Natural Sweet Almond Oil as an Effective Green Inhibitor for Aluminum Corrosion in Sulfuric Acid Medium

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Natural sweet almond oil (SA oil) was inspected as a safe and green inhibitor for the corrosion of aluminum (Al) in 1.0 M H₂SO₄ solution. The protection efficacy of SA oil was detected from mass loss, geometric hydrogen evolution reaction, potentiodynamic polarization and electrochemical impedance spectroscopy techniques. All the corrosion parameters gained from these techniques emphasize the good inhibiting action of SA oil. The outcomes demonstrates that the protection efficacy rises with rising the doses of SA oil and decline temperature. It is reached to 93.62 % at 450 ppm of SA oil. The protection process is explicated by the adsorption of SA oil on the Al surface according to Langmuir isotherm. The polarization method classifies this oil as a mixed type and mainly anodic ($\beta_a > \beta_c$). The adsorption of SA oil onto the Al surface is spontaneous due to the negative values of $\Delta G_{ads}$. From the impact of temperature, the activation and adsorption thermodynamics functions were computed and interpreted.

Keywords: Green inhibitor, Sweet Almond oil, Corrosion, Aluminum, Polarization, Adsorption

1. INTRODUCTION

Pure aluminum (Al) and its alloys are used in many technological applications due to their special advantages such as low density and good appearance, good corrosion protection, high thermal and electrical conductivity corrosion protection [1,2]. H₂SO₄ solutions are generally applied for pickling, chemical or electrochemical etching of Al. Unluckily, these processes cause corrosion of Al. To preserve
aluminum from corrosion, scientists have turned to several methods, the most remarkable of which is the addition of corrosion inhibitors. There are various corrosion inhibitors are used to diminish the corrosion rate of Al. Most of these molecules are organic compounds [3-15]. It was found from the literature review that these compounds are effective in protecting Al from corrosion attack due to their potent adsorption on the Al surface, but the disadvantages of these compounds are that they are toxic and harmful to human health and the environment, as well as their high price and high economic costs. Therefore, it is not recommended to use it. Therefore, scientists turned to use the natural inhibitions of the leaves, roots or oils of natural plants for the inhibition of metals and alloys in aqueous solutions [16-22]. One of the most important features of these natural compounds is that they are environmentally friendly and harmless to human health, as well as economically profitable, as they are cheap compared to synthetic organic compounds. It is also characterized by the chemical composition of it contains effective compounds and groups that have a high adsorption force on the surface of the metal and thus have a high inhibition efficacy [23-25].

In this context. The present work is focuses on the use of a safe, natural sweet seed oil (SA oil) as an inhibitor for the corrosion of Al in 1.0 M H2SO4 instead of the usual hazardous organic compounds. Mass loss (ML), gasometric hydrogen evolution reaction (HE), potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy techniques were utilized to demonstrate the inhibitory strength of SA oil. The impact of rising temperature and thermodynamic functions for the activation and adsorption processes were inspected.

2. EXPERIMENTAL METHODS

Al metal with higher purity of 99.999% produced by the aluminum factory in Nag Hammadi - Arab Republic of Egypt was utilized in this manuscript. Al sheets with dimension 1.0 × 2.6 × 0.12 cm was used in the chemical measurements (ML and HER). For electrochemical measurements (PDP and EIS), a cylindrical rod of Al was embedded in Araldite with uncovered surface area 0.34 cm² was used. Before any measurement, the electrode (rod or sheet) was polished with certain levels of sand paper, degreased with acetone, washed with double distilled water. At the end dried between two filter papers. All the chemical used for preparing the investigated solutions were of analytical grade and all the measurements were done at 27 ± 1°C.

The ML methods were performed out as described formerly [26]. The Al sheets were immersed in 50 ml of the test solution during 10 hours. The reaction vessel used for HER and the procedure for detection of the dissolution rate of Al in the acid solution at the same described formally [13, 27]. For PDP and EIS measurements were done using an electrochemical cell containing three holes A saturated calomel electrode (SCE), Pt counter electrode, and Al electrode as working electrode were inserted in the holes. PDP were performed using a PS remote Potentiostate with PS software for determination of the corrosion parameters.

