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ADSORPTION MECHANISM AND SYNERGISTIC INHIBITIVE EFFECT OF *Telfairia occidentalis* FOR THE CORROSION OF MILD STEEL IN HCl

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ABSTRACT

The extract from the leaves of *Telfairia occidentalis* was investigated as corrosion inhibitor in 1MHCL solution using gravimetric technique at the temperature range of 303-333K. The joint effect of iodide ion and extract of *Telfairia occidentalis* was also investigated. From the result obtained, values of inhibition efficiency ranged from 44.3 to 89.8%, 63.4 to 90.07%, 80.4 to 91.63% and 82.6 to 94.0% at temperature of 303, 313, 323 and 333K respectively, showing that inhibition efficiency of the extract of *Telfairia occidentalis* increased with increasing temperature. The increase in inhibition efficiency as temperature increased suggests that mechanism of adsorption is chemisorption. Also, the inhibition efficiency of the extract increased synergistically on addition of potassium iodide (KI). The inhibition potential of extract of *Telfairia occidentalis* is attributed to presence of tannin, phlobatannin, flavonoid, alkaloid, cyanogenic glycosides and amino acid in the extract. The heat of adsorption value obtained ranged from 51.70 to 33.89KJ mol^{-1} indicating the adsorption of the inhibitor on surface of mild steel is endothermic. The adsorption behavior of the inhibitor was well described by Langmuir and Frumkin isotherm models.

Keywords: Corrosion, mild steel, inhibition, adsorption, *Telfairia occidentalis.*

INTRODUCTION

Industrial processes such as pickling and descaling use acid solutions for removal of undesirable scale or rust from metal surfaces. During these processes, there is contact between these metals and the acid solution resulting to gradual destruction of the metals. This has brought about the use of inhibitor which can counteract the corrosive action of such aggressive environments [1, 2, 3, 4]. Among the various methods of controlling corrosion, the use of inhibitors is one of the most practical ways for protecting metals and alloys against corrosion especially in acidic environment [5, 6]. Adsorption inhibitors are usually organic substances containing polar functional groups with nitrogen, sulphur and or oxygen in the conjugated system. These substances adsorbs on the metal surface with the polar group acting as the reaction centre for the adsorption process and the resulting adsorption layer functions as a barrier, isolating the metal from the corrodent. However, known hazard effects, of most synthetic corrosion inhibitors are the motivation for the use of natural product of plant origin as corrosion inhibitor. Extract of naturally occurring products are environmentally acceptable, readily available and biodegradable in nature [7, 8]. Also, synergistic effects of addition halide ions to acid solution containing organic compounds as inhibitor are often carried out to enhance the effectiveness of such organic compound. Telfairia occidentalis commonly known as fluted pumpkin is a creeping vegetable shrub that spread low across the ground with large lobed leaves, and long twisting tendrils [9]. It belongs to the family of Cucurbitacae. In West African sub-region, the leaves of Telfairia occidentalis are consumed for its nutritious value. The aim of the present study is to investigate the inhibitive potential of extract of Telfairia occidentalis leaves on mild steel corrosion in HCl, as well as synergistic effect of potassium iodide using gravimetric method.

Materials and methods

Materials Preparation: Mild steel of composition (wt %) Mn (0.6), P (0.36), C (0.15), Si (0.03) and Fe (98.86) were used for this study. The sheet was mechanically pressed cut to form different coupons, each of dimension, 3×3×0.1cm. Each coupon was degreased by washing with ethanol, rinsed with acetone and allowed to dry in the air before preservation in a dessicator. All reagents used for the study were analytical grade and double distilled water was used for their preparation.

Extraction of Plant Extract: Stock solutions of the plant extract were prepared by boiling weighed amount of the dried and ground leaves of Telfaria occidentalis for 2hours, under reflux, in 1MHCl. After 2 hours, the solution was cooled and filtered. The stock solution concentrations were determined by drying the residue and weighing it to obtain the amount of material extracted. From the stock solution obtained, inhibitor test solutions were prepared in the concentration range of 25-1000mg/l by diluting with 1M HCl.

Chemical Analysis: Phytochemical analysis of the ethanol and aqueous extracts of Telfaria occidentalis was carried out according to the method reported by [10].

