

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 metallic 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.

Ereromastax polysperma is a medicinal plant in the family Acanthaceae. It is locally called Edem iduduot by the Efik and Ibibio speaking people of Nigeria. The traditional medicinal uses of the plant in eastern Nigeria have been documented [11 – 13]. The phytochemical screening of *Ereromastax polysperma* leaf extract showed the presence of tannins, phenol, flavonoid, alkaloid, saponin and sterol [14]. The aim of this work was to evaluate the inhibitory effect of *Ereromastax polysperma* leaf extract on mild steel corrosion in H₂SO₄ solution.

2. MATERIALS AND METHODS

2.1 Test Materials

Mild steel sheet used for this work was obtained in Calabar, Nigeria. It had the following chemical composition (weight %): C (0.12), Mn (0.85), S (0.06), P (0.05), Si (0.09) and Fe (98.83). 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. They were then 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 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. They were then ground to powder. The dried ground sample of *Eremomastax polysperma* leaf was macerated with 90% ethanol for seven days at room temperature in a 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.

2.3 Weight Loss Method

Previously weighed mild steel coupons were suspended with the aid of glass hooks and rods and immersed in 100 ml of 1 M H₂SO₄ solution (blank) and in 1 M H₂SO₄ solution containing 1.0 g/L – 4.0 g/L *Eremomastax polysperma* leaf extract (inhibitor) in open beakers. In each experiment, one mild steel 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 mild steel 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 weight loss was recorded and used to compute the inhibition efficiency, I(%) [15]:

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

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

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

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

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

2.4 Hydrogen Evolution Method

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

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].

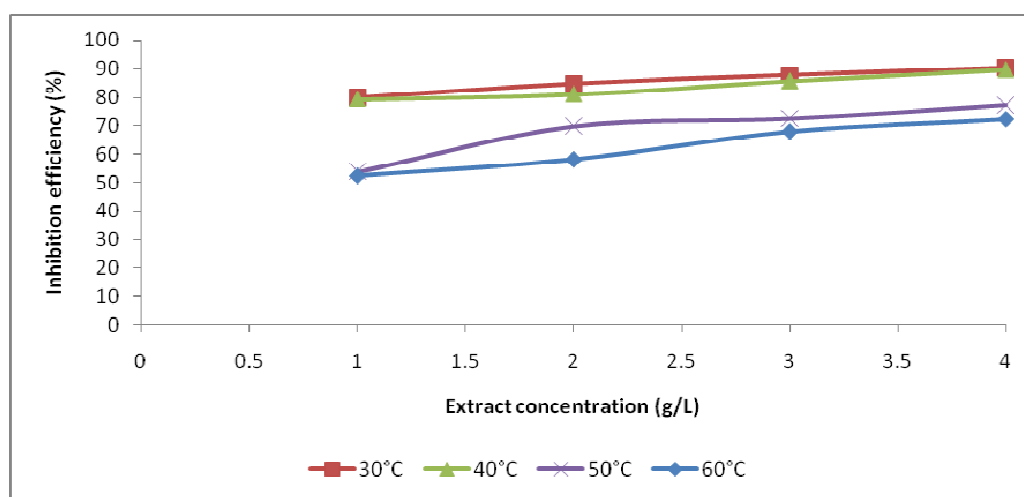
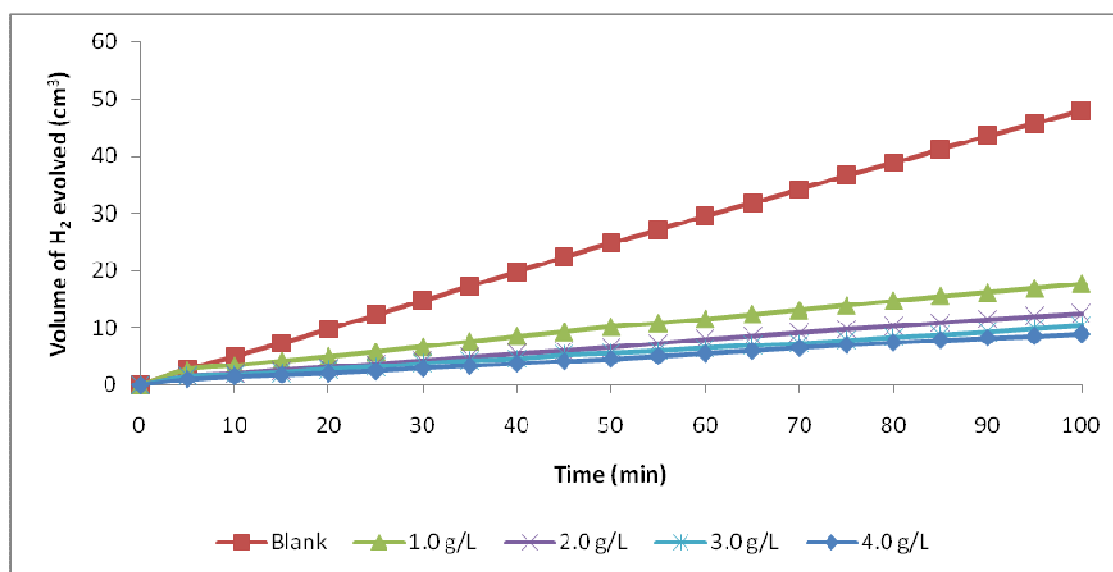


