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Research Article

Comparative study on the corrosion inhibition of mild steel by *Maesobatrya barteri* leaf and root extracts in acidic medium

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Abstract The inhibition action of *Maesobatrya barteri* leaf (LF) and root (RT) extracts on mild steel corrosion in 1M H_2SO_4 solution was studied using weight loss method. The results obtained reveal that the extracts functioned as good inhibitors of mild steel in H_2SO_4 solution. Inhibition efficiency was found to increase with increase in extract concentration and temperature, and followed the trend: LF > RT. Chemical adsorption mechanism has been proposed for the adsorption of the plant extracts onto mild steel surface. Thermodynamic parameters revealed that the adsorption of the extracts onto metal surface was endothermic and spontaneous. The experimental data for the LF extract obeyed the Langmuir adsorption isotherm while that of the RT extract followed the Freundlich adsorption isotherm.

Keywords Corrosion inhibition, *Maesobatrya barteri*, Weight loss, Chemisorption, Extract

Introduction

The exposure of metals to corrosive media is inevitable in certain industrial processes. Some of these processes include pickling, oil well acidizing, descaling and anodizing. The exposed metal consequently corrodes in these media. In order to minimize the loss of the metal and/or the corrosive solutions, inhibitors are usually added to the corrosive solution. The traditional inhibitors used are synthesized organic compounds containing heteroatoms such as N, S, O and/or P. The use of such inhibitors nowadays is limited due to safety concerns, as some of them are toxic and environmentally unfriendly.

Due to the cost - effectiveness of using inhibitors over other means of corrosion control, research emphasis has now shifted to the use of naturally occurring substances, especially of plant origin, as corrosion inhibitors. Such an interest is due to their biodegradability, non-toxicity, cheapness, and availability on demand. Moreover, plant extracts contain organic nitrogen, oxygen and/or sulphur in the combined form [1]. Extracts from different parts of plants have been reported as good inhibitors of mild steel corrosion in acidic media, namely, leaf extracts [2-3], seed extracts [4-5], fruit extracts [6-7], flower extracts [8-9], stem bark extracts [10-11], and root extracts [12-13].

Maesobatrya barteri is commonly called Bush cherry in English and go by other names among the different ethnic groups in Nigeria viz Nyanyatet (Efik/Ibibio) and Uvune (Igbo). It is a medicinal plant belonging to the family Euphorbiaceae. It has broad leaves and succulent berries which are edible. The traditional medicinal uses of parts of *Maesobatrya barteri* by the people of south eastern Nigeria have been documented [14-15].

Previous work [16-17] in our group revealed that *Maesobatrya barteri* leaf and root extracts are good inhibitors of aluminium corrosion in acidic medium. No work has been reported on the inhibition effect of *Maesobatrya barteri* extracts on mild steel corrosion. As part of our effort in the global search for eco-friendly inhibitors, this work aims at comparing the inhibition effect of *Maesobatrya barteri* leaf and root extracts on the corrosion of mild steel in H_2SO_4 solution.

Materials and Method

Test materials

Mild steel sheet used for this work was obtained in Calabar, Nigeria. The sheet was mechanically press cut into 5 cm x 4 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.

Preparation of *Maesobatrya barteri* leaf and root extracts

Fresh leaves and roots of *Maesobatrya barteri* were collected from the Main Campus of University of Uyo, Uyo, Nigeria. *Maesobatrya barteri* leaf and root extracts were prepared as previously reported [16-17]. Extract concentrations of 0.5 g/L, 1.0 g/L, 1.5 g/L, 2.0 g/L, and 4.0 g/L respectively in 1M H_2SO_4 solution were used for the weight loss studies at 30°C – 60°C.

Weight loss measurements

Previously weighed mild steel coupons were suspended with the aid of glass hooks and rods and immersed in 100ml of 1M H_2SO_4 solution (blank) and in 1M H_2SO_4 solution containing 0.5 g/L – 4.0 g/L *Maesobatrya barteri* leaf and root extracts, respectively, 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 corrodent concentration was kept at 1M H_2SO_4 and the volume of the test solution used was 100 mL. The difference between the initial weight of coupons and the weight of coupons after corrosion was taken as the weight loss which was used to compute the inhibition efficiency, I(%) [18]:

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

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

The corrosion rate (CR) was calculated using the formula [3]:

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

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

Results and Discussion

Effect of extract concentration on inhibition efficiency

Figure 1 depicts the effect of *Maesobatrya barteri* leaf and root extracts on mild steel corrosion in 1M H_2SO_4. The inhibition efficiency at a particular temperature increased with increase in extract concentration. This indicates a strong interaction between the mild steel surface and the extracts [19]. The highest inhibition efficiencies of 84.38% and 64.19%, were obtained at 60°C in the presence of the LF and RT extracts, respectively, revealing that the leaf extract was a better inhibitor of mild steel corrosion in H_2SO_4 solution than the root extract counterpart (Figure 2).

