CORROSION INHIBITION OF ALUMINUM COUPON IN HCL SOLUTION USING *TELFAIRIA OCCIDENTALIS* STALK EXTRACT.

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Abstract
This work studied the corrosion inhibition of aluminum using ethanoic extract of *Telfairia occidentalis* stalk. Significance of this work is that locally sourced biomass will be used to inhibit corrosion of Aluminum coupon in HCL solution. The aluminum coupon was subjected to corrosion with 0.1M and 0.2M HCL solutions and gravimetric method was used to study the corrosion rate. Phytochemical analysis was done on the stalk to ascertain its inhibition potential. Effect of inhibitor concentration, and time on both inhibition efficiency and corrosion rate was studied. Kinetics and thermodynamic studies were done. It was observed that *Telfairia Occidentali s*talk contains saponin and tannins which indicates inhibition potency of the sample. Inhibition efficiency was found to increase as inhibitor concentration was increased while corrosion rate decreased. As time was increased, it was observed that weight loss increased while corrosion rate decreased. The reaction was found to be first order while adsorption isotherm followed Langmuir model. Negative Gibbs free energy suggested that the reaction was spontaneous, while negative enthalpy confirmed it to be exothermic in nature. This study has proved that *Telfairia Occidentalis* stalk extract inhibited the corrosion of Aluminum coupon in HCL solution.

Keywords: Aluminum, Corrosion, Inhibitor, *Telfairia Occidentalis,* Weight loss

1.0 Introduction
Corrosion has a great impact in the industries, which makes it a crucial obstacle that needs to be solved. The need for corrosion inhibitors is sometimes a must in order to control unacceptably high corrosion rates. The use of inhibitors is one of the most efficient methods for protection against corrosion especially in acid solutions to avoid metal dissolution [1]. In addition to selecting corrosion resistant alloys and using internally lined pipes and/or vessels, chemical inhibition is a commonly used approach to control internal corrosion reactions due to the various corrosive environments. Corrosion inhibitors have been used massively in industries in order to reduce the corrosion rate of many metals. The few thousands of articles and

publications issued about corrosion and its prevention every year makes one understand the importance of corrosion prevention [2].

An inhibitor is a substance (or a combination of substances) added in a very low concentration to treat the surface of a metal that is exposed to a corrosive environment that terminates or diminishes the corrosion of a metal. These are also known as blockers, due to their adsorption properties.

The term "green inhibitor" or "eco-friendly inhibitors" refers to the substances that have biocompatibility in nature. The inhibitors like plant extracts presumably possess biocompatibility due to their biological origin [3]. Pumpkin is a tropical vine grown in West Africa such as Ghana and Nigeria as leafy vegetable and for its edible seeds. The plant is drought-tolerant, dioeciously perennial that is usually grown trellised. The young shoots and leaves of the female plant are the main ingredients of a Nigeria soup, edikang ikon. The plant is cultivated largely in many parts of Nigeria more especially in Ebonyi State, where the soil supports its growth. Common names of the plant include fluted gourd, fluted pumpkin and Ugu [4].

2.0 Materials and methods

Aluminum sheet, hydrochloric acid solution, pumpkin stalk extract, distilled water, water bath, Gallenkamp USA electronic weighing balance.

2.1 Preparation of stalk extract

The fresh stalk of pumpkin (*Telfairia Occidentalis*) was harvested in a local farm in Nkwelle Ezunaka of Anambra state, washed under running water to remove dust and other particles that may act as contaminants. It was shade dried for 24 hours to remove moisture, pulverized into tiny pieces to increase surface area. Stalk was processed by cold extraction method using 99% absolute ethanol as solvent.

2.2 Corrosion study for the inhibition process

Gravimetric method (weight loss) was used for the corrosion study according to the work done by Mohammed, 2011 [5]. In this method, the weight of the coupon was taken initially after which it was suspended in HCL solution. The final weight of the coupon was taken when the time elapsed. The weight loss was calculated as the difference in weight.

The corrosion rate, surface coverage and the inhibition efficiency (%IE) were calculated using formulae below;

$$CR\left(\frac{mm}{y}\right) = \frac{87.6x10^4 W}{D.A.T} \quad (1)$$

$$Surface\ coverage = \frac{(CR_U - CR_i)}{CR_u} \quad (2)$$

$$Inhibition\ Efficiency = \frac{CR_u - CR_i)}{CR_u} x\ 100 \quad (3)$$

Where W is the weight loss (mg), CR_u and CR_i are the corrosion rates of the aluminum coupons in absence and presence of inhibitor respectively, D is the density of aluminum coupon. A is the sectional area (Cm^2) and T is the contact time (hr).