Gravimetric Experiment: Two pre-weighed mild steel coupon was completely immersed in 250ml of the test solution in an open beaker. The beaker was inserted into a water bath maintained at 30^{o}C. After 2 hours, the coupon was withdrawn from the test solution, washed with washing liquor, rinsed in acetone and dried in air before reweighing. The weight loss was taken to be the difference between the weight of the coupon after immersion and its initial weight. The experiment was repeated at 40, 50 and 60^{o}C respectively, and in each case the test was conducted in aerated solutions and run in duplicate. From the weight loss results, the inhibition efficiency (% I) of the inhibitor, degree of surface coverage (θ) and corrosion rates (CR) were determined using equations 1, 2, and 3 respectively.

$$\% I = \left(1 - \frac{W_1}{W_2}\right) \times 100 \quad (1)$$

$$\theta = 1 - \frac{W_1}{W_2} \quad (2)$$

$$\mathrm{CR}\ (\mathrm{gcm^{-2}h^{-1}}) = \frac{\mathrm{W}}{\mathrm{At}} \quad (3)$$

Where W_1 and W_2 are the weight losses (g/dm^3) for mild steel in the presence and absence of inhibitor, A is the area of the mild steel coupon (cm^2), t is the time of immersion (hours) and W is the weight loss of mild steel after time t.

RESULTS AND DISCUSSION

Phytochemical analysis: Table 1 shows the phytochemical constituents of aqueous and ethanol extract of Telfairia occidentalis. The results obtained indicate that tannin, phlobatannins, flavonoid, alkaloids, amino acid were present in the ethanol extract of

Telfairia occidentalis but absent in the aqueous extract of Telfairia occidentalis. This indicates that the inhibition efficiency of the extract is due to the presence of these phytochemical components.

Table 1: Phytochemical constituents of aqueous and ethanol extracts of Telfairia occidentalis.

Phytochemicals	Aqueous extract	Ethanol extract
Tannins	-	+++
phlobatannins	-	++
Flavonoid	-	++
Alkaloid	-	+++
Cyanogenic glycosides	-	-
Amino acid	-	++

Effect of inhibitor concentration: The variation of average weight loss and inhibition efficiency with different concentrations of Telfaria occidentalis extract for corrosion of mild steel in 1MHCl at 30°C is shown in Figures 1 and 2 respectively. It can be seen from Fig. 1 that weight loss of mild steel decreased with increase in the concentration of Telfaria occidentalis extract, indicating that this extract inhibit the corrosion of mild steel in HCl.

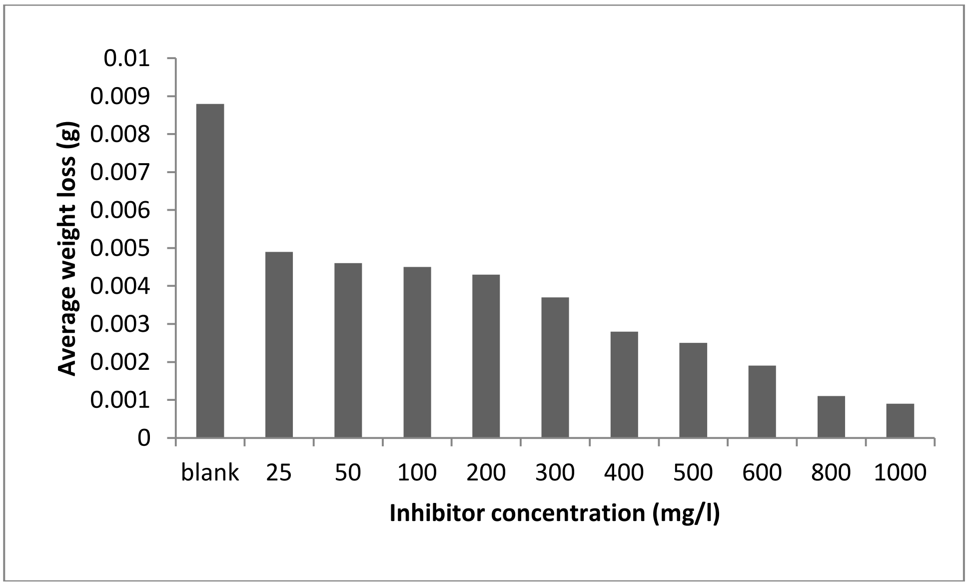

Figure 1: Variation of weight loss of mild steel in 1MHCl with different concentrations of Telfairia occidentalis extract at 30°C.