Effect of temperature on inhibition efficiency

Table 1 shows the effect of temperature on the inhibition effect of *Maesobatrya barteri* extracts on mild steel corrosion in 1M H_2SO_4 solution. An increase in temperature led to an increase in the inhibition efficiency of both the LF and RT extracts. An increase in inhibition efficiency with increase in temperature indicates that the extracts were more effective in inhibiting mild steel corrosion at higher temperatures that at lower ones. Furthermore, an increase in inhibition efficiency with increase in temperature is indicative of a chemical adsorption (chemisorption) mechanism.

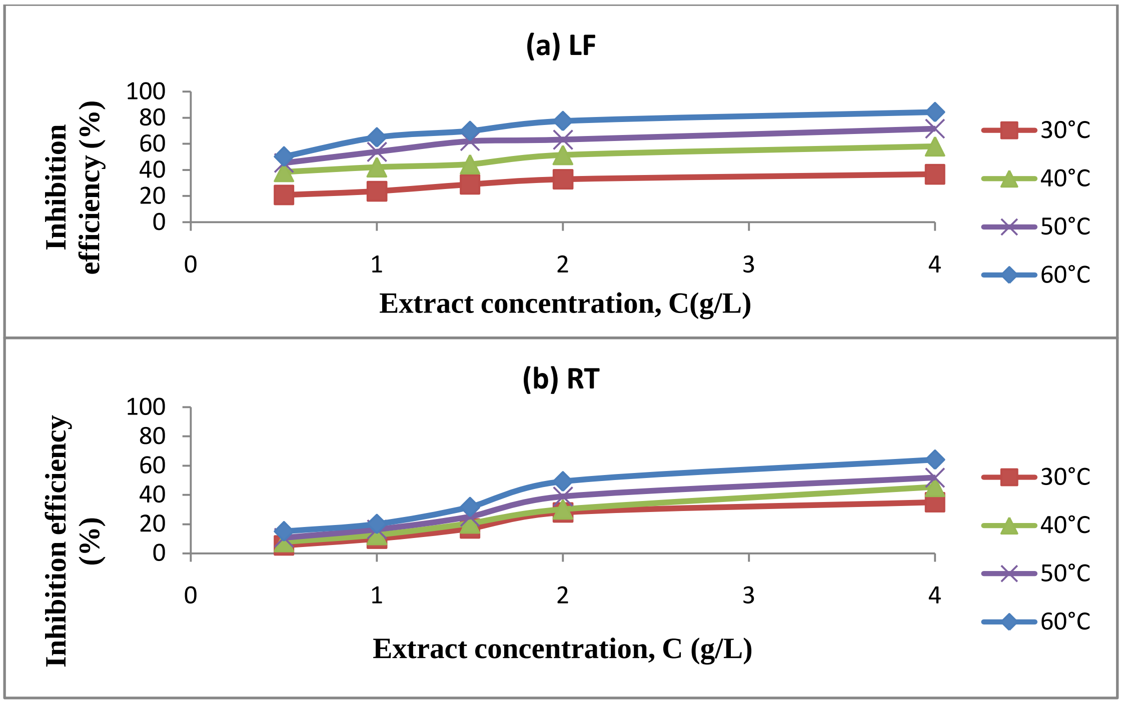

Figure 1: A plot of inhibition efficiency against concentrations of (a) LF and (b) RT extracts of Maesobatrya barteri for mild steel corrosion in 1M H_2SO_4 solution

