Original Research Article

Inhibition of Mild Steel Corrosion in Acidic Medium by *Telfairia occidentalis* Rind Extract

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ABSTRACT

Telfairia occidentalis rind extract has been studied as a potential green inhibitor for mild steel corrosion in 1 M H_2SO_4 using weight loss and hydrogen evolution methods. The results of the investigation reveal that *Telfairia occidentalis* rind extract is a good inhibitor of mild steel corrosion in sulphuric acid solution. The inhibition efficiency increases with increase in rind extract concentration but decrease with increase in temperature. The calculated thermodynamic parameters reveal that the corrosion inhibition process was endothermic and spontaneous. Physical adsorption has been proposed for the adsorption of *Telfairia occidentalis* rind extract onto mild steel surface. The adsorption of the extract on mild steel surface obeys the Langmuir adsorption isotherm.

Keywords: Telfairia occidentalis, mild steel, corrosion inhibition, physisorption, Langmuir isotherm

1. INTRODUCTION

Corrosion of metals is a global phenomenon that has received enormous attention and concern, due to its degrading effects on metallic structures and infrastructure. Mild steel, which is widely used in industries, is often exposed to aggressive environments during industrial processes such as picking, descaling and acid cleaning, which results in its corrosion [1]. The cost of replacing corroded metallic equipment is usually very high. In order to protect metals in aggressive environments, the use of corrosion inhibitors is practiced globally [1]. Corrosion inhibitors are compounds containing nitrogen, oxygen, sulphur and/or phosphorus [2]. Though many synthetic organic and inorganic compounds have been reported to exhibit good anti-corrosive property [3-5], their usage has been discouraged due to their toxicity, which makes them environmentally unfriendly. Thus safety and environmental concern have prompted researchers to find eco-friendly corrosion inhibitors from natural products such as plant extracts containing phytochemicals like alkaloids, saponins, terpenes, tannins, etc, which are rich in oxygen, sulphur and nitrogen [6]. Besides being eco-friendly, plant extracts are renewable, readily available, cheap and biodegradable. Some of the plant extracts which have been investigated by researchers as showing good anti-corrosive property on mild steel in acidic medium include; *Stachytarpheta indica* leaf extract [7], *Phoenix dactylifera* seed extract [8], watermelon rind extract [9], *Piper longum* fruit extract [10], Fenugreek seed extract [11], and *Gmelina arborea* stem bark extract [12].

Telfairia occidentalis commonly called fluted pumpkin in English, Ikong-ubong by the Efik/Ibibio and ugu by the Igbo ethnic groups in Nigeria belongs to the family *Cucurbitaceae*. The climbing vegetable has edible leaves borne on tender shoots. The shoots also bear large gourd fruits containing edible seeds [13]. The seeds are used for cultivation. The seeds are housed by a big gourd which is used as feed for herbivores such as pigs and goats. The shoot (stem) and leaves have been found to be rich in antioxidants and have antimicrobial properties [14]. The leaf and shoot are also used in herbal medicine by the people of Nigeria. The need for the discovery of efficient eco-friendly corrosion inhibitors cannot be over-emphasised. No work has been reported on the anti-corrosive property of *Telfairia occidentalis* rind extract on mild steel. The aim of this work was to investigate the corrosion inhibition effect of *Telfairia occidentalis* rind extract on mild steel corrosion in H_2SO_4 solution.

2. MATERIAL AND METHODS

2.1 Test materials

Mild steel sheet used for this work was obtained from Kenjohnson Metals, Uyo, 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 4 cm coupons for the weight loss method and 2 cm x 4 cm for the hydrogen evolution studies. Mill scales on these coupons were removed by polishing 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 moisture – free desiccator before use in corrosion studies.

2.2 Preparation of *Telfairia occidentalis* rind extract

Fresh rinds of *Telfairia occidentalis* were collected from Itam Market in Uyo, Akwa Ibom State, Nigeria. They were washed and oven – dried at 50°C until constant weight. They were then ground to powder. As reported in literature [15], the dried ground sample of *Telfairia occidentalis* rind was macerated with 90% ethanol for seven days, with intermittent stirring, at room temperature in 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 brownish rind extract in the beaker. Extract concentrations of 0.5 g/L, 1.0 g/L, 1.5 g/L and 2.0 g/L respectively were prepared using 1 M H_2SO_4 solution for both the weight loss and hydrogen evolution studies.

