Performance of Avocado Seeds as New Green Corrosion Inhibitor for 7075-T6 Al Alloy in a 3.5% NaCl Solution: Electrochemical, Thermodynamic, Surface and Theoretical Investigations

M. Radi1*, R. Melian1, M. Galai1*, N. Dkhirche1, E. Ech-chihbi2 and M. Ebn Touhami1

1Advanced Materials and Process Engineering Laboratory, Faculty of Science, Ibn Tofail University, P. O. Box 133-14000 Kenitra, Morocco
2Laboratory of Organometallic, Molecular Materials and Environment, Faculty of Science, Sidi Mohamed Ben Abdellah University, P. O. Box 1796, Fez, Morocco
*Corresponding authors: galaimouhsine@gmail.com / radi.morad@gmail.com

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Abstract
AS inhibition effect on the corrosion behavior of AA in a 3.5% NaCl solution was herein studied using electrochemical, thermodynamic, surface analysis and DFT (B-3LYP, at 6-31G (d, p)) techniques. The obtained results showed that AS inhibited AA corrosion process. Maximum IE(%) of around 85% was reached with AS C of 1 g/L, and it was stable as T increased from 298 to 328 K. Furthermore, AS acted as a mixed-type inhibitor through electrostatic interaction (physical adsorption), which was more dominant than chemical adsorption, between the charged molecules and the AA surface. EIS measurements confirmed these results. SEM coupled with EDX showed that AS were preferentially adsorbed onto the AA surface. AFM results demonstrated that Rₐ values were reduced from 338 μm to 79 nm. X-RD offered suitable support to PDP and EIS studies. There was an excellent agreement between experimental and computed data. Pc effectiveness was investigated by DFT studies, having followed the order: GA > D-M.

Keywords: 3.5% NaCl, AA, AFM, AS, DFT, EDX, EIS, corrosion, IE(%), PDP, SEM and X-RD.

Introduction*
AA 7000 series (Al-Zn-Mg), with 7075-T6 at the head, are widely used for structural parts, due to their excellent mechanical properties/weight ratio and manufacturing cost. However, these alloys are likely to be affected by the corrosion phenomenon, mostly localized, mainly due to intermetallic particles of different compositions, which cause the creation of new phases with electrochemical properties very different from those of the Al matrix. These particles, such as Mg₂Si, MgZn₁₂, Al₇Cu₂Fe, Al₄CuMg, Al₂Cu and Al₃Fe, promote micro-coupling, which is often the main cause of localized corrosion [1-4]. The metallic surface is energetically heterogeneous, due to local disordering. The

* The abbreviations and symbols definition lists are in pages 441-442.
particles that are anodic, concerning the matrix, tend to dissolve. The particles that are cathodic promote the matrix dissolution. Cu and Fe are more cathodic than the Al matrix, which causes galvanic corrosion. The combination of different layers helps protect materials against corrosion in a sustainable way. However, when damage is initiated, the coatings can no longer protect the bare metal. Corrosion inhibitors are substances that decrease metals reaction with their environment, when added at low C to corrosive media. An inhibitor can function by adsorption onto the metal surface, thus reducing CR. Most synthetic inhibitors have good corrosion inhibiting properties, but their majority are toxic to the environment, and can cause temporary or permanent damage to organs, such as the kidneys or the liver, or disrupt the body enzyme system. Therefore, due to environmental concerns, plants are increasingly seen as a source of green corrosion inhibitors. They are used to protect metals and alloys from aggressive environments, replacing toxic chemicals. Several studies on the development of green inhibitors have been carried out for application in the protection of metals and alloys against corrosion [5-7]. Avocado (*Persea Americana*) belongs to the *Lauraceae* family. AS have many health benefits, due to their composition [8]. They are considered a natural source of proteins, antioxidants, vitamins (B1, B2, B3, C, A and E), minerals (P, Ca, Zn, Na, Fe, K and Cu) polyunsaturated fatty acids and trace elements [9]. The present study aimed to research and exploit a natural inhibitor for the corrosion inhibition of AA, in 3.5% NaCl, used in the aeronautical industry. Compared to IE(%) values of other inhibitors, such as *Phoenix dactylifera L.* (63%) [10], plant-derived cationic dye (78%) [11] and Berberine (80%) [12], those obtained in this work have reached satisfactory values.

**Experimental part**

**Inhibitor preparation**

AS were washed for eliminating impurities, dried at 50 °C, in order to prevent deterioration of physical and chemical properties, and, then, powdered by grinding. The powder was sifted and analyzed by FTIR. The samples FTIR spectra were recorded with a VERTEX 70 device, at the wavelength range from 400 to 4000 cm\(^{-1}\), in ATR mode. The powder was pelletized at about 1% by wt. in KBr previously stored in an oven at 100 °C, and under a pressure of about 1000 psi.