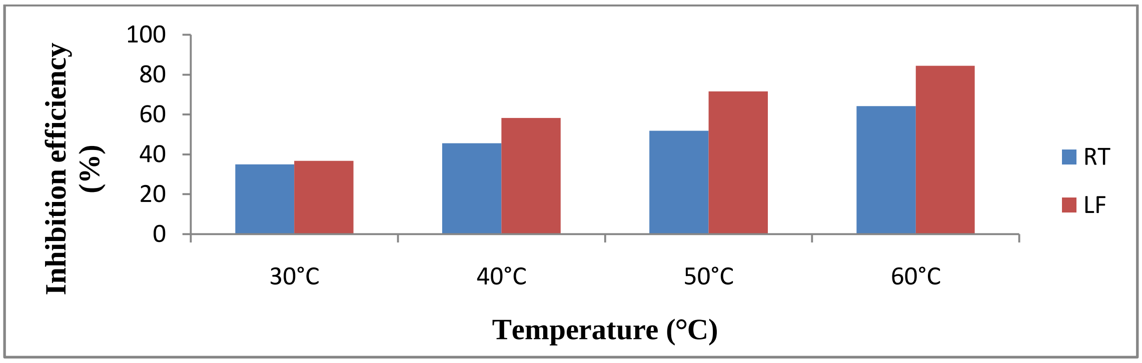

Figure 2: Maximum inhibition efficiency for mild steel corrosion in 1M H_2SO_4 containing 4.0 g/L Maesobatrya barteri LF and RT extracts at different temperatures

Table 1: Calculated values of weight loss, corrosion rate and inhibition efficiency for mild steel corrosion in 1M H_2SO_4 solution containing *Maesobatrya barteri* leaf (LF) and root (RT) extracts at 30°C – 60°C

Plant's part	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	0.3545	0.5629	0.8532	1.6042	2.2156	3.5181	5.3325	10.0263	-	-	-	-
	0.5 g/L	0.2800	0.3456	0.4650	0.7989	1.7500	2.1600	2.9063	3.5094	21.02	38.60	45.50	50.20
	1.0 g/L	0.2701	0.3256	0.3936	0.5615	1.6881	2.0350	2.4600	3.5094	23.81	42.16	53.87	65.00
LF	1.5 g/L	0.2514	0.3121	0.3230	0.4813	1.5713	1.9506	2.0188	3.0081	29.08	44.55	62.14	77.50
	2.0 g/L	0.2374	0.2721	0.3138	0.3609	1.4838	1.7006	1.9613	2.2556	33.03	51.66	63.22	77.50
	4.0 g/L	0.2243	0.2350	0.2421	0.2506	1.4019	1.4688	1.5131	1.5663	36.73	58.25	71.62	84.38
	0.5 g/L	0.3355	0.5196	0.7616	1.3641	2.0969	3.2475	4.7600	8.5256	5.36	7.69	10.74	14.97
	1.0 g/L	0.3189	0.4923	0.7129	1.2827	1.9931	3.0769	4.4556	8.0169	10.04	12.54	16.44	20.04
RT	1.5 g/L	0.2941	0.4477	0.6393	1.0965	1.8381	2.7981	3.9956	6.8531	17.04	20.47	25.07	31.65
	2.0 g/L	0.2552	0.3934	0.5215	0.8162	1.5950	2.4588	3.2594	5.1013	28.01	30.11	38.88	49.12
	4.0 g/L	0.2306	0.3067	0.4112	05745	1.4413	1.9169	2.5700	3.5906	34.95	45.51	51.80	64.19

The values of the activation energy (E_a) for mild steel corrosion in 1M H_2SO_4 solution in the presence and absence of *Maesobatrya barteri* leaf and root extracts, respectively, were obtained using the alternative formulation of Arrhenius equation [16]:

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

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 (Figure 3) and the results presented in Table 2. Table 2 shows that the E_a values in the presence of both the leaf and root extracts were lower than the E_a value of the blank (41.4636 kJ mol^{-1}). The decrease in the E_a values in the presence of the extract indicates chemical adsorption while the reverse signifies physical adsorption [20].