3.0 Results and Discussions

3.1 Effect of inhibitor concentrations on the corrosion inhibition

Figures 1 shows the effect of inhibitor concentration on the weight loss at different temperatures. The result shows that weight loss decreased as the inhibition concentration increased and equally decreased as temperature decreased.

Figure 2 shows the effect of inhibition concentration on the corrosion rate at different temperatures. It was observed that corrosion rate decreased as temperature decreased and inhibitor concentration increased. This is in line with the work done by Nwabanne and Okafor 2011 [6].

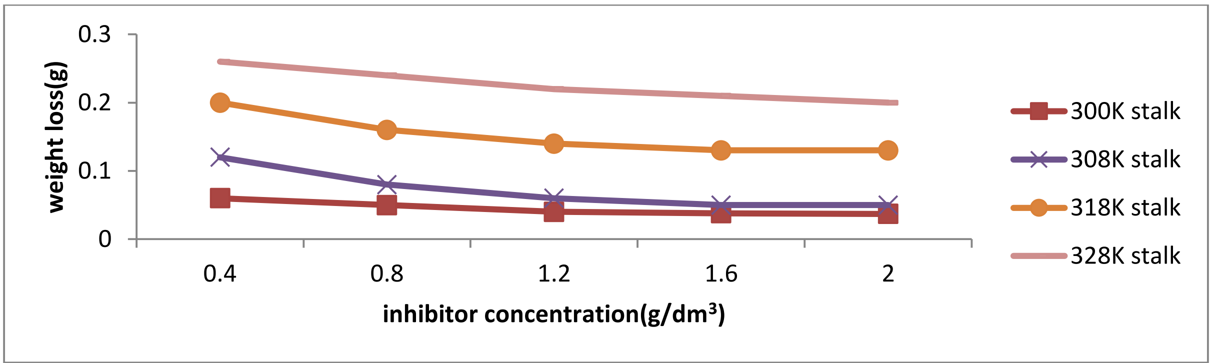

Figure 1: Effect of inhibitor concentrations at various temperatures on the weight loss.

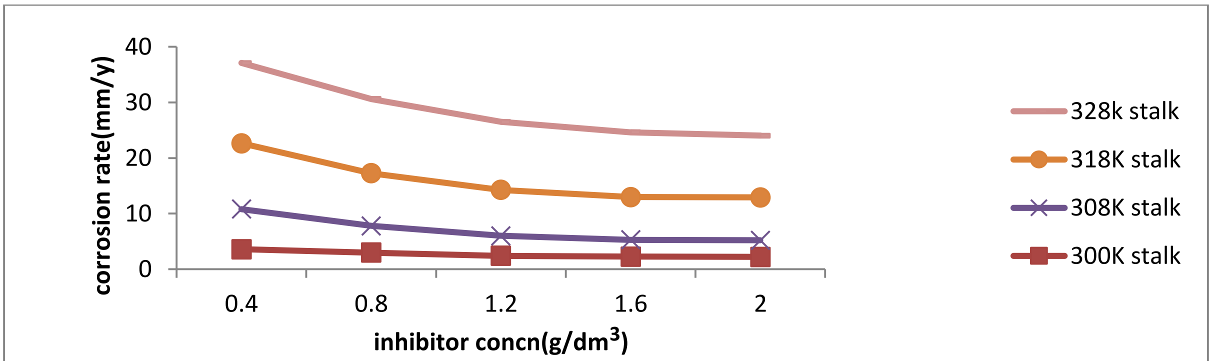

Figure 2: Effect of inhibitor concentrations on the Corrosion rate at different temperatures.

Figure 3 shows the effect of inhibition concentration on inhibition efficiency at different temperatures. It was observed that inhibition efficiency increased with an increase in inhibition concentration and decreased with an increase in temperature. This means that the stalk extract adsorbed on the surface of the aluminum by physical adsorption mechanism thereby inhibiting further corrosion attack. This was in agreement with the work done by Eddy et al., 2009 [7].