**Materials and solutions**

A conventional electrochemical cell with three electrodes was used. The WW (AA) had an area of 1 cm\(^2\), and it was prepared by grinding abrasive paper (gradation from 220 to 2000). Ag/AgCl (3 M C in Cl\(-\)) were used as RE, while Pt was the CE. Then, the samples were rinsed and degreased with acetone. Before each analysis, they were immersed in an electrochemical cell and stabilized for 2 h. AS easily dissolved with distilled water, at ambient T. AS C of 0.25, 0.5, 0.75 and 1 g/L were prepared in a 3.5% NaCl solution. AA had the following composition (wt%): Zn (5.81), Mg (2.62), Cu (1.59), Cr (0.19), Mn (0.01), Ti (0.02), Si (0.08), Fe (0.23) and Al (balance).
**Polarization measurements**

The WW was immersed in the solution for 2 h, until $E_{ocp}$ was constant, as a function of time. The cathodic polarization curve was registered from $E_{ocp}$ towards the negative direction, with a SR of 1 mV/s. After this scan, the same electrode remained in the solution until $E_{corr}$ steady state ($E_{ocp} \pm 0.02$ V) was achieved. Afterwards, the anodic polarization curve was registered from $E_{ocp}$ towards the anodic domain, with the same scanning speed. These measurements were done utilizing a PGZ100 potentiostat, controlled by a PC. For each essay, three independent experiments were performed. The Tafel extrapolation method of the linear cathodic domain was utilized to extract the corrosion kinetic parameters. $\eta(\%)$ was extracted from $i_{corr}$ values, using the following equation:

$$\eta = \left(\frac{i^0_{corr} - i_{corr}}{i^0_{corr}}\right) \times 100$$

where $i^0_{corr}$ and $i_{corr}$ are values in AS absence and presence, respectively.

**EIS measurements**

EIS was performed employing a transfer function analyzer (Voltalab PGZ 100, Radiometer Analytical) over the frequency range from 100 kHz to 0.01 Hz, with 10 points per decade. The applied amplitude of the AC signal was 30 mV. All experiments were performed at the circuit E. The obtained impedance data were investigated within the equivalent circuit, using Bouckamp’s program [13]. $\eta(\%)$ was evaluated from $R_p$ values by:

$$\eta(\%) = \left(\frac{R^0_p - R_p}{R_p}\right) \times 100$$

where $R^0_p$ and $R_p$ represent values in AS absence and presence, respectively.

**Surface study**

Using a SEM model (JOEL JSM-5500), micrographs of the corroded and protected AA surfaces were obtained. The samples surface $R_a$ was measured with an AFM (Nano Surf), in non-contact mode, and the images were processed using Gwyddion software. AA surfaces were examined using X-RD X'Pert Pro MPD model.

**Computational study**

**DFT calculations**

AS major constituents are GA and D-M. The two major molecules were optimized by utilizing DFT-B3LYB method. B3LYP and 6-31G (d, p) basis set, operated with Gaussian 09 software, were used in gas and aqueous media. The solvation model using IEFPCM was also employed to examine the water molecules solvent effect. For the considered AS molecules, $E_{HOMO}$, $E_{LUMO}$, $\Delta E$, $\eta$, $\chi$ and $\Delta N$ were computed. Quantum chemical descriptors were determined according to the following equations [14,15]:

$$\Delta E_{gap} = E_{LUMO} - E_{HOMO}$$
According to Pearson, $\phi$ and $\eta$ are equal to 4.82 and 0 eV, respectively. Fukui indices are useful predictors of reactive sites for nucleophilic and electrophilic attacks [16, 17].

\[
f_k^*= P_k(N+1) - P_k(N) \text{ for nucleophilic attack} \tag{7}
\]

\[
f_k^- = P_k(N) - P_k(N-1) \text{ for electrophilic attack} \tag{8}
\]

where $P_k(N)$, $P_k(N + 1)$ and $P_k(N-1)$ are the molecule neutron, anion and cation, respectively. MPA was used to express Fukui functions in the present study.

**Results and discussion**

**AS characterization and chemical composition**

Fig. 1 shows AS vibration bands.

![Figure 1. AS IR spectra.](image)

Spectra data for AS FTIR are presented in Table 1.
Table 1. Most characteristic AS IR bands.

<table>
<thead>
<tr>
<th>Wave number cm(^{-1})</th>
<th>Bond</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>3214</td>
<td>(\nu O-H)</td>
<td>0.74</td>
</tr>
<tr>
<td>2940</td>
<td>(\nu C-H)</td>
<td>0.84</td>
</tr>
<tr>
<td>2113</td>
<td>(C=C)</td>
<td>0.95</td>
</tr>
<tr>
<td>1737</td>
<td>(\nu C=C)</td>
<td>0.91</td>
</tr>
<tr>
<td>1614</td>
<td>(\nu C=C)</td>
<td>0.83</td>
</tr>
<tr>
<td>1379</td>
<td>(\delta s(CH_3))</td>
<td>0.80</td>
</tr>
<tr>
<td>1079</td>
<td>C-O</td>
<td>0.67</td>
</tr>
<tr>
<td>1017</td>
<td>(\nu O-H)</td>
<td>0.53</td>
</tr>
</tbody>
</table>

AS IR spectra are presented in Fig. 1. IR peaks of O–H (3214 cm\(^{-1}\)) vibrations were identified. IR band at 2940 cm\(^{-1}\) was attributed to the C–H stretching vibration, and the 2113 cm\(^{-1}\) absorption band is characteristic of C=C stretching vibrations. In addition, a vibration band at 1614 cm\(^{-1}\) was attributed to C=C, and the absorption band at 1079 cm\(^{-1}\) is characteristic of C–O stretching vibrations. Regarding AS extract chemical composition, [18] reported that it is essentially composed of 10% GA and 5% D-M, which represents 90% of the inhibitor.

