

## **SUPPLEMENTARY MATERIALS**

### **Impact of aqueous extract *Artemisia herba-alba* leaves as a green inhibitor against acid activation of 2024 aluminum alloy**

**Nacer Hechiche<sup>1</sup>. Gérald Culioli<sup>2</sup>. Abdelaziz Kadri<sup>1</sup>. Dalila Boughrara<sup>1</sup>. Amar Saal<sup>3</sup>  
.F.Xavier Perrin<sup>4</sup>**

<sup>1</sup> Laboratoire de physique et chimie des matériaux, Université Mouloud Mammeri, Tizi-Ouzou, Algérie

<sup>2</sup> Institut Méditerranéen de Biodiversité et d'Ecologie Marine et Continentale, UMR CNRS-IRD, Aix-Marseille Université, Avignon, France

<sup>3</sup> Laboratoire de Chimie Théorique Computationnelle Et Photonique, USTHB, Algiers ,  
Algeria

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## 1 Adsorption isotherms

In addition to Langmuir isotherm, the following adsorption models were tested to evaluate the model that best fits the surface coverage data:

Temkin isotherm

$$K_{ads}C = e^{f\theta} \quad (1)$$

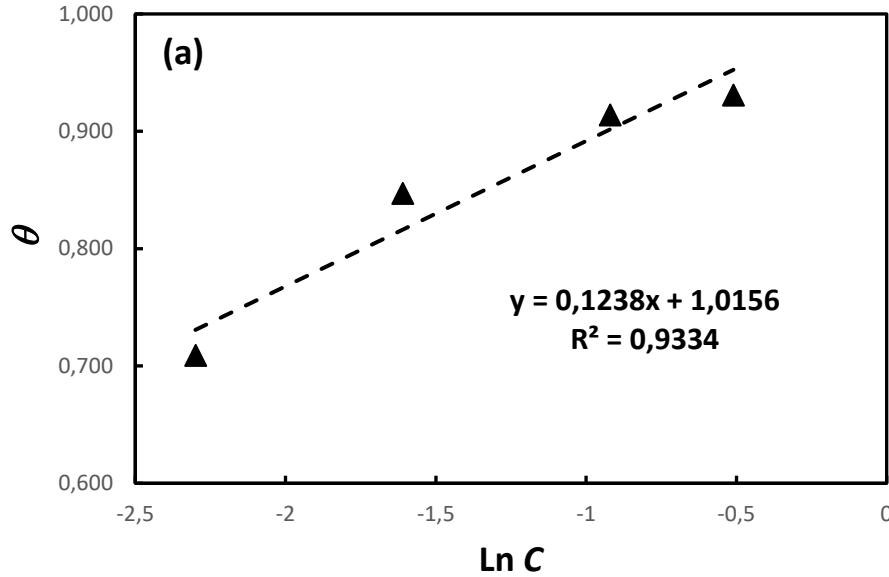
Freundlich isotherm

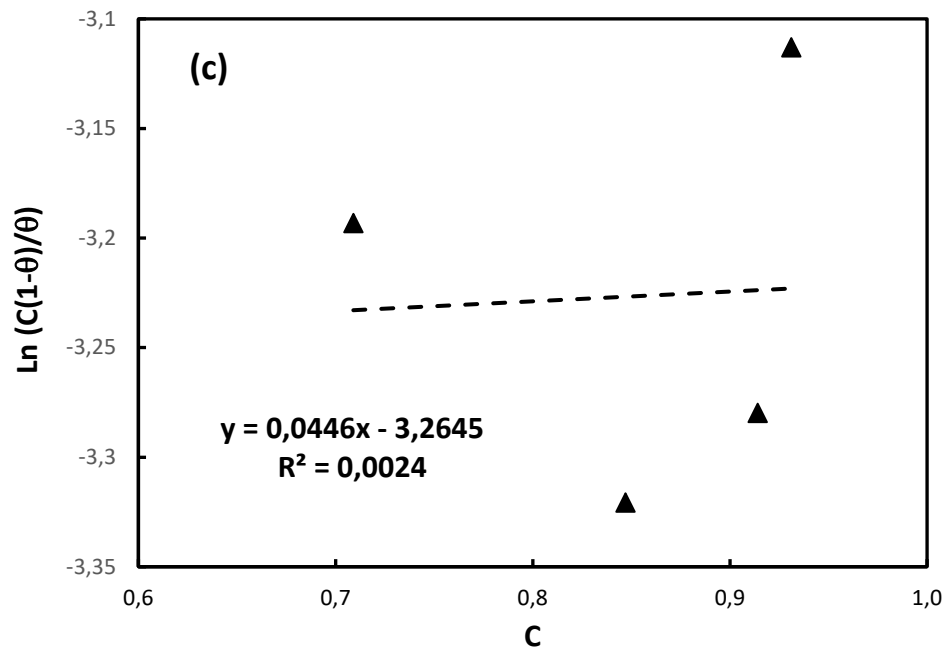
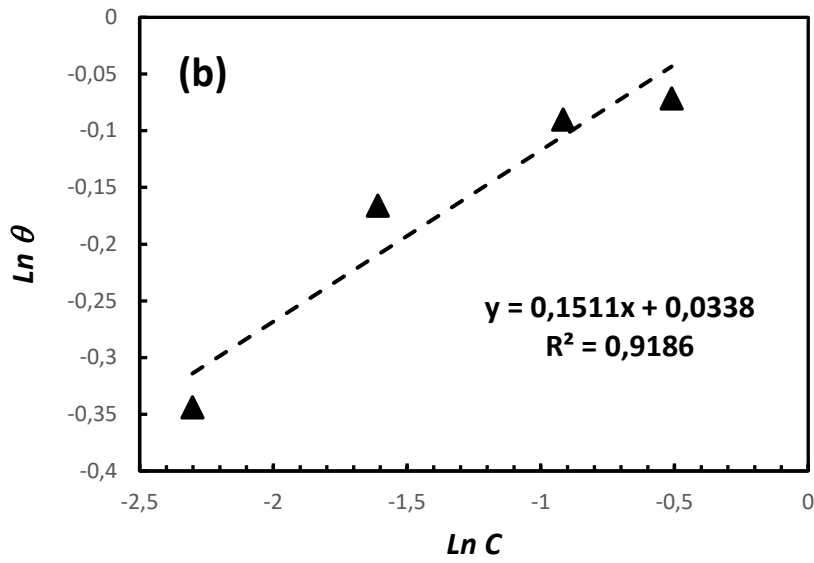
$$K_{ads}C^{\frac{1}{n}} = \theta \quad (2)$$

Frumkin isotherm

$$K_{ads}C = \frac{\theta}{1-\theta} e^{f\theta} \quad (3)$$

Where  $K_{ads}$  is the adsorption equilibrium constant (in L/g),  $C$  the mass concentration,  $f$  the molecular interaction parameter between corrosion inhibitor molecules and  $n$  the Freundlich empirical constant.





