

Original Research Article

Mild Steel Corrosion Inhibition by *Eremomastax polysperma* Leaf Extract in Acidic Medium

ABSTRACT

The inhibition of mild steel corrosion in 1 M H₂SO₄ solution by *Eremomastax polysperma* leaf extract has been studied using weight loss and hydrogen evolution techniques. The results obtained show that *Eremomastax polysperma* leaf extract is a good inhibitor of mild steel corrosion in H₂SO₄ 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 on mild steel surface. Thermodynamic parameters reveal that the corrosion inhibition process in the presence of the extract was endothermic and occurred spontaneously. The adsorption of *Eremomastax polysperma* leaf extract on mild steel surface best fitted the Langmuir adsorption isotherm.

Keywords: [Corrosion inhibition, *Eremomastax polysperma*, Mild steel, Physisorption, Weight loss, Hydrogen evolution, Langmuir isotherm]

1. INTRODUCTION

The present day high operational cost of extracting metals from their ores has made it imperative to protect existing metallic structures from corrosion. Corrosion weakens the mechanical strength of metals leading to equipment breakdown or failure [1]. The use of corrosion inhibitors for the protection of metals in aggressive media is a standard practice globally. Compounds containing nitrogen, sulphur, oxygen and/or phosphorous have been reported as good inhibitors of mild steel corrosion in acidic media [2 - 6]. The use of traditional inhibitors (i.e. synthesised organic and inorganic compounds) is now limited due to environmental safety concerns, as some of them are toxic and environmentally - unfriendly. The desire for biodegradable, cheap, renewable and environmentally - friendly corrosion inhibitors has led to the extraction of inhibitors from natural products, especially of plant origin. Plant extracts contain phytochemicals such as saponins, alkaloids, terpenes, tannins, etc, which are rich sources of organic nitrogen, sulphur and oxygen. Many workers have reported high inhibition efficiencies of mild steel corrosion by leaves extracts in acidic medium [1, 7 - 10]. Unfortunately, some of the reported plants are known to grow only in certain regions of the world. Importation of extracts of such plants for use in other regions of the world is not only expensive but time consuming. Hence, the need for the local sourcing of efficient eco-friendly corrosion inhibitors cannot be over-emphasised.

29 *Eremomastax polysperma* is a medicinal plant in the family Acanthaceae. It is locally called Edem
30 iduduot by the Efik and Ibibio speaking people of Nigeria. The traditional medicinal uses of the plant in
31 eastern Nigeria have been documented [11 – 13]. The phytochemical screening of *Eremomastax*
32 *polysperma* leaf extract showed the presence of tannins, phenol, flavonoid, alkaloid, saponin and
33 sterol [14].

34 The aim of this work was to evaluate the inhibitory effect of *Eremomastax polysperma* leaf extract on
35 mild steel corrosion in H₂SO₄ solution. H₂SO₄ solution is widely used industrially in the pickling of iron
36 and steel because it is less fuming than other mineral acids. Additionally, the choice of 30°C – 60°C for
37 this work was to simulate the temperature for the pickling process.

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39 **2. MATERIALS AND METHODS**

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41 **2.1 Test Materials**

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43 Mild steel sheet used for this work was obtained in Calabar, Nigeria. It had the following chemical
44 composition (weight %): C (0.12), Mn (0.85), S (0.06), P (0.05), Si (0.09) and Fe (98.83). The sheet
45 was mechanically press - cut into 4 cm x 5 cm coupons, and polished to mirror finish using different
46 grades of silicon carbide papers. The coupons were degreased in absolute ethanol, dipped in acetone
47 before air-drying. They were then stored in a moisture – free desiccator before use in corrosion
48 studies.

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50 **2.2 Preparation of *Eremomastax polysperma* Leaf Extract**

51 Fresh leaves of *Eremomastax polysperma* were collected from a farm in Nung Oku Ibesikpo, Akwa
52 Ibom State, Nigeria and authenticated by a plant taxonomist in the Department of Botany and
53 Ecological Studies, University of Uyo, Nigeria. They were washed and air – dried at 30°C for seven
54 days. They were then ground to powder. The dried ground sample of *Eremomastax polysperma* leaf
55 was macerated with 90% ethanol for seven days at room temperature in a glass trough with cover.
56 The mixture was then filtered. The filtrate was evaporated at 40°C in a water bath to constant weight,
57 leaving a dark green extract (paste) in the beaker.