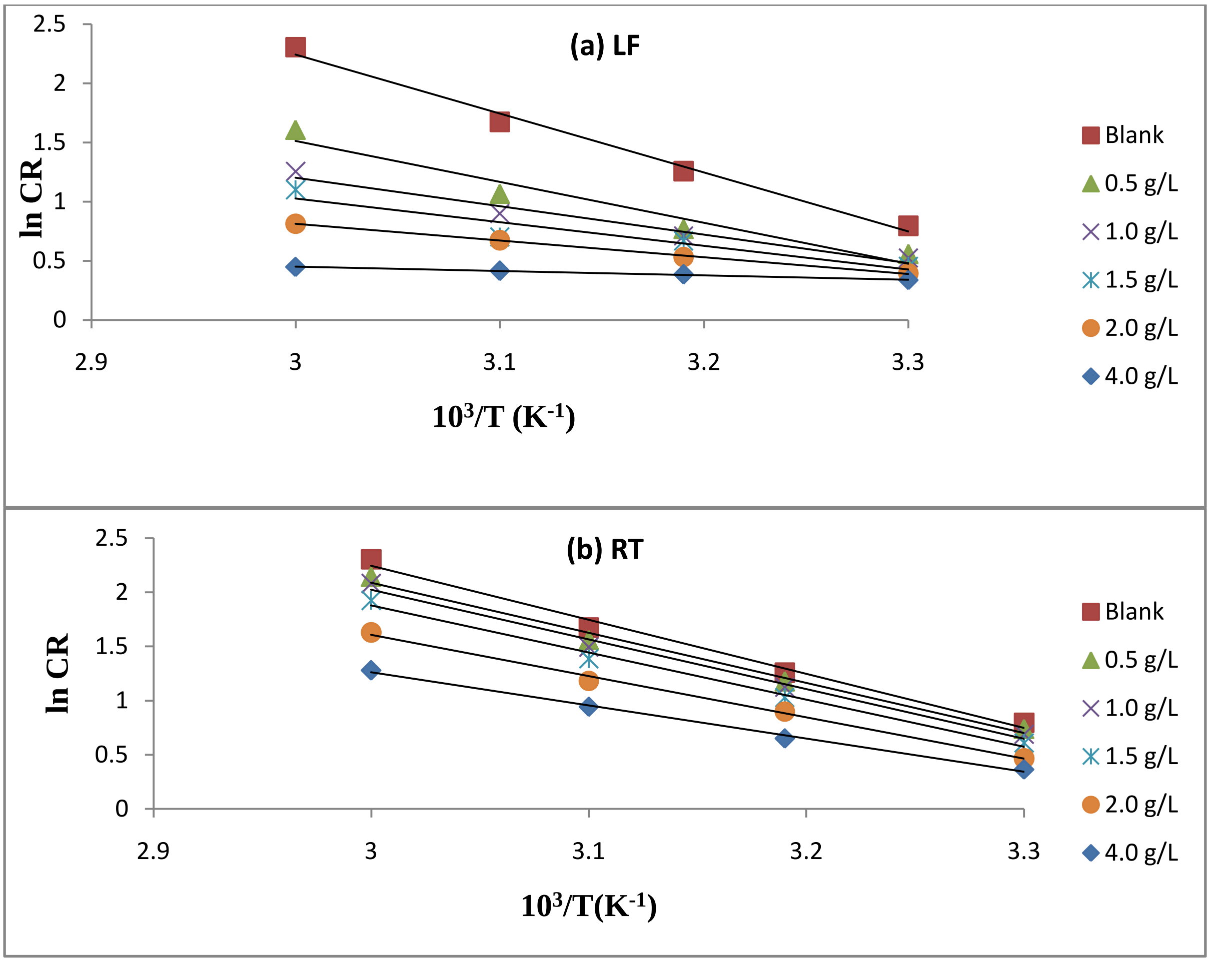

Figure 3: Plot of ln CR vs. 1/T (Arrhenius plot) for mild steel corrosion in 1M H_2SO_4 in the absence and presence of (a) LF and (b) RT extracts of Maesobatrya barteri

The values of enthalpy of activation ($\Delta H°_{ads}$) and entropy of activation ($\Delta S°_{ads}$) were obtained from an alternative formulation of the transition state equation [3]:

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

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 $-\Delta H°_{ads}/R$ and intercepts of [ln (R/Nh) + $\Delta S°_{ads}/R$] from which the values of $\Delta H°_{ads}$ and $\Delta S°_{ads}$ were calculated and listed in Table 2. The positive values of $\Delta H°_{ads}$ both in the blank and in the presence of extracts indicate the endothermic nature of the mild steel corrosion process. The negative values of entropies ($\Delta S°_{ads} < 0$) indicate a decrease in the disorderliness of the system which implies an ordered layer of extract on mild steel surface.

Table 2: Calculated values of thermodynamic parameters for mild steel corrosion in 1M H_2SO_4 solution in the absence and presence of (a) LF and (b) RT extracts of *Maesobatrya barteri*

Plant's part	Extract concentration	E_a (kJ mol^{-1})	$\Delta H°_{ads}$ (kJ mol^{-1})	$\Delta S°_{ads}$ (J K^{-1} mol^{-1})
	1M H_2SO_4 (Blank)	41.4636	38.8247	- 110.6992
	0.5 g/L	28.7673	26.1251	- 154.8882
	1.0 g/L	19.9718	17.3314	- 183.8425
LF	1.5 g/L	16.6679	14.0482	- 195.1445
	2.0 g/L	11.7286	9.0889	- 211.8166
	4.0 g/L	3.0505	0.4106	- 240.8524
	0.5 g/L	38.4963	35.8566	- 120.8955
	1.0 g/L	38.1297	35.4866	- 122.5434
RT	1.5 g/L	36.1085	33.4680	- 129.8148
	2.0 g/L	31.6863	29.0491	- 145.3229
	4.0 g/L	25.4103	22.7712	- 167.0349