GA and D-M chemical compositions are presented in Fig. 2. These major AS compounds contain C–O, C=C, C–H and O–H groups, all of which have been identified by FTIR spectroscopy.

![Figure 2. GA and D-M chemical composition.](image)

**Electrochemical measurements**

**PDP measurements**

PDP measurements were carried out in a large E domain, in order to study AS effect on the partial anodic and cathodic reactions, at a SR of 1 mV/s.

Fig. 3 shows the polarization curve for AA in a 3.5% NaCl solution without and with AS, at different C (0.25, 0.5, 0.75 and 1 g/L).

In AS absence, the curve is characterized by different electrochemical reactions. On the anodic side, the branch is characterized by a strong increase in J, due to the propagation of galvanic and pitting corrosion localized on the AA surface (eq. 9). On the cathodic side, the plateau observed is associated with dissolved O reduction in the solution (eq. 10). The limiting J is in the order of \(10^{-1}\) mA/cm\(^2\). The increase in J for the lowest cathodic E corresponds to the water reduction reaction (eq. 11).

\[
\text{Al} \rightarrow \text{Al}^{3+} + 3e^- \quad (9)
\]
\[
\text{O}_2 + 4\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad (10)
\]
\[
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad (11)
\]
In AS presence, the anodic branch was characterized by a wide plateau of 320 mV, with a slightly positive slope, suggesting that the alloy was probably not in the passive state, but rather covered with a very protective film.

On the cathodic side, \( J \) associated with dissolved O reduction was decreased by almost two decades, compared to the reference. This strong decrease was due to the formation of a passive film on the matrix, which provided a pronounced barrier effect that limited O reduction on the intermetallic particles [19-21].

![Figure 3.](image-url)

**Figure 3.** Polarization curves for AA without and with AS, in various \( C \), after 2 h of immersion, at 298 K. The scan rate is \( |dE/dt| = 1 \text{ mV/s}^{-1} \).

Table 2 presents electrochemical parameters: \( E_{corr} \), \( i_{corr} \), \( \beta_c \) and IE(%). Tafel extrapolation method of the linear cathodic part, in both AS absence and presence, was used. IE(%) was obtained from the relation in Eq (1).

<table>
<thead>
<tr>
<th>( C ) (g/L)</th>
<th>( E_{corr} ) (mV/Ag/AgCl)</th>
<th>( i_{corr} ) (( \mu A \text{ cm}^{-2} ))</th>
<th>( \beta_c ) (mV/dec(^{-1}))</th>
<th>IE(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>774±0.1</td>
<td>10.8±0.3</td>
<td>359±1</td>
<td>-</td>
</tr>
<tr>
<td>0.25</td>
<td>735±0.4</td>
<td>6.8±0.1</td>
<td>298±4</td>
<td>37.0</td>
</tr>
<tr>
<td>0.50</td>
<td>729±0.6</td>
<td>5.5±0.2</td>
<td>295±2</td>
<td>49.0</td>
</tr>
<tr>
<td>0.75</td>
<td>730±0.2</td>
<td>5.2±0.5</td>
<td>290±5</td>
<td>51.8</td>
</tr>
<tr>
<td>1.00</td>
<td>733±0.1</td>
<td>1.4±0.1</td>
<td>293±1</td>
<td>87.0</td>
</tr>
</tbody>
</table>

The results reported in Table 2 show that \( i_{corr} \) decrease as AS \( C \) increased. The same is true for CR. IE(%) reached a maximum value of about 87% at 1 g/L AS. This is related to the low recorded \( i_{corr} \), which was about 1.4 \( \mu A/cm^2 \). AS addition slightly modified \( E_{corr} \) values. Compared to other inhibitors, such as *Phoenix dactylifera* L. (63%) [10] and plant-derived cationic dye (78%) [11], AS IE(%) obtained during this study was significant, improving the protection against AA corrosion.
**EIS**

EIS diagrams obtained at OCP of AA, after 2 h immersion in 3.5% NaCl without and with AS, at 298 ±2 K, are shown in Fig. 4. These diagrams were obtained after $E_{corr}$ was stable, which allowed for a well-defined low-frequency of the diagram.

![Figure 4. Nyquist plots of AA without and with different C of AS in 3.5% NaCl.](image)

EIS diagrams, in the complex plane depiction of the Nyquist diagram presented in Fig. 4, are characterized by capacitive loops in the high and medium frequencies. The first capacitive loop is the load transfer resistance, which is parallel to the high-frequency capacitor, while the second one, at the medium frequency region, was originated from the formed oxide film.

The impedance diagrams also show an inductive loop at low frequencies. However, according to the work of [22-24], an inductive loop can be obtained under certain conditions, if the overall reaction consists of two electrochemical reactions involving an adsorbed intermediate. Moreover, this mechanism agrees with the work of [25], who have shown that the inductive loop of impedance diagrams is due to an adsorption process.