**Figure S1** . Linearized (a) Temkin isotherm, (b) Freundlich isotherm, and (c) Frumkin isotherm (temperature: 25 °C)

## 2- Actual free energy of adsorption for natural extracts

The molar concentration of the active inhibitor molecule,  $c$  is given by Equation (4),

$$c = \frac{xC}{M_{inh}} \quad (4)$$

where  $x$  is the weight fraction of the active inhibitor in the natural extract,  $C$  is the mass concentration (in g/L) of the natural extract and  $M_{inh}$  is the molecular weight of the inhibitor.

The adsorptive equilibrium constant ( $K_{ads,1}$ ) in  $L g^{-1}$  is thus related to the adsorptive equilibrium constant ( $K_{ads,2}$ ) in  $L mol^{-1}$  through Equation (5) :

$$K_{ads,2} = \frac{M_{inh}}{x} K_{ads,1} \quad (5)$$

The free adsorption enthalpies defined from the mass or molar concentrations are given in Equation (6) and (7), respectively :

$$\Delta G_{ads,1}^0 = -RT \ln(K_{ads,1} C_{H_2O}) \quad (6)$$

$$\Delta G_{ads,2}^0 = -RT \ln(K_{ads,2} c_{H_2O}) \quad (7)$$

$$\text{with } C_{H_2O} = M_{H_2O} c_{H_2O}$$

To compare the relative values of  $\Delta G_{ads,1}^0$  and  $\Delta G_{ads,2}^0$  it is sufficient to compare the exponential terms:

$$\frac{K_{ads,2} c_{H_2O}}{K_{ads,1} C_{H_2O}} = \frac{M_{inh}}{M_{H_2O} x}$$

we can anticipate that  $K_{ads,2} c_{H_2O}$  will be greater than  $K_{ads,1} C_{H_2O}$  and therefore that  $\Delta G_{ads,2}^0$  will be more negative than  $\Delta G_{ads,1}^0$  given that  $M_{inh} > M_{H_2O}$  and  $x < 1$ .