2.3 Phytochemical screening of *Telfairia occidentalis* rind extract

Phytochemical screening of *Telfairia occidentalis* ethanol rind extract was performed using standard procedures reported in literature [16 - 17].

2.4 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 H_2SO_4 solution (blank) and in 1 M H_2SO_4 solution containing 0.5 g/L – 2.0 g/L *Telfairia occidentalis* rind extract (inhibitor), 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 inhibition efficiency I(%) was calculated using the formula [18]:

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

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.

The corrosion rate (CR) was calculated using the equation:

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

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

2.5 Hydrogen Evolution Method

The reaction vessel and procedure for measuring the corrosion process by this method are as described by Abakedi and Asuquo [6].Two mild steel coupons weighing 8.0 g were dropped into 100 ml of 1 M H_2SO_4 solution (blank).The volume of H_2 gas evolved from the corrosion reaction was recorded every 60 seconds for 60 minutes. The same experiment was repeated in the presence of 0.5 g/L – 2.0 g/L *Telfairia occidentalis* rind extract (inhibitor) in 1 M H_2SO_4 solution.

The hydrogen evolution rate R_H was calculated using the equation:

$$R_H\ (cm^3 min^{-1}) = \left(\frac{V_1 - V_0}{t_1 - t_0}\right) \quad (3)$$

where v_1 and v_0 are the volumes of hydrogen gas evolved at time t_1 and t_0, respectively.

The inhibition efficiency by the hydrogen evolution method was obtained through the formula [19]:

$$I(\%) = \left(1 - \frac{R_{Hi}}{R_{H0}}\right) \times 100 \quad (4)$$

where RH_o and RH_i are the rates of evolution of H_2 gas in the absence and presence of extract, respectively, at a specified time.

3. RESULTS AND DISCUSSION

3.1 Results of Phytochemical Screening of *Telfairia occidentalis* Rind Extract

The results of the phytochemical analysis of ethanol *Telfairia occidentalis* rind extract are presented in Table 1.

Table 1. Phytochemical Composition of *Telfairia occidentalis* Rind Extract

Test	Observation	Inference
Frothing	Stable foam formed	Saponin present
Borntrager's	Colour of lower layer turned pink	Anthraquinone present
Dragendorff's	No red precipitate formed	Alkaloid absent
Extract + $FeCl_3$	Dark bluish-black precipitate	Tannin present
Extract + $Pb(CH3COO)_2$	Yellow precipitate formed	Flavonoid present
Extract + HCHO + dil. HCl + KOH	Bulky precipitate formed	Phlobatannin present
Keller Killiani's	No brown ring was formed	Deoxy-sugar absent

3.2 Effect of *Telfairia occidentalis* Rind Extract Concentration on Inhibition Efficiency

The variation of the inhibition efficiency with concentration of rind extract in 1 M H_2SO_4 solution is shown in Fig.1. At a particular temperature, it is observed that the inhibition efficiency increased with increase in rind extract concentration. The maximum inhibition efficiency of the rind extract was

89.00% at extract concentration of 2.0 g/L at 30°C. The effect of *Telfairia occidentalis* rind extract (TORE) on the volume of H_2 gas evolved with time for the mild steel corrosion in 1 M H_2SO_4 at 30°C are shown in Fig. 2. It is observed that increase in the rind extract concentrations led to a decrease in the volume of H_2 gas evolved at a particular time. Table 2 reveals that the calculated values of inhibition efficiency in the presence of TORE increased with increase in extract concentration. The maximum inhibition efficiency was 90.94% at extract concentration of 2.0 g/L. The inhibition efficiencies obtained from both the weight loss and hydrogen evolution methods followed a similar trend. An increase in inhibition efficiency with increase in inhibitor concentration indicates a strong interaction between the mild steel surface and the inhibitor [3].The corrosion inhibiting effect of the extract can be attributed to the phytochemical constituents of the extract. However, It is not clear if the inhibitory effect of the extract is due to particular constituent(s) of the extract or due to a synergistic effect of the constituents. This is because constituents of some extracts (e.g. alkaloid fraction, saponin fraction, etc) are known to be effective as corrosion inhibitors [20].