The capacitive loops sizes, out of phase concerning the real axis, increased with higher AS C. $R_p$ values, determined from the medium frequency limits on the Nyquist diagrams, confirmed a satisfactory protective capacity at 1 g/L AS. The metal/electrolyte interface modeling was carried out through an equivalent electrical circuit (Fig. 5).

Two equivalent circuits were applied using a Bouckamp program. As shown in Fig. 5, the capacitor was substituted through a CPE, which offered a different frequency response. CPE impedance is represented by the following equation [26]:

$$Z_{CPE} (\omega) = Q^{-1}(j\omega)^{-n}$$  \hspace{1cm} (12)

where Q is a constant in $\Omega$/cm$^2$/s$^n$, $\omega$ is the angular frequency in rad/s$^{-1}$and n is CPE exponent (-1 < n < 1). $Z_{CPE}$ can represent either an inductance, or a Warburg impedance, or a capacitance or a resistance (n = -1, 0 and 0.5, respectively). The following elements from the suggested equivalent circuits are: $R_s$, $R_f$, $R_{ct}$, $n_f$, $n_{ct}$, CPE$_f$ and CPE$_{dl}$.

$R_p$ was calculated by the following equation:

$$R_p = R_f + R_{ct}$$  \hspace{1cm} (13)
Figure 5. Equivalent circuit model used for fitting experimental EIS data.

Electrochemical parameters and IE(%) values, for different AS C, obtained by EIS, and using the equivalent circuit, are given in Table 3.

Table 3. Impedance parameters for AA in a 3.5 %NaCl solution without and with AS.

<table>
<thead>
<tr>
<th>Medium</th>
<th>C g/L</th>
<th>$R_s$ Ω/cm²</th>
<th>$Q_f$ Ω⁻¹ S⁻¹/cm²</th>
<th>$n_f$</th>
<th>$R_t$ Ω/cm²</th>
<th>$Q_t$ Ω⁻¹ S⁻¹/cm²</th>
<th>$n_t$</th>
<th>$R_{ct}$ Ω/cm²</th>
<th>$R_f$ Ω/cm²</th>
<th>$R_p$ Ω/cm²</th>
<th>$L$ (H)</th>
<th>IE(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-</td>
<td>12.5±0.3</td>
<td>170.3±0.12</td>
<td>1</td>
<td>107±0.2</td>
<td>-</td>
<td>-</td>
<td>1111.0±2.4</td>
<td>1218</td>
<td>16.0±1.3</td>
<td>211</td>
<td>-</td>
</tr>
<tr>
<td>AS</td>
<td>0.25</td>
<td>5.0±0.1</td>
<td>72.1±0.23</td>
<td>0.885</td>
<td>879±0.3</td>
<td>130.8±0.31</td>
<td>0.575</td>
<td>1039.0±5.3</td>
<td>1918</td>
<td>1550.0±4.3</td>
<td>193</td>
<td>36.5</td>
</tr>
<tr>
<td>AS</td>
<td>0.50</td>
<td>4.5±0.2</td>
<td>44.8±0.34</td>
<td>0.805</td>
<td>275.5±0.6</td>
<td>66.9±0.45</td>
<td>0.525</td>
<td>2093.0±6.1</td>
<td>2360</td>
<td>2080.0±7.3</td>
<td>314</td>
<td>48.5</td>
</tr>
<tr>
<td>AS</td>
<td>0.75</td>
<td>4.0±0.3</td>
<td>66.4±0.13</td>
<td>0.856</td>
<td>619.0±4.0</td>
<td>150.6±0.72</td>
<td>0.687</td>
<td>1879.0±5.2</td>
<td>2498</td>
<td>2140.0±5.3</td>
<td>351</td>
<td>51.2</td>
</tr>
<tr>
<td>AS</td>
<td>1.00</td>
<td>4.6±0.1</td>
<td>12.7±0.15</td>
<td>0.739</td>
<td>4542.0±0.1</td>
<td>16.7±0.53</td>
<td>0.948</td>
<td>4426.0±3.4</td>
<td>8968</td>
<td>7948.0±2.3</td>
<td>505</td>
<td>86.4</td>
</tr>
</tbody>
</table>

From the obtained parameters, it can be seen that AS addition decreased $Q_{ct}$ and $Q_f$ values and increased $R_{ct}$ and $R_f$. The significant decrease in the capacitance values is often ascribed to a reduction in the dielectric constant or a rise in the double electric layer thickness, due to AS molecules adsorption onto the AA surface [27-29]. IE(%) and $R_p$ values increased with AS addition, indicating the formation of an insulated adsorption layer. This phenomenon suggests that the charge transfer process was impeded when the uncovered area available for this process decreased, which can be explained by AS molecules adsorption at the metal/electrolyte interface [30].

**T effect**

**Polarization curves**

In general, T has a remarkable effect on corrosion phenomena. CR increases when the test T increases, which induces changes in the inhibitors action [31, 32]. PDP study of AA in NaCl without and with AS (1 g/L), at T from 298 to 328 K, was herein conducted. The corresponding obtained PDP curves are shown in Fig. 6.

