

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.

35 2. MATERIALS AND METHODS

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37 2.1 Test materials

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

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44 2.2 Preparation of *Eremomastax polysperma* Leaf Extract

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

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54 2.3 Weight Loss Method

55 Previously weighed aluminium coupons were suspended with the aid of glass hooks and rods and
 56 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
 57 *Eremomastax polysperma* leaf extract (inhibitor) in open beakers. In each experiment, one aluminium
 58 coupon per beaker was used. The beakers were then placed in a thermostatic water bath maintained at
 59 30°C, 40°C, 50°C, and 60°C, respectively. The aluminium coupons were retrieved from the test solutions
 60 after four (4) hours and scrubbed with bristle brush under running water. They were dipped in acetone
 61 and air - dried before reweighing. The difference between the weight at a given time and the initial weight
 62 of the coupons was taken as the weight loss which was used to compute the corrosion rate given by the
 63 equation [2]:

64

$$65 \quad CR \text{ (mg cm}^{-2}\text{hr}^{-1}\text{)} = \left(\frac{W}{At} \right) \quad (1)$$

66

66 where W is the weight loss (mg), A is the total surface area (cm²) while t is the exposure time (hours).

67

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

70

$$71 \quad I(\%) = \left(\frac{W_0 - W_1}{W_0} \right) \times 100 \quad (2)$$

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72 where W₀ and W₁ are the weight losses of aluminium coupons in the absence and presence of inhibitors,
 73 respectively, in the corrodent at the same temperature

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74 2.4 Thermometric method

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

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

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83 where T_m and T_i are the maximum and initial temperatures, respectively, while 't' is the time (min) taken to
84 reach the maximum temperature. The inhibition efficiency, I(%) was evaluated from percentage reduction
85 in the reaction number via the equation:
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$$I (\%) = \left(\frac{\text{RN}_0 - \text{RN}_1}{\text{RN}_0} \right) \times 100 \quad (4)$$

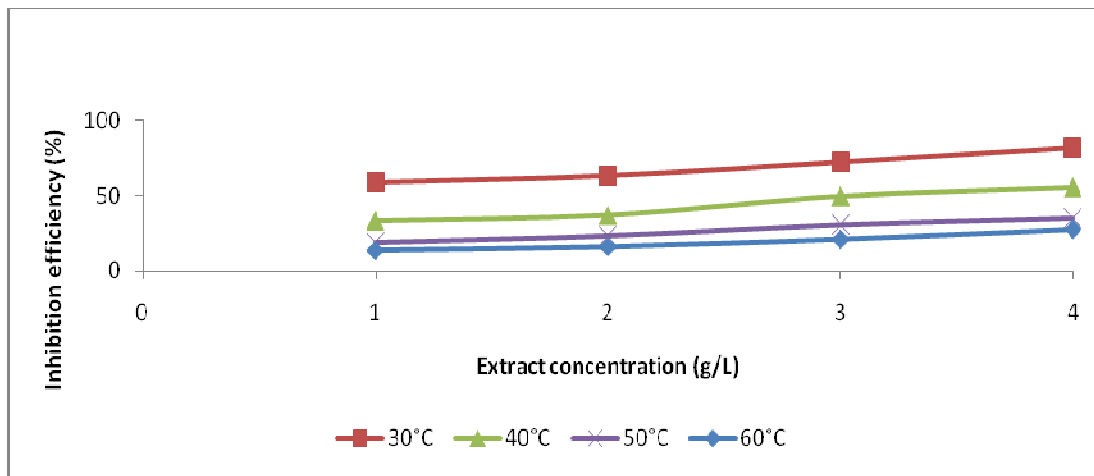
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88 where RN_0 is the reaction number in the absence of inhibitors (blank) and RN_1 is the reaction number in
89 the presence of studied inhibitor.