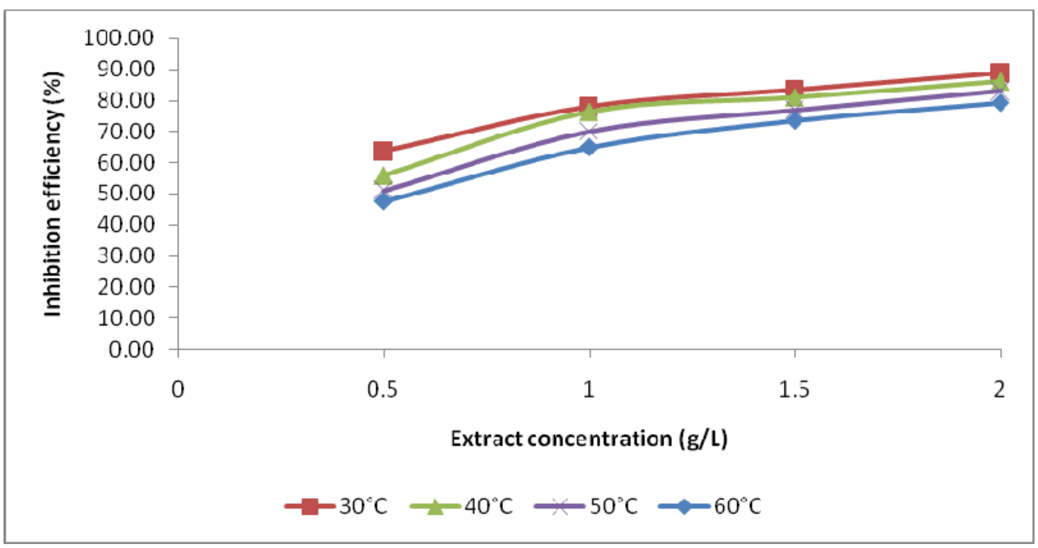


Fig. 1. Variation of inhibition efficiency (%) with *Telfairia occidentalis* rind extract concentration (g/L) for mild steel corrosion in 1 M H_2SO_4 at different temperatures

Table 2. Effect of *Telfairia occidentalis* rind 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)	**H_2 Evolution Rate (cm^3/min)**	**Inhibition Efficiency (%)**
Blank	0.4967	-
0.5	0.1983	60.07
1.0	0.1083	78.19
1.5	0.0717	85.57
2.0	0.0450	90.94