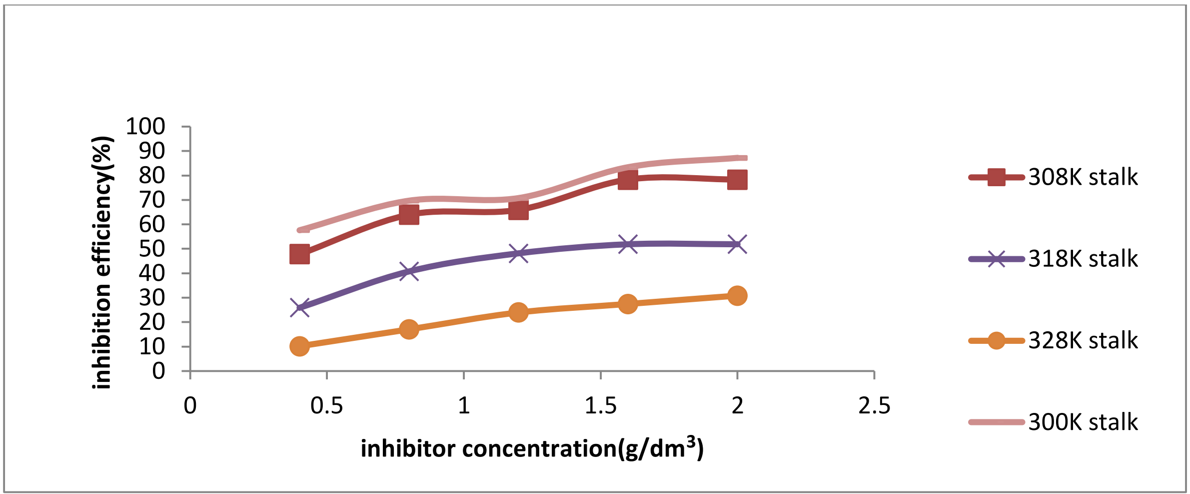

Figure 3: Effect of inhibitor concentration on inhibition efficiency at different temperatures.

The increase in the temperature of the system causes a decrease in the inhibition efficiency and surface coverage and also increase in the corrosion rate of the aluminum specimen. This may be due to the fact that the film forming at the aluminum surface becomes weak as the temperature increases.

3.2 Effect of time on the corrosion inhibition

Figures 4 and 5 show the effect of time on weight loss for different inhibitor concentrations for 0.1M and 0.2M HCL solutions. The results show that weight loss increased as time was increased with and without the inhibitor. It was equally observed that weight loss decreased as inhibitor concentration increased. This shows that the extract of *Telfairia Occidentalis* inhibits the corrosion of aluminum in 0.1M and 0.2M HCL corroding environments [8].

It was observed from Figures 6 and 7 that effect of time on corrosion rate had reverse effect. Increase in time decreased the corrosion rate. Corrosion rate was equally seen to decrease as the concentration of inhibitor increased for both 0.1M and 0.2M HCL solutions.