Fig.1. Effect of *Eremomastax polysperma* leaf extract concentration on the inhibition efficiency of mild steel corrosion in 1 M H₂SO₄ at different temperatures

3.2 Hydrogen Evolution Measurements

Fig. 2 illustrates the effect of *Eremomastax polysperma* leaf extract on the volume of H₂ gas evolved in the corrosion of mild steel in 1 M H₂SO₄. It is observed that, at a given time, as the leaf extract concentration increases, the volume of H₂ 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

108 *Eremomastax polysperma* leaf extract. The inhibition efficiencies obtained by both the weight loss and
109 hydrogen evolution methods followed a similar trend.



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112 **Fig. 2. Variation of volume of H₂ gas evolved (cm³) with time (min) for mild steel corrosion in 1**
113 **M H₂SO₄ in the absence and presence of *Eremomastax polysperma* leaf extract at 30 °C**

114 **Table 1. Effect of *Eremomastax polysperma* leaf extract concentration on inhibition efficiency**
115 **of mild steel in 1 M H₂SO₄ 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

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3.3 Effect of Temperature on Inhibition Efficiency

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 H_2SO_4 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.

The activation energies (E_a) of mild steel corrosion in 1M H_2SO_4 solution, with and without inhibitors, were obtained from the gradients of $\ln CR$ vs. $1/T$ plots (Fig. 3) and the results are 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 (42.8578 kJ mol⁻¹). The increase in the E_a values in the presence of the extract indicates physical adsorption while the reverse signifies physical adsorption [22 - 23].

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

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 ₂ SO 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

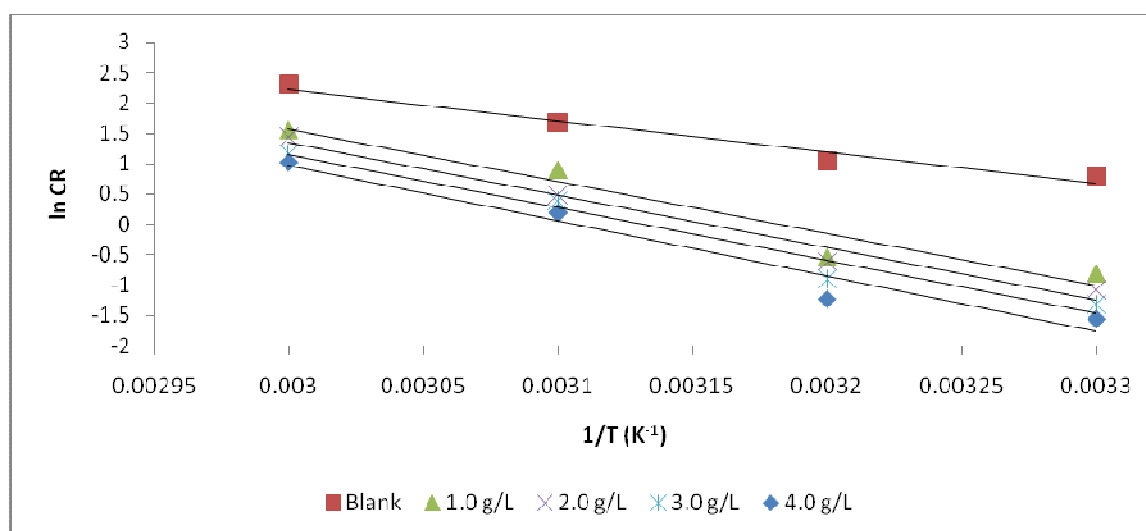


Fig. 3. Plot of ln CR vs. 1/T (Arrhenius plot) for mild steel corrosion in 1 M H₂SO₄ in the absence and presence of *Eremomastax polysperma* leaf extract