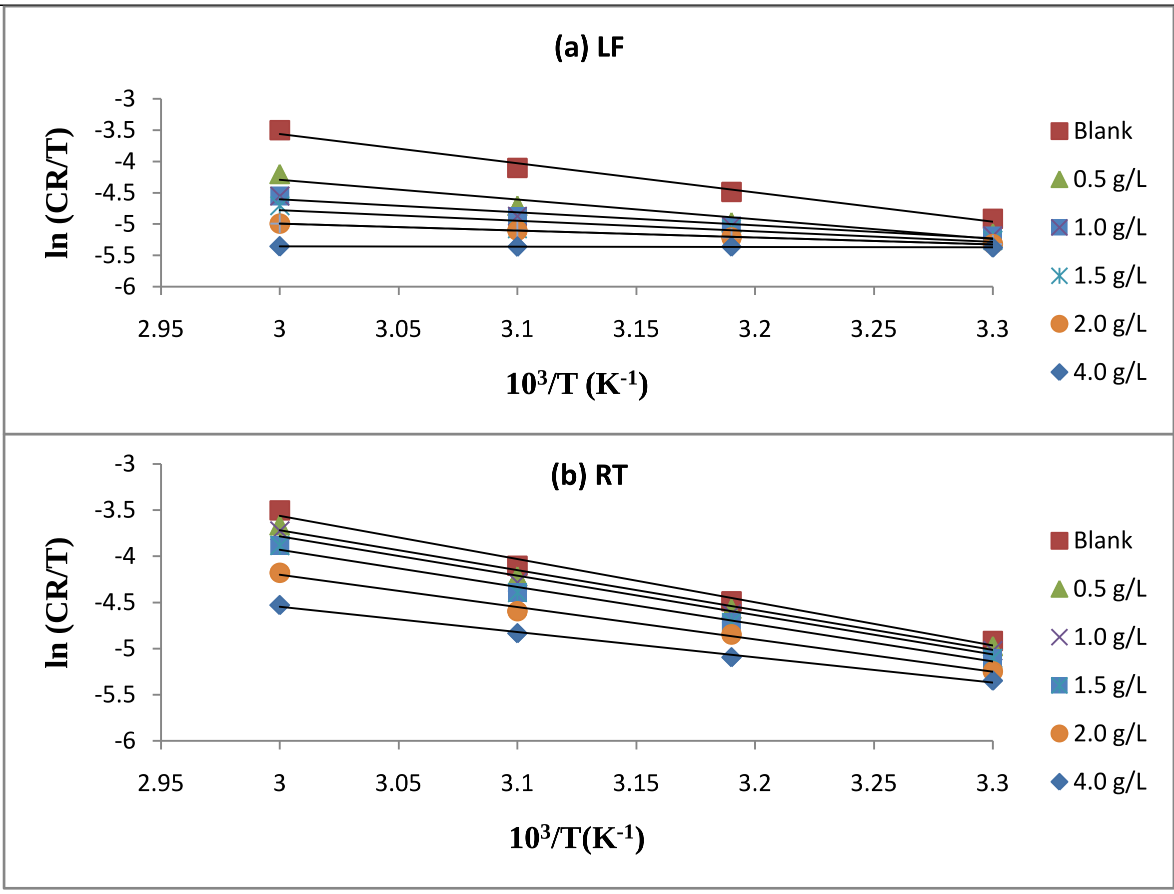

Figure 4: Plot of ln (CR/T) vs. 1/T (Transition state plot) for mild steel corrosion in 1M H_2SO_4 solution in the absence and presence of (a) LF and (b) RT extracts of Maesobatrya barteri

Adsorption isotherm

The nature or type of interaction at the metal – solution interface can be deduced by the adsorption isotherm obeyed. Several adsorption isotherms were assessed in order to fit the experimental data obtained. The best fit for the adsorption of *Maesobatrya barteri* leaf extract on mild steel surface was obtained by the modified Langmuir isotherm defined as:

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

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 as shown in Figure 5 reveals that the adsorption of *Maesobatrya barteri* leaf extract on mild steel surface in 1M H_2SO_4 solution obeyed the Langmuir adsorption isotherm.