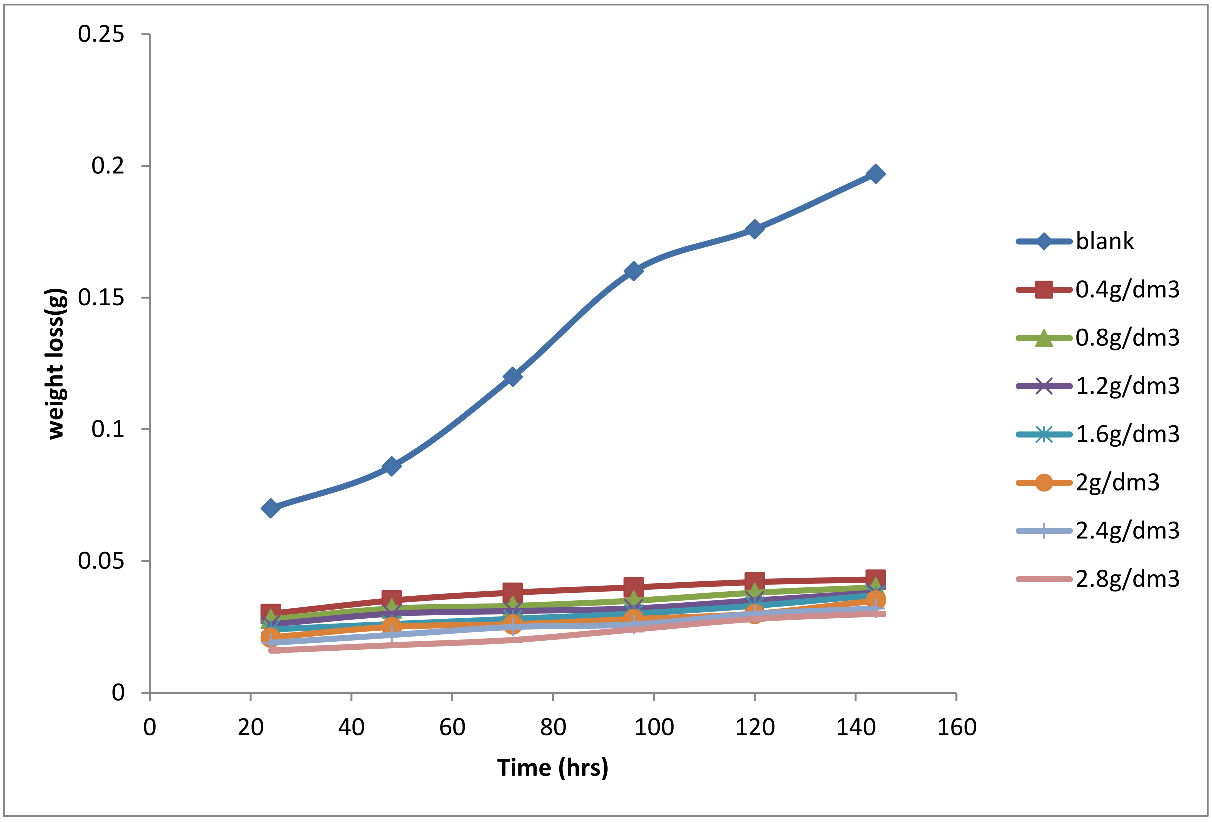

Figure 4: weight loss of blank and different concentrations of stalk extract with 0.1M HCl at 300k.

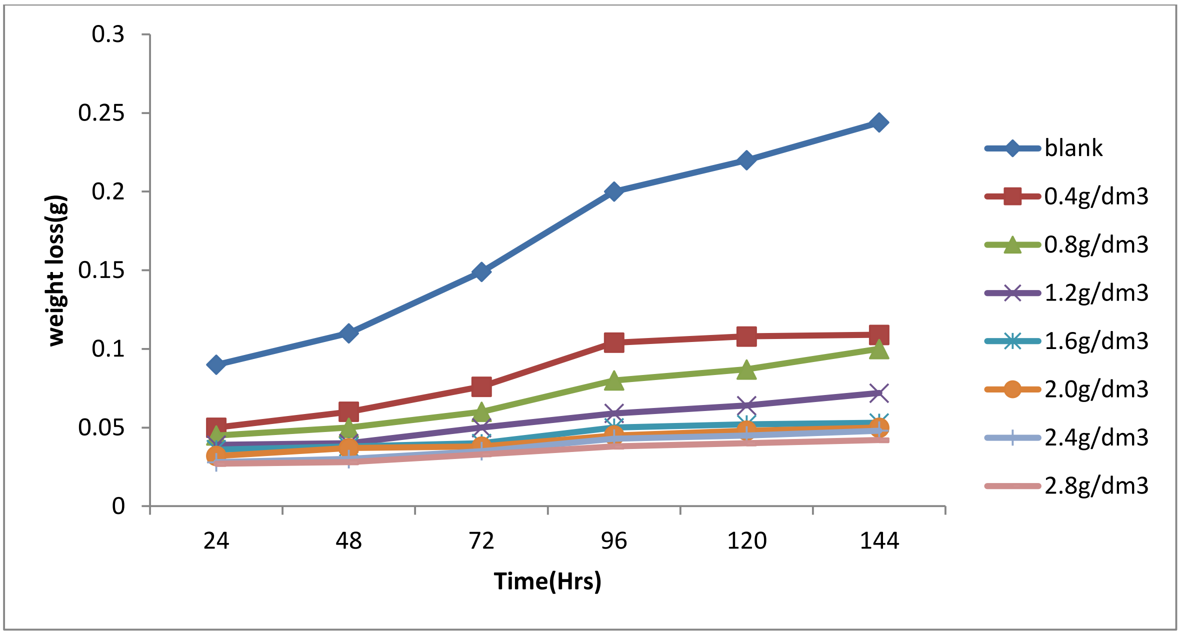

Figure 5: weight loss of blank and different concentrations of stalk extract with 0.2M HCl at 300K.