From Fig. 2, inhibition efficiency increased from 44.3 to 89.8% as inhibitor concentration increased from 25 to 1000mg/l. The result shows that Telfaria occidentalis extract was effective in retarding the rate of corrosion of mild steel in the examined corrosive media. According to Oguzie [11], the increase in inhibition efficiency with an increase in the extract concentration is due to a higher degree of surface coverage resulting from enhanced inhibitor adsorption. The presence of phytochemical constituents in the plant extract such as tannins, alkaloids, protein, amino acids and pigments are also known to exhibit the inhibiting action and their adsorption on the metal surface reduced the surface area available for corrosion [12].

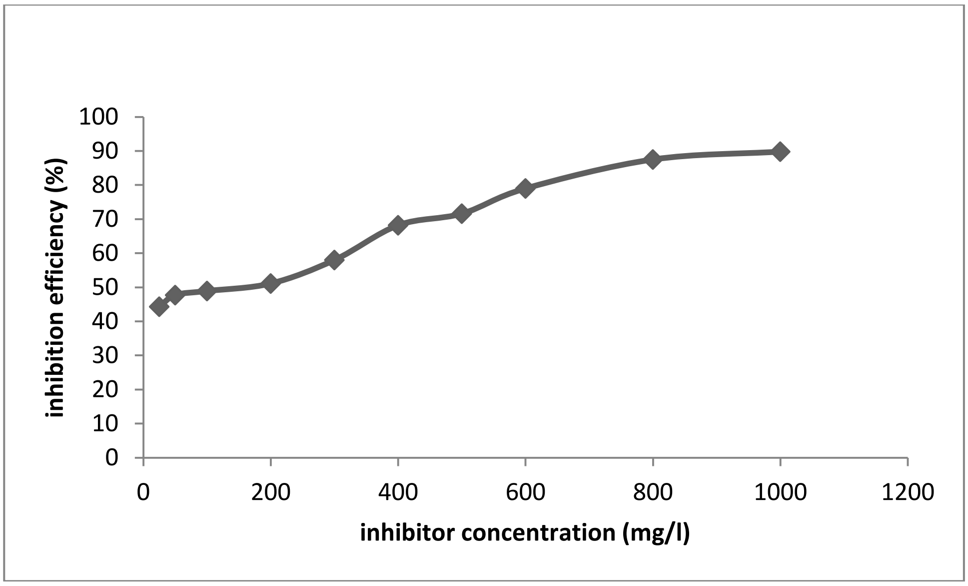

Figure 2: Variation of inhibition efficiencies with different concentrations of Telfairia occidentalis extract in 1MHCL at 30°C.

Effect of temperature: The effect of temperature (T) on the rate of corrosion (CR) of mild steel was investigated using Arrhenius equation (4) [3, 13].

$$CR = Aexp(-{}^{E_a}/_{RT}) \quad (4)$$

Where CR is the corrosion rate of mild steel, A is Arrhenius or pre-exponential factor, E_a is the activation energy, R is the gas constant and T is the temperature. Taking logarithm of both sides of Equation (4), yields Equation (5).

$$\log(CR) = logA - E_a/2.303RT \quad (5)$$

A linear graph was obtained by plotting $\log(CR)$ against 1/T as shown in Figure (3).