The actual free energy of adsorption is more negative than the value calculated from mass concentrations of the aqueous extract of AHA (-25.3  $kJ \cdot mol^{-1}$ ). A simple calculation based on isofraxidin as the only active compound in the extract and present at 10% by mass in the extract conducted by example at a  $\Delta G_{ads,2}^0$  value of -37.2  $kJ \cdot mol^{-1}$ .

### 3- Chemical compounds detected by LC-MS/MS

**Table S1** Chemical compounds detected by LC-MS/MS of the AEAHA

| <i>m/z</i><br>(+ mode) | RT (min) | Ion formula   | Mass error<br>(ppm) | $m\sigma^a$       | Putative annotation                             |
|------------------------|----------|---|---------------------|-------------------|---|
| 156.0423               | 0.7      | C <sub>5</sub> H <sub>6</sub> N <sub>3</sub> O <sub>3</sub> | -9.6                | 26.3              | -   |
| 118.0864               | 0.72     | C <sub>5</sub> H <sub>12</sub> NO <sub>2</sub>              | -1.0                | 8.2               | Valine  |
| 124.0395               | 0.80     | C <sub>6</sub> H <sub>6</sub> NO <sub>2</sub>               | -1.9                | 7.5               | Nicotinic acid                                  |
| 102.0551               | 0.80     | C <sub>4</sub> H <sub>8</sub> NO <sub>2</sub>               | -1.3                | 3.4               | -   |
| 132.1021               | 0.85     | C <sub>6</sub> H <sub>14</sub> NO <sub>2</sub>              | +0.2                | 7.3               | Isoleucine/leucine                              |
| 127.0503               | 0.89     | C <sub>5</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub> | +0.8                | 3.5               | Thymine   |
| 267.1590               | 1.65     | C <sub>15</sub> H <sub>23</sub> O <sub>4</sub>              | +0.5                | 7.1               | Sesquiterpene (Deoxyartemisinin or isomer)      |
| 137.0597               | 1.69     | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub>                | +0.1                | 3.4               | 4-Hydroxyacetophenone                           |
| 167.1066               | 1.71     | C <sub>10</sub> H <sub>15</sub> O <sub>2</sub>              | +0.1                | 16.3              | Monoterpene                                     |
| 265.1437               | 1.98     | C <sub>15</sub> H <sub>21</sub> O <sub>4</sub>              | -1.2                | n.d. <sup>b</sup> | Sesquiterpene (Ludovicin B, Barrelin or isomer) |
| 121.0649               | 2.02     | C <sub>8</sub> H <sub>9</sub> O                             | +0.5                | 13.5              | Acetophenone                                    |
| 153.1275               | 2.23     | C <sub>10</sub> H <sub>17</sub> O                           | +0.1                | 3.3               | Monoterpene (Thuyone or isomer)                 |
| 257.1024               | 2.26     | C <sub>12</sub> H <sub>17</sub> O <sub>6</sub>              | -1.6                | 6.6               | -   |
| 185.1173               | 3.43     | C <sub>10</sub> H <sub>17</sub> O <sub>3</sub>              | -0.6                | 7.2               | Monoterpene                                     |
| 225.1097               | 3.45     | C <sub>12</sub> H <sub>17</sub> O <sub>4</sub>              | +11.1               | 19.7              | -   |
| 257.1021               | 3.62     | C <sub>12</sub> H <sub>17</sub> O <sub>6</sub>              | -1.0                | 8.1               | -   |
| 155.1067               | 3.77     | C <sub>9</sub> H <sub>15</sub> O <sub>2</sub>               | -1.4                | 5.3               | -   |
| 137.0600               | 5.07     | C <sub>8</sub> H <sub>9</sub> O <sub>2</sub>                | -1.1                | 4.4               | -   |
| 267.1593               | 5.22     | C <sub>15</sub> H <sub>23</sub> O <sub>4</sub>              | -0.8                | 7.5               | Sesquiterpene (Deoxyartemisinin or isomer)      |
| 265.1433               | 5.43     | C <sub>15</sub> H <sub>21</sub> O <sub>4</sub>              | -0.7                | n.d.              | Sesquiterpene (Ludovicin B, Barrelin or isomer) |
| 283.1543               | 5.78     | C <sub>15</sub> H <sub>23</sub> O <sub>5</sub>              | -0.1                | 33.8              | Sesquiterpene (Artemisinin or isomer)           |
| 181.0858               | 6.11     | C <sub>10</sub> H <sub>13</sub> O <sub>3</sub>              | +0.8                | 25.8              | Monoterpene                                     |
| 315.1440               | 6.46     | C <sub>15</sub> H <sub>23</sub> O <sub>7</sub>              | -0.4                | 7.4               | Sesquiterpene                                   |
| 285.1696               | 7.38     | C <sub>15</sub> H <sub>25</sub> O <sub>5</sub>              | +0.1                | 5.0               | Sesquiterpene (Dihydroartemisinin or isomer)    |
| 227.1277               | 7.63     | C <sub>12</sub> H <sub>19</sub> O <sub>4</sub>              | +0.2                | 15.6              | -   |
| 135.1168               | 7.70     | C <sub>10</sub> H <sub>15</sub>                             | +0.3                | 4.7               | Monoterpene                                     |
| 183.1014               | 7.81     | C <sub>10</sub> H <sub>15</sub> O <sub>3</sub>              | +0.7                | n.d.              | Monoterpene                                     |
| 121.1011               | 7.87     | C <sub>9</sub> H <sub>13</sub>                              | -1.9                | 26.2              | -   |
| 185.1172               | 8.07     | C <sub>10</sub> H <sub>17</sub> O <sub>3</sub>              | +0.4                | 6.8               | Monoterpene                                     |