58 **2.3 Weight Loss Method**

59 Previously weighed mild steel coupons were suspended with the aid of glass hooks and rods and
60 immersed in 100 ml of 1 M H₂SO₄ solution (blank) and in 1 M H₂SO₄ solution containing 1.0 g/L – 4.0

61 g/L *Eremomastax polysperma* leaf extract (inhibitor) in open beakers. In each experiment, one mild
 62 steel coupon per beaker was used. The beakers were then placed in a thermostatic water bath
 63 maintained at 30°C, 40°C, 50°C, and 60°C, respectively. The mild steel coupons were retrieved from
 64 the test solutions after four (4) hours and scrubbed with bristle brush under running water. They were
 65 dipped in acetone and air - dried before reweighing. The weight loss was recorded and used to
 66 compute the inhibition efficiency, I(%) [15]:

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

67
 68

69 where W_0 and W_1 are the weight losses of the mild steel coupons in the absence and presence of
 70 extract, respectively, in 1 M H_2SO_4 at the same temperature.

71 The corrosion rate (CR) was calculated using the formula [16]:

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

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

74 **2.4 Hydrogen Evolution Method**

75 The reaction vessel and procedure for measuring the corrosion process by this method are as
 76 described in literature [17]. A 100 cm^3 of 1 M H_2SO_4 solution was introduced into the reaction vessel
 77 connected to a burette through a delivery tube. The initial volume of air in the burette was recorded.
 78 Two mild steel coupons weighing 8.0 g were dropped into the 1 M H_2SO_4 solution and the reaction
 79 vessel quickly closed to prevent any escape of hydrogen gas. The volume of H_2 gas evolved from the
 80 corrosion reaction was monitored by the depression (in cm^3) in the paraffin oil level. The depression in
 81 paraffin oil level was monitored every 60 seconds for 100 minutes. The same experiment was
 82 repeated in the presence of 1.0 g/L – 4.0 g/L *Eremomastax polysperma* leaf extract in 1 M H_2SO_4
 83 solution.

84 The inhibition efficiency I(%) was calculated using the equation [18]:

$$I(\%) = \left(\frac{V_0 - V_1}{V_0} \right) \times 100 \quad (3)$$

where V_0 and V_1 are the volumes of H_2 gas evolved in the absence and presence of inhibitor, respectively, at a specified time.

3. RESULTS AND DISCUSSION

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

Fig. 1 shows that at a particular temperature the inhibition efficiency increased with increase in the concentration of *Eremomastax polysperma* leaf extract. The maximum inhibition efficiency of the leaf extract was 90.42% at extract concentration of 4.0 g/L at 30°C. An increase in inhibition efficiency with increase in inhibitor concentration indicates a strong interaction between the mild steel surface and the inhibitor [19].

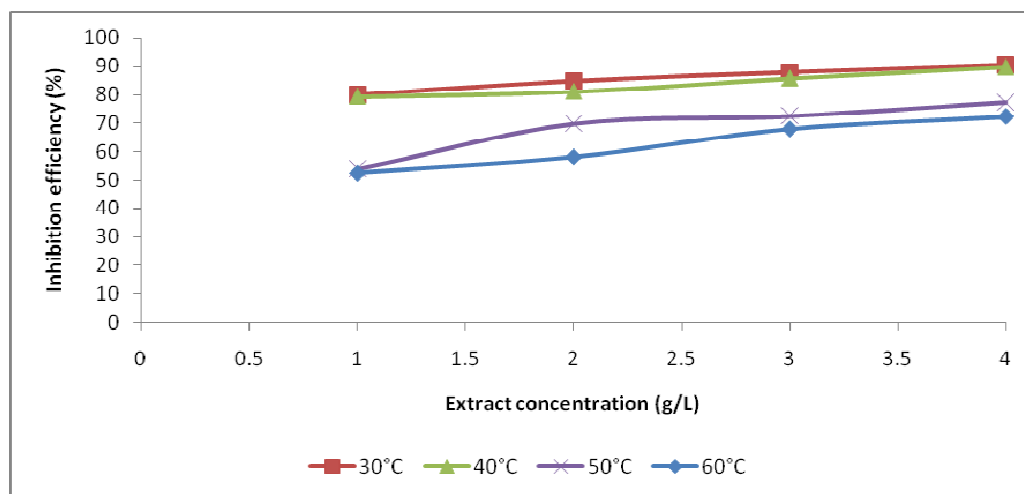


Fig.1. Effect of *Eremomastax polysperma* leaf extract concentration on the inhibition efficiency of mild steel corrosion in 1 M H_2SO_4 at different temperatures

