# Adsorption and Inhibition Effect of Eremomastax polysperma Leaf Extract on Aluminium Corrosion in Acidic Medium

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**Original Research Paper**

# Adsorption and Inhibition Effect of *Eremomastax polysperma* Leaf Extract on Aluminium Corrosion in Acidic Medium


**ABSTRACT**

The inhibition of aluminium corrosion in hydrochloric acid solution by *Eremomastax polysperma* leaf extract has been studied using weight loss and thermometric methods. The results obtained reveal that *Eremomastax polysperma* leaf extract significantly inhibited the corrosion of aluminium in HCl solution. The inhibition efficiency increased with increase in extract concentration but decreased with increase in temperature. Physical adsorption has been proposed for the adsorption of the leaf extract onto aluminium surface. The adsorption of *Eremomastax polysperma* leaf extract onto aluminium surface obeyed the modified Langmuir adsorption isotherm. Thermodynamic parameters reveal that the corrosion inhibition process in the presence of *Eremomastax polysperma* leaf extract was endothermic and spontaneous.


*Keywords: Corrosion inhibition, Eremomastax polysperma, aluminium, Langmuir isotherm, physisorption, weight loss, thermometric.*

## 1. INTRODUCTION

One of the consequences of corrosion of a metal is the weakening of its mechanical strength [1]. The breakdown of equipment due to the corrosion of its metallic components is a regular occurrence in industry. In the petroleum industry, for instance, the shutdown of refineries for turn-around maintenance due to corrosion of vital components is a common industrial practice. Efforts geared at reducing the corrosion of metals in contact with aggressive environments led to the discovery of some inorganic and synthesised organic compounds as corrosion inhibitors. Although many of these compounds inhibit the corrosion of metals excellently in various media, their usage is being discouraged in recent time because of their toxicity and non-environmentally friendly characteristics. The quest for efficient eco-friendly corrosion inhibitors as replacement for the traditional inhibitors is now focused on natural products. Some leaves extracts have been reported as good inhibitors of aluminium corrosion in acidic media [2 – 7]. The search for more efficient eco-friendly inhibitors of aluminium corrosion in acidic medium is ongoing since among the known inhibitors, there is none that offers a 100% inhibition efficiency on aluminium corrosion in acidic medium.

*Eremomastax polysperma* (Efik/Ibibio name: Edem ididuot) is a medicinal plant belonging to the family Acanthaceae. Its used in traditional medicine by the people of Nigeria has been documented [8 - 9]. The phytochemical analysis of *Eremomastax polysperma* leaf extract showed the presence of phenol, flavonoids, saponins, sterol tannins and alkaloids [10]. Previous studies [11] revealed that *Eremomastax polysperma* leaf extract is a good inhibitor of mild steel corrosion in acidic medium. The aim of this work was to assess the inhibitory effect of *Eremomastax polysperma* leaf extract on aluminium corrosion in acidic medium.

## 2. MATERIALS AND METHODS

### 2.1Test materials

Aluminium sheet used for this work was obtained from System Metal Industries Limited, Calabar, Nigeria. It was mechanically press - cut into 4 cm x 5 cm coupons. These coupons were polished to mirror finish using different grades of silicon carbide papers. The coupons were degreased in absolute ethanol, dried in acetone and stored in a moisture – free desiccator before use in corrosion studies.

### 2.2 Preparation of *Eremomastax polysperma* Leaf Extract

Fresh leaves of *Eremomastax polysperma* were collected from a farm in Nung Oku Ibesikpo, Akwa Ibom State, Nigeria. They were plucked, washed and air – dried at 30°C for seven days. They were then ground to powder. The dried ground sample of *Eremomastax polysperma* was macerated with 90% ethanol for seven days at room temperature in a large glass trough with cover. The mixture was then filtered. The filtrate was evaporated at 40°C in a water bath to constant weight, leaving a dark green extract in the beaker. Extract concentrations of 1.0 g/L, 2.0 g/L, 3.0 g/L, and 4.0 g/L respectively in 0.5 M HCl solution were used for the weight loss studies at 30°C, 40°C, 50°C and 60°C. The same extract concentrations were used in 2 M HCl solution for the thermometric tests.

