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# Adsorption characteristics and inhibition effect of *Jatropha tanjorensis* leaf extracts on aluminium corrosion in hydrochloric acid solution

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**Abstract**
The inhibition of corrosion of aluminium in hydrochloric acid by *Jatropha tanjorensis* ethanol leaf extract (JELE) and *Jatropha tanjorensis* acetone leaf extract (JALE) has been studied using weight loss and thermometric methods. JELE exhibited a higher inhibition efficiency than JALE at 1.0 g/L – 5.0 g/L extract concentrations studied. The inhibition efficiency by both extracts increased with increase in extract concentration. The inhibition efficiency of JELE increased with increase in temperature while that of JALE decreased with increase in temperature. The adsorption of both extracts conformed to the Langmuir adsorption isotherm. Thermodynamic data obtained revealed that the adsorption process was both endothermic and spontaneous.

**Keywords:** *jatropha tanjorensis*, inhibition efficiency, corrosion, extract, solvent, langmuir isotherm

## 1. Introduction

One of the consequences of the corrosion of a metal is the degradation of the metal and/or its properties thereby reducing its usefulness for practical applications. In order to increase the service life of a metallic structure in contact with an aggressive environment such as during descaling, pickling, oil well acidizing, etc, its rate of corrosion has to be reduced. Amongst the methods of corrosion control, the use of corrosion inhibitors is quite cost - effective. Due to a stricter environmental safety legislations in many countries, there is a higher demand for eco-friendly corrosion inhibitors over the traditional inhibitors globally. This has kindled the interest of researchers on natural products as a veritable source of eco-friendly corrosion inhibitors. Several leaves extracts [1-10] have been reported as potential inhibitors of aluminium corrosion in acidic media. The solvent used in preparing the extract for corrosion inhibition studies is often pre-determined by the researchers. Limited work has been done on the effect of the type of solvent used on the inhibition efficiency of the extract obtained.

*Jatropha tanjorensis* is a medicinal plant belonging to the family Euphorbiaceae. In southern Nigeria, its leaves are used in herbal medicine [11]. Preliminary phytochemical screening of *Jatropha tanjorensis* leaf extract indicated the presence of tannin, flavonoid, anthraquinone, alkaloid, cardiac glycoside and saponin [12]. Previous work [13] revealed that *Jatropha tanjorensis* leaf extract inhibited the corrosion of mild steel in acidic medium. The aim of this work was to assess the inhibition efficiencies of *Jatropha tanjorensis* ethanol leaf extract (JELE) and *Jatropha tanjorensis* acetone leaf extract (JALE) on the corrosion of aluminium in hydrochloric acid solution.

## 2. Materials and Methods

### 2.1 Test Materials

Aluminium sheet used for this work had the following chemical composition (weight %): Cu (0.03), Si (0.13),Mn (0.05), Fe (0.09). Mg (0.10) and Al (99.60). The sheet was mechanically press - cut into 4 cm x 5 cm coupons, and polished to mirror finish using different grades of silicon carbide papers. The coupons were degreased in absolute ethanol, dipped in acetone before air-drying. Before use for corrosion studies, the prepared coupons were stored in a moisture – free desiccator.

### 2.2 Preparation of *Jatropha tanjorensis* leaf extracts

*Jatropha tanjorensis* leaves were obtained from a farm in Ikot Ekpene, Akwa Ibom State, Nigeria and authenticated by a plant taxonomist in the Department of Botany and Ecological Studies, University of Uyo, Nigeria. They were washed and air – dried at 30°C for seven days and ground to powder. The powdered leaf was divided into two parts. One part was macerated in 90% ethanol while the other part was macerated in acetone. The respective mixtures were stirred intermittently and then filtered after 72 hours. The separate filtrates were evaporated to constant weights at 40°C in a water bath, to obtain *Jatropha tanjorensis* ethanol leaf extract (JELE) and *Jatropha tanjorensis* acetone leaf extract (JALE).

### 2.3 Weight loss method

Aluminium coupons, which had been cleaned and weighed, were suspended with the aid of glass hooks and rods and immersed in 100 $cm^3$ of 0.5 M HCl solution (blank) and in 0.5 M HCl solution containing 1.0 g/L – 5.0 g/L JELE and JALE, respectively, in open beakers. Each beaker contained one aluminium coupon. The beakers were maintained at 30°C, 40°C, 50°C, and 60°C, respectively, by placing them in a thermostatic water bath. After four hours, the aluminium coupons were retrieved from the test solutions and cleaned by scrubbing with bristle brush under running water before dipping in acetone and air – dried. The washed coupons were reweighed.