3.2 Hydrogen Evolution Measurements

Fig. 2 illustrates the effect of *Eremomastax polysperma* leaf extract on the volume of H_2 gas evolved in the corrosion of mild steel in 1 M H_2SO_4 . It is observed that, at a given time, as the leaf extract concentration increases, the volume of H_2 gas evolved decreases. This indicates that the extract

inhibits the corrosion process by adsorbing on the metal surface, forming protective thin films which reduce/stop the electron transfer process on the metal surface [20]. Table 1 contains the calculated values of inhibition efficiency for the inhibition process containing *Eremomastax polysperma* leaf extract. Table 1 reveals that the inhibition efficiency increased with increase in the concentration of *Eremomastax polysperma* leaf extract. The inhibition efficiencies obtained by both the weight loss and hydrogen evolution methods followed a similar trend.

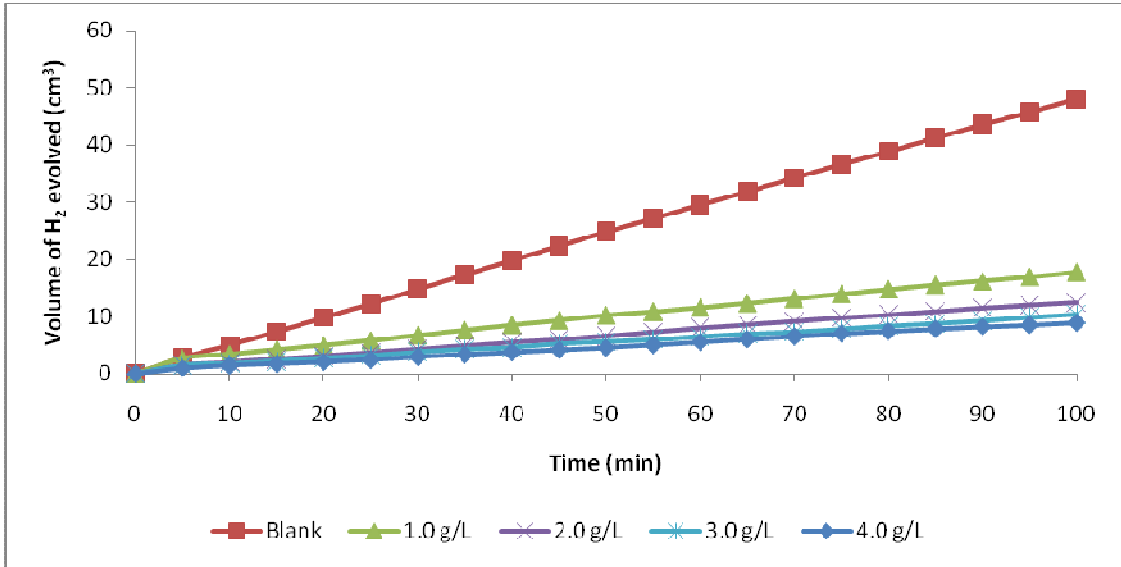


Fig. 2. Variation of volume of H_2 gas evolved (cm^3) with time (min) for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of *Eremomastax polysperma* leaf extract at 30°C

Table 1. Effect of *Eremomastax polysperma* leaf extract concentration on inhibition efficiency of mild steel in 1 M H_2SO_4 solution at 30°C (Hydrogen evolution measurements)

Extract concentration (g/L)	Volume of H ₂ evolved (cm ³)	Time taken (min)	Inhibition efficiency (%)
Blank	48.00	100	-
1.0	17.70	100	63.13
2.0	12.50	100	73.95
3.0	10.20	100	78.75
4.0	9.00	100	81.25

3.3 Effect of Temperature on Inhibition Efficiency

Table 2 reveals an increase in the corrosion rate of mild steel in H₂SO₄ solution with increase in temperature. This shows that the reactants acquired more energy and overcame the activation energy barrier more easily with an increase in temperature than at lower temperatures. Additionally, Table 2 shows that the inhibition efficiency decreased with increase in temperature at the extract concentrations studied (Table 2). This indicates weakening of adsorption bonds between mild steel surface and inhibitor as well as a physical adsorption process [21].