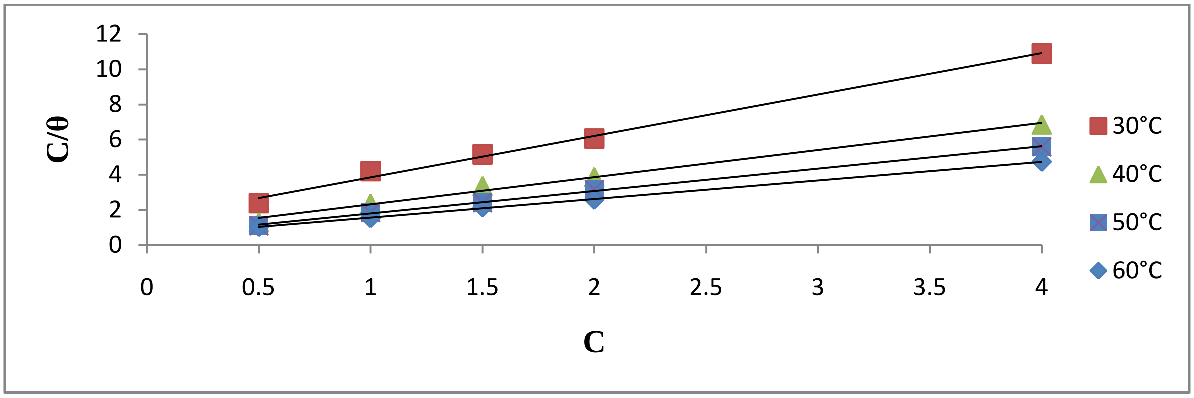

Figure 5: Plot of C/θ vs. C (Langmuir isotherm) for mild steel corrosion in 1M H_2SO_4 solution containing Maesobatrya barteri leaf extract

The adsorption of *Maesobatrya barteri* root extract obeyed the Freundlich adsorption isotherm equation [21]:

$$\log\theta = n \log C + \log K_{ads} \qquad (6)$$

where θ is the degree of surface coverage, K_{ads} is the equilibrium adsorption constant, C is the inhibitor concentration and n is the interaction parameter. Figure 6 reveals linear plots of log θ vs. log C, with gradients of 'n' and intercepts of log K_{ads}. The equilibrium adsorption constant, K_{ads}, is related to the standard free energy of adsorption (ΔG°_{ads}) by the formula [19, 22]:

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G^{\circ}_{ads}}{RT}\right) \qquad (7)$$

where 55.5 is the molar concentration of water in the solution, R is the universal gas constant while T is the absolute temperature.

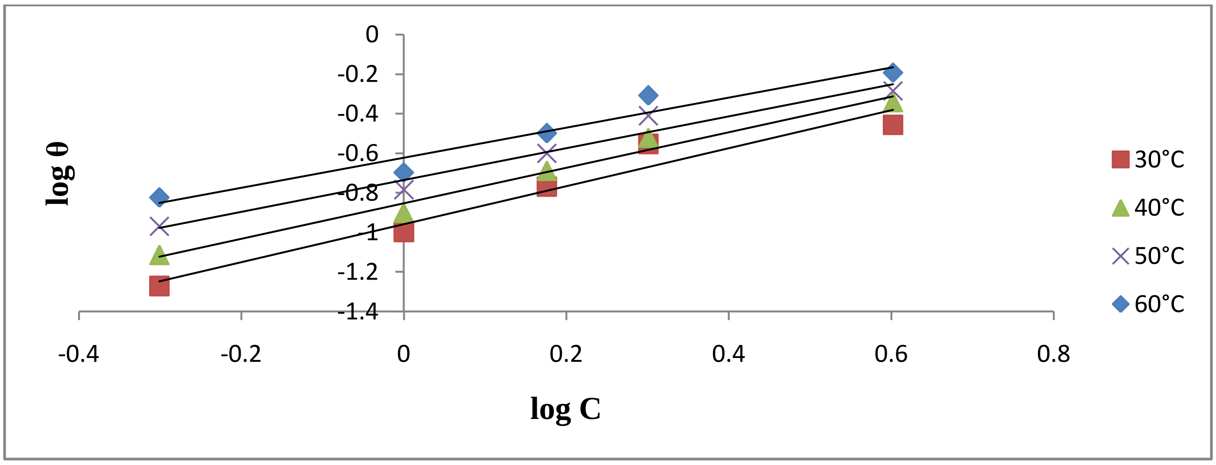

Figure 6: Plot of log θ vs log C (Freundlich isotherm) for mild steel corrosion in 1M H_2SO_4 solution containing Maesobatrya barteri root extract

