

# Inhibition of Copper Corrosion by Acid Extracts of *Gnetum africana* and *Musa acuminata* Peel

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**Abstract**– The inhibition of copper corrosion by *Gnetum africana* (GA) and *Musa acuminata* (MA) peel under various concentrations of HNO<sub>3</sub> at different temperatures of 303K and 333K was studied by weight loss method. The inhibition efficiencies of both *Gnetum africana* and *Musa acuminata* peel increase with increase in concentration and decrease with increase in temperature and period of immersion. The inhibition efficiency of *Gnetum africana* was greater than that of *Musa acuminata* peel for otherwise identical conditions. Values of activation energy of the inhibited corrosion reaction of copper for both *Gnetum africana* and *Musa acuminata* peel were greater than the value obtained for the blank. Thermodynamic consideration revealed that adsorption of both inhibitors on copper surface was spontaneous, physically controlled and occurred according to Langmuir adsorption isotherms.

**Keywords**– Corrosion Inhibitors, *Gnetum africana*, *Musa acuminata* Peel and Copper

## I. INTRODUCTION

Copper and its alloys are good corrosion resistance in water and have excellent heat conductivity, but these corrode easily in acid solutions. Copper and its alloys are broadly used in heating systems and condensers [1]. However, these systems should be regularly cleaned due to inlays of carbonates and oxides. Dilute acids are normally used to clean these surfaces. In order to prevent the corrosion of copper metals, corrosion inhibitors are generally added to the acids. The use of inhibitors is an important method of protecting materials against deterioration compound. Inhibitors are chemicals that often work by adsorbing themselves on the metallic surface by forming a film [2-6]. Most corrosion inhibitors are either synthesized from cheap raw materials or are chosen from organic compounds containing electronegative functional groups and  $\pi$ -electrons in triple or conjugated double bonds. The presence of aromatic rings and hetero atoms (such as S, N, O and P) are the major adsorption centers for these inhibitors [3]. Broad spectra of organic compounds are available as corrosion inhibitors. Of these, only very few are actually used in practice. This is partly due to the fact that desirable properties of an inhibitor usually extend beyond those simply related to metal protection. Considerations of cost, toxicity, availability and environmental friendliness are of considerable importance. Accordingly, the replacement of some toxic, expensive chemical inhibitors by inhibitors obtained from natural sources is necessary. Apart from being

readily available, cheap and a renewable source of materials, naturally occurring substances are eco-friendly and ecologically acceptable. Naturally occurring substances are biodegradable and do not contain heavy metals or other toxic compounds. Therefore, the present study is aimed at investigating the adsorption and inhibitive properties of the acid extracts of *Gnetum africana* and *Musa acuminata* peel.

## II. MATERIALS AND METHOD

### A. Metal Preparation

The sheet employed in this work was made of pure copper (99.9%). The copper sheet was mechanically pressed cut into different coupons of dimension 5x1.5x0.01cm. Each coupon polished and drilled at one end, was degreased in ethanol, dried in acetone and preserved in a dessicator. Solutions were prepared using analer reagents and distilled water.

### B. Extraction of Inhibitor

Samples of the inhibitors were obtained from Akwata axis of Ogbete Main Market Enugu. The leaves and the peels were rinsed with distilled water, dried and ground. 1g of each ground inhibitor sample was soaked for 24 hours in different concentrations (1M, 1.5M, 2M and 2.5M) of 150ml of HNO<sub>3</sub> to obtain a mixture. Then it was filtered. The filtrate obtained from the mixture served as the stock solution of inhibitor extract. The same procedure was used to obtain extracts for 2g and 3g of the samples.

## III. RESULTS AND DISCUSSION

### A. Effects of Time, Inhibitor Concentration and Temperature on Corrosion Rate (CR) and Inhibition Efficiency (IE)

Fig. 1 shows the variation of weight loss with time for the corrosion of copper in 2.5MHNO<sub>3</sub> in the absence and presence of various concentrations of acid extracts of *Gnetum africana* and *Musa acuminata* peel at 303k. Similar plots (not shown) were obtained at 333k. There exists generic increase in weight loss as the time increases. Observation of Fig. 1 shows a relative decrease in weight loss of copper in the presence of *Gnetum africana* and *Musa acuminata* peel when compared to that of the blank. Also from fig.1, it is evident that weight loss decreases with increase in the concentration of the acid extracts of *Gnetum africana* and *Musa acuminata*. 3g of GA

and 1g of MA recorded the least and highest weight loss, respectively.