The values of the activation energy (E_a) for mild steel corrosion in 1 M H₂SO₄ solution in the presence and absence of *Eremomastax polysperma* leaf extract, respectively, were obtained using the alternative formulation of Arrhenius equation [20]:

$$\ln CR = \frac{-E_a}{RT} + \ln A \quad (3)$$

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

139 The activation energies (E_a) of mild steel corrosion in 1M H_2SO_4 solution, with and without inhibitors,
 140 were obtained from the gradients of $\ln CR$ vs. $1/T$ plots (Fig. 3) and the results are presented in Table
 141 3. Table 3 shows that the E_a values in the presence of the leaf extract were higher than the E_a value
 142 of the blank ($42.8578 \text{ kJ mol}^{-1}$). The increase in the E_a values in the presence of the extract indicates
 143 physical adsorption while the reverse signifies chemical adsorption [22 - 23].

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146 **Table 2. Calculated values of corrosion rate and inhibition efficiency for mild steel corrosion in**
 147 **1 M H_2SO_4 in the absence and presence of different concentrations of *Eremomastax***
 148 ***polysperma* leaf extract**

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Extract conc.	Weight loss				Corrosion rate				Inhibition efficiency			
(g/L)	(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
1M H_2SO_4	0.355	0.454	0.853	1.604	2.2187	2.8375	5.3312	10.0250	-	-	-	-
1.0	0.071	0.094	0.394	0.764	0.4450	0.5875	2.4625	4.7750	80.00	79.29	53.81	52.37
2.0	0.054	0.086	0.258	0.672	0.3375	0.5375	1.6125	4.2000	84.78	81.05	69.75	58.10
3.0	0.043	0.065	0.235	0.513	0.2687	0.4062	1.4687	3.2062	87.88	85.68	72.45	68.01
4.0	0.034	0.047	0.194	0.443	0.2125	0.2937	1.2125	2.7687	90.42	89.64	77.25	72.38

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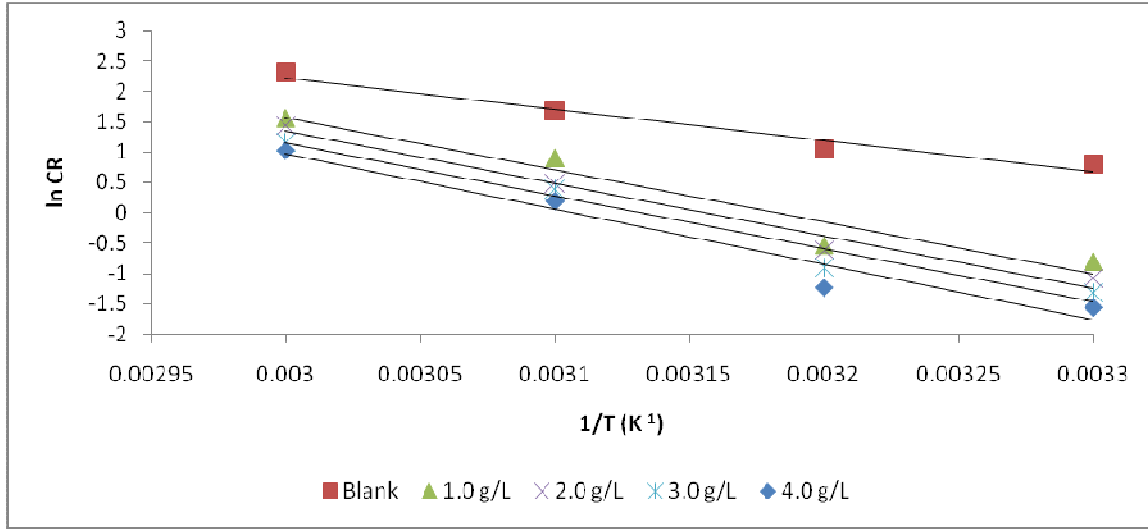


Fig. 3. Plot of ln CR vs. 1/T (Arrhenius plot) for mild steel corrosion in 1 M H₂SO₄ in the absence and presence of *Eremomastax polysperma* leaf extract

The values of enthalpy of activation ($\Delta H^\circ_{\text{ads}}$) and entropy of activation ($\Delta S^\circ_{\text{ads}}$) were obtained from an alternative formulation of the transition state equation [24]:

$$\ln\left(\frac{\text{CR}}{T}\right) = \left[\ln\left(\frac{R}{Nh}\right) + \frac{\Delta S^\circ_{\text{ads}}}{R}\right] - \frac{\Delta H^\circ_{\text{ads}}}{RT} \quad (4)$$

where CR is the corrosion rate, T is the absolute temperature, R is the universal gas constant, h is the Planck's constant, and N is the Avogadro's number. Fig. 4 shows linear plots of $\ln(\text{CR}/T)$ vs. $1/T$ with gradients of $(-\Delta H^\circ_{\text{ads}}/R)$ and 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 in Table 3. The positive values of $\Delta H^\circ_{\text{ads}}$ indicate that mild steel corrosion inhibition was an endothermic process. Additionally, the negative values of $\Delta S^\circ_{\text{ads}}$ show a decrease in the disorderliness of the system, indicating an ordered layer of extract on mild steel surface.