The inhibition efficiency $I_{WL}$ (%) was calculated using the formula [14]:

$$I_{WL}(\%) = \left(1 - \frac{W_1}{W_0}\right) \times 100 \quad (1)$$

Where $W_0$ and $W_1$ are the weight losses of the aluminium coupons in the absence and presence of extract, respectively, in HCl at the same temperature.

The corrosion rate (CR) of aluminium in 0.5 M HCl solution was evaluated using equation (2) [15]:

$$CR\ (mg\ cm^{-2} hr^{-1}) = \left(\frac{W}{At}\right) \quad (2)$$

where W is the weight loss (mg), A is the total surface area ($cm^2$) while t is the exposure time (hours).

### 2.4 Thermometric Method

The thermometric tests were performed following similar instruments and methods described by other workers [16]. The corrodent was 50 $cm^3$ of 2 M HCl. The initial temperature in all experiments was kept at 30.0°C. The change in temperature with time was recorded using a calibrated thermometer (0 - 100°C) to the nearest ± 0.1°C.

The reaction number (RN) was computed using equation (3) [17]:

$$RN\ (°C\ min^{-1}) = \frac{T_m - T_i}{t} \quad (3)$$

where $T_m$ and $T_i$ are the maximum and initial temperatures, respectively, while 't' is the time (min) taken to reach the maximum temperature.

The inhibition efficiency, $I_{TM}$ (%) was calculated using the equation:

$$I_{TM}(\%) = \left(1 - \frac{RN_1}{RN_0}\right) \times 100 \quad (4)$$

where $RN_0$ and $RN_1$ are the reaction numbers in the absence of inhibitor (blank) and in the presence of inhibitor, respectively.

## 3. Results and Discussion

### 3.1 Effect of *Jatropha tanjorensis* leaf extracts concentration on inhibition efficiency

Figure 1 shows the effect of concentrations of (a) *Jatropha tanjorensis* ethanol leaf extract (JELE) and (b) *Jatropha tanjorensis* acetone leaf extract (JALE), respectively, on inhibition efficiency of aluminium corrosion in 0.5 M HCl solution. It is observed that the inhibition efficiency increased with increase in the concentration of both leaf extracts. The maximum inhibition efficiency of JELE was 88.96% at 60°C at extract concentration of 5.0 g/L while that of JALE was 48.48% at 30°C at extract concentration of 5.0 g/L. Therefore, JELE inhibited the corrosion of aluminium better than JALE. The results of the thermometric tests on aluminium corrosion in 2 M HCl solution in the absence and presence of JELE and JALE, respectively, are illustrated in Figure 2. Inspection of Figure 2 reveals that as the concentration of the extracts increased, the time required to reach the maximum temperature ($T_m$) increased while the maximum temperature decreased. This resulted in increase in the inhibition efficiencies with increase in both JELE and JALE concentrations, respectively (Table 1). An increase in inhibition efficiency with increase in inhibitor concentration is an indication that the extract adsorbed on the metal surface and formed a protective film which reduced the electron transfer process on the metal surface [18]. Furthermore, it is evident from these data that the solvent used for the extraction greatly affected the inhibition efficiency obtained. The ethanol leaf extract (JELE) exhibited a higher inhibition efficiency than the acetone leaf extract (JALE) of *Jatropha tanjorensis.*

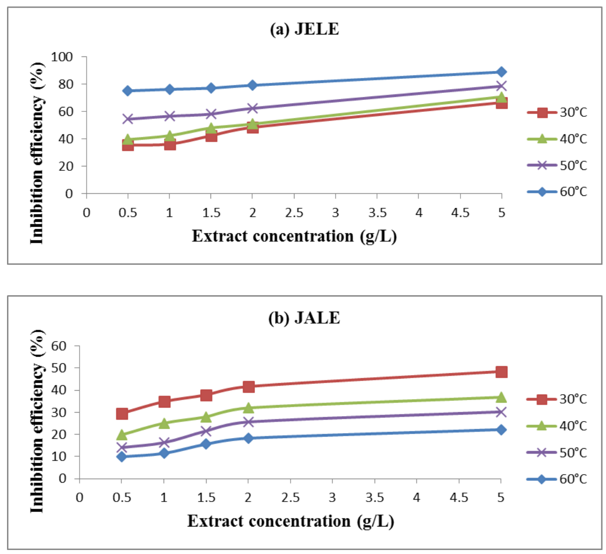



**Fig 1:** Effect of concentrations of (a) JELE and (b) JALE on inhibition efficiency of aluminium corrosion in 0.5 M HCl solution at 30°C – 60°C