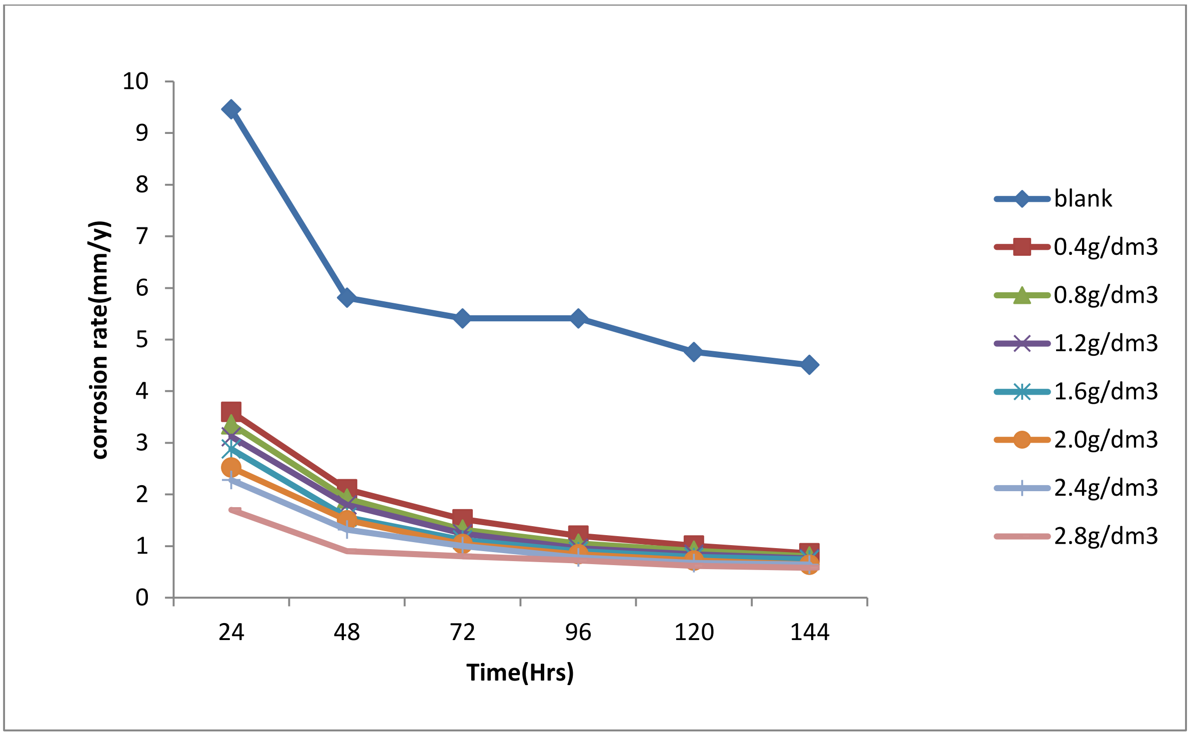

Figure 6: Effect of time on the corrosion rate at different inhibitor concentrations in 0.1M HCl solution at 300K.