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

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

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 $\ln (CR/T)$ 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 ΔH°_{ads} and ΔS°_{ads} were calculated and listed in Table 3. The positive values of ΔH°_{ads} indicate that mild steel corrosion inhibition was an endothermic process. Additionally, the negative values of ΔS°_{ads} show a decrease in the disorderliness of the system, indicating an ordered layer of extract on mild steel surface.

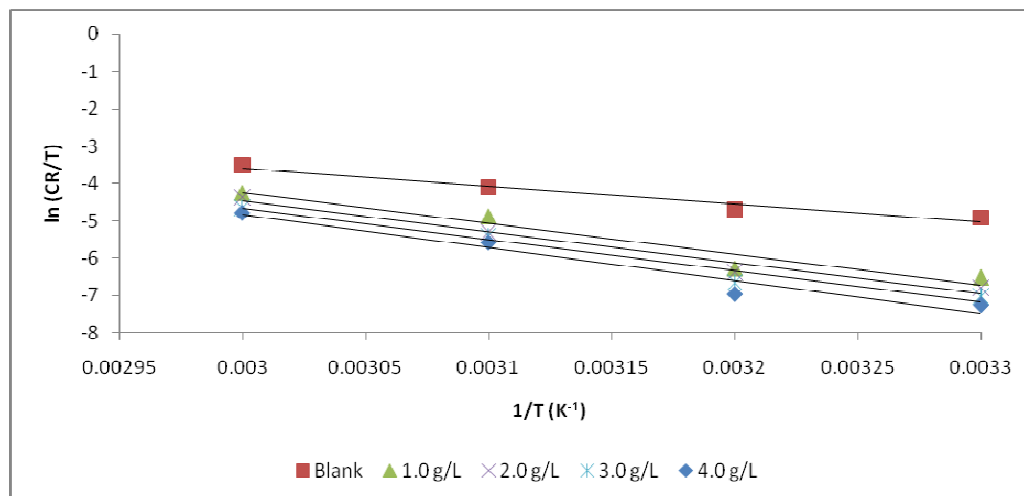


Fig. 4. Plot of $\ln (CR/T)$ vs. $1/T$ (transition state plot) for mild steel corrosion in 1 M H_2SO_4 solution in the absence and presence of *Eremomastax polysperma* leaf extract

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)	$\Delta H^\circ_{\text{ads}}$ (kJ mol ⁻¹)	$\Delta S^\circ_{\text{ads}}$ (J K ⁻¹ mol ⁻¹)
1M H ₂ SO 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:

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

where C is the inhibitor concentration, θ is the degree of surface coverage while K_{ads} is the equilibrium adsorption constant. 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 H₂SO₄ solution obeyed the Langmuir adsorption isotherm. The values of K_{ads} were evaluated from the intercept of the graph and presented in Table 4. K_{ads} is related to the standard free energy of adsorption ($\Delta G^\circ_{\text{ads}}$) by the formula [25]:

$$\Delta G^\circ_{\text{ads}} = -RT \ln(55.5K_{\text{ads}}) \quad (6)$$

where 55.5 is the molar concentration of water in the solution in mol dm⁻³.

The negative values of $\Delta G^\circ_{\text{ads}}$ reveal that the mild steel corrosion inhibition process by *Eremomastax polysperma* leaf extract occurred spontaneously. Generally, values of $\Delta G^\circ_{\text{ads}}$ 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 $\Delta G^\circ_{\text{ads}}$ 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.

