</td>
<td>0.7</td>
<td>313</td>
<td>8</td>
<td>0.054</td>
<td>0.751</td>
<td>69.62</td>
</tr>
<tr>
<td>7</td>
<td>6</td>
<td>0.5</td>
<td>1.2</td>
<td>323</td>
<td>4</td>
<td>0.081</td>
<td>2.253</td>
<td>57.41</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>1.5</td>
<td>1.2</td>
<td>303</td>
<td>4</td>
<td>0.041</td>
<td>1.126</td>
<td>69.62</td>
</tr>
<tr>
<td>6</td>
<td>8</td>
<td>1.5</td>
<td>0.2</td>
<td>323</td>
<td>4</td>
<td>0.122</td>
<td>3.379</td>
<td>37.13</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>0.5</td>
<td>1.2</td>
<td>303</td>
<td>4</td>
<td>0.054</td>
<td>1.502</td>
<td>55.7</td>
</tr>
</tbody>
</table>
3. 7. Mathematical models of the inhibition efficiency

The equation (4), in terms of coded factors can be used to make predictions about the response forgiven levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels of the factors are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients. The Model F-value of 35.36 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, D, AB, CD, A^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model. The "Pred R-Squared" of 0.8100 is in reasonable agreement with the "Adj R-Squared" of 0.9431; i.e. the difference is less than 0.2. "Adeq Precision" measures the signal to noise ratio.
A ratio greater than 4 is desirable. Your ratio of 21.680 indicates an adequate signal. This model can be used to navigate the design space.

The final equations in terms of coded and actual factors are represented by eqns. (7) and (8).

Inhibition Efficiency = +68.24 b+2.89 A+11.99 C+5.49 D+1.88 AB+0.50 AC+1.04 AD-1.29 BC+0.033 BD-1.78 CD-7.72 A^2-3.05 B^2 C^2-1.62 D^2 (7)

Inhibition Efficiency = -1165.98194+26.61336 Acid Conc.+113.98465 Inhibitor Conc.+7.26918 Temperature +16.42354 Time +7.52000 Acid Conc. * Inhibitor Conc. +0.10050 Acid Conc. * Temperature +0.52125 Acid Conc. * Time -0.25750 Inhibitor Conc. * Temperature +0.016250 Inhibitor Conc. * Time -0.044625 Temperature * Time -30.86526 Acid Conc. ^2-12.18526 Inhibitor Conc. ^2-0.011313 Temperature^2 -0.10102 Time^2 (8)

Table 6. ANOVA Response for inhibition efficiency of Al in H\textsubscript{2}SO\textsubscript{4} medium with CAL extract.
3. 8. Results of the optimum inhibition efficiency.

To confirm the validity of the results, additional experimental were conducted. The chosen conditions for the concentrations, temperatures and time are listed in Table 5, along with the predicted and measured inhibition efficiencies. As shown in table the measured inhibition efficiencies were close to the predicted values. It shows that RSM approach was appropriate for optimizing the corrosion inhibition process Table 7.

Table 7. Validation of optimal results for corrosion inhibition of aluminium in H$_2$SO$_4$ by CAL extracts.

<table>
<thead>
<tr>
<th>Acid Conc.</th>
<th>Inhibitor Conc. (g/L)</th>
<th>Temperature (k)</th>
<th>Time (hr)</th>
<th>Predicted IE (%)</th>
<th>Experimental IE (%)</th>
<th>Percentage error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.49</td>
<td>1.00</td>
<td>303.60</td>
<td>11.71</td>
<td>78.78</td>
<td>79.56</td>
<td>0.01</td>
</tr>
</tbody>
</table>

3. 9. Surface morphology

Optical microscope test revealed that when a smooth surface of aluminium alloy is immersed in 0.5 M H$_2$SO$_4$ acid media for hours, in absence of CAL extract, corrosion pits were created on the surface of the aluminium due to aggressive attack of H$_2$SO$_4$ solution [40-48]. A mutilated surface with flakes of dark spots is observed Figure 6 (a) which indicates deposition of corrosion products and/or chloride ions on the surface. But in the presence of inhibitor as shown in Figure 6 (b), smooth layers were recognize due to adsorption of organic molecules
present in the extract at most active sites. On the basis of the information provided by the optical microscope, it can be concluded that plant extract protect aluminium surface in acid environment forming good protective film on the surface of the metal. The outcome of this process revealed that the adsorption of the extract molecules is spontaneously stable and is linked with the mechanism of physisorption.

![Figure 6. Micro photograph obtained by optical microscope for surface morphology of aluminium (a) corroded in 0.5 M H₂SO₄ and (b) with 1000 gl⁻¹ inhibitor concentration.](image)

4. CONCLUSIONS

1) The results of the phytochemical analysis of the CAL extracts exhibit powerful inhibitive properties of phytocompounds that acts as good inhibitor for corrosion of aluminum in 0.5 M H₂SO₄ solution.

2) The adsorption process of CAL extract on the surface of the aluminum is spontaneous, stable and follows Langmuir adsorption isotherm.

3) The FT-IR results affirmed existence of both cathodic and anodic reactions for the tested CAL extracts and as such acted as mixed-type inhibitor.

4) The CAL extract provide some protection against pitting corrosion of aluminum in the presence of aggressive solutions, and the level of protection increased with subsequent increase in extract concentrations.

5) The CAL extracts revealed optimum corrosion protection efficiency of 78.43 (%) at optimal inhibition concentration of 1.00 gl⁻¹, temperature of 303.62 k and time of 11.71 (hs).
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References