90 **3. RESULTS AND DISCUSSION**

91 **3.1 Effect of *Eremomastax polysperma* Leaf Extract Concentration on Inhibition**
 92 **Efficiency**

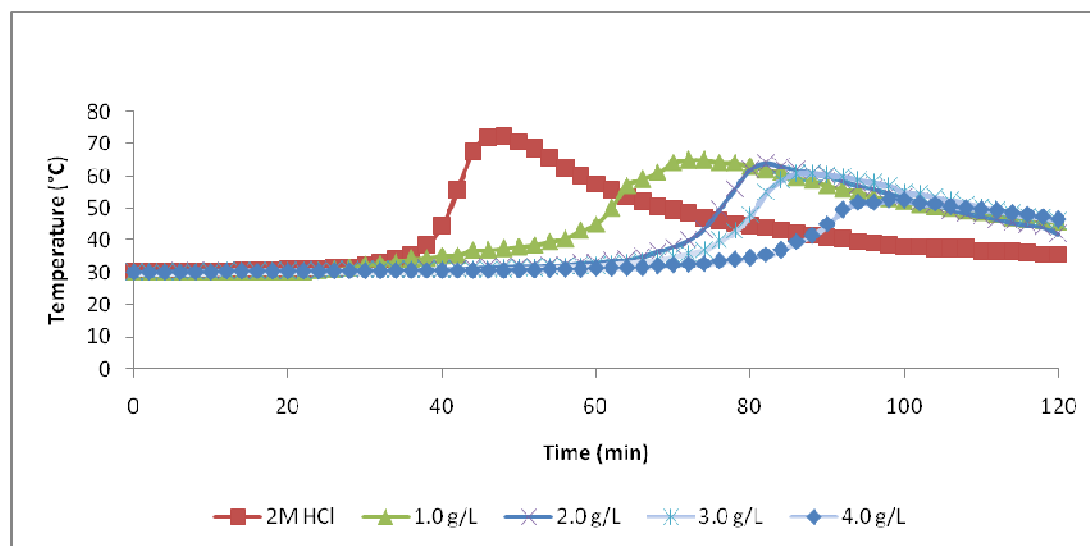
93 Fig. 1 illustrates the effect of *Eremomastax polysperma* leaf extract on aluminium corrosion in 0.5 M HCl.
 94 The inhibition efficiency at a particular temperature increased with increase in extract concentration. The
 95 highest inhibition efficiency of 81.78% was obtained at 30°C at 4.0 g/L *Eremomastax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

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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



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

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

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130 **3.3 Effect of temperature on inhibition efficiency**

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

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

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

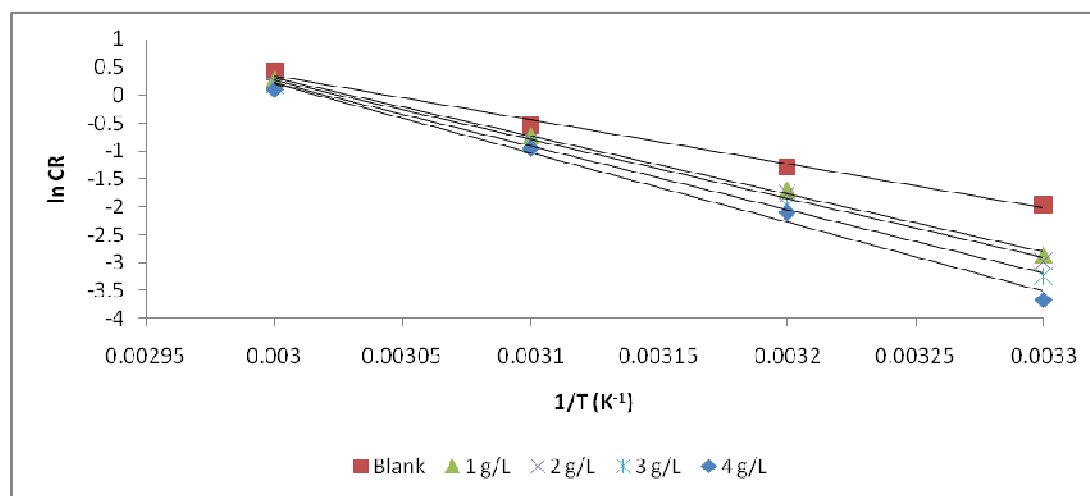
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142 where CR is the corrosion rate, R is the universal gas constant, T is the absolute temperature while A is
143 the pre-exponential factor.