![Figure 6](image-url)
J was higher with an increase in T from 298 to 328 K. The curves of the cathode and anode were consistent with an equivalent mechanism within the whole T range. AA $E_{\text{corr}}$ was little modified by the increase in T to 328 K, in 3.5% NaCl without and with AS.

$E_{\text{corr}}$, $i_{\text{corr}}$, $\beta_c$ and IE(%) values are summarized in Table 4. In general, throughout the studied range, T higher values caused an increase in $i_{\text{corr}}$. The $i_{\text{corr}}$ evolution in only 3.5% NaCl confirmed an increasing metallic dissolution with higher T. Nevertheless, the rise in $i_{\text{corr}}$ with higher T, in AA presence, was much smaller than in the uninhibited solution. These results confirm and complement those obtained by EIS. AS showed better (IE%) in the studied T range (308, 318 and 328 K).

### Table 4. AA electrochemical parameters in 3.5 % NaCl with and without AS, at different T.

<table>
<thead>
<tr>
<th>Medium</th>
<th>T (K)</th>
<th>$E_{\text{corr}}$ mV/Ag/AgCl</th>
<th>$i_{\text{corr}}$ µA/cm$^2$</th>
<th>$\beta_c$ mV/dec$^{-1}$</th>
<th>$\beta_a$ mV/dec$^{-1}$</th>
<th>IE(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>298</td>
<td>774</td>
<td>10.8</td>
<td>359</td>
<td>216</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>773</td>
<td>76.7</td>
<td>302</td>
<td>157</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>716</td>
<td>143.6</td>
<td>235</td>
<td>186</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>731</td>
<td>171.1</td>
<td>247</td>
<td>182</td>
<td>-</td>
</tr>
<tr>
<td>AS</td>
<td>298</td>
<td>733</td>
<td>1.4</td>
<td>293</td>
<td>155</td>
<td>87.0</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>796</td>
<td>10.9</td>
<td>274</td>
<td>151</td>
<td>85.7</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>796</td>
<td>23.2</td>
<td>286</td>
<td>144</td>
<td>83.8</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>823</td>
<td>32.9</td>
<td>290</td>
<td>159</td>
<td>80.7</td>
</tr>
</tbody>
</table>

**Thermodynamic studies**

The Arrhenius-type dependence observed between $i_{\text{corr}}$ and T allowed to calculate the corrosion process $E_a$ value at different T, in AS absence and presence. Fig. 7 illustrates the $i_{\text{corr}}$ logarithm ($\ln CR$) variation as a function of the absolute T inverse ($1/T$). This $\ln i_{\text{corr}} = f (1/T)$ variation was linear for different C of both uninhibited and inhibited media. From the Arrhenius relation 7, we can calculate $E_a$ for different C of the solutions without and with AS [33-35].

\[
\ln (i_{\text{corr}}) = \ln (K) - \frac{E_a}{RT}
\]  

(14)

where R is the universal gas constant and K is the Arrhenius pre-exponential constant. The values collected from the slope of the linear plots are presented in Table 5, where it is seen that $E_a$ value for the studied AS C was higher than that of the uninhibited solution. The increased $E_a$ in AS presence may also be interpreted as physical adsorption.

Indeed, an enormous energy barrier within the inhibited solution was associated with physical adsorption or weak chemical bonding of AS with the AA surface [36, 37]. An alternative formula of the Arrhenius equation allows $\Delta H_a$ and $\Delta S_a$ determination, according to the following equation (15):

\[
I_{\text{corr}} = \frac{RT}{Nh} \exp \left( \frac{\Delta S_a}{R} \right) \exp \left( -\frac{\Delta H_a}{RT} \right)
\]  

(15)

where N is Avogadro’s number and h is Plank’s constant.
Fig. 6 illustrates \( L_n (i_{corr}/T) \) variation as a function of the inverse \( T \) (1/T). The obtained lines have a slope equal to \(-\Delta H_a/R\), and an ordinate at the origin equal to \( L_n (R/Nh) + (\Delta S_a/R) \). From these equations, we can therefore calculate \( \Delta H_a \) and \( \Delta S_a \) values, which are given in Table 5.

\[
\frac{L_n (i_{corr}/T)}{T} = \frac{-\Delta H_a}{R} + \frac{L_n (R/Nh) + (\Delta S_a/R)}{T}
\]

\( \Delta H_a \) positive signs reflect the endothermic nature of the AA dissolution process. Indeed, increased \( \Delta H_a \), in AS presence, corresponds to a decrease in AA dissolution [38]. Additionally, Table 5 shows that \( \Delta S_a \) value was higher in AS presence than in its absence, which suggests that a rise in disorder occurred during the transition from the reactant to the activated complex, during the corrosion process [39, 40].

**SEM**

The surface morphologies of AA samples, in 3.5% NaCl without and with AS, were analyzed by SEM. The surface compositions were determined from their EDX spectra. Figs. 8 and 9 show SEM-EDX of AA corroded and inhibited surfaces, after 2 h of immersion in 3.5% NaCl. SEM image of AA surface in 3.5% NaCl without AS (Fig. 8) shows the extreme degradation around the intermetallic particles.