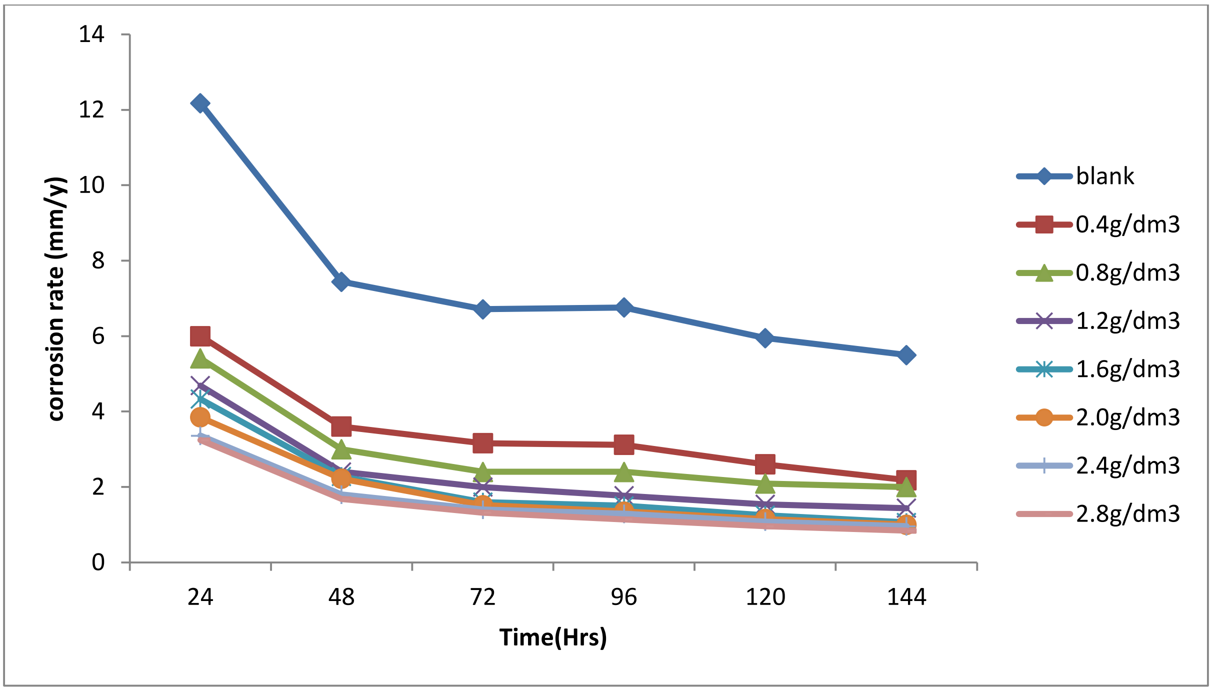

Figure 7: Effect of time on the corrosion rate at different inhibitor concentrations in 0.2M HCl solution at 300K.

3.3 Kinetics study for the corrosion inhibition

Weight losses obtained were fitted to first order, second order and rate law kinetics model for both 0.1M and 0.2 M HCL solutions using different inhibitor concentrations. Table 1 shows the kinetic parameters obtained. It was observed that all the inhibitor concentrations have correlation coefficients greater than 0.9 for both 0.1M and 0.2M HCL solutions for all the models but first order recorded the highest. This suggested to a greater extent that the reaction followed first order.

Table 1. Kinetics parameters for all the models

Inhibitor Conc (g/100mls)	0.4	0.8	1.2	1.6	2.0	2.4	2.8
0.1 M HCL First Order							
K	-0.002	-0.002	-0.002	-0.003	-0.009	-0.004	-0.005
R^2	0.901	0.965	0.0959	0.991	0.957	0.981	0.989
Second Order							
K	-0.078	-0.083	-0.09	-0.119	-0.140	-0.172	
R^2	0.879	0.954	0.941	0.997	0.949	0.983	
Rate Law							
K	0.00	1E-04	9E-05	0.00	0.00	0.00	0.00
R^2	0.937	0.979	0.959	0.976	0.952	0.986	0.982
0.2M HCL First Order							
K	-0.007	-0.007	-0.005	-0.003	-0.003	-0.004	-0.004
R^2	0.900	0.978	0.968	0.917	0.959	0.958	0.951
Second Order							
K	-0.094	-0.108	-0.107	-0.084	-0.094	-0.134	-0.125
R^2	0.878	0.964	0.953	0.918	0.946	0.947	0.953
Rate Law							
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00
R^2	0.917	0.975	0.915	0.968	0.968	0.964	0.964

3.4 Adsorption isotherm for the corrosion inhibition process

Langmuir, Freundlich, Temkin and El-Awady models were used to investigate the nature of adsorption of stalk extract on the Aluminum Surface. Table 2 shows the isotherm parameters.

Langmuir Isotherm model had its correlation coefficient (R^2) close to unity which suggests that data fits Langmuir isotherm properly. Its closeness to unity indicates a higher correlation between the variables; surface coverage and inhibitor concentrations [9]. This is also in accordance with the findings of Shanmugam etal.,[10]. The application of Langmuir isotherm indicates that there is no interaction between the adsorbate and adsorbent [11], [6]. The negative values of ΔG suggest that the adsorption of inhibitors on aluminum surface is a spontaneous process. Generally, the adsorption type is regarded as physisorption. High value of Kad at lower temperature reflects the high adsorption ability of the extract on aluminum surface. The negative "a" value obtained on Temkin isotherm shows that repulsion force exists on the surface. The values of "K" increased at increased temperature which shows a chemical adsorption which is not in line with Langmuir isotherm.