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

Extract Conc.	Weight Loss				Corrosion Rate				Inhibition Efficiency			
	(g)				(mg cm ⁻² hr ⁻¹)				(%)			
	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

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



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

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

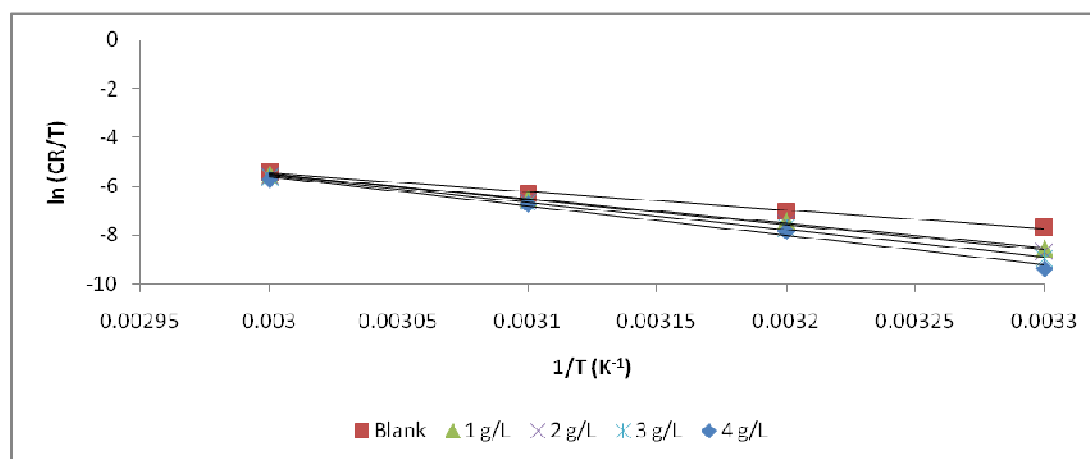
$$\ln\left(\frac{CR}{T}\right) = \left[\ln\left(\frac{R}{Nh}\right) + \frac{\Delta S^\circ_{\text{ads}}}{R} \right] - \frac{\Delta H^\circ_{\text{ads}}}{RT} \quad (6)$$

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

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

Extract concentration	E_a (kJ mol ⁻¹)	$\Delta H^\circ_{\text{ads}}$ (kJ mol ⁻¹)	$\Delta S^\circ_{\text{ads}}$ (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

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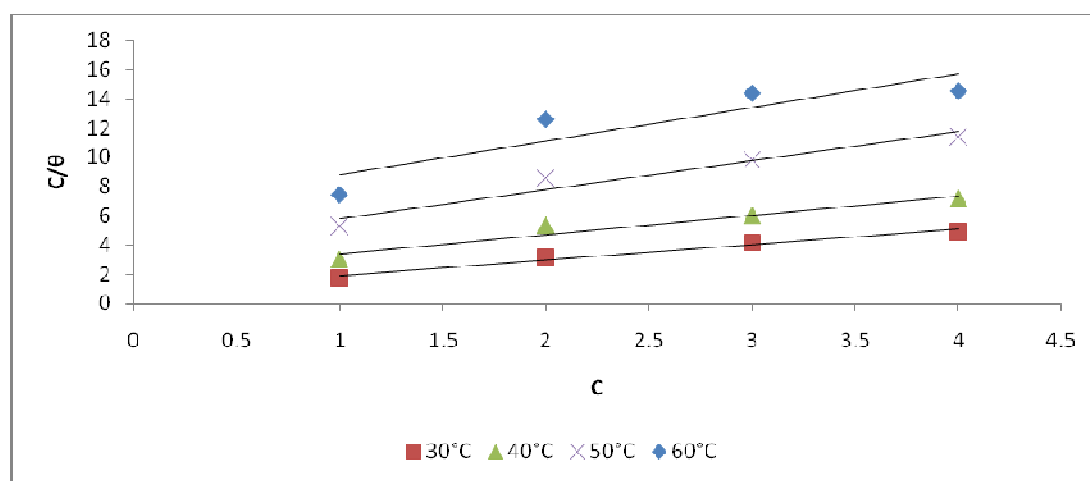
170 **Fig. 4. Plot of $\ln(CR/T)$ vs. $1/T$ (Transition state plot) for aluminium corrosion in 0.5 M HCl solution**
 171 **in the absence and presence of *Eremomastax polysperma* leaf extract**