### 2.3 Weight Loss Method

Previously weighed aluminium coupons were suspended with the aid of glass hooks and rods and immersed in 100 mL of 0.5 M HCl solution (blank) and in 0.5 M HCl solution containing 1.0 g/L – 4.0 g/L *Eremomastax polysperma* leaf extract (inhibitor) in open beakers. In each experiment, one aluminium coupon per beaker was used. The beakers were then placed in a thermostatic water bath maintained at 30°C, 40°C, 50°C, and 60°C respectively. The aluminium coupons were retrieved from the test solutions after four (4) hours and scrubbed with bristle brush under running water. They were dipped in acetone and air - dried before reweighing. The difference between the weight at a given time and the initial weight of the coupons was taken as the weight loss which was used to compute the corrosion rate given by the equation [2]:

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

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

The inhibition efficiency I(%) of *Eremomastax polysperma* leaf extract in 0.5 M HCl was calculated using the formula [12]:

$$I(\%) = \left(\frac{W_0 - W_1}{W_0}\right) \times 100 \qquad (2)$$

where $W_0$ and $W_1$ are the weight losses of aluminium coupons in the absence and presence of inhibitors, respectively, in the corrodent at the same temperature

### 2.4 Thermometric method

The reaction vessel and procedure for determining the corrosion behaviour by this method is as described in literature [13 - 14]. The corrodent concentration was kept at 2 M HCl. The volume of test solution used was 50 mL. The initial temperature in all experiments was kept at 30.0°C. The progress of corrosion reaction was monitored by determining the changes in temperature with time using a calibrated thermometer (0 - 100°C) to the nearest ± 0.1°C. This method enabled the computation of the reaction number (RN) defined as [14]:

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

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(%) was evaluated from percentage reduction in the reaction number via the equation:

$$I\ (\%) = \left(\frac{RN_0 - RN_1}{RN_0}\right) \times 100 \qquad (4)$$

where $RN_0$ is the reaction number in the absence of inhibitors (blank) and $RN_1$ is the reaction number in the presence of studied inhibitor.

## 3. RESULTS AND DISCUSSION

### 3.1 Effect of *Eremomastax polysperma* Leaf Extract Concentration on Inhibition Efficiency

Fig. 1 illustrates the effect of *Eremomastax polysperma* leaf extract on aluminium corrosion in 0.5 M HCl. The inhibition efficiency at a particular temperature increased with increase in extract concentration. The highest inhibition efficiency of 81.78% was obtained at 30°C at 4.0 g/L *Eremomastax polysperma* leaf extract concentration. Fig. 2 depicts the thermometric results for aluminium corrosion in 2 M HCl solution in the absence (blank) and in the presence of *Eremomastax polysperma* leaf extract. Inspection of Fig. 2 shows that as the concentration of the leaf extract increases, the time (t) required to reach the maximum temperature increases while the maximum temperature ($T_m$) decreases. The calculated values of reaction number (RN) and inhibition efficiency I(%) for aluminium corrosion in 2 M HCl containing *Eremomastax polysperma* leaf extract are contained in Table 1. Table 1 reveals that the inhibition efficiency by the thermometric method increased with increase in the leaf extract concentration. The inhibition efficiency by the thermometric method followed the same trend as that obtained by the weight loss measurements.

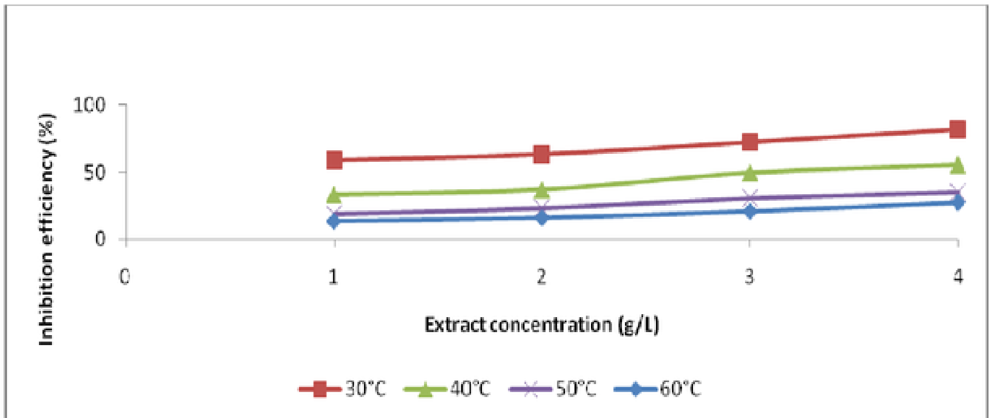


**Fig.1. Effect of *Eremomastax polysperma* leaf extract concentration on the inhibition efficiency of aluminium corrosion in 0.5 M HCl solution at different temperatures**