The chemical components of SA oil are shown in Table 1.
Table 1. The chemical constituents of SA oil

<table>
<thead>
<tr>
<th></th>
<th>Oleic Acid 69%</th>
<th>Linoleic Acid 17%</th>
<th>Saturated Fatty Acids</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>14%</td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSION

3.1. PDP measurement

Fig. 1 displays the PDP curves of the Al electrode in 1.0 M H₂SO₄ free solutions as well as when it contains different concentrations of SA oil ranging between 50 to 450 ppm. Clearly from the Fig 1 that, Tafel type behavior is observed. There is a transition region in which the current nearly constant or slowly changed to a negative or positive direction (cathodic or anodic curves). Beyond this zone, the potential increases quickly with current (Tafel region). The presence of SA oil increased the cathodic and anodic overvoltage and mainly caused a parallel displacement to the most negative and positive trends, respectively, of the free curve. Thus, the SA oil affects both cathodic hydrogen evolution and the anodic dissolution of Al.

Figure 1. PDP curves for Al electrode in 1M H₂SO₄ as well as when it contains certain concentrations of the SA oil. 1) 0.00ppm 2) 50ppm 3) 150ppm 4) 250ppm 5) 350 ppm 6) 450 ppm SA oil
The corrosion functions were derived from these curves such as anodic ($\beta_a$) and cathodic ($\beta_c$) Tafel slopes ($\beta_a$) corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$) and protection efficacy ($P_{PDP}$ %)

$$P_{PDP} \% = \left[ 1 - \frac{I_{inh}}{I_f} \right] 100$$

(1)

Where, $I_{inh}$ and $I_f$ are the corrosion current densities in the blank 1.0 MH$_2$SO$_4$ solutions and as well as in the occurrence of certain concentrations of SA oil. These functions are recorded in the Table 2. The analysis of the corrosion functions in this table showed that, with increasing doses of SA oil the $\beta_a$ & $\beta_c$ values are approximately constant. The change is about 9 mV and 14 mV in the case of $\beta_a$ and $\beta_c$ respectively. This demonstrates that SA oil apparently affects both the cathodic H$_2$ evolution and anodic Al corrosion reactions and also no difference in the value of $E_{corr}$, the change nearly 19 mV. These data confirm that he SA oil acted as a mixed inhibitor and mainly anodic ($\beta_a > \beta_c$) [28]. The $I_{corr}$ values, reduce and the $%P$ values increase. The $P\%$ reached to 93.62% at 450 ppm of AS oil. This demonstrates that the tested SA oil was a good inhibitor of Al corrosion in 1.0 M H$_2$SO$_4$ solutions.

### Table 2. Corrosion parameters gained from the PDP curves of the Al electrode in 1M H$_2$SO$_4$ solution and as well as when it contains different concentrations of the SA oil.

<table>
<thead>
<tr>
<th>Extract Conc. (ppm)</th>
<th>$-\beta_c$, mV dec.-1</th>
<th>$\beta_a$, mV dec.-1</th>
<th>$-E_{corr}$, mV,(SCE)</th>
<th>$I_{corr}$, (µA/cm2)</th>
<th>$P_{PDP}$%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1M H$_2$SO$_4$</td>
<td>340</td>
<td>654</td>
<td>799</td>
<td>180</td>
<td>-</td>
</tr>
<tr>
<td>1M H$_2$SO$_4$ +50ppm</td>
<td>336</td>
<td>650</td>
<td>794</td>
<td>80</td>
<td>57.45</td>
</tr>
<tr>
<td>1M H$_2$SO$_4$+150 ppm</td>
<td>333</td>
<td>645</td>
<td>790</td>
<td>52</td>
<td>72.34</td>
</tr>
<tr>
<td>1M H$_2$SO$_4$+250 ppm</td>
<td>330</td>
<td>652</td>
<td>785</td>
<td>36</td>
<td>80.85</td>
</tr>
<tr>
<td>1M H$_2$SO$_4$+350 ppm</td>
<td>326</td>
<td>648</td>
<td>783</td>
<td>22</td>
<td>88.29</td>
</tr>
<tr>
<td>1M H$_2$SO$_4$+450 ppm</td>
<td>332</td>
<td>546</td>
<td>780</td>
<td>12</td>
<td>93.62</td>
</tr>
</tbody>
</table>