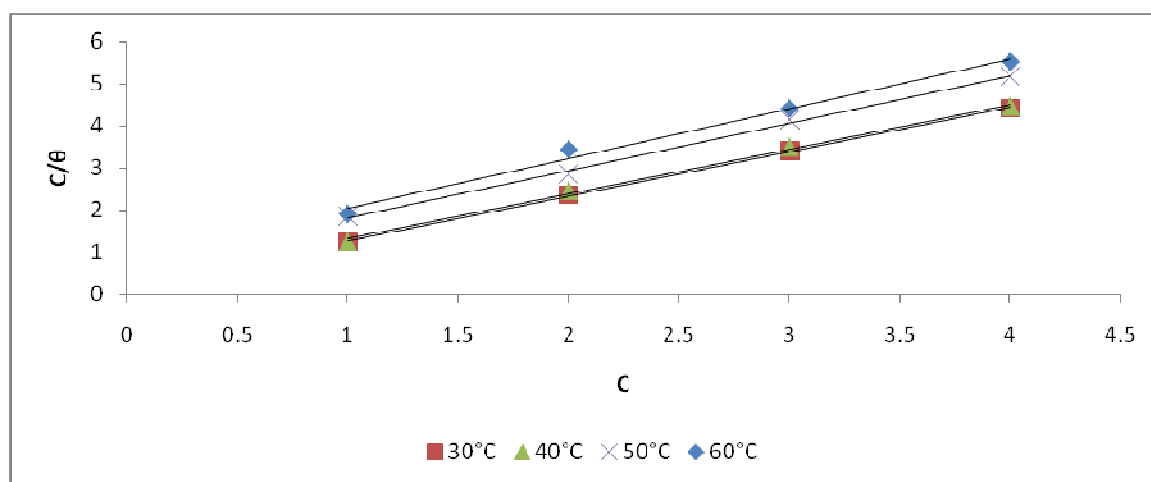


Fig. 5. Plot of C/θ vs. C (Langmuir isotherm) for mild steel corrosion in 1 M H_2SO_4 solution containing *Eremomastax polysperma* leaf extract

Table 4. Some parameters of the linear regression of Langmuir adsorption isotherm for mild steel corrosion in 1 M H_2SO_4 solution containing *Eremomastax polysperma* leaf extract

Temperature	R^2	n	$1/K_{ads}$ ($g\ L^{-1}$)	K_{ads} ($g^{-1}L$)	ΔG°_{ads} ($kJ\ mol^{-1}$)
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 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 ΔG°_{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.

REFERENCES

1. Abakedi OU, Ekpo VF, John EE. Corrosion inhibition of mild steel by *Stachytarpheta indica* leaf extract in acid medium. Pharmaceut. Chem. J. 2016;3(1): 165 – 171.
2. Ibisi NE, Amadi SO. Corrosion inhibition of mild steel in HCl using methylene blue as inhibitor. Int. J. Res. Chem. Environ. 2016;6(1): 38 – 41.
3. Mabrouk EM, Shokry H, Abu Al-Naja KM. inhibition of aluminum corrosion in acid solution by mono- and bis-azo naphthylamine dyes. Part 1. Chem. Met. Alloys. 2011;4: 98 – 106.
4. Ita BI, Abakedi OU. Corrosion of mild steel in acidic medium and its inhibition by 2 -hydroxy – 1 - naphthaldehyde – 4 - phenylsemicarbazone and 2, 4 –dihydroxylbenzaldehyde – 4 - phenylsemicarbazone. Bull. Electrochem. 2006;22(4): 145 – 148.
5. Dadgarnezhad A, Sheikhsheoie I, Baghaei F. Corrosion inhibitory effects of a new synthetic symmetrical Schiff-base on carbon steel in acid media. Anti-Corros. Methods Mater. 2004;51(4): 266 – 271.
6. Elewady GY, El-Said IA, Fouda AS. Anion surfactants as corrosion inhibitors for aluminum dissolution in HCl solutions. Int. J. Electrochem. Sci. 2008;3:177 – 190.
7. Abakedi OU, Asuquo JE, James MA, Ituen NE. Comparative study on the corrosion inhibition of mild steel by *Maeseobatrya barteri* leaf and root extracts in acidic meedium. J. Sci. Eng. Res. 2016;3(5): 153 – 160.
8. Victoria SN, Prasad R, Manivannan R. Psidium guajava leaf extract as green corrosion inhibitor for mild steel in phosphoric acid. Int. J. Electrochem. Sci. 2015;10: 2220 – 2238.
9. Patel NS, Jauhari S, Mehta GN. Mild steel corrosion inhibition by *Bauhinia purpurea* leaves extract in 1 N sulphuric acid. Arabian J. Sci. Eng. 2009; 34(2C): 61 – 69.
10. Al-Mhyawi SR. Inhibition of mild steel corrosion using Juniperus plants as green inhibitor. African J. Pure Appl. Chem. 2014;8(1): 9 – 22.
11. Pandey BP. Textbook of botany: angiosperms. 1st ed. New Delhi: S. Chand Group; 2006.
12. Bassey ME, Effiong EO. Preliminary investigation of herbs used in paediatric care among the people of Akwa Ibom State, Nigeria. J. Nat. Prod. Plant Resour. 2011;1(3): 33 – 42.
13. Mboso OE, Eyong EU, Odey MO, Osakwe E. Comparative phytochemical screening of *Eremomastax speciosa* and *Eremomastax polysperma*. J. Nat. Prod. Plant Resour. 2013;3(2): 37 – 41.
14. Uyoh EA, Chukwurah PN, Ita EE, Oparaugo V, Erete C. Evaluation of nutrients and chemical composition in underutilized *Eremomastax* (Lindau.) species. Int. J. Med. Arom. Plants. 2014;4(2): 124 – 130.
15. Ibok UJ, Ekpe UJ, Abakedi OU, Offiong OE. Inhibition of the corrosion of aluminium in hydrochloric acid solutions by aromatic thiosemicarbazone derivatives. Tropical J. Appl. Sci. 1993;3: 54 – 62.