The parameters of the linear regression of both the Langmuir and Freundlich adsorption isotherms are presented in Table 3. The values of K_{ads} increased with increase in temperature for both LF and RT extracts, with LF exhibiting higher K_{ads} values. An increase in the values of K_{ads} with increase in temperature shows that the extracts adsorbed more strongly onto mild steel surface with increase in temperature [3]. This is supported by an increase in the inhibition efficiency with increase in temperature. Additionally, the higher K_{ads} values for the LF extract imply that the LF extract adsorbed more strongly and offered a better inhibition on mild steel surface in H_2SO_4 solution than the RT extract. The ΔG°_{ads} values for both extracts are negative, indicating that the adsorption of both *Maesobatrya barteri* leaf and root extracts onto mild steel surface occurred spontaneously. Furthermore, the values of $\Delta G°_{ads}$ for the LF extract (the better inhibitor) being more negative than their RT extract counterparts indicate that the more effective an inhibitor, the more negative its $\Delta G°_{ads}$ values.

Table 3: Some parameters of the linear regression of Langmuir and Freundlich adsorption isotherms for mild steel corrosion in 1M H_2SO_4 solution containing *Maesobatrya barteri* extracts

Plant's part	Temperature	Langmuir model				
		R^2	n	$1/K_{ads}$	K_{ads} ($g^{-1}L$)	$\Delta G°_{ads}$ (kJ mol^{-1})
	303K	0.9939	2.35	1.5027	0.6655	- 9.0920
LF	313K	0.9915	1.55	0.7707	1.2975	- 11.1295
	323K	0.9986	1.27	0.5348	1.8699	- 12.4664
	333K	0.9994	1.06	0.503 6	1.9857	- 13. 0188
		Freundlich Model				
		R^2	n	log K_{ads}	K_{ads} ($g^{-1}L$)	$\Delta G°_{ads}$ (kJ mol^{-1})
	303K	0.9500	0.96	- 0.9589	0.1099	- 4.5551
RT	313K	0.9808	0.90	- 0.8531	0.1402	- 5.3391
	323K	0.9652	0.80	- 0.7352	0.1840	- 6.2397
	333K	0.9473	0.76	- 0.6229	0.2383	- 7.1489

Conclusion

On the basis of this study, the following conclusions could be drawn:

1. The leaf (LF) and root (RT) extracts of *Maesobatrya barteri* appreciably inhibited the corrosion of mild steel in H_2SO_4 solution.
2. The inhibition efficiencies of the plant extracts increased with increase in extract concentration and temperature and followed the trend: LF > RT.
3. Based on the trend of inhibition efficiency with temperature and from the calculated values of activation energy, the *Maesobatrya barteri* leaf and root extracts adsorbed chemically onto the mild steel surface.
4. The adsorption of the LF extract obeyed the Langmuir adsorption isotherm while the RT extract followed the Freundlich adsorption isotherm.

References

[1]. Abakedi, O. U., Moses, I. E., & Asuquo, J. E. (2016). Adsorption and inhibition effect of *Maesobatrya barteri* leaf extract on aluminium corrosion in hydrochloric acid solution. *J. Sci. Eng. Res.*, *3*(1): 138 – 144.

[2]. Abakedi, O. U**.,** Ekpo, V. F., & John, E. E. (2016). Corrosion inhibition of mild steel by *Stachytarpheta indica* leaf extract in acid solution. *Pharmaceut. Chem. J.*, *3*(1): 165 – 171.

[3]. Abakedi, O. U**.,** & Asuquo, J. E. (2016). Inhibition of mild steel corrosion by *Microdesmis puberula* leaf extract in 1M H_2SO_4 solution. *Am. Chem. Sci. J.*, *16* (1):1 –8.

[4]. Noor, E. A. (2008). Comparative study on the corrosion inhibition of mild steel by aqueous extract of Fenugreek seeds and leaves in acidic solutions. *J. Eng. Appl. Sci*., *3*(1), 23 – 30.

[5]. Al–Turkustani, A. M., Al – Sawat, R. M., Al – Ghamdi, N. S., Al – Harbi, E. M., Al–Gamdi, M. A., & Al–Solmi, S. A. (2013). Corrosion behaviour of mild steel in acidic solution using aqueous seed extract of *Phoenix dactylifera* L. (Date seeds). *J. Chemica Acta*, *2*: 53 – 61.