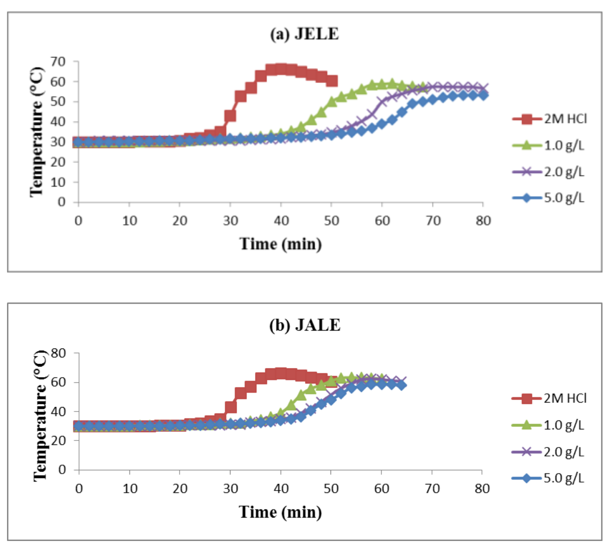



**Fig 2:** Variation of temperature (°C) with time (min) in 2 M HCl for aluminium corrosion solution in the absence and presence of (a) JELE and (b) JALE, respectively

**Table 1:** Thermometric data for aluminium corrosion in 2 M HCl solution in the absence and presence of (a) JELE and (b) JALE, respectively

| Extract concentration | Initial temperature $T_i$ (°C) | Maximum temperature $T_m$ (°C) | Time taken to reach maximum temp. t (min) | Reaction number RN (°C $min^{-1}$) | Inhibition efficiency (%) |
|---|---|---|---|---|---|
| 2 M HCl | 30.0 | 66.5 | 39 | 0.9359 | - |
| 1.0 g/L JELE | 30.0 | 59.0 | 62 | 0.4677 | 50.03 |
| 2.0 g/L JELE | 30.0 | 57.5 | 70 | 0.3929 | 58.02 |
| 5.0 g/L JELE | 30.0 | 53.3 | 78 | 0.3051 | 67.40 |
| 1.0 g/L JALE | 30.0 | 63.5 | 55 | 0.6091 | 34.92 |
| 2.0 g/L JALE | 30.0 | 62.4 | 58 | 0.5586 | 40.31 |
| 5.0 g/L JALE | 30.0 | 58.8 | 62 | 0.4645 | 50.37 |

### 3.2 Effect of temperature on inhibition efficiency

Effect of temperature on inhibition efficiency of JELE and JALE, respectively, was assessed by performing the weight loss tests at 30°C - 60°C. The data obtained are presented in Table 2. It is observed that the inhibition efficiency of JELE increased with increase in temperature. Conversely, an increase in temperature led to a decrease in the inhibition efficiency of JALE. JELE was more effective as an inhibitor at higher temperatures while JALE was more effective at lower temperatures. This observation could be attributed to the type of phytochemical components extracted by the solvents used for the extraction.

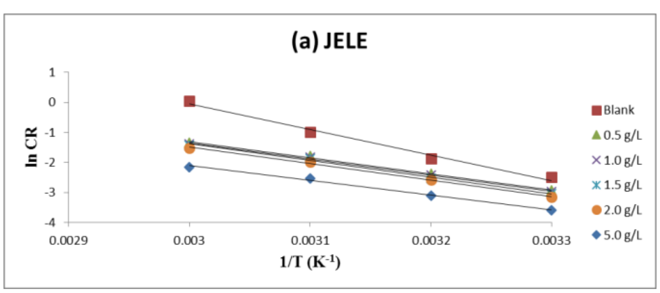
**Table 2:** Weight loss data for aluminium corrosion in 0.5 M HCl solution in the absence and presence of *(*a) JELE and (b) JALE, respectively, at 30°C - 60°C