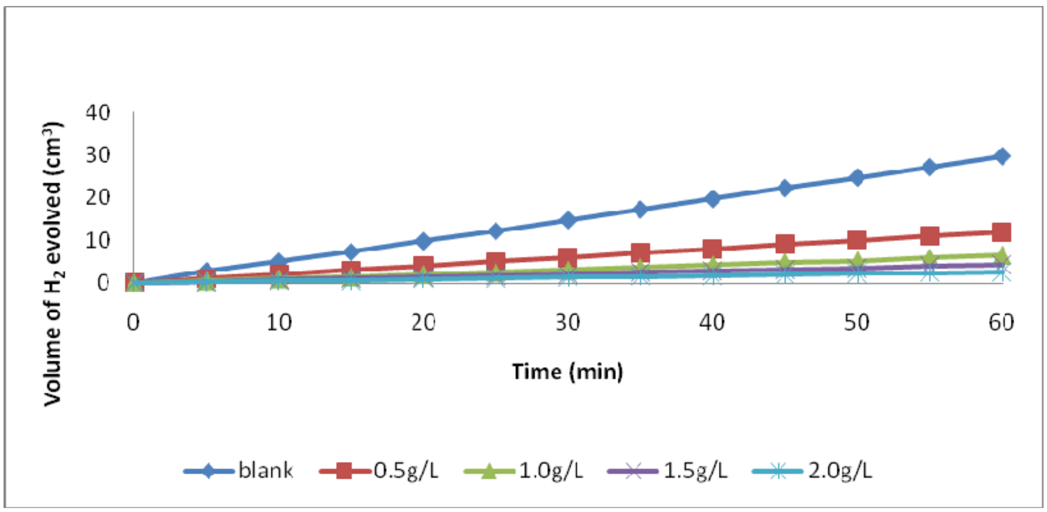


Fig. 2. Variation of volume of H_2 gas evolved (cm^3) with time (min) for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of *Telfairia occidentalis* rind extract at 30°C

3.3 Effect of Temperature on inhibition Efficiency

The effect of temperature on the inhibition effect of *Telfairia occidentalis* rind extract on mild steel corrosion in 1 M H_2SO_4 solution are shown Table 3. It is observed that an increase in temperature resulted in a decrease in the inhibition efficiency. The decrease in inhibition efficiency indicates that the extract was more effective in inhibiting mild steel corrosion at lower temperatures than at higher temperatures. Furthermore, a decrease in inhibition efficiency with increase in temperature signifies physical adsorption of the extract on mild steel surface. The adsorption of an inhibitor at the metal solution interface involves the displacement of water molecules adsorbed at the metal surface [21]:

$$Inh_{(sol)} + nH_2O_{(ads)} \rightarrow Inh_{(ads)} + nH_2O_{(sol)} \quad (5)$$

The inhibitor can combine with freshly generated Fe^{2+} ions on the steel surface to form metal-inhibitor complexes:

$Fe \rightarrow Fe^{2+} + 2e^-$ (6)

$Fe^{2+} + inh \rightarrow (Fe\text{-}Inh)_{ads}$ (7)

If the complex is formed by electrostatic interaction between Fe^{2+} and the charged inhibitor, the bond formed would be weak. On the other hand, if the complex formed is associated with charge sharing or transfer from the inhibitor to the metal, the bond formed would be strong. An increase in the temperature of the system can result in instability of the Fe-Inh complex leading to poor inhibition of corrosion at higher temperatures, if the complex is soluble at high temperature.

Table 3. Weight loss data for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of different concentrations of *Telfairia occidentalis* rind extract at 30°C – 60°C

Extract Concentration	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
Blank	2.5102	5.2078	9.0203	20.8336	-	-	-	-
0.5 g/L	0.9141	2.3008	4.4156	10.9258	63.59	55.82	51.05	47.56
1.0 g/L	0.5555	1.2367	2.7063	7.2313	77.87	76.25	69.99	65.29
1.5 g/L	0.4133	0.9945	2.0883	5.4992	83.54	80.90	79.85	73.60
2.0 g/L	0.2758	0.7266	1.5328	4.3109	89.01	86.05	83.01	79.31

3.4 Thermodynamic Consideration

The alternative formulation of Arrhenius equation was used to obtain the activation energy (E_a) values for mild steel corrosion in 1 M H_2SO_4 in the presence and absence of TORE [17]:

$$\ln CR = \frac{-E_a}{RT} + \ln A \quad (8)$$

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

Plots of ln CR against 1/T for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of different concentrations of TORE are presented in Fig. 3. The values of the activation energies (E_a)

were obtained from the gradients of the plots and are presented in Table 4. Table 4 reveals that the E_a values in the presence of the extract were higher than the E_a value of the blank (57.355 kJ/mol), indicating an increase in the energy barrier of the reaction in the presence of the TORE when compared to the blank. These higher activation energies imply slower reaction rate for the corrosion of mild steel in H_2SO_4 solutions in the presence of the extract than in its absence. The higher E_a values in the H_2SO_4-TORE medium signifies physical adsorption [22]. It can therefore be proposed that *Telfairia occidentalis* rind extract physically adsorbed onto the mild steel surface.