|          |       |   |      |      |   |
|----------|-------|---|------|------|---|
| 181.0859 | 8.26  | C <sub>10</sub> H <sub>13</sub> O <sub>3</sub>  | +0.3 | 10.6 | Monoterpene   |
| 229.1435 | 8.40  | C <sub>12</sub> H <sub>21</sub> O <sub>4</sub>  | -0.5 | 10.3 | -   |
| 414.2120 | 8.44  | C <sub>20</sub> H <sub>32</sub> NO <sub>8</sub> | +0.7 | 19.0 | -   |
| 285.1697 | 8.48  | C <sub>15</sub> H <sub>25</sub> O <sub>5</sub>  | -0.3 | 24.2 | Sesquiterpene (Dihydroartemisinin or isomer)  |
| 595.1654 | 8.53  | C <sub>27</sub> H <sub>31</sub> O <sub>15</sub> | +0.5 | 7.6  | Flavonoid (Vicenin-2)   |
| 179.1066 | 8.66  | C <sub>11</sub> H <sub>15</sub> O <sub>2</sub>  | +0.6 | 5.1  | -   |
| 193.0500 | 8.73  | C <sub>10</sub> H <sub>9</sub> O <sub>4</sub>   | +0.1 | 6.1  | Coumarin (Scopoletin)   |
| 565.1556 | 8.79  | C <sub>26</sub> H <sub>29</sub> O <sub>14</sub> | -0.8 | 4.4  | Flavonoid (Schafotoside/Isoschafotoside)  |
| 249.1487 | 8.83  | C <sub>15</sub> H <sub>21</sub> O <sub>3</sub>  | -0.7 | n.d. |   |
| 565.1552 | 8.91  | C <sub>26</sub> H <sub>29</sub> O <sub>14</sub> | -0.1 | 1.0  | Flavonoid (Schafotoside/Isoschafotoside)  |
| 149.0960 | 8.92  | C <sub>10</sub> H <sub>13</sub> O               | +0.6 | 1.4  | Monoterpene   |
| 208.1332 | 8.94  | C <sub>12</sub> H <sub>18</sub> NO <sub>2</sub> | 0.0  | 7.1  | -   |
| 267.1587 | 9.04  | C <sub>15</sub> H <sub>23</sub> O <sub>4</sub>  | +1.0 | 15.6 | Sesquiterpene (Deoxyartemisinin or isomer)  |
| 223.0599 | 9.14  | C <sub>11</sub> H <sub>11</sub> O <sub>5</sub>  | +0.4 | 11.8 | Coumarin (Fraxidin/Isofraxidin)   |
| 231.1380 | 9.15  | C <sub>15</sub> H <sub>19</sub> O <sub>2</sub>  | -0.1 | 11.2 | Sesquiterpene (10-epi-Gazaniolide or isomer)  |
| 163.1117 | 9.22  | C <sub>11</sub> H <sub>15</sub> O               | +0.3 | 2.6  | -   |
| 433.1136 | 9.24  | C <sub>21</sub> H <sub>21</sub> O <sub>10</sub> | -1.6 | 3.3  | Flavonoid (Vitexin/Isovitexin)  |
| 569.3310 | 9.31  | C <sub>30</sub> H <sub>49</sub> O <sub>10</sub> | +1.8 | 5.2  | Sesquiterpene (C <sub>15</sub> H <sub>24</sub> O <sub>5</sub> ) (observed as dimer)<br>(Dihydroartemisinin or isomer) |