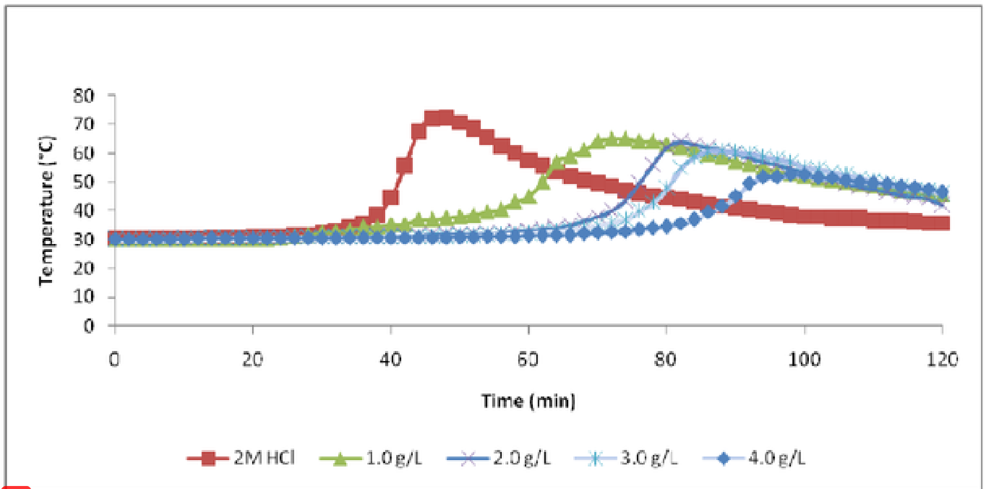


**Fig. 2. Temperature – time curves for aluminium corrosion in 2 M HCl obtained in absence and presence of *Eremomastax polysperma* leaf extract**

**Table 1. Effect of *Eremomastax polysperma* leaf extract on inhibition efficiency of aluminium corrosion in 2 M HCl solution (Thermometric measurements)**

| Extract concentration C (g $L^{-1}$) | 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 I (%) |
|---|---|---|---|---|---|
| Blank | 30.0 | 72.5 | 48 | 0.8854 | - |
| 1.0 | 30.0 | 65.0 | 72 | 0.4861 | 45.09 |
| 2.0 | 30.0 | 64.2 | 82 | 0.4171 | 52.89 |
| 3.0 | 30.0 | 61.0 | 88 | 0.3523 | 60.21 |
| 4.0 | 30.0 | 52.7 | 98 | 0.2316 | 73.84 |

### 3.3 Effect of temperature on inhibition efficiency

The effect of temperature on the inhibition effect of *Eremomastax polysperma* leaf extract on aluminium corrosion in 0.5 M HCl solution is shown in Table 2. It is observed that an increase in temperature led to a decrease in the inhibition efficiency of the extract. A decrease in inhibition efficiency with increase in temperature indicates that *Eremomastax polysperma* leaf extract was more effective in inhibiting aluminium corrosion at lower temperatures that at higher temperatures. Furthermore, a decrease in inhibition efficiency with increase in temperature indicates a physical adsorption (physisorption) mechanism.