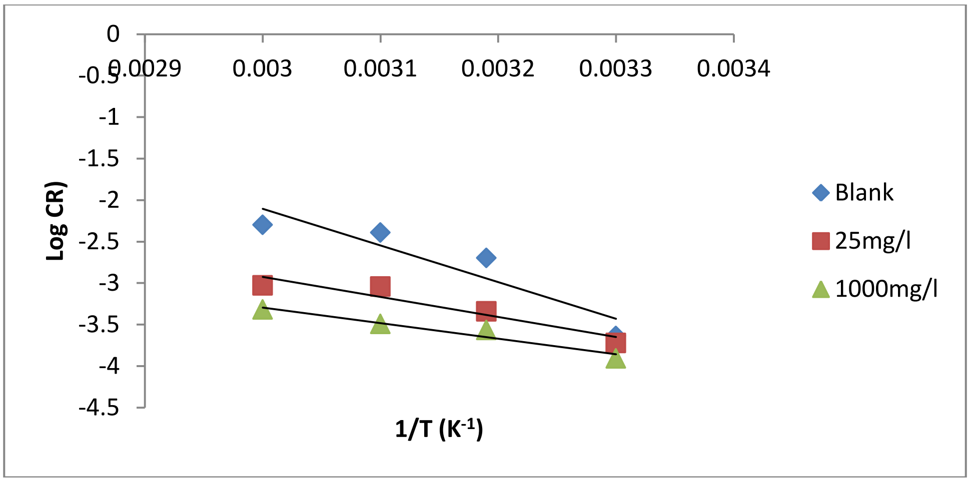

Figure 3: Activation energy plot for the corrosion of mild steel in 1MHCl.

Values of activation energy obtained from the slope of the linear plot ranged from 84.61 to 78.47Jmol^{-1} as presented in Table 2. According to Oguzie [11], unchanged or lowered value of E_a in inhibited system compared to the blank is indicative of chemisorption possibly because some of the energy is used up in the chemical reaction. E_a tends to decrease in the presence of an inhibitor by decreasing the available reaction area (geometric blocking effect), thereby decreasing the corrosion rate. The corrosion rates of mild steel in the absence and presence of Telfaria occidentalis extract and inhibition efficiencies of various concentrations of Telfaria occcidentalis at different temperatures were recorded in Table 1. The results obtained showed that the rate of corrosion of mild steel decreased with increase in the concentration of inhibitor but increased with increase in temperature, while the inhibition efficiency of extract of T. occidentalis increased with increasing temperature. This suggests that the adsorption of extract of T.occidentalis on mild steel surface is consistent with the mechanism of chemical adsorption. According to Ebenso et al. [14], for physical adsorption mechanism, inhibition efficiency of an inhibitor decreases with temperature, while for chemical adsorption mechanism, inhibition efficiency increases with temperature.

Table 2: Corrosion rates and inhibition efficiencies of different Telfaria occidentalis extract at different temperature.

System (mg/l)	Corrosion rate $\times 10^{-4}$ ($gcm^{-2}h^{-1}$)				Inhibition efficiency (%)			
	30^{o}C	40^{o}C	50^{o}C	60^{o}C	30^{o}C	40^{o}C	50^{o}C	60^{o}C
Blank	2.30	20.75	40.63	53.74				
25	1.28	7.59	9.08	9.37	44.3	63.4	80.4	82.6
1000	1.18	2.72	3.22	4.81	89.8	90.07	91.63	94.0

The transition state equation was used calculate some thermodynamic parameters (enthalpy of adsorption, ΔHads and entropy of adsorption ΔSads) according to Equation (6) [6].

$$CR/_T = R/_{N_A h} \times \exp\left(^{\Delta S_{ads}}/_{2.303R}\right) \times \exp\left(^{\Delta H_{ads}}/_{RT}\right) \qquad (6)$$

Where N_A is the Avogadro's number, h is plank's constant while other terms retain their previous meanings.
Taking logarithm of both sides of Equation (6), Equation (7) is obtained.

$$\log\left(CR/_T\right) = log\, R/_{N_A h} + {}^{\Delta S_{ads}}/_{2.303R} - {}^{\Delta H_{ads}}/_{2.303RT} \qquad (7)$$

A linear graph was obtained by plotting log (CR/T) against 1/T as shown in Figure 4 with slopes and intercepts equal to $-\Delta H_{ads}/2.303R$ and ($\log R/N_A h + \Delta S_{ads}/2.303R$) respectively.