### 3.2. EIS TECHNIQUE

The EIS technology was implemented in the electrochemical processes of Al corrosion in 1 M H$_2$SO$_4$ solution and its inhibition using sweet almond oil. Figs. 2 and 3 shows the Nyquist and Bode diagrams of Al electrode in 1.0 M H$_2$SO$_4$ without and with some concentrations of the SA oil, respectively. EIS spectra shows the usual one single depressed semicircle [29,] and the semicircle diameter show an increase with the amount of the additive. The shape of the resulted spectra always gives an indication to the mechanism which is, controlled by the charge transfer resistance and don’t change by the amount of additive. Fig.4 shows the equivalent circuit fitting this model. The circuit consists of the corrosion solution resistance Rs, the charge transfer resistance $R_{ct}$, and the constant phase element, double layer capacitance $C_{dl}$. Table 3, shows the increase of the values of $R_{ct}$ with the increase the doses of SA oil, and this increase could be due to the construction of adherent film on the Al surface. This is because, the addition of SA oil increases the adsorption of the active constituents of SA oil over the Al surface which causes a decrease in charge transfer between the Al surface and the H$_2$SO$_4$ medium [30]. Furthermore, the decrease in $C_{dl}$ values with an increase the doses of SA oil, which normally results
from a decrease in the dielectric constant. This can be attributed to the adsorption of the components of the oil onto the Al/electrolyte interface, thereby protecting the aluminum from the aggressive medium. According to Helmholtz model given by the subsequent equation [31]:

$$C_{dl} = \frac{\varepsilon \varepsilon_0}{\delta} A$$

where $\delta$ is the thickness of the protective layer, $\varepsilon$ is the dielectric constant, $\varepsilon_0$ is the vacuum permittivity and $A$ is the effective area of the electrode.

Figure 2. Nyquist plots for the Al electrode in 1M H$_2$SO$_4$ as well as when it contains different concentrations of SA oil. 1) 0.00ppm 2)50ppm 3) 150ppm 4) 250ppm 5) 350 ppm 6) 450 ppm SAoil

Figure 3. Bode plots for the Al electrode in 1M H$_2$SO$_4$ as well as when it contains certain concentrations of SA oil; 1) 0.00ppm 2) 50ppm 3) 150ppm 4) 250ppm 5) 350 ppm 6) 450 ppm SA oil
The values of protection efficacy ($P_{EIS}%$) listed in Table 3 using the following equation below:

$$P_{EIS}% = \frac{R_{ct}^0}{R_{ct}}$$

From the corrosion data in Table 3 show that protection efficacy rises with rising concentration of the oil. These results confirms that the investigated SA oil is a promising inhibitor for Al in H$_2$SO$_4$ solution.

For further investigations, the Bode and phase angle plots are represented in Fig.4 as shown, the impedance modulus, have an increase with the increase of the oil amount at low frequencies, and hence proving the adsorption of SA oil on the Al- surface and in turn improving the inhibitory action against H$_2$SO$_4$ solution. Also, the appearance of a single peak in the phase angle plots that demonstrate the presence of a single time constant at the Al / solution interface.

### Table 2. EIS parameters obtained from the Al electrode in 1M H$_2$SO$_4$ solution and as well as when it contains different concentrations of the extract