| Extract conc | Corrosion rate (mg $cm^{-2}$ $hr^{-1}$) | | | | Inhibition efficiency (%) | | | |
|---|---|---|---|---|---|---|---|---|
| | 30°C | 40°C | 50°C | 60°C | 30°C | 40°C | 50°C | 60°C |
| 0.5 M HCl | 0.0825 | 0.1544 | 0.3681 | 1.0531 | - | - | - | - |
| 0.5 g/L JELE | 0.0531 | 0.0931 | 0.1675 | 0.2612 | 35.60 | 39.67 | 54.50 | 75.19 |
| 1.0 g/L JELE | 0.0506 | 0.0875 | 0.1593 | 0.2500 | 38.64 | 43.32 | 56.70 | 76.26 |
| 1.5 g/L JELE | 0.0475 | 0.0800 | 0.1537 | 0.2406 | 42.42 | 48.18 | 58.23 | 77.15 |
| 2.0 g/L JELE | 0.0425 | 0.0756 | 0.1387 | 0.2187 | 48.48 | 51.01 | 62.31 | 79.23 |
| 5.0 g/L JELE | 0.0275 | 0.0450 | 0.0787 | 0.1162 | 66.66 | 70.85 | 78.61 | 88.96 |
| 0.5 g/L JALE | 0.0581 | 0.1237 | 0.3162 | 0.9487 | 29.54 | 19.84 | 14.09 | 9.91 |
| 1.0 g/L JALE | 0.0537 | 0.1156 | 0.3081 | 0.9325 | 34.85 | 25.10 | 16.30 | 11.45 |
| 1.5 g/L JALE | 0.0500 | 0.1106 | 0.2887 | 0.8887 | 39.40 | 28.34 | 21.56 | 15.61 |
| 2.0 g/L JALE | 0.0481 | 0.1050 | 0.2737 | 0.8606 | 41.66 | 31.98 | 25.63 | 18.28 |
| 5.0 g/L JALE | 0.0425 | 0.0975 | 0.2569 | 0.8194 | 48.48 | 36.84 | 30.22 | 22.19 |

The activation energy ($E_a$) of the corrosion process in the absence and presence of extract was determined using the alternative formulation of the Arrhenius equation [18]:

$$\ln CR = \frac{-E_a}{RT} + \ln A \quad (5)$$

where A is the pre-exponential factor, CR is the corrosion rate, T is the temperature in Kelvin while R is the universal gas constant.



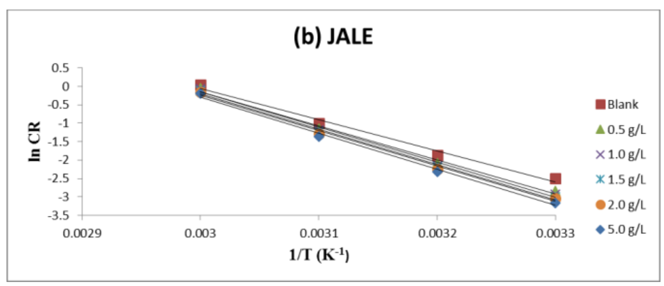




**Fig 3:** Arrhenius plot (ln CR vs. 1/T) for aluminium corrosion in 0.5 M HCl in the absence and presence of (a) JELE and (b) JALE

Figure 3 shows that the Arrhenius plot for aluminium corrosion in 0.5 M HCl in the absence and presence of JELE and JALE, respectively, are linear. The $E_a$ values were evaluated from the gradients of the graph and presented in Table 3. The $E_a$ values in the presence of JELE were lower than the $E_a$ of the blank (70.74 kJ $mol^{-1}$) while those of JALE were higher than $E_a$ of the blank. It has been reported by other workers [19, 20] that higher values of $E_a$ in the presence of inhibitor compared to that in its absence is due to physisorption while the reverse is attributed to chemisorption.