The average value of R^2 obtained with Freundlich adsorption isotherm model were relatively close to unity which indicate a strong correlation between the two variables [12]. Also, its rate constant decreased with increased temperature which shows a physical adsorption.

The obtained values of 1/y for El-Awady is greater than one showing that a given stalk molecule occupies more than one active site. Values of $^1/_y$ greater than unity implied the formation of multi layers of the inhibitor on the metal surface. It was also seen from the table that the value of k_{ad} decreases with increase in temperature indicating that adsorption of *Telfaria occidentalis* stalk on the aluminum surface was unfavorable at higher temperatures [13]. The negative value of ΔG_{ads} showed that the adsorption of the inhibitor on the surface of the aluminum was spontaneous.

Table 2: Isotherm parameters for corrosion inhibition using stalk extract

	300K	300K	318K	328K
LANGMUIR				
K	2.571	2.326	1.131	0.297
ΔG(KJ/mol)	-25.697	-23.869	-11.983	-3.246
R^2	0.970	0.984	0.988	0.982
TEMKIN				
K	3.548	4.571	7.907	25.586
R^2	0.930	0.938	0.962	0.989
FREUNDLICH				
N	0.248	0.299	0.459	0.707
K	0.724	0.649	0.419	0.197
R^2	0.937	0.929	0.950	0.991
EL-AWADY				
1/y	1.066	1.164	1.372	1.164
K	2.944	2.004	0.736	0.248
R^2	0.889	0.929	0.957	0.985

The apparent activation energies (Ea) for the corrosion process in absence and presence of plant extracts were evaluated from Arrhenius equation [13].

$$CR = Ae^{-Ea/RT} \quad (4)$$

Where CR is the corrosion rate of metal, A is the Arrhenius or pre-exponential factor, Ea is the activation energy, R is the gas constant and T is the temperature. A plot of log CR which is the corrosion rate obtained by weight loss against $^1/_T$ gives a straight line with a slope of – Ea/2.303R, where Ea is the activation energy. Values of Ea and A were obtained from the slopes and intercept of the Arrhenius plot respectively.

Table 3: Values of Ea for corrosion using stalk extract in 0.2M HCL.

Inhibitor concentration (g/dm^3)	Ea (KJ/Mol)
uninhibited	6443.01
0.4	29333.42
0.8	42985.33
1.2	51563.25
1.6	57288.25
2.0	55277.80

From Table 3, Ea for inhibited solution were higher than those for uninhibited solution. The higher values of Ea indicated that the dissolution of metal was slow in the presence of the extract. The increase in activation energy could be attributed to an appreciable decrease in the adsorption of the inhibitor on the metal surface with increase in temperature [15]. Due to more desorption of inhibitor molecules at higher temperatures, the greater surface area of metal comes in constant with aggressive environment, resulting in an increase of corrosion rates with temperature [16]. Furthermore, the enthalpy and entropy of adsorption were also calculated as in Table 4.

Table 4: Thermodynamic parameters for the corrosion inhibition of Aluminum

ΔG(KJ/Mol)	T(K)	(ΔS)	(ΔH)	R^2
-104668.59	308	4588	-2×10^6	0.986
-49477.70	318			
-12895.00	328			

The negative values of ΔH reflected the exothermic nature of the aluminum dissolution process. It is also in accordance with the work done by Shanableh 2009 [17]. Negative value of Gibb's free energy suggested that the reaction was spontaneous in nature.

Conclusion

From the results of this study, we can conclude that ethanolic extract of stalk of *Telfairia occidentali*s is an effective inhibitor of aluminum corrosion in 0.1M and 0.2M hydrochloric acid solution at 300K. The addition of the extracts to the system led to significant decrease in the rate of corrosion. This proves that the use of *Telfairia occidentalis* stalk reduces the corrosion rate in the 0.1M and 0.2M HCL corrosive media. The adsorption behavior obeyed Langmuir, Freundlich and El-Awady's adsorption isotherm model though Langmuir recorded highest correlation coefficient. The thermodynamic properties studied suggested that the process of film formation with the extracts were higher than the destruction of the metal surface and that the adsorption process is exothermic.

References

[1] Sorkhasi, H. A. Seifzadeh, D. Hosseini, M. G. (2008). EIS and Polarization Studies to Evaluate the Inhibition Effect of 3H-Phenothiazin-3-one, 7-dimethylamine on Mild Steel Corrosion in IM HCl solution. Corrosion Science., 50: 33-63.