<table>
<thead>
<tr>
<th>Oil Conc. (ppm)</th>
<th>$C_{dl}$, $\mu$F cm$^{-2}$</th>
<th>$R_{ct}$, ohm cm$^{-2}$</th>
<th>$P_{EIS} %$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1M H$_2$SO$_4$</td>
<td>66.22</td>
<td>32.6</td>
<td>-</td>
</tr>
<tr>
<td>1M H$_2$SO$_4$ +50ppm</td>
<td>59.12</td>
<td>75.5</td>
<td>56.82</td>
</tr>
<tr>
<td>1M H$_2$SO$_4$ +150 ppm</td>
<td>53.07</td>
<td>115.4</td>
<td>71.75</td>
</tr>
<tr>
<td>1M H$_2$SO$_4$ +250 ppm</td>
<td>50.44</td>
<td>155.2</td>
<td>79.00</td>
</tr>
<tr>
<td>1M H$_2$SO$_4$ +350 ppm</td>
<td>46.88</td>
<td>250.6</td>
<td>86.99</td>
</tr>
<tr>
<td>1M H$_2$SO$_4$ +450 ppm</td>
<td>42.66</td>
<td>380.8</td>
<td>91.43</td>
</tr>
</tbody>
</table>

### 3.3. H$_2$ evolution reaction measurements

The dissolution of Al sheet in 1M H$_2$SO$_4$ solution alone as well as when containing some concentration of sweet almond oil was inspected by H$_2$ evolution reaction measurements.

Fig.5 displays the relationship between the H$_2$ evolved during the dissolution reaction and the reaction time. Obviously from this Fig. we found that the volume of evolved H$_2$ rises with reaction time. At the beginning of the curve, the evolution rate of H$_2$ is slow until it is reached at a certain time the evolution rate of H$_2$ increases rapidly due to the destruction of the oxide film formed on the surface of Al.. The time is defined as the induction time [13, 27]. Adding a certain concentration of sweet almond oil diminishes the of H$_2$ evolution. The higher the concentration of sweet almond oil, the more variation
in the rate of H₂ evolution was observed. Since the Al sheet is easily dissolved in 1M H₂SO₄ solution with hydrogen liberation according to the next equation:

\[
2\text{Al} + 3\text{H}_2\text{SO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3 + 3\text{H}_2
\]  

(4)

The rate of H₂ liberation is related to the corrosion rate of Al. Therefore, the slope of the straight line was taken after the induction time to measure the corrosion rate of Al in free H2SO4 \( (R_{\text{un}}) \) and in the presence inhibitor \( (R_{\text{in}}) \).

The protection efficacy \( (\%\ P_{\text{HE}}) \) is determined from measurements of the H₂ evolution reaction by applying the subsequent equations:

\[
\%\ P_{\text{HE}} = \left[ 1 - \frac{R_{\text{in}}}{R_{\text{un}}} \right] \times 100
\]  

(5)

The values of rate gained from the H₂ evolution reaction measurements are registered in Table 3. Obviously from Table 3 that \( \%\ P_{\text{HE}} \) values increases with the augmentation of the concentricity of the sweet almond oil reaching 92.15% at 450 ppm of the oil.

**Figure 5.** The relationship between the H₂ evolved during the dissolution of Al sheet in a free 1.0 M HCl solution and when it contains some doses of SA oil. 1) 0.00ppm 2) 50ppm 3) 150ppm 4) 250ppm 5) 350 ppm 6) 450 ppm SA oil

**Table 3.** Corrosion parameters acquired from hydrogen evolution reaction

<table>
<thead>
<tr>
<th>Oil Conc. (ppm)</th>
<th>( R ) (ml/min.)</th>
<th>( P_{\text{HE}} )%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1M H₂SO₄</td>
<td>0.433</td>
<td>-</td>
</tr>
<tr>
<td>1M H₂SO₄ +50ppm</td>
<td>0.192</td>
<td>55.56</td>
</tr>
<tr>
<td>1M H₂SO₄+150 ppm</td>
<td>0.130</td>
<td>69.97</td>
</tr>
<tr>
<td>1M H₂SO₄+250 ppm</td>
<td>0.091</td>
<td>78.98</td>
</tr>
<tr>
<td>1M H₂SO₄+350 ppm</td>
<td>0.060</td>
<td>86.14</td>
</tr>
<tr>
<td>1M H₂SO₄+450 ppm</td>
<td>0.034</td>
<td>92.15</td>
</tr>
</tbody>
</table>
3.4. Mass loss (ML) technique

3.4.1. Impact of sweet almond oil concentrations

The impact of some concentrations of sweet almond oil ranging from 50 to 450 ppm on the corrosion of Al sheet in 1.0M H₂SO₄ solution was estimated by ML method. The corrosion rate of Al relied on the surface area of the sheet used, the immersed time, concentrations of both the aggressive H₂SO₄ solution and investigated oil. ML of Al was determined in mg after immersing in fixed time 10 hours in the free 1M H₂SO₄ solution and with the addition some concentration of almond oil.