**Table 5.** \( E_a, \Delta H_a \) and \( \Delta S_a \) values for AA in NaCl without and with AS.

<table>
<thead>
<tr>
<th>Medium</th>
<th>( E_a ) (kJ/mol)</th>
<th>( \Delta H_a ) (kJ/mol)</th>
<th>( \Delta S_a ) (J/mol.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>73.3</td>
<td>70.7</td>
<td>15.9</td>
</tr>
<tr>
<td>1 g/L</td>
<td>83.9</td>
<td>81.3</td>
<td>34.4</td>
</tr>
</tbody>
</table>

\( E_a \) and \( \Delta H_a \) values were determined using the Arrhenius equation. The values of \( \Delta S_a \) indicate an increase in disorder during the transformation from the reactant to the activated complex, during the corrosion process.

**Figure 7.** AA Arrhenius plots without and with 1 g/L AS.

**Figure 8.** Surface morphology and EDX of AA after immersion for 2 h in NaCl without AS.
Fig. 10 shows SEM-EDX of AA surface, after 20 h immersion in 3.5% NaCl with AS. In AS presence (Fig. 9 and 10), the AA matrix almost did not suffer corrosion attack by NaCl. This is in accordance with AS higher corrosion IE(%), as observed from electrochemical measurements.

![Fig. 9. Surface morphology and EDX of AA after 2 h immersion in 3.5% NaCl with 1g/L AS.](image1)

![Fig. 10. Surface morphology and EDX of AA after 20 h immersion in 3.5% NaCl with 1 g/L AS.](image2)

EDX analysis of the corrosion products created on the AA surfaces is presented in Table 6. P, N and S peaks appearance designate that the minority of AS were adsorbed onto the AA. P appearance is associated to the presence of diverse bioactive compounds comprising vitamins (A, C, E and B (vitamin B1) [8] and minerals (P, Ca, Zn, K, Na, Fe and Cu) [17]. Therefore, these results confirm those attained from electrochemical measurements.

<table>
<thead>
<tr>
<th>Element</th>
<th>Blank</th>
<th>AS (2 h)</th>
<th>AS (20 h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>9.40</td>
<td>9.55</td>
<td>18.51</td>
</tr>
<tr>
<td>N</td>
<td>-</td>
<td>0.39</td>
<td>1.54</td>
</tr>
<tr>
<td>O</td>
<td>16.70</td>
<td>12.86</td>
<td>24.43</td>
</tr>
<tr>
<td>Mg</td>
<td>2.19</td>
<td>2.65</td>
<td>1.65</td>
</tr>
<tr>
<td>Al</td>
<td>53.01</td>
<td>72.24</td>
<td>51.25</td>
</tr>
<tr>
<td>P</td>
<td>-</td>
<td>0.02</td>
<td>0.25</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td>Cu</td>
<td>0.49</td>
<td>0.37</td>
<td>0.52</td>
</tr>
<tr>
<td>Zn</td>
<td>2.52</td>
<td>1.91</td>
<td>1.82</td>
</tr>
</tbody>
</table>

**AFM**

AFM allowed knowing electrochemical interactions at the nanometric, or even atomic, scale. It is an essential tool for the study of interface phenomena, such as corrosion [41-44]. Micrographs of the AA surface without and with AS (1 g/L) are presented in three dimensions (Fig. 11).
**Figure 11.** 3D AFM images of AA after 24 h immersion in NaCl: (a) without and (b) with 1 g/L AS.

Fig. 11a shows that the AA surface in 3.5% NaCl without AS suffered severe damage, while with it, $R_a$ was significantly reduced (Fig. 12).

**Figure 12.** $R_a$ variation of AA after 24 h immersion in NaCl without and with AS (1 g/L).

$R_a$ of the AA surface immersed in 3.5% NaCl without and with AS was 338.17 and 79.3 μm, respectively. $R_a$ reduction confirmed the formation of a film by AS, which covered the entire AA surface (Table 7).

<table>
<thead>
<tr>
<th>Table 7. $R_a$ and $S_a$ values derived from AFM.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>$R_a$ (μm)</td>
</tr>
<tr>
<td>$S_a$ (nm)</td>
</tr>
</tbody>
</table>

**X-RD analysis**

X-RD has been performed for determining the products developed on the AA surface. AA X-RD patterns, after 20 h immersion in NaCl without and with AS (1 g/L), are displayed in Fig. 13.
Figure 13. X-RD patterns of AA in NaCl without and with 1 g/L AS.

X-RD patterns determined three significant peaks: the one from Al was the strongest; the MgZn$_2$ precipitate peak was very weak; and the intensity of that from Al(OH)$_3$ was reduced in AS presence, indicating that it protected the alloy [45-47]. There were some other AS compounds which X-RD could not identify. The theoretical studies would help us to illustrate it.

**DFT calculations**

After the experimental investigation was performed with AS, the theoretical study was executed to compare its components. GA and D-M have been theoretically examined through DFT calculations, for explaining the IE(%) structural parameters. Geometrical optimization structure, HOMO and LUMO, are presented in Fig. 14.