| 285.1694 | 9.37  | C <sub>15</sub> H <sub>25</sub> O <sub>5</sub>  | +1.0 | 9.6  | Sesquiterpene (Dihydroartemisinin or isomer)  |
| 265.1434 | 9.53  | C <sub>15</sub> H <sub>21</sub> O <sub>4</sub>  | +0.0 | n.d. | Sesquiterpene (Ludovicin B, Barrelin or isomer)   |
| 299.1483 | 9.62  | C <sub>15</sub> H <sub>23</sub> O <sub>6</sub>  | +2.1 | 15.5 | Sesquiterpene (Hydroxyartemisin or isomer)  |
| 799.4637 | 9.67  | C <sub>45</sub> H <sub>67</sub> O <sub>12</sub> | -1.2 | 65.3 | Sesquiterpene (C <sub>15</sub> H <sub>22</sub> O <sub>4</sub> ) (observed as trimer)<br>(Deoxyartemisinin or isomer)  |
| 231.1380 | 9.75  | C <sub>15</sub> H <sub>19</sub> O <sub>2</sub>  | -0.3 | n.d. | Sesquiterpene (10-epi-Gazaniolide or isomer)  |
| 167.1067 | 9.81  | C <sub>10</sub> H <sub>15</sub> O <sub>2</sub>  | -0.2 | n.d. | Monoterpene   |
| 219.1743 | 9.83  | C <sub>15</sub> H <sub>23</sub> O               | 0.0  | 9.7  | Sesquiterpene (Artemisinic aldehyde or isomer)  |
| 265.1436 | 9.85  | C <sub>15</sub> H <sub>21</sub> O <sub>4</sub>  | -0.6 | n.d. | Sesquiterpene (Ludovicin B, Barrelin or isomer)   |
| 308.1852 | 9.96  | C <sub>17</sub> H <sub>26</sub> NO <sub>4</sub> | +0.2 | 12.5 | -   |
| 533.3116 | 9.98  | C <sub>30</sub> H <sub>45</sub> O <sub>8</sub>  | -1.3 | 6.7  | Sesquiterpene (C <sub>15</sub> H <sub>22</sub> O <sub>4</sub> ) (observed as dimer)<br>(Deoxyartemisinin or isomer)   |
| 249.1482 | 10.05 | C <sub>15</sub> H <sub>21</sub> O <sub>3</sub>  | +1.4 | 28.0 | Sesquiterpene   |
| 267.1589 | 10.23 | C <sub>15</sub> H <sub>23</sub> O <sub>4</sub>  | +0.6 | 4.4  | Sesquiterpene (Deoxyartemisinin or isomer)  |
| 177.0544 | 10.31 | C <sub>10</sub> H <sub>9</sub> O <sub>3</sub>   | +1.4 | 0.4  | Monoterpene   |
| 151.1117 | 10.37 | C <sub>10</sub> H <sub>15</sub> O               | -1.3 | 14.9 | Monoterpene   |
| 251.1642 | 10.46 | C <sub>15</sub> H <sub>23</sub> O <sub>3</sub>  | 0.0  | 10.3 | Sesquiterpene (Artabin, Temisin or isomer)  |
| 167.0701 | 10.57 | C <sub>10</sub> H <sub>15</sub> O <sub>2</sub>  | +1.4 | 17.8 | Monoterpene   |