The corrosion rate (Rcorr.) in mg.cm⁻¹.min⁻¹ was determined by applying the subsequent equation [32, 33]:

\[
R_{corr} = \frac{M_{un} - M_{in}}{A \times t}
\]  
(6)

where, \(M_{un}\) and \(M_{in}\) are the mass reduction of Al sheet in free H₂SO₄ solution and in the presence of the inhibitor (almond oil), A is the surface area of the Al sheet and t is the immersion time in hours.

The protection efficacy (\(P_{ML}\)) and surface coverage (\(\theta\)) which denote the part of the Al surface covered by the almond oil were computed from the mass loss method utilizing the subsequent equations:

\[
P_{ML} \% = \left[1 - \frac{R_{corr, in}}{R_{corr, un}}\right] \times 100
\]
(7)

\[
\theta = \left[1 - \frac{R_{corr, in}}{R_{corr, un}}\right] \times 100
\]
(8)

where, \(R_{corr, in}\) and \(R_{corr, un}\) are the corrosion rate gained from ML measurements in 1.0M H₂SO₄ solution and when including the SA oil, respectively.

The computed values of corrosion parameters such as, \(\Delta M\), \(R_{corr}\), \(P_{ML}\)\% and \(\theta\) are collected in Table 3. Obviously, from this Table, with increasing the concentration of sweet almond oil, the ML values are reduced, which led to increase the values of \(\% I\) and \(\theta\). These outcomes confirm the inhibitory strength of the examined sweet almond oil. The \(\% I\) values reached 93.01% at 450 ppm or the sweet almond oil. The \(\% I\) values gained from the ML technique were nearly identical to those gained from PDP, EIS, and H₂ measurements. This emphasizes the accuracy of the corrosion data acquired from different methods and confirms the inhibitory power of sweet almond oil.

### Table 3. Influence of increasing temperature on the corrosion parameters acquired from the ML method for corrosion of Al in 1.0 M H₂SO₄ alone and with addition certain concentrations of SA oil

<table>
<thead>
<tr>
<th>Temperature °K</th>
<th>Conc. of oil (ppm)</th>
<th>ML (mg)</th>
<th>(R_{corr} \times 10^{-2}) mg cm⁻² h⁻¹</th>
<th>(\theta)</th>
<th>(P_{ML}) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>0.00</td>
<td>0.152</td>
<td>6.082</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.067</td>
<td>2.671</td>
<td>0.561</td>
<td>56.08</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.041</td>
<td>1.672</td>
<td>0.725</td>
<td>72.51</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>0.027</td>
<td>1.094</td>
<td>0.820</td>
<td>82.01</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>0.018</td>
<td>0.729</td>
<td>0.880</td>
<td>88.01</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>0.011</td>
<td>0.425</td>
<td>0.930</td>
<td>93.01</td>
</tr>
<tr>
<td>308</td>
<td>0.00</td>
<td>0.222</td>
<td>8.895</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.111</td>
<td>4.434</td>
<td>0.502</td>
<td>50.15</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0.071</td>
<td>2.862</td>
<td>0.678</td>
<td>67.82</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>0.056</td>
<td>2.256</td>
<td>0.746</td>
<td>74.64</td>
</tr>
</tbody>
</table>
### 3.4.2. Determination of the activation thermodynamic functions

The thermodynamic activation functions were derived from the impact of high temperature on the corrosion of Al sheets in the free 1.0M H$_2$SO$_4$ solution and also, when it contained different doses of SA oil utilizing ML methods. The corrosion parameters gained from the influence of temperature were recorded in Table 4. The outcomes illustrated that, with rising the temperature, the difference in ML and $R_{orr}$ increases while the $P_{ML \%}$ and $\theta$ values are diminished. This demonstrates that the adsorbent layer created on the Al surface is reduced and the adsorption of SA oil on the Al surface is physical.