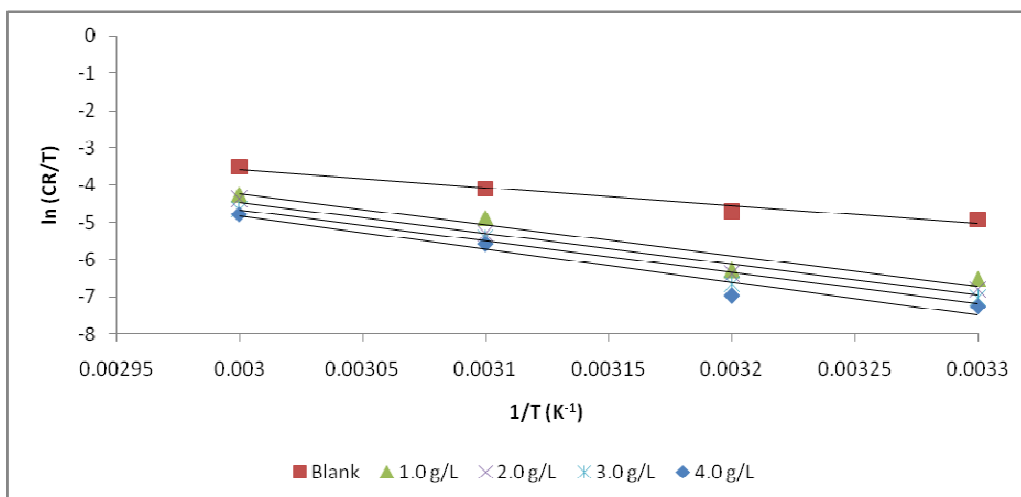


Fig. 4. Plot of $\ln (CR/T)$ vs. $1/T$ (transition state plot) for mild steel corrosion in 1 M H_2SO_4 solution in the absence and presence of *Eremomastax polysperma* leaf extract

Table 3. Calculated values of thermodynamic parameters for mild steel corrosion in 1 M H_2SO_4 solution in the absence and presence of *Eremomastax polysperma* leaf extract

Extract concentration	E_a (kJ mol ⁻¹)	ΔH°_{ads} (kJ mol ⁻¹)	ΔS°_{ads} (J K ⁻¹ mol ⁻¹)
1M H_2SO_4 (Blank)	42.8578	40.2447	- 106.5755
1.0 g/L	71.0930	68.4882	- 27.3680
2.0 g/L	72.0142	69.4044	- 26.3870
3.0 g/L	72.5189	69.9066	- 26.6198
4.0 g/L	75.8154	73.2031	- 18.0979

3.4 Adsorption Isotherm

The best fit for the adsorption of *Eremomastax polysperma* leaf extract on mild steel surface was obtained by the modified Langmuir isotherm defined as:

$$\frac{C}{\theta} = nC + \frac{n}{K_{ads}} \quad (5)$$

where C is the inhibitor concentration, θ is the degree of surface coverage while K_{ads} is the equilibrium adsorption constant. The degree of surface coverage of mild steel by *Eremomastax polysperma* leaf extract is presented in Table 4. It is noticed that the degree of surface coverage increased with increase in extract concentration but decreased with increase in temperature. Linear plot of C/θ vs. C (Fig. 5) shows that the adsorption of *Eremomastax polysperma* leaf extract on mild steel surface in 1 M H_2SO_4 solution obeyed the Langmuir adsorption isotherm. The values of K_{ads} were evaluated from the intercept of the graph and presented in Table 5. K_{ads} is related to the standard free energy of adsorption (ΔG_{ads}°) by the formula [25]:

$$\Delta G_{ads}^\circ = -RT \ln(55.5K_{ads}) \quad (6)$$

where 55.5 is the molar concentration of water in the solution in mol dm^{-3} .