Consequently, the adsorption of JELE onto aluminium surface is proposed to occur by chemical adsorption (chemisorption) while that of JALE occurred by physical adsorption (physisorption).
The values of enthalpy of activation ($\Delta H^\circ_{ads}$) and entropy of activation ($\Delta S^\circ_{ads}$) were evaluated from the transition state equation [14]:

$$\ln\left(\frac{CR}{T}\right) = \left[\ln\left(\frac{R}{Nh}\right) + \frac{\Delta S^\circ_{ads}}{R}\right] - \frac{\Delta H^\circ_{ads}}{RT} \qquad (6)$$

where T is the temperature in Kelvin, R is the universal gas constant, CR is the corrosion rate, N is the Avogadro's number and h is Planck's constant.
Linear plots of ln (CR/T) vs. 1/T were obtained (Figure 4), from which the values of $\Delta H^\circ_{ads}$ and $\Delta S^\circ_{ads}$ were evaluated from the gradients ($-\Delta H^\circ_{ads}/R$) and intercepts [$\ln(R/Nh) + \Delta S^\circ_{ads}/R$], respectively, and presented in Table 3. The positive values of $\Delta H^\circ_{ads}$ both in the absence and presence of the extract reveal that the corrosion and corrosion inhibition of aluminium in HCl solution was endothermic in nature. A decrease in the disorderliness of the system and an ordered layer of extract on the metal surface could be deduced due to the negative values of $\Delta S^\circ_{ads}$ obtained [21].

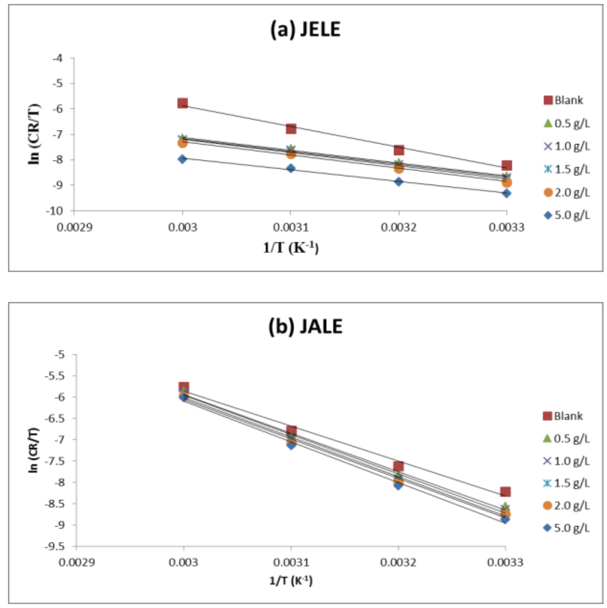



**Fig 4:** Transition state plot (ln CR/T vs. 1/T) for aluminium corrosion in 0.5 M HCl in the absence and presence of (a) JELE and (b) JALE

**Table 3:** Thermodynamic parameters for aluminium corrosion in 0.5 M HCl in the absence and presence of (a) JELE and (b) JALE, respectively

| Extract concentration | $E_a$ (kJ mol$^{-1}$) | $\Delta H^\circ_{ads}$ (kJ mol$^{-1}$) | $\Delta S^\circ_{ads}$ (JK$^{-1}$ mol$^{-1}$) |
|---|---|---|---|
| 0.5 M HCl | 70.74 | 68.13 | -41.88 |
| 0.5 g/L JELE | 44.62 | 42.00 | -130.67 |
| 1.0 g/L JELE | 44.83 | 42.21 | -130.44 |
| 1.5 g/L JELE | 45.90 | 43.28 | -127.56 |
| 2.0 g/L JELE | 45.91 | 43.29 | -128.28 |
| 5.0 g/L JELE | 40.59 | 37.98 | -149.49 |
| 0.5 g/L JALE | 77.74 | 74.85 | -22.43 |
| 1.0 g/L JALE | 79.35 | 76.73 | -16.89 |
| 1.5 g/L JALE | 79.75 | 77.14 | -16.09 |
| 2.0 g/L JALE | 79.91 | 77.29 | -15.98 |
| 5.0 g/L JALE | 81.86 | 79.25 | -10.46 |

### 3.3 Adsorption studies

The adsorption of JELE and JALE onto aluminium surface obeyed the modified Langmuir adsorption isotherm:

$$\frac{C}{\theta} = \frac{n}{K_{ads}} + nC \qquad (7)$$

where θ is the degree of surface coverage, C is the inhibitor concentration and $K_{ads}$ is the adsorption equilibrium constant.
Straight line graphs of C/θ vs. C were obtained (Figure 5), which confirmed that the adsorption of JELE and JALE, respectively, onto aluminium surface conformed to the Langmuir adsorption isotherm. The values of $K_{ads}$ were evaluated from the intercept of the graph while the values of n were obtained from the gradients. Both values are presented in Table 4.