<table>
<thead>
<tr>
<th>318</th>
<th>350</th>
<th>0.037</th>
<th>1.506</th>
<th>0.831</th>
<th>83.07</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>450</td>
<td>0.024</td>
<td>0.948</td>
<td>0.893</td>
<td>89.34</td>
</tr>
<tr>
<td>0.00</td>
<td>0.265</td>
<td>10.645</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.154</td>
<td>6.196</td>
<td>0.418</td>
<td>41.79</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>0.113</td>
<td>4.527</td>
<td>0.575</td>
<td>57.47</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>0.092</td>
<td>3.689</td>
<td>0.653</td>
<td>65.34</td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>0.072</td>
<td>2.874</td>
<td>0.730</td>
<td>73.00</td>
<td></td>
</tr>
<tr>
<td>450</td>
<td>0.047</td>
<td>1.896</td>
<td>0.822</td>
<td>82.19</td>
<td></td>
</tr>
</tbody>
</table>

| 328  | 0.00 | 0.324 | 12.982| -     | -     |
|      | 50   | 0.219 | 8.806 | 0.322 | 32.16 |
|      | 150  | 0.167 | 6.686 | 0.485 | 48.49 |
|      | 250  | 0.134 | 5.390 | 0.585 | 58.48 |
|      | 350  | 0.112 | 4.476 | 0.655 | 65.52 |
|      | 450  | 0.074 | 2.976 | 0.771 | 77.07 |

**Figure 6.** The relationship between log $R_{corr}$ and 1000/T for the dissolution of Al sheet in free 1.0M H$_2$SO$_4$ as well as it contained various doses of SA oil. 1) 0.5M H$_2$SO$_4$  2) 50ppm  3) 150ppm  4) 250ppm  5) 350ppm  6) 450ppm SA oil
Figure 7. The relationship between log $R_{\text{corr}}/T$ and 1000/T for the dissolution of Al sheet in free 1.0 M H$_2$SO$_4$ as well as it contained certain doses of SA oil. 1) 0.5M H$_2$SO$_4$  2) 50ppm  3) 150ppm  4) 250ppm  5) 350ppm  6) 450ppm SA oil

The thermodynamic activation functions e.g. the activation energy ($E_a^\circ$), the enthalpy of activation ($\Delta H^\circ$) and the entropy of activation ($\Delta S^\circ$) for the corrosion of Al sheets in free 1.0 M H$_2$SO$_4$ solution and also, when includes some doses of SA oil were determined from Arrhenius and the alternative Arrhenius equations [34,35]:

\[
\frac{R_{\text{corr}}}{A} = \exp\left(-\frac{E_a^\circ}{RT}\right)
\]

\[
\frac{R_{\text{corr}}}{A} \cdot \frac{N\hbar}{R} = \exp\left(\frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \cdot \frac{1}{T}\right)
\]

where, R is the gas constant, A is the frequency factor, h is the Plank's constant and N is the Avogadro's number.

The activation energy was determined from Fig.6 which presents the relationship between (log $R_{\text{corr}}/T$) for the corrosion of Al sheet in 1.0 M H$_2$SO$_4$ -free solution and containing certain doses of SA oil. $E_a^\circ$ values were computed from the slope of the straight lines of Fig 5 and tabulated in Table 5. Clearly from Table 5, $E_a^\circ$ values increase with increasing doses of SA oil. This shows that the corrosion of Al under these conditions is controlled by activation. The increase of $E_a^\circ$ due to the formation of adsorbent barrier layer on the surface of Al. This layer keeps the Al corrosion from the acid attack by preventing the charge/mass transfer reaction that present on the Al surface [23]. $E_a^\circ$ values more than 20kJ/mol assure the physical adsorption of SA oil on the Al surface.