The values of the activation energy ($E_a$) for aluminium corrosion in 0.5 M HCl solution in the presence and absence of *Eremomastax polysperma* leaf extract, respectively, were obtained using the alternative formulation of Arrhenius equation [15]:

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

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

**Table 2. Calculated values of weight loss, corrosion rate and inhibition efficiency for aluminium corrosion in 0.5 M HCl solution containing *Eremomastax polysperma* leaf extract at 30°C – 60°C**

| Extract Conc. | Weight Loss (g) | | | | 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 | 30°C | 40°C | 50°C | 60°C |
| Blank | 0.0225 | 0.0442 | 0.0946 | 0.2428 | 0.1406 | 0.2763 | 0.5913 | 1.5175 | - | - | - | - |
| 1.0 g/L | 0.0092 | 0.0294 | 0.0766 | 0.2103 | 0.0575 | 0.1838 | 0.4788 | 1.3144 | 59.11 | 33.48 | 19.03 | 13.39 |
| 2.0 g/L | 0.0082 | 0.0277 | 0.0725 | 0.2043 | 0.0513 | 0.1731 | 0.4531 | 1.2769 | 63.56 | 37.33 | 23.36 | 15.86 |
| 3.0 g/L | 0.0062 | 0.0222 | 0.0657 | 0.1922 | 0.0388 | 0.1388 | 0.4106 | 1.2013 | 72.44 | 49.77 | 30.55 | 20.84 |
| 4.0 g/L | 0.0041 | 0.0196 | 0.0615 | 0.1760 | 0.0256 | 0.1225 | 0.3844 | 1.1000 | 81.78 | 55.66 | 34.99 | 27.51 |

The activation energies ($E_a$) of aluminium corrosion in 0.5 M HCl solution, with and without inhibitors, were obtained from the gradients of ln CR vs. 1/T plots (Figure 3) and the results presented in Table 3. Table 3 shows that the $E_a$ values in the presence of the leaf extract were higher than the $E_a$ value of the blank (65.65 kJ $mol^{-1}$). The increase in the $E_a$ values in the presence of the extract indicates physical adsorption while the reverse signifies chemical adsorption [16]. Consequently, the adsorption of *Eremomastax polysperma* leaf extract onto aluminium surface occurred by a physical adsorption mode.

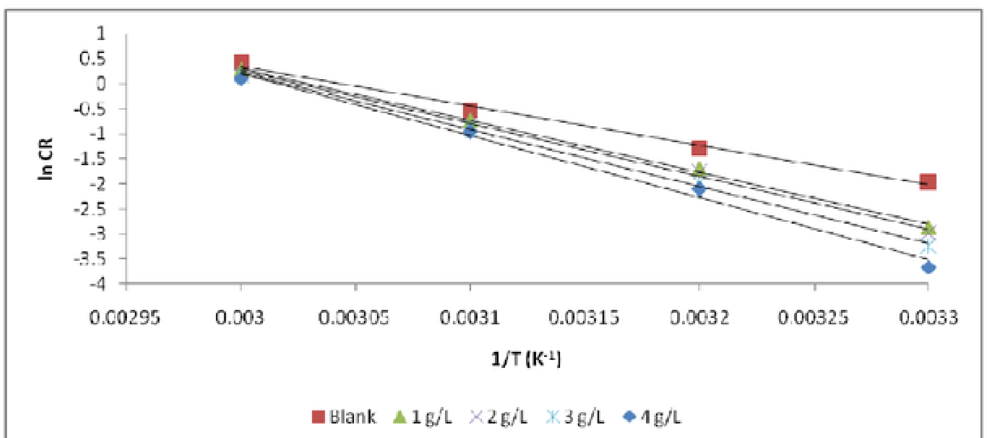


**Fig. 3. Plot of ln CR vs. 1/T (Arrhenius plot) for aluminium corrosion in 0.5 M HCl in the absence and presence of *Eremomastax polysperma* leaf extract**

The values of enthalpy of activation ($\Delta H^{\circ}_{ads}$) and entropy of activation ($\Delta S^{\circ}_{ads}$) were obtained from an alternative formulation of the transition state equation [11]:

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

where CR is the corrosion rate, $E_a$ is the activation energy, T is the absolute temperature, A is the Arrhenius pre-exponential factor, R is the universal gas constant, h is the Planck's constant, and N is the Avogadro's number. Figure 4 shows linear plots of ln (CR/T) vs. 1/T with gradients of ($-\Delta H^{\circ}_{ads}$/R) and intercepts of [ln (R/Nh) + $\Delta S^{\circ}_{ads}$/R] from which the values of $\Delta H^{\circ}_{ads}$ and $\Delta S^{\circ}_{ads}$ were calculated and listed in Table 3. The positive values of $\Delta H^{\circ}_{ads}$ both in the blank and in the presence of extracts indicate the endothermic nature of the aluminium corrosion process. The positive values of $\Delta S^{\circ}_{ads}$ in the presence of the leaf extract indicate an increase in the disorderliness of the extract on aluminium surface.