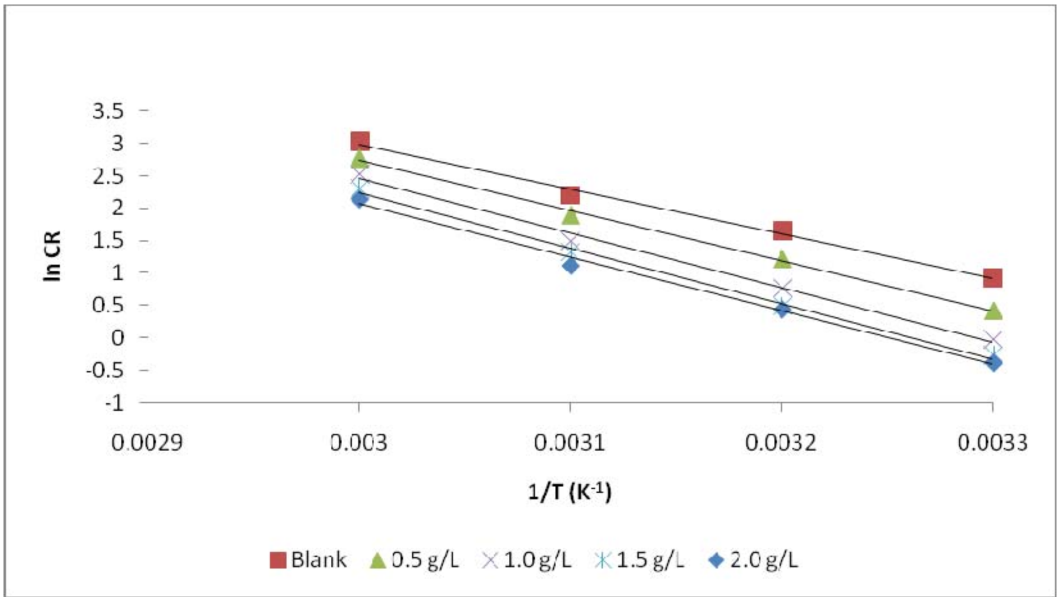


Fig.3. Plot of ln CR against 1/T (Arrhenius plot) for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of *Telfairia occidentalis* rind extract

In order to establish the mode of adsorption of the inhibitors on the mild steel surface, the values of enthalpy of activation (ΔH^o_{ads}) and entropy of activation (ΔS^o_{ads}) were obtained from an alternative formulation of the transition state equation [6]:

$$\ln\left(\frac{CR}{T}\right) = \left[\ln\left(\frac{R}{Nh}\right) + \frac{\Delta S^{\circ}_{ads}}{R}\right] - \frac{\Delta H^{\circ}_{ads}}{RT} \qquad (8)$$

where CR is the corrosion rate, T is temperature in Kelvin, R is the universal gas constant, N is Avogadro's number, A the Arrhenius pre-exponential factor, while h is the Planck's constant. Fig 4 indicates the plots of ln (CR/T) against 1/T for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of different concentrations of TORE. The values of ΔH^o_{ads} were obtained from slopes and intercepts of the plots and are presented in Table 4. The values of ΔH^o_{ads} in the blank and in the presence of the extract were positive. The positive values of ΔH^o_{ads} both in the blank and in the presence of extracts signify the endothermic nature of the mild steel corrosion process. It has been explained by some workers [23] that since in an endothermic reaction the molecules absorb heat from the surrounding, therefore increasing the number of molecules (by increasing the extract concentration) leads to an increase in the amount of heat absorbed. Hence, the observed increase in the values of ΔH^o_{ads} as extract concentration increases. The negative values of ΔS^o_{ads} indicate a decrease in the disorderliness of the adsorption process of TORE on mild steel surface.