|          |       |  |      |      |   |
|----------|-------|--|------|------|---|
| 151.1116 | 10.59 | C <sub>10</sub> H <sub>15</sub> O              | +1.2 | 8.3  | Monoterpene   |
| 447.2381 | 10.62 | C <sub>25</sub> H <sub>35</sub> O <sub>7</sub> | -0.7 | 36.2 | -   |
| 333.2633 | 10.72 | C <sub>18</sub> H <sub>37</sub> O <sub>5</sub> | +0.8 | 5.3  | -   |
| 301.0713 | 10.79 | C <sub>16</sub> H <sub>13</sub> O <sub>6</sub> | -0.4 | 7.8  | Flavonoid (Hispidulin, Cirsiliol, Tectorigenin or isomer) |
| 331.0814 | 10.85 | C <sub>17</sub> H <sub>15</sub> O <sub>7</sub> | -0.4 | 9.7  | Flavonoid (Jaceosidin, Iristectorigenin or isomer)        |
| 247.1324 | 10.90 | C <sub>15</sub> H <sub>19</sub> O <sub>3</sub> | +0.9 | 12.9 | Sesquiterpene (Santonin, Lumisantonin or isomer)          |
| 271.1882 | 10.97 | C <sub>15</sub> H <sub>27</sub> O <sub>4</sub> | +8.1 | 6.3  | Sesquiterpene   |
| 361.0918 | 11.02 | C <sub>18</sub> H <sub>17</sub> O <sub>8</sub> | -0.2 | 7.7  | Flavonoid (Irigenin or isomer)                            |
| 251.1641 | 11.03 | C <sub>15</sub> H <sub>23</sub> O <sub>3</sub> | +0.3 | 8.9  | Sesquiterpene (Artabin, Temisin or isomer)                |
| 347.1856 | 11.14 | C <sub>20</sub> H <sub>27</sub> O <sub>5</sub> | -0.8 | n.d. | Diterpene   |
| 203.1796 | 11.18 | C <sub>15</sub> H <sub>23</sub>                | -0.6 | 3.5  | Sesquiterpene   |
| 135.1166 | 11.23 | C <sub>10</sub> H <sub>15</sub>                | +4.7 | n.d. | Monoterpene   |
| 345.0974 | 11.40 | C <sub>18</sub> H <sub>17</sub> O <sub>7</sub> | -1.6 | 8.0  | Flavonoid (Cirsilineol, Eupatilin or isomer)              |
| 221.1900 | 11.49 | C <sub>15</sub> H <sub>25</sub> O              | +0.1 | 7.2  | Sesquiterpene (Artemisinic alcohol or isomer)             |
| 249.1487 | 11.51 | C <sub>15</sub> H <sub>21</sub> O <sub>3</sub> | -0.5 | n.d. | Sesquiterpene (Taurin, Artemorin or isomer)               |
| 375.1078 | 11.53 | C <sub>19</sub> H <sub>19</sub> O <sub>8</sub> | -1.0 | 3.4  | Flavonoid (Casticin or isomer)                            |
| 333.2067 | 11.75 | C <sub>20</sub> H <sub>29</sub> O <sub>4</sub> | -1.9 | n.d. | Diterpene   |
| 219.1747 | 11.79 | C <sub>15</sub> H <sub>23</sub> O              | 2.3  | 14.6 | Sesquiterpene (Artemisinic aldehyde or isomer)            |
| 233.1543 | 11.81 | C <sub>15</sub> H <sub>21</sub> O <sub>2</sub> | -3.1 | 8.1  | Sesquiterpene (dihydroartemisinic acid or isomer)         |

<sup>a</sup>Constructor statistical match factor (comparison of theoretical and experimental isotopic patterns). <sup>b</sup>n.d.: Not determined.