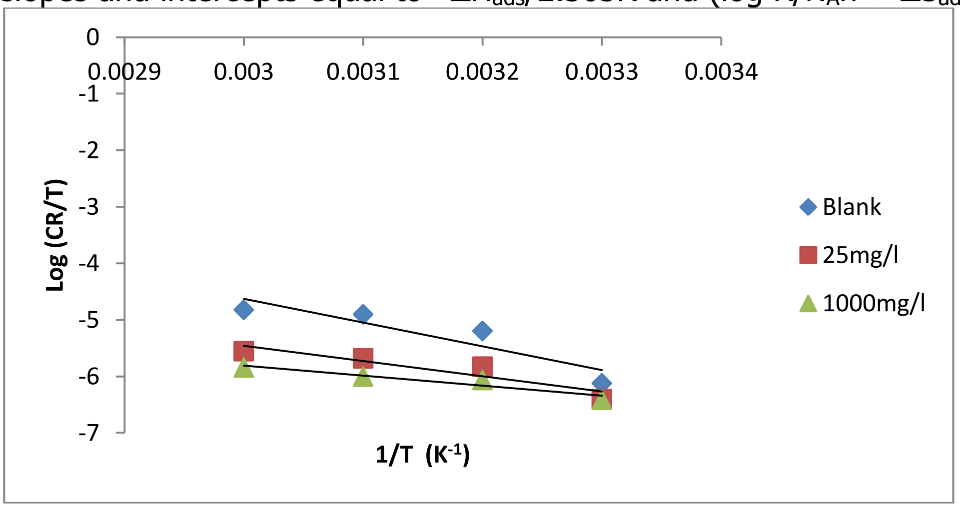

Figure 4: Plot of log (CR/T) against 1/T for corrosion of mild steel in 1MHCl.

Calculated values of ΔH_{ads} and ΔS_{ads} obtained from slope and intercept of the linear graph are presented in Table 3. Enthalpy of adsorption ΔH_{ads} decreased from 51.70 to 33.89KJmol^{-1} as inhibitor concentration increased from 25 to 1000mg/l. This positive value of ΔH_{ads} indicates that adsorption of extract of Telfaria occidentalis on surface of mild steel is endothermic, while the entropy of adsorption ΔS_{ads} decreased from -147.01 to -207.19 KJ mol^{-1} as inhibitor concentration increased from 25 to 1000mg/l, suggesting that there was association of the inhibitor's molecules instead of dissociation [15].

Table 3: Thermodynamic parameters for corrosion of mild steel in 1MHCL

System mg/l	E_a KJ mol^{-1}	R^2	ΔH_{ads}KJ/mol	ΔS_{ads} J/mol	R^2
Blank	84.61	0.852	80.28	152.20	0.823
25	80.22	0.896	51.70	-147.01	0.860
1000	78.47	0.942	33.89	-9.61	0.905

Adsorption isotherms

The data obtained for degree of surface coverage was used to test for applicability of Langmuir and Frumkin isotherm.

Langmuir adsorption isotherm can be expressed according to Equation (8) [16].

$$\frac{C}{\theta} + \frac{1}{K} + C \qquad (8)$$

Where C is the inhibitor concentration, θ is degree of surface coverage and K is the adsorption equilibrium constant. Taking logarithm of both sides of Equation (8) yields Equation (9).

$$\log(C/\theta) = logC - logK \qquad (9)$$

A plot of $\log(C/\theta)$ against $logC$ as shown in Figure 5 yielded straight line, indicating that Langmuir adsorption isotherm was obeyed [17]. Adsorption equilibrium constant K calculated from the intercept of the linear plot was presented in Table 3.

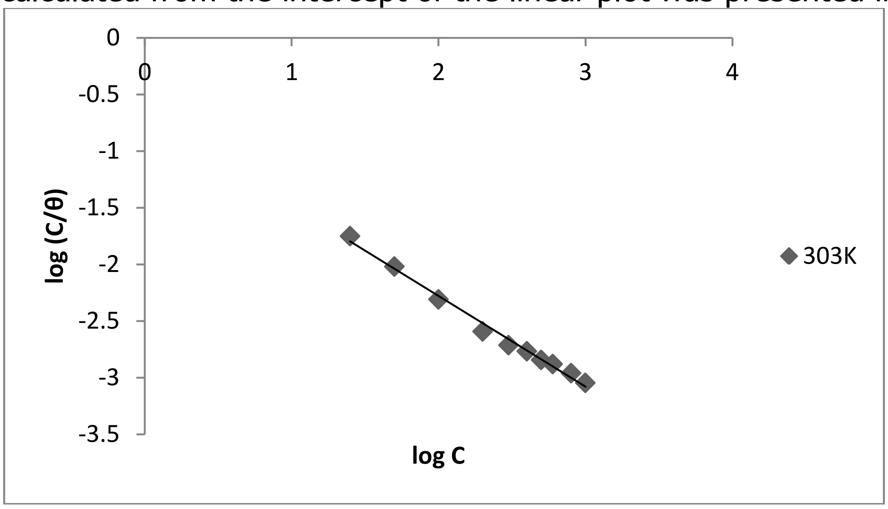

Figure 5: Langmuir adsorption isotherm plot for corrosion of mild steel in 1MHCl

Frumkin adsorption isotherm can be expressed according to Equation (10) [3, 16].