From Table 5, $E_a^\circ$ values rises with rising doses of SA oil, which indicates that the corrosion of Al under these conditions is controlled by activation. Increased $E_a^\circ$ due to the formation of adsorbent barrier layer on the surface of Al. This layer keeps the Al corrosion from the acid attack by preventing the charge/mass transfer reaction that present on the Al surface [23]. $E_a^\circ$ values more than 20kJ/mol assure the physical adsorption of SA oil on the Al surface.

The $\Delta H^\circ$ and $\Delta S^\circ$ values were determined from the slope and intercept of the linear relationship between log $R_{\text{corr}}/T$ versus 1000/T as displays in Fig7. These values were recorded in Table 5. From this table, it is evident that The values of $\Delta H^\circ$ are positive and increases with the increasing the doses of
SA oil. This clarifies that the endothermic nature of Al corrosion and the occurrence of SA oil diminishes Al corrosion in 1.0 M H₂SO₄. Negative ΔS° values demonstrate that the activated complex in the rate-limiting step represents a binding rather than dissociation, reflecting the occurrence of more ordering, and the transition from the substrate to complex activation.

Table 5: Thermodynamics activation functions for Al in free 1.0 MH₂SO₄ solutions and in occurrence of certain doses of AS oil

<table>
<thead>
<tr>
<th>Conc. of oil (ppm)</th>
<th>Eₐ° kJ mol⁻¹</th>
<th>ΔH° kJ mol⁻¹</th>
<th>-ΔS° J mol⁻¹ K⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>16.34</td>
<td>13.40</td>
<td>388.76</td>
</tr>
<tr>
<td>50</td>
<td>27.85</td>
<td>24.89</td>
<td>392.55</td>
</tr>
<tr>
<td>150</td>
<td>34.46</td>
<td>32.75</td>
<td>399.35</td>
</tr>
<tr>
<td>250</td>
<td>39.20</td>
<td>37.62</td>
<td>406.33</td>
</tr>
<tr>
<td>350</td>
<td>53.52</td>
<td>51.69</td>
<td>410.18</td>
</tr>
<tr>
<td>450</td>
<td>56.44</td>
<td>55.61</td>
<td>415.52</td>
</tr>
</tbody>
</table>

3.5. Interpretation of the inhibitory process

The inhibitory strength of SA oil towards the corrosion of Al in 1.0 M H₂SO₄ solution was inspected by some chemical and electrochemical methods. All specific corrosion functions confirmed that SA oil served as an efficient corrosion inhibitor for Al in 1.0 MH₂SO₄ solution. The main advantage of any compound to be a good corrosion inhibitor is its capability to adsorb on the metal surface by substituting water molecule. In this way, the amount of active sites exposed to acidic solutions is reduced and leads to a reduced corrosion rate. The adsorption strength and the P% values calculated from different techniques depend on the chemical composition, concentration, and the number of active adsorption centers in the investigated natural SA oil. The type of metal used, the temperature, the type and concentration of the corrosive solutions.

The tested SA oil inhibits the corrosion of Al in 1.0 M HCl solution by adsorption onto the Al surface. The adsorption process can be considered as a replacement operation between the SA oil in the aqueous phase [SA(aq)] and water molecules at the Al surface [H₂O(Al sur.)] to give SA oil adsorbed on the surface of Al [SA(Al sur.)] and thus increased protection efficacy due to next equation:

\[
\text{AS } \text{(aq)} + \alpha \text{H}_2\text{O(Al sur.}) \rightarrow \text{AS (Al sur.)} + \alpha \text{H}_2\text{O(aq)} \quad (11)
\]

where, α is the size ratio and simply equals the amount of adsorbed water molecules replaced by a single inhibitor molecule.