172 **3.4 Adsorption Isotherm**

173 The adsorption of *Eremomastax polysperma* leaf extract on aluminium surface conformed to the modified
 174 Langmuir adsorption isotherm equation [17]:
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$$\frac{C}{\theta} = \frac{n}{K_{ads}} + nC \tag{7}$$

176 where C is the inhibitor concentration, θ is the degree of surface coverage while K_{ads} is the equilibrium
 177 constant of the adsorption process. Fig. 5 reveals linear plots of C/θ . vs. C, with gradients of 'n' and
 178 intercepts of $1/K_{ads}$. The linear plots have 'n' values (gradients) greater than 1, indicating that the extract
 179 occupied more than one adsorption site on the metal surface [15]. Furthermore, values of 'n' greater than
 180 1 implies multi-layer coverage of the metal's surface by the extract. The values of K_{ads} were evaluated
 181 from the intercept of the graph and presented in Table 4. The decrease in the values of K_{ads} with increase
 182 in temperature indicates that *Eremomastax polysperma* leaf extract became loosely adsorbed onto
 183 aluminium surface as the temperature was increased. This assertion is supported by an increase in the
 184 entropy of the system as temperature increased (Table 3).
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 188 **Fig. 5. Plot of C/θ vs. C (Langmuir isotherm) for aluminium corrosion in 0.5 M HCl solution**
 189 **containing *Eremomastax polysperma* leaf extract**
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192 K_{ads} is related to the standard free energy of adsorption (ΔG°_{ads}) by the formula
 193 [18]:

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

194 where 55.5 is the molar concentration of water in the solution, R is the universal gas constant while T is
 195 the absolute temperature. The thermodynamic parameters for the adsorption of *Eremomastax*
 196 *polysperma* leaf extract on aluminium surface are shown in Table 4. The negative values of ΔG°_{ads} reveal
 197 that the aluminium corrosion inhibition process by *Eremomastax polysperma* leaf extract occurred
 198 spontaneously. Generally, values of ΔG°_{ads} less negative than -20 kJ mol^{-1} indicate physical adsorption
 199 while those more negative than -40 kJ mol^{-1} indicate chemical adsorption [19 - 20]. Consequently, the
 200 values of ΔG°_{ads} obtained in this work being less negative than -20 kJ mol^{-1} coupled with a decrease in
 201 the inhibition efficiency with increase in temperature indicates a physical adsorption process.
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205 **Table 4. Some parameters of the linear regression of Langmuir adsorption isotherm for aluminium**
 206 **corrosion in 0.5 M HCl solution containing *Eremomastax polysperma* leaf extract**
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Temperature	R ²	n	1/K _{ads} (g L ⁻¹)	K _{ads} (g ⁻¹ L)	ΔG ^o _{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

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4. CONCLUSION

211 This work reveals that *Eremomastax polysperma* leaf extract is a good inhibitor of aluminium corrosion in
212 HCl solution. The inhibition efficiency was found to increase with increase in extract concentration but
213 decreased with increase in temperature. Based on a decrease in the inhibition efficiency with increase in
214 temperature, higher E_a values in the extract compared to the blank and ΔG^o_{ads} values being less negative
215 than - 20 kJ mol⁻¹, physical adsorption (physisorption) mechanism has been proposed for the adsorption
216 of *Eremomastax polysperma* leaf extract on aluminium surface. The negative values of ΔG^o_{ads} reflect the
217 spontaneity of the corrosion inhibition process while the positive values of ΔH^o_{ads} revealed the
218 endothermic nature of the adsorption process. The adsorption of *Eremomastax polysperma* leaf extract
219 onto aluminium surface conformed to the modified Langmuir adsorption isotherm.

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