**Table 3. Calculated values of thermodynamic parameters for aluminium corrosion in 0.5 M HCl solution in the absence and presence of *Eremomastax polysperma* leaf extract**

| Extract concentration | $E_a$ (kJ $mol^{-1}$) | $\Delta H^{\circ}_{ads}$ (kJ $mol^{-1}$) | $\Delta S^{\circ}_{ads}$ (J $K^{-1}$ $mol^{-1}$) |
|---|---|---|---|
| 0.5 M HCl (Blank) | 65.65 | 63.04 | - 53.84 |
| 1.0 g/L | 86.02 | 83.40 | 6.84 |
| 2.0 g/L | 88.20 | 85.58 | 13.20 |
| 3.0 g/L | 94.67 | 92.05 | 32.21 |
| 4.0 g/L | 103.28 | 100.66 | 57.87 |

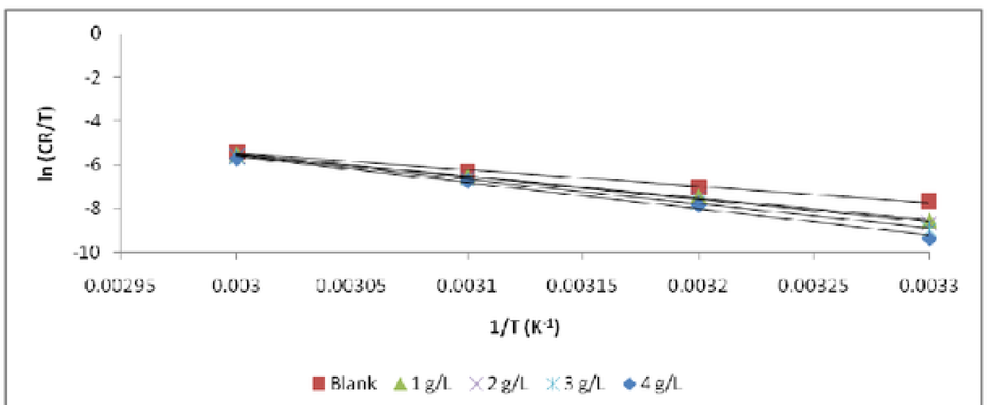


**Fig. 4. Plot of ln (CR/T) vs. 1/T (Transition state plot) for aluminium corrosion in 0.5 M HCl solution in the absence and presence of *Eremomastax polysperma* leaf extract**

### 3.4 Adsorption Isotherm

The adsorption of *Eremomastax polysperma* leaf extract on aluminium surface conformed to the modified Langmuir adsorption isotherm equation [ 17]:

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

where C is the inhibitor concentration, θ is the degree of surface coverage while $K_{ads}$ is the equilibrium constant of the adsorption process. Fig. 5 reveals linear plots of C/θ. vs. C, with gradients of 'n' and intercepts of $1/K_{ads}$. The linear plots have 'n' values (gradients) greater than 1, indicating that the extract occupied more than one adsorption site on the metal surface [15]. Furthermore, values of 'n' greater than 1 implies multi-layer coverage of the metal's surface by the extract. The values of $K_{ads}$ were evaluated from the intercept of the graph and presented in Table 4. The decrease in the values of $K_{ads}$ with increase in temperature indicates that *Eremomastax polysperma* leaf extract became loosely adsorbed onto aluminium surface as the temperature was increased. This assertion is supported by an increase in the entropy of the system as temperature increased (Table 3).