![Figure 14. Geometrical optimization structure, HOMO and LUMO for GA (a, b, c) and D-M (d, e, f) at DFT/6-31G(d,p) in the aqueous phase.](image-url)
It is seen that HOMO and LUMO electron density is distributed over GA molecule, indicating that it represents both nucleophilic and electrophilic centers from which the electron can be transferred from/to the AA vacant 3-d orbit. However, in D-M case, HOMO is distributed all over it, while LUMO is concentrated on the propanone group, which represents the electrophilic center that accepts electrons transferred by retrodonation from the AA surface.

Some quantum chemical descriptors, including ΔE, σ, η, χ and ΔN, in both gas and aqueous phases, were also quantified (Table 8). $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ refer to the tested compound electron donation and receiving ability to/from AA atomic orbitals. HOMO higher value indicates that AS have an excellent ability for donating electrons to the AA surface vacant d-orbitals. In comparison, LUMO lower value implies that AS has an affinity for accepting electrons from the d-orbitals of the metal surface. It can be noticed from Table 8 that HOMO theoretical order in the gas and aqueous phases is GA > D-M, suggesting that the former had good electron-donating properties. ΔE is another fundamental descriptor that elucidates the inhibitor reactivity towards the metal surface. As ΔE diminishes, the inhibitor molecule reactivity is enhanced (higher IE) [48].

From Table 8, ΔE values obtained in both gas and aqueous phases follow the order D-M > GA, indicating that the latter has more reactivity than that of D-M.

Table 8. Various descriptors quantum chemical for GA and D-M molecules in both gas and aqueous phases.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Gas phase</th>
<th>Aqueous phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{HOMO}}$ (eV)</td>
<td>-7.403</td>
<td>-7.354</td>
</tr>
<tr>
<td>$E_{\text{LUMO}}$ (eV)</td>
<td>-1.391</td>
<td>-1.370</td>
</tr>
<tr>
<td>ΔE (eV)</td>
<td>6.011</td>
<td>5.983</td>
</tr>
<tr>
<td>η (eV)</td>
<td>3.005</td>
<td>2.991</td>
</tr>
<tr>
<td>σ (eV$^{-1}$)</td>
<td>0.332</td>
<td>0.334</td>
</tr>
<tr>
<td>χ (eV)</td>
<td>4.397</td>
<td>4.362</td>
</tr>
<tr>
<td>ΔN</td>
<td>0.070</td>
<td>0.076</td>
</tr>
<tr>
<td>µ (D)</td>
<td>3.815</td>
<td>6.534</td>
</tr>
</tbody>
</table>

According to χ equalization principle [49], D-M with high χ reflected lower reactivity than that of GA. Based on literature [50, 51], it is known that an inhibitor molecule can donate its electron to a metallic surface if ΔN > 0 and < 0. However, ΔN order in the aqueous phase was GA (0.197) > D-M (0.076), suggesting that the former had higher ΔN towards the AA surface atoms than that of the latter. The present investigation showed that µ of GA and D-M did not have a significant order, and that the magnitudes of the mentioned descriptors for both molecules had the same trend in gas and aqueous phases. Consequently, these molecules, especially GA, may have been responsible for experimentally recorded AS IE(%)..

Local reactivity descriptors (Fukui indices)

Fukui indices are important to recognize electrophilic and nucleophilic reactive centers within the same molecule [52]. Fig. 15 displays the graphical outcomes of
neutral GA and D-M molecules electrophilic/nucleophilic attacks, in terms of atom-condensed Fukui functions (Table 9) in the aqueous medium.

![Figure 15](image)

**Figure 15.** Schematic representation of Fukui indices $f_k^+$ (blue) and $f_k^-$ (red) for the considered molecules in the aqueous medium.

**Table 9.** Fukui functions and their dual descriptors for the considered molecules in the aqueous medium.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>D-M</th>
<th>GA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$f_k^+$</td>
<td>$f_k^-$</td>
</tr>
<tr>
<td>C1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C2</td>
<td>-0.02679</td>
<td>0.01255</td>
</tr>
<tr>
<td>C3</td>
<td>0.01557</td>
<td>0.02180</td>
</tr>
<tr>
<td>C4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C5</td>
<td>-0.01105</td>
<td>0.01397</td>
</tr>
<tr>
<td>C6</td>
<td>-</td>
<td>0.08702</td>
</tr>
<tr>
<td>C7</td>
<td>0.00618</td>
<td>0.01830</td>
</tr>
<tr>
<td>C8</td>
<td>-0.00072</td>
<td>0.01260</td>
</tr>
<tr>
<td>C10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C11</td>
<td>-0.00006</td>
<td>-0.00294</td>
</tr>
<tr>
<td>C12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C13</td>
<td>0.27468</td>
<td>0.00967</td>
</tr>
<tr>
<td>O1</td>
<td>0.02303</td>
<td>0.02221</td>
</tr>
<tr>
<td>O4</td>
<td>0.03929</td>
<td>0.05665</td>
</tr>
<tr>
<td>O6</td>
<td>0.00493</td>
<td>0.11951</td>
</tr>
<tr>
<td>O8</td>
<td>0.00301</td>
<td>0.08545</td>
</tr>
<tr>
<td>O9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O10</td>
<td>0.00164</td>
<td>0.07402</td>
</tr>
<tr>
<td>O11</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O12</td>
<td>0.00202</td>
<td>0.10349</td>
</tr>
<tr>
<td>O14</td>
<td>0.18375</td>
<td>0.08428</td>
</tr>
</tbody>
</table>