Some adsorption isotherms were applied to select the best isotherms by inserting the values of θ (ML) obtained from the ML method in various isotherm. We found that the convenient adsorption is Langmuir isotherm by applying this equation:

\[
\frac{C_{SA}}{\theta} = \frac{1}{K_{ads}} + C_{SA} \quad (12)
\]

Where, C_SA is the concentration of SA oil, K_ads is the equilibrium constant of adsorption.
Fig. 7 presents the relationship between $\frac{C_{SA}}{\theta}$ and $C_{SA}$ for Al corrosion in 1.0 M H$_2$SO$_4$ solution and also when containing certain doses of SA oil at different temperatures. A straight line was gained with slope almost equal one. This elucidates that the adsorption of SA oil on the Al surface is subjected to Langmuir isotherm, which means the absence of any interaction between the adsorbent species [36].

\[ \frac{C_{SA}}{\theta} = K_{ads} \]

The $K_{ads}$ values were computed from the intercept of the of the Langmuir relation and equal to 32.2, 19.6, 11.1 and $8.3 \times 10^{-3}$ at 298, 308, 318 and 328 K, respectively. The large values of $K_{ads}$ at low temperature and diminished at high temperature. This demonstrates a large ability of the SA oil to be adsorbed on the Al surface by increasing the barrier film created on the Al surface and thus decrease $R_{corr}$ values.

\[ K = \frac{1}{55.5} \exp \left( -\frac{\Delta G_{ads}}{RT} \right) \]

The free energy of adsorption ($\Delta G_{ads}$) was evaluated from the subsequent equation:

\[ \Delta G_{ads} = -RT \ln 55.5 K \]

Where, 55.5 equal the concentricity of water in mol/l.

The evaluated values of $\Delta G_{ads}$ are equal to $-38.63$, $-37.30$, $-35.96$ and $-33.08$ kJ mol$^{-1}$ at temperature 298, 308, 318 and 328 K, respectively. These values demonstrate that the adsorption of SA oil onto the Al surface is spontaneous owing to the negative labeling of $\Delta G_{ads}$. As previously described [38]. These values decline with elevating temperature. These outcomes agree with the $P$ % values which decrease in high temperatures. The adsorption of additives on the metal surface is chemical when the $\Delta G_{ads}$ values are smaller than $-40$ kJ mol$^{-1}$, while they are physically when $\Delta G_{ads}$ values are more than $-20$ kJ mol$^{-1}$. This clarifies that the adsorption of SA oil on the Al surface on the surface of Al is a mixture of chemical and physical adsorption.

The enthalpy of adsorption ($\Delta H_{ads}$) can be computed from Van't Hoff equation [38]:

\[ \Delta H_{ads} = -\frac{R}{\theta} \frac{\partial \ln (\theta)}{\partial (1/T)} \]
\[
\log K_{ads} = \frac{\Delta H_{ads}}{2.303 \, RT} + C
\]  
(14)
where \(C\) is constant

The plots between \(\log K_{ads}\) and \(1000/T\) (Van't Hoff diagram) for the adsorption of SA oil on the Al surface in MH\(_2\)SO\(_4\) is presented in Fig.9.

**Figure 9.** Van't Hoff diagram for the adsorption of SA oil on the Al surface in 1.0 M H\(_2\)SO\(_4\)

From the slope of the straight line gained in Van't Hoff diagram. We can determine the values of \(\Delta H^0_{ads}\) and equal to 42.12 kJ mol\(^{-1}\). This demonstrates that the adsorption of SA oil on the Al surface is endothermic. The entropy of adsorption (\(\Delta S_{ads}\)) was computed from the subsequent equation:

\[
\Delta S_{ads} = \frac{\Delta H_{ads} - \Delta G_{ads}}{T}
\]  
(15)

The computed values of \(\Delta S_{ads}\) are equal to 0.270, 0.258 0.245 and 0.229 kJ mol\(^{-1}\). The positive signs of \(\Delta S_{ads}\) clarified the more randomness at the Al/electrolyte interface during the adsorption of SA oil on the Al surface. This higher disorder is due to more water molecules may desorbed from the Al surface by AS oil

### 4. CONCLUSIONS

1- SA oil act as excellent corrosion inhibitor for Al in 1.0 M MH\(_2\)SO\(_4\) solution.
2- All the corrosion parameters emphasize the inhibitory effect of SA oil.
3- The protection efficacy increases with increasing the doses of SA oil and declines temperature.
4- SA oil is adsorbed on the Al surface according to Langmuir isotherm.
5- Polarization parameters proved that the SA oil act as mixed inhibitor.
6- EIS parameters data demonstrate the corrosion reaction is controlled by charge transfer.
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References