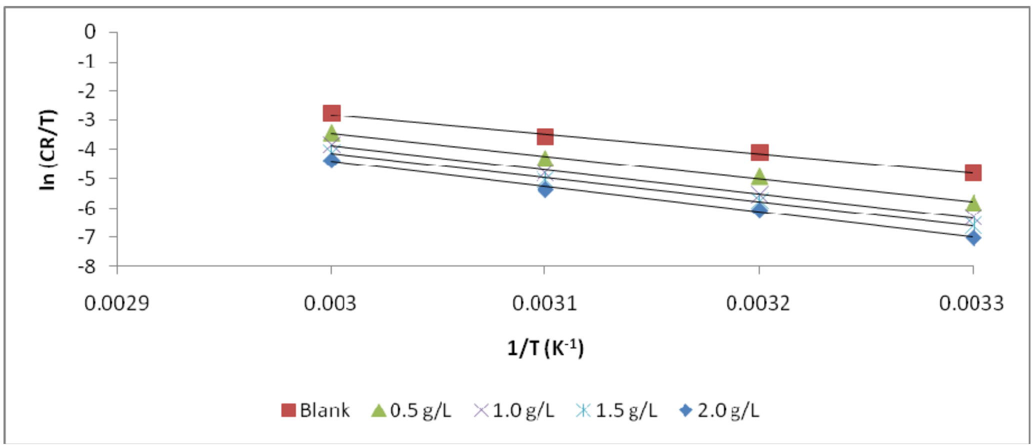


Fig.4. Plot of ln (CR/T) against 1/T (Transition state plot) for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of *Telfairia occidentalis* rind extract

Table 4. Calculated values of thermodynamic parameters for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of *Telfairia occidentalis* rind extract

Extract Concentration	E_a (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (JK^{-1} mol^{-1})
Blank	57.355	54.711	-56.888
0.5 g/L	67.305	64.664	-32.161
1.0 g/L	70.524	67.885	-26.216
1.5 g/L	70.728	68.088	-27.746
2.0 g/L	76.449	72.142	-17.618

3.6 Adsorption Studies

Several adsorption isotherms such as the Langmuir,Temkin, Freundlich and El-awady isotherms were tested using the weight loss measurements. The best fit for the adsorption of TORE on mild steel surfaces were found to obey the Langmuir adsorption isotherm given as [24]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (10)$$

where θ is the degree of surface coverage, C is the concentration of inhibitor and K_{ads} is the equilibrium constant of the adsorption process. Fig. 5 reveals linear plots of C/θ against C with gradient of 'n' and $1/K_{ads}$ as intercepts. Values of K_{ads} (Table 5) were found to decrease with increase in temperature, indicating that TORE became loosely adsorbed onto the mild steel surface with increase in temperature.

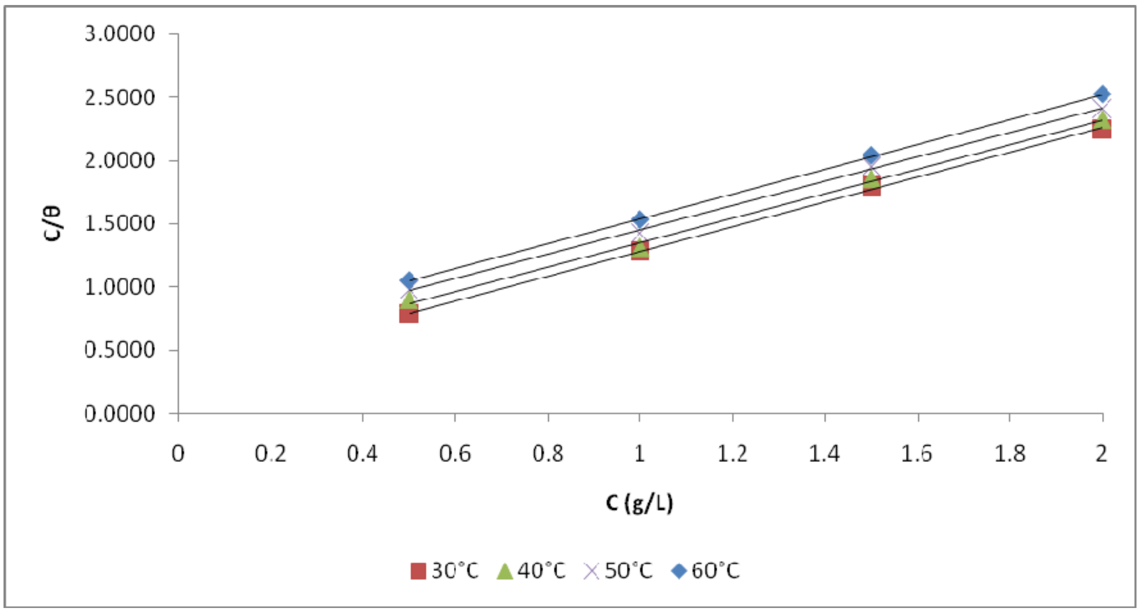


Fig.5. Plot of C/θ against C (Langmuir isotherm) for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of *Telfairia occidentalis* rind extract