According to the schematic representation of Fukui indices, it is visible that almost all the GA molecule atoms interacted, as electrophilic and nucleophilic sites, i.e., higher values of $f_k^+$ and $f_k^-$ were obtained. However, in D-M molecule case, C(13), O(14), O(4) and O(1) acted as major locations for nucleophilic behavior, and all its O atoms acted as major centers, with electrophilic conduct.

Fukui functions second order ($f_k^2$), also called dual descriptor, provides an easy and intuitive approach to chemical reactivity [53], and it can be evaluated using the following equation (16):

$$f_k^2 = f_k^+ \cdot f_k^-$$

(16)

Fukui functions and their dual descriptors are shown in Fig.16.
It was reported that if $f_k^2 < 0$, it will tend to transfer electrons to the metal surface, while if $f_k^2 > 0$, it will accept electrons from the metal [54]. As shown in Table 9 and Fig. 16, the most active sites for D-M and GA electron-accepting centers had the following sequence: C(13) > O(14) > C(11) > O(1) and C(7) > O(8) > C(5) > C(1) > O(9), respectively. However, the most active sites for D-M and GA donating active centers followed the order: O(6) > O(12) > O(8) > O(10) > C(2) > C(5) > O(4) > C(9) > C(7) > C(3) and O(10) > O(11) > C(6) > O(12) > C(4) > C(2) > C(3), respectively.

Conclusions

Electrochemical, thermodynamic, surface analysis and theoretical studies were used to characterize AS IE(%) on AA corrosion in a 3.5% NaCl solution. The following conclusions were drawn from this study:

- AS were an excellent green corrosion inhibitor for AA in a neutral 3.5% NaCl medium.
- AS IE(%) measured by EIS reached up 87% at 1 g/L inhibitor C.
- Polarization curves showed that AS is a mixed type inhibitor.
- AS adsorption onto the AA surface followed Langmuir’s isotherm. Thermodynamic parameters showed that AS was highly adsorbed onto the AA surface.
- The study of the AA surface morphology and roughness by SEM/EDX and AFM showed a stable and insoluble adherent deposit.
Theoretical calculations showed that there was a correlation between AS molecular structure and its IE(%). They suggest that the effectiveness of AS Pc constituents studied through DFT pursued the sequence: GA > D-M.

Authors’ contributions
M. Radi: wrote the paper. R. Melian: conceived and designed the analysis. M. Galai: collected the data. N. Dkhirche: performed the analysis. E. Ech-chihbi: performed the analysis. M. Ebn Touhami: conceived and designed the analysis.

Abbreviations
AA: 7075-T6 Al alloy
AC: alternating current
AFM: atomic force microscope
AgCl: silver chloride
Al$_2$Cu: aluminum bronze
Al$_3$Fe: iron aluminide
AS: avocado seeds
ATR: attenuated total reflection mode
C: concentration
CE: counter electrode
CPE: constant phase element
CR: corrosion rate
DFT: density functional theory
DM: D-mannoheptulose
E: potential
E$_a$: activation energy
E$_{corr}$: corrosion potential
EDX: energy dispersive X-ray
E$_{HOMO}$: energy of the highest occupied molecular orbital
EIS: electrochemical impedance spectroscopy
E$_{HOMO}$: energy of the highest unoccupied molecular orbital
E$_{LUMO}$: energy of the lowest unoccupied molecular orbital
E$_{ocp}$: circuit potential evolution
FTIR: Fourier transform infrared spectroscopy
GA: gallic acid
i$_{corr}$: corrosion current density
IE(%): inhibition efficiency
IEFPCM: integral equation formalism variant of the polarizable continuum model
J: current density
KBr: potassium bromide
L: inductance
Mg$_2$Si: magnesium silicide
MgZn$_2$: dizinc magnesium
MPA: Mulliken population analysis
NaCl: sodium chloride
OCP: open circuit potential
Pc: phytochemicals
PDP: potentiodynamic polarization
Symbols definition

\( \Psi \): pound-force per square inch
\( \mathbf{Q}_c \): double layer capacitance of the inhibitors film
\( \mathbf{Q}_{ct} \): Al double layer capacitance
\( \mathbf{R}_a \): average roughness
\( \mathbf{R}_{ct} \): charge transfer resistance
\( \mathbf{RE} \): reference electrode
\( \mathbf{R}_L \): resistance of the inductive loop
\( \mathbf{R}_p \): polarization resistance
\( \mathbf{S}_a \): average surface roughness
\( \mathbf{SEM} \): scanning electron microscopy
\( \mathbf{SR} \): scan rate
\( \mathbf{T} \): temperature
\( \mathbf{WE} \): working electrode
\( \mathbf{X-RD} \): X-ray diffraction

References