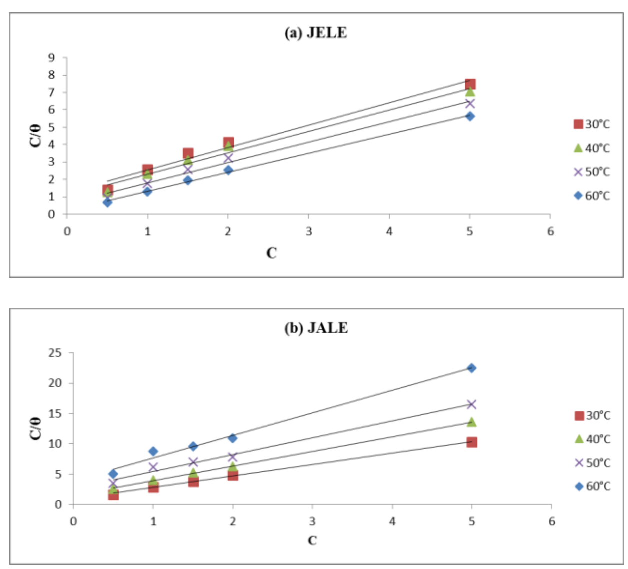



**Fig 5:** Langmuir isotherm plot for the adsorption of (a) JELE and (b) JALE onto aluminium in 0.5 M HCl solution at 30°C - 60°C

The standard free energy of adsorption ($\Delta G_{ads}$) was calculated using equation (8) [22];

$$\Delta G^{\circ}_{ads} = -RT \ln(55.5K_{ads}) \quad (8)$$

where T is the absolute temperature, R is the universal gas constant and 55.5 is the molar concentration of water in the solution. The values of $\Delta G^{\circ}_{ads}$ obtained for both JELE and JALE are negative (Table 4). Negative values of $\Delta G^{\circ}_{ads}$ indicate that the extracts adsorbed spontaneously onto aluminium surface.

**Table 4:** Langmuir isotherm parameters for the adsorption of (a) JELE and (b) JALE onto aluminium surface in 0.5 M HCl solution at 30°C - 60°C

| Extract | Temperature | $R^2$ | n | $1/K_{ads}$ (g $L^{-1}$) | $K_{ads}$ (g-1 L) | $\Delta G^{\circ}_{ads}$ (kJ $mol^{-1}$) |
|---|---|---|---|---|---|---|
| JELE | 30°C | 0.9766 | 1.28 | 1.265 | 0.791 | -9.526 |
| | 40°C | 0.9795 | 1.23 | 1.066 | 0.938 | -10.287 |
| | 50°C | 0.9886 | 1.17 | 0.621 | 1.610 | -12.066 |
| | 60°C | 0.9976 | 1.09 | 0.240 | 4.167 | -15.068 |
| JALE | 30°C | 0.9989 | 1.89 | 0.916 | 1.092 | -10.339 |
| | 40°C | 0.9990 | 2.42 | 1.476 | 0.678 | -9.439 |
| | 50°C | 0.9905 | 2.77 | 2.646 | 0.378 | -8.172 |
| | 60°C | 0.9890 | 3.72 | 3.934 | 0.254 | -7.328 |

## 4. Conclusion

Based on this work, the following conclusions could be made:

1. Both *Jatropha tanjorensis* ethanol leaf extract (JELE) and *Jatropha tanjorensis* acetone leaf extract (JALE) significantly inhibited the corrosion of aluminium in HCl solution, with JELE exhibiting a higher inhibition efficiency than JALE.
2. The adsorption of both extracts obeyed the modified Langmuir adsorption isotherm.
3. JELE was more effective as an inhibitor of aluminum corrosion in HCl solution at higher temperatures while JALE was more effective at lower temperatures.
4. The positive values of $\Delta H^{\circ}_{ads}$ and the negative values of $\Delta G^{\circ}_{ads}$ reveal that the adsorption of JELE and JALE, respectively, was both endothermic and spontaneous.
5. Chemisorption is proposed to account for the adsorption of JELE onto aluminium surface while JALE adsorbed via physisorption mechanism.

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