The standard free energy of adsorption (ΔG^{o}_{ads}) was calculated using equation (11) [3]:

$$K_{ads} = \frac{1}{55.5}\exp\left(\frac{-\Delta G^{o}_{ads}}{RT}\right) \qquad (11)$$

where R is the universal gas constant, 55.5 is the molar concentration of water in the solution, T is the temperature in Kelvin while K_{ads} is the equilibrium constant of adsorption.

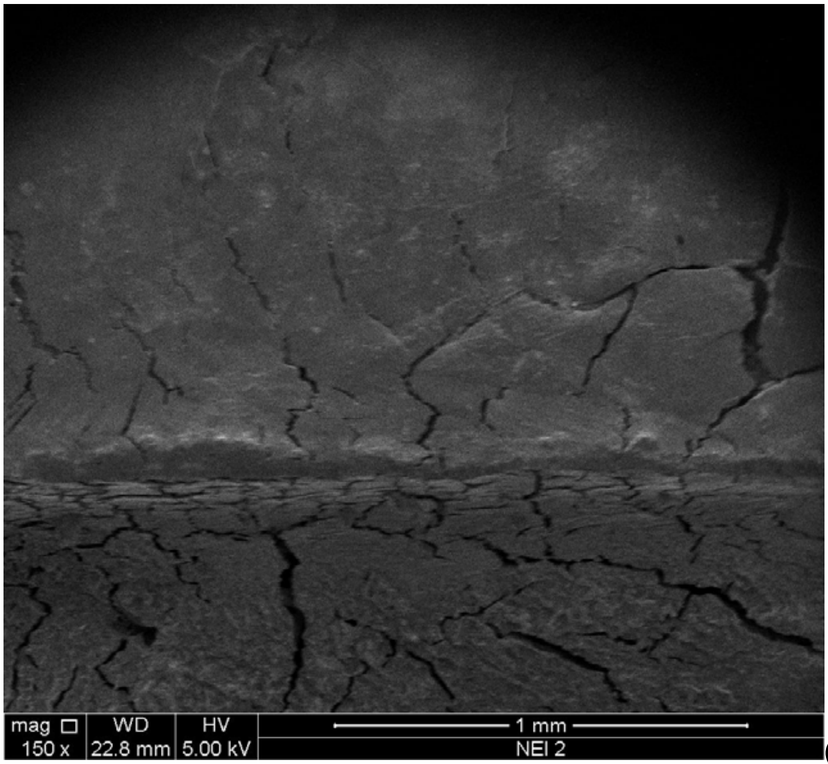
Table 5. Some parameters of the linear regression of Langmuir adsorption isotherm for mild steel corrosion in 1 M H_2SO_4 containing *Telfairia occidentalis* rind extract

Temperature	R^2	n	l/K_{ads} (g/L)	K_{ads} ($g^{-1}L$)	$\Delta G°_{ads}$ (kJ mol^{-1})
303K	0.9990	0.98	0.3050	3.2787	-13.110
313K	0.9977	0.97	0.3893	2.5687	-12.908
323K	0.9991	0.96	0.4891	2.0446	-12.707
333K	0.9999	0.98	0.5563	1.7976	-12.744

The negative values of ΔG^o_{ads} shown in Table 5 indicate that mild steel corrosion inhibition by TORE occurred spontaneously. Values of ΔG^o_{ads} less negative than -20 kJ mol^{-1} indicate physical adsorption while values of ΔG^o_{ads} more negative than -40 kJ mol^{-1} are attributed to chemical adsorption of inhibitor onto the metal surface [25 – 26]. Since the values of ΔG^o_{ads} obtained in this study are less negative than -20 kJ mol^{-1}, physical adsorption of the extract onto mild steel surface has been proposed. This is further supported by a decrease in the inhibition efficiency with increase in temperature.