- 252 16. Abakedi OU. Inhibition of aluminium corrosion in hydrochloric acid solution by *Stachytarpheta*
253 *indica* leaf extract. J. Sci. Eng. Res. 2016;3(3): 105 – 110.
- 254 17. Onuchukwu AI, Mshelia PB. The production of oxygen gas: a student catalysis experiment. J.
255 Chem. Edu. 1985;62(9): 809 – 811.
- 256 18. Ita BI, Abakedi OU. Inhibition of zinc corrosion in 2 M H₂SO₄ by thiosemicarbazone
257 derivatives. Int. J. Sci. Technol. 2006;5: 55 – 57.
- 258 19. Ita BI, Abakedi OU, Osabor VN. Inhibition of mild steel corrosion in hydrochloric acid by 2-
259 acetylpyridine and 2-acetylpyridine phosphate. Glo. Adv. Res. J. Eng. Technol. Innov.
260 2013;2(3): 84 – 89.
- 261 20. Abakedi OU, Moses IE. Aluminium corrosion inhibition by *Maeseobatrya barteri* root extract in
262 hydrochloric acid solution. Am. Chem..Sci. J. 2016;10(3):1 – 10.
- 263 21. Abakedi OU, Moses IE, Asuquo JE. Adsorption and inhibition effect of *Maeseobatrya barteri*
264 leaf extract on aluminium corrosion in hydrochloric acid solution. J. Sci. Eng. Res. 2016;3(1):
265 138 – 144.
- 266 22. Awad MI. Eco-friendly corrosion inhibitors: inhibitive action of quinine for low carbon steel in 1
267 M HCl. J. Appl. Electrochem. 2006; 1163 – 1168.
- 268 23. Bentiss F, Bouanis M, Mernari B, Trainel M, Vezin H, Lagrennee M. Understanding the
269 adsorption of 4*H*-1,2,4-triazole derivatives on mild steel surface in molar hydrochloric acid.
270 Appl. Surf. Sci. 2007;253: 3696 – 3704.
- 271 24. Abakedi OU, Asuquo JE. Corrosion inhibition of mild steel in 1 M H₂SO₄ solution by
272 *Microdesmis puberula* leaf extract. Am. Chem. Sci. J. 2016;16(1): 1 – 8.
- 273 25. Cang H, Fei Z, Shao J, Shi W, Xu Q. Corrosion inhibition of mild steel by aloes extract in HCl
274 solution medium. Int. J. Electrochem. Sci. 2013;8: 720 – 734.
- 275 26. Kamis E, Belluci F, Latanison RM, El-Ashry ESH. Acid corrosion inhibition of nickel by 2-
276 (triphenylphosphoryl) succinic anhydride. Corros. 1991;47(9): 677 – 686.
- 277 27. Bilgic S, Sahin M. The corrosion inhibition of austenitic chromium-nickel steel in H₂SO₄ by 2-
278 butyn-1-ol. Mater. Chem. Phys. 2001;70(3): 290 – 295.
- 280 28. Ebenso EE. Effect of halide ions on the corrosion inhibition of mild steel in H₂SO₄ using
281 methyl red – Part I. Bull. Electrochem. 2003;19(5): 209 – 216.