[2] Oguzie, E.E,(2012). Corrosion Inhibitive Effect and Adsorption behavior of *HibiscusSabdariffa* on Mild Steel in Acidic Media. Portugaliae Electrochemica Acta., 26: 303-314.

[3] Jerkiewicz, G. Borodzinski, J.J. Chrzanowski, W. and Conway, B.E. (1995). Examination of Factors Influencing Promotion of H Absorption into Metals by Site-Blocking Elements. J. Electrochem Soc., 142: 3755-3763.

[4] Nurul Izni Kairi, &Jain Kassin. (2013). Effect of Temperature on the Corrosion Inhibition of Mild Steel in 1M HCl Solution by *curcuma longa* extract. Int.J.Electrochem.Sci., 8:7138-7155

[5] Mohamed, Y., Youssef, C., Taleb, H., I (2011) Corrosion Inhibition of Mild Steel using Potato Peel Extract in 2M HCl Solution. *Int. J. Electrochem. Sci.,* 6 (2011) 6542 - 6556

[6] Nwabanne, J.T and Okafor, V. N. Inhibition of the Corrosion of Mild Steel in Acidic Medium by Vernonia Amygdalina: Adsorption and Thermodynamics Study. Journal of Emerging Trends in Engineering and Applied Sciences (JETEAS) 2 (4): 619-625

[7]. Eddy, N.O., Ibok, U. J., Ebenso, E. E., El Nemr, A., El Ashry, et S.H. (2009). Quantum chemical study of the inhibition of the corrosion of mild steel in Sulfuric acid by some antibiotics. J. Mol. Model. 15 (9): 1085-1092

[8] Odiongenyi, A.O., Odoemelam, S.A., Eddy, N.O.(2009). Corrosion inhibition and adsorption properties of ethanol extract of Vernonia Amygdalina for the corrosion of mild steel in H2SO4. Portugalia Electrochim.Acta. 27(1): 33-45.

[9] Bentiss, F. Lebrini, M. Vezin, H. Chai, F. Traisnel, M. and Lagrene, M. (2005). Enhanced Corrosion Resistance of Carbon Steel in normal Sulfuric acid Medium by some Macrocyclic polyether Compounds containing a 1,3,4-thiadiazole moiety AC impedeance and Computational studies. Corr. Sci., 51: 2165 – 2173.

[10] Sangeetha M, Rajendran S, Sathiyabama J, and Prabhaka P. (2012) Asafoetida Extract (ASF) as green corrosion inhibitor for mild steel in sea water Vol. 1 (5), pg 14

[11] Ashassi-Sorkhabi, H., Majidi, M.R., Seyyedi, K. (2004). Investigation of inhibitive action of amino acids against steel corrosion in HCl solution. Appl. Surf. Sci. 225: 176-185.

[12] Abdullah, A (2008) Adsorption Isotherm of some Triazoles as corrosion inhibitiors of mild steel in Acids. Dayila University – College of Engineering. AL-Faith. No. 32. 2008.

[13] Obot, I, B., Obi, N. O., Egbedi, S.A. Umoren Adsorption characteristics and corrosion inhibitive properities of Clotrimozole for Aluminum corrosion in Hydrochloric Acid. Int. J. Electrochem. Sci; 4 (2009) 363-877.

[14] Vasudha, V. G. and Shanmuya, P. K. (2013). *Polyalthia Longifolia* as a Corrosion Inhibitor for Mild Steel in HCl Solution. Research Journal for Chemical Sciences., 3: 21-26.

[15] Szaven, T. and Brand, A. (1981). Adsorption of Oleates of various Amines on Iron in Acidic Solution. Electrochem. Acta., 26: 1253-1256.

[16] Herrag, L. Hammouti, B. Elkadi, S. Aouniti, A. Jama, C. Vezin, H. and Bentiss, F. (2010). Adsorption Properties and Inhibition of Mild Steel Corrosion in Hydrochloric solution by some newly Synthesized diamine derivative: Experimental and Theoretical Investigations. Corros. Sci.,52: 3042-3051.

[17] Shanableh, Alaa (2011) "Studies on natural extracts as inhibitors of mild steel corrosion in 1M HCl Solution. A thesis in Chemical Engineering Sharjah, UAE