3.7 Scanning Electron Microscopy (SEM) Analysis

SEM analysis was carried out to investigate the surface morphology of mild steel coupons immersed in 1 M H_2SO_4 solution in the absence and presence of 2.0 g/L *Telfairia occidentalis* rind extract (TORE) for four (4) hours at 30°C. Fig. 6(a) reveals a damage mild steel surface due to severe corrosion of mild steel in the blank. Conversely, Fig. 6(b) reveals that mild steel surface corroded less in the presence of the extract relative to the blank, as reflected in a smoother surface. This indicates that the extract protected the mild steel surface by adsorbing on it.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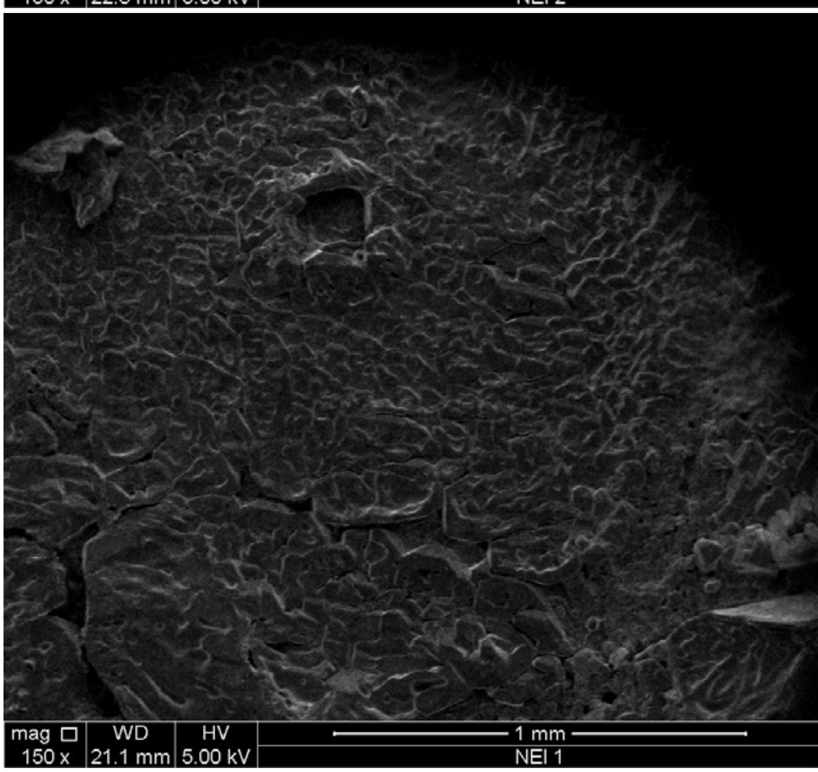
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1 mm
NEI 1
(B)

Fig. 6. SEM image of mild steel surface immersed for 4 hours in (a) 1 M H_2SO_4 solution (Blank) and (b) 1 M H_2SO_4 solution containing 2.0 g/L *Telfairia occidentalis* rind extract

4. CONCLUSION

The following conclusions can be drawn from this work: *Telfairia occidentalis* rind extract is a good inhibitor for mild steel in H_2SO_4 solution at 30°C – 60°C. The inhibition efficiency increased with increase in extract concentration but decreased with increase in temperature. The higher values of activation energy (E_a) in the extract relative to the blank coupled with a decrease in inhibition efficiency with increase in temperature in addition to the $\Delta G°_{ads}$ of the process being less negative than -20 kJ mol^{-1}, physical adsorption has been proposed for the adsorption of the extract onto mild steel surface. The positive values of $\Delta H°_{ads}$ and the negative values of $\Delta G°_{ads}$, respectively, indicate the endothermic and spontaneous nature of adsorption of the extract on mild steel surface. The adsorption of the extract on mild steel surface obeyed the Langmuir adsorption isotherm.

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