Table 4. Calculated values of degree of surface coverage of mild steel by *Eremomastax polysperma* leaf extract in 1 M H_2SO_4 solution

Extract concentration	Degree of surface coverage (θ)			
	30°C	40°C	50°C	60°C
1.0 g/L	0.80	0.79	0.54	0.52
2.0 g/L	0.85	0.81	0.70	0.58
3.0 g/L	0.88	0.86	0.72	0.68
4.0 g/L	0.90	0.90	0.77	0.72

The negative values of ΔG_{ads}° reveal that the mild steel corrosion inhibition process by *Eremomastax polysperma* leaf extract occurred spontaneously. Generally, values of ΔG_{ads}° less negative than -20 kJ mol^{-1} indicate physical adsorption while those more negative than -40 kJ mol^{-1} indicate chemical adsorption [26 - 28]. Consequently, the values of ΔG_{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.

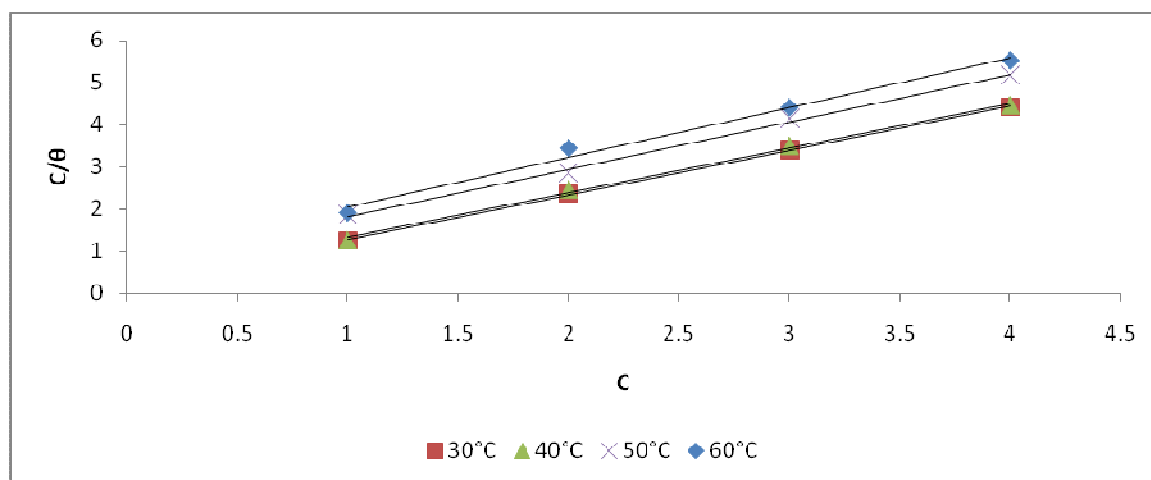


Fig. 5. Plot of C/θ vs. C (Langmuir isotherm) for mild steel corrosion in $1 \text{ M H}_2\text{SO}_4$ solution containing *Eremomastax polysperma* leaf extract

Table 5. Some parameters of the linear regression of Langmuir adsorption isotherm for mild steel corrosion in $1 \text{ M H}_2\text{SO}_4$ solution containing *Eremomastax polysperma* leaf extract

Temperature	R^2	n	$1/K_{\text{ads}} (\text{g L}^{-1})$	$K_{\text{ads}} (\text{g}^{-1}\text{L})$	$\Delta G^{\circ}_{\text{ads}} (\text{kJ mol}^{-1})$
303K	0.9996	1.06	0.2176	4.5956	-13.9598
313K	0.9973	1.06	0.2638	3.7908	-13.9195
323K	0.9980	1.12	0.7030	1.4225	-11.7321
333K	0.9902	1.18	0.8675	1.1527	-11.5130

4. CONCLUSION

On the basis of this study, the following conclusions could be drawn: *Eremomastax polysperma* leaf extract appreciably inhibited the corrosion of mild steel in H_2SO_4 solution. The inhibition efficiency increased with increase in *Eremomastax polysperma* leaf extract concentration but decreased with increase in temperature. Based on a decrease in inhibition efficiency with temperature, higher E_a

values in the extract compared to the blank and the $\Delta G^{\circ}_{\text{ads}}$ values being less negative than -20 kJ mol⁻¹, physically adsorption has been proposed for the adsorption of *Eremomastax polysperma* leaf extract onto mild steel surface. The adsorption of the extract obeyed the Langmuir adsorption isotherm.

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