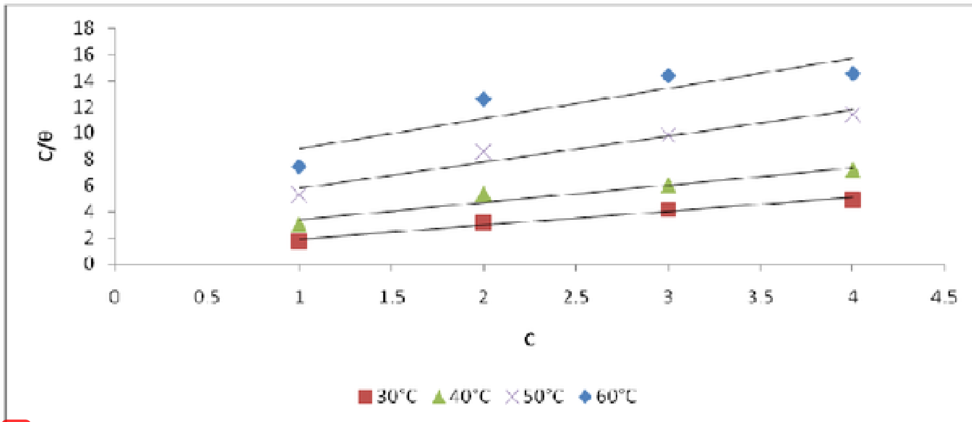


**Fig. 5. Plot of C/θ vs. C (Langmuir isotherm) for aluminium corrosion in 0.5 M HCl solution containing *Eremomastax polysperma* leaf extract**

$K_{ads}$ is related to the standard free energy of adsorption ($\Delta G^\circ_{ads}$) by the formula [18]:

$$K_{ads} = \frac{1}{55.5}\exp\left(\frac{-\Delta G^\circ_{ads}}{RT}\right) \qquad (8)$$

where 55.5 is the molar concentration of water in the solution, R is the universal gas constant while T is the absolute temperature. The thermodynamic parameters for the adsorption of *Eremomastax polysperma* leaf extract on aluminium surface are shown in Table 4. The negative values of $\Delta G^\circ_{ads}$ reveal that the aluminium corrosion inhibition process by *Eremomastax polysperma* leaf extract occurred spontaneously. Generally, values of $\Delta G^\circ_{ads}$ less negative than -20 kJ $mol^{-1}$ indicate physical adsorption while those more negative than -40 kJ $mol^{-1}$ indicate chemical adsorption [19 - 20]. Consequently, the values of $\Delta G^\circ_{ads}$ obtained in this work being less negative than -20 kJ $mol^{-1}$ coupled with a decrease in the inhibition efficiency with increase in temperature indicates a physical adsorption process.

**Table 4. Some parameters of the linear regression of Langmuir adsorption isotherm for aluminium corrosion in 0.5 M HCl solution containing *Eremomastax polysperma* leaf extract**

| Temperature | $R^2$ | n | $1/K_{ads}$ ($g\ L^{-1}$) | $K_{ads}$ ($g^{-1} L$) | $\Delta G^{\circ}_{ads}$ ($kJ\ mol^{-1}$) |
|---|---|---|---|---|---|
| 303K | 0.9779 | 1.06 | 0.82 | 1.22 | - 10.62 |
| 313K | 0.9355 | 1.33 | 2.07 | 0.48 | - 8.54 |
| 323K | 0.9511 | 1.98 | 3.82 | 0.26 | - 7.17 |
| 333K | 0.8054 | 2.30 | 6.50 | 0.15 | - 5.87 |

## 4. CONCLUSION

This work reveals that *Eremomastax polysperma* leaf extract is a good inhibitor of aluminium corrosion in HCl solution. The inhibition efficiency was found to increase with increase in extract concentration but decreased with increase in temperature. Based on a decrease in the inhibition efficiency with increase in temperature, higher $E_a$ values in the extract compared to the blank and $\Delta G^{\circ}_{ads}$ values being less negative than – 20 kJ $mol^{-1}$, physical adsorption (physisorption) mechanism has been proposed for the adsorption of *Eremomastax polysperma* leaf extract on aluminium surface. The negative values of $\Delta G^{\circ}_{ads}$ reflect the spontaneity of the corrosion inhibition process while the positive values of $\Delta H^{\circ}_{ads}$ revealed the endothermic nature of the adsorption process. The adsorption of *Eremomastax polysperma* leaf extract onto aluminium surface conformed to the modified Langmuir adsorption isotherm.

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