$$\log\{[C] \times (\theta/1-\theta)\} = 2.303logK + 2\alpha\theta \qquad (10)$$

Where ɑ is the lateral interaction term describing the interaction in adsorbed layer? The plot of $\log\{[C] \times (\theta/1-\theta)$ against θ was linear as shown in Figure 6, suggesting that

Frumkin adsorption isotherm was obeyed. The adsorption parameter α calculated from the slope of the graph as recorded in Table 4 was positive indicating the attractive behavior of the inhibitor on the mild steel surface [18, 19].

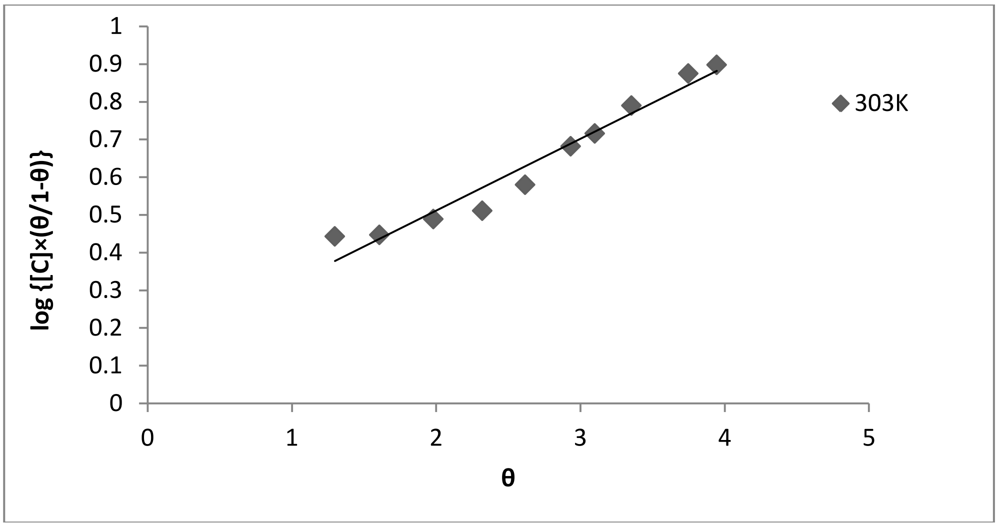

Figure 6: Frumkin adsorption isotherm plot for corrosion of mild steel in 1MHCl

Table 4: Adsorption isotherm parameters for corrosion of mild steel in 1MHCl

Isotherm	Temperature	R^2	LogK	α
Langmuir	303K	0.991	0.680	
Frumkin	303K	0.953	0.056	0.095

Synergistic study

The combined effect of addition of 5mM of potassium iodide (KI) with different concentration of Telfaria occidentalis in 1MHCl was also studied. The result of the study shows that there was a decrease in weight loss and corrosion rate as concentration of the extract with KI increased, resulting in remarkable increase in inhibition efficiency of the extract and surface coverage as shown in Table 5. According to Umoren and Ebenso (2008), synergism of corrosion inhibitors is either due to interaction between components of the inhibitors or due to interaction between the inhibitor and one of the ions present in aqueous solution.

Table 5: Synergistic effects of addition of 5mM KI in 1MHCl containing different concentrations of Telfairia occidentalis extract.

System (mg/l)	Corrosion rate×10^{-3} ($gcm^{-2}h^{-1}$)	Inhibition efficiency (%)	Surface coverage (θ)
Blank	3.39	39.2	0.392
25mg/l +KI	2.63	52.3	0.523
50mg/l +KI	2.45	55.7	0.557

CONCLUSION

This study shows that the extract from leaves of Telfairia occidentalis can be used as excellent inhibitor for mild steel corrosion in 1MHCl. The inhibition efficiency of this extract increased with increasing temperature suggesting chemisorption mechanism. Also, the inhibition efficiency of these extract was found to increase in the presence of KI. The phytochemical component in the extract of this inhibitor was attributed for its inhibition efficiency. The adsorption of Telfairia occidentalis molecules on mild steel surfaces was found to obey Langmuir and Frumkin adsorption isotherm.

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