[6]. Kamaraj, P. Arthanareeswari, M. Arockiaselvi, J. Vennila, R. & Ilamathi, P. (2014). *Podophyllum hexandrum* fruit extract as corrosion inhibitor of mild steel in 1N HCl. *Indian J. Appl. Sci*., *4*(6): 57 – 59.

[7]. Singh, A. Singh, V. K., & Quraishi, M. A. (2013). Inhibition of mild steel corrosion in HCl solution using Pipali (*Piper longum*) fruit extract. *Arab J. Sci. Eng*., *38*: 85 – 97.

[8]. Thilagathy, P. & Saratha, R. (2015). Mirabilis Jalapa flowers extract as corrosion inhibitor for the mild steel corrosion in 1M HCl. *IOSR J. Appl. Chem*., *8*(1): 30 – 35.

[9]. Rajendran, A. & Karthikeyan, C. (2012). The inhibitive effect of extract of flowers of *Cassia auriculata* in 2M HCl on the corrosion of aluminium and mild steel. *Int. J. Plant Res*., *2*(1): 9 – 14.

[10]. Priyadarshini, B. Stella, S.M. . Stango, A.X Subramanian, B. Vijayalakshmi, U. (2015). Corrosion resistance of mild steel in acidic environment; Effect of *Peltophorum ptetocarpum* extract. *Int. J. ChemTech. Res.*,*7*(2): 518 – 525.

[11]. Nnanna, I. A. Uchenna, K. O. Nwosu, F. O. Ihekoronye, & U. Eti, E. P. (2014). *Gmelina arborea* bark extracts as a corrosion inhibitor for mild steel in an acidic environment. *Int. J. Mater. Chem.*,*4*(2): 34 – 39.

[12]. Abdel-Fatah, H. T. M. Hassan, A. A. M. Saadi, Z. A. Shetify, M. M. . El-Sehiety, H. E. E. (2014). Corrosion inhibition of mild steel in an acidic medium by *Salvadora persica* (Miswak) – Part 1: in sulphamic acid. *Chem. Sci. Trans*., *3*(1): 221 – 231.

[13]. Okafor, P. C. Ebenso, E. E. & Ekpe, U. J. (2010). *Azadirachta indica* extracts as corrosion inhibitor for mild steel in acid medium. *Int. J. Electrochem. Sci*., *5*: 978 –993.

[14]. Durugbo, E. U. (2013). Medico – ethnobotanical inventory of Ogii, Okigwe Imo State, South Eastern Nigeria – I. *Glo. Adv. Res. J. Med. Plants,2*(2): 30 – 44.

[15]. Ajibesin, K. K. (2012). Ethnobotanical survey of plants used for skin diseases and related ailments in Akwa Ibom State, Nigeria. *Ethnobot. Res. Appl.*,*10*: 463 – 522.

[16]. Abakedi, O. U. & Moses, I. E. (2016). Aluminium corrosion inhibition by *Maesobatrya barteri* root extract in hydrochloric acid solution. *Am. Chem. Sci. J.*, *10* (3): 1 – 10.

[17]. Abakedi, O. U.**,** Moses, I. E. & Asuquo, J. E. (2016). Adsorption and inhibition effect of *Maesobatrya barteri* leaf extract on aluminium corrosion in hydrochloric acid solution. *J. Sci. Eng. Res.*, *3*(1): 138 – 144.

[18]. Ibok, U. J., Ekpe, U. J., Abakedi, O. U., & Offiong, O. E. (1993). Inhibition of the corrosion of aluminium in hydrochloric acid solutions by aromatic thiosemicarbazone derivatives. *Tropical J. Appl. Sci., 3*: 54 – 62.

[19]. Ita, B. I., Abakedi, O. U., & Osabor, V. N. (2013). Inhibition of mild steel corrosion in hydrochloric by 2-acetylacetylpyridine and 2-acetylacetylpyridine phosphate. *Glo. Adv. Res. J. Eng. Technol. Innov., 2*(3): 84 – 89.

[20]. Awad, M. I. (2006). Eco-friendly corrosion inhibitors: inhibitive action of quinine for low carbon steel in 1M HCl. *J. Appl. Electrochem., 36*: 1163 – 1168.

[21]. Al-Bonayan, A. M. (2015). Corrosion inhibition of carbon steel in hydrochloric acid solution by Senna-Italica extract. *IJRRAS, 22*(2): 49 – 64.

[22]. Moussa, M. N. H., El – Far, A. A., & El – Shafei, A. A. (2007). The use of water-soluble hydrazones as inhibitors for the corrosion of C-steel in acidic medium. *Mater. Chem. Phys., 105*: 105 – 113.