The results of corrosion rate evaluated by Eq. (1) are displayed in Table 1.

$$\text{Corrosion Rate (CR)} = \frac{w_i - w_f}{A \times t} (\text{g/cm}^2 \cdot \text{hr}) \quad (1)$$

Where  $w_i$  and  $w_f$  are the initial and final weight, respectively,  $A$  is the surface area ( $\text{cm}^2$ ) of the coupon and  $t$  is exposure time (hours).

The results are evaluated for different temperatures and inhibitor concentrations. Results shown in Table 1 indicate that corrosion rate of copper was reduced in the presence of the inhibitors when compared to that of the blank. Corrosion rates were also observed to increase with increase in temperature both in the absence and presence of the inhibitors. It is known that there is characteristic increase in temperature as the temperature increases. Also from Table 1, it is evident that corrosion rates decrease with increase in the concentration of the inhibitors. This confirms that acid extracts of *Gnetum africana* and *Musa acuminata* peel are adsorption inhibitors for the corrosion of copper in  $\text{HNO}_3$  [3]. The result of inhibition efficiency shown in table 1 is evaluated using Eq. (2) [4].

$$\text{Inhibition Efficiency (IE)} = \left( 1 - \frac{w_I}{w_A} \right) \times 100 \quad (2)$$

Where  $w_I$  = weight loss in the presence of inhibitor

$w_A$  = weight loss in the absence of inhibitor

From Table 1, it is clearly seen that inhibition efficiency increased in the presence of the inhibitors when compared to that of the blank. Inhibition efficiency also increases with increase in the concentration of the acid extracts of the inhibitors. Table 1 also revealed that inhibition efficiency decreases with increase in temperature, an indication of physical adsorption mechanism [7]. Also from Table 1, it is evident that rate of corrosion in the presence of *Musa acuminata* peel is higher than in the presence of *Gnetum africana*. The higher value of inhibition efficiency obtained from *Gnetum africana* corroborates this finding. The variations in the inhibition efficiencies can be attributed to variations in the phytochemical constituents of the acid extracts of the inhibitors presented in Tables 8 and 9.

### B. Corrosion Adsorption

The adsorption characteristics of acid extracts of *Gnetum africana* and *Musa acuminata peel* were studied by fitting experimental data obtained from weight loss measurements into different adsorption isotherms. The test indicates that Langmuir adsorption isotherm best described the adsorption characteristics of acid extracts of *Gnetum africana* and *Musa acuminata peel*. Hence, no further consideration of other models was attempted. The Langmuir adsorption isotherm is given by Eq. (3), which can also be linearised as shown in Eq. (4) [8]:

$$C/\theta = 1 / (K_L + C) \quad (3)$$

$$\text{Log (C/}\theta) = \text{Log C} - \text{Log } K_L \quad (4)$$

Where  $C$  (g/l) is the concentration of the inhibitor in the bulk electrolyte,  $\theta$  is the degree of surface coverage of the inhibitors and  $K_L$  is the Langmuir equilibrium constant of adsorption for the inhibitors. Plots of  $\text{log (C/}\theta)$  versus  $\text{log C}$  generated linear graph for the evaluation of  $\text{log } K_L$  from the intercept. Values of adsorption parameters deduced from Langmuir adsorption isotherms are recorded in Tables 2 and 3. The results indicated that the slopes and  $R^2$  values were very close to unity which also indicated strong adherence to the assumptions of Langmuir isotherm. Therefore, there is no interaction between the adsorbed species [9].

### C. Corrosion Thermodynamics

The thermodynamic parameter,  $\Delta G$  for corrosion adsorption was calculated using the values of  $K_L$  substituted into Eq. (5) from Eq. 4 [10]:

$$\Delta G_{\text{ads}} = 2.303RT \log (55.5K_L) \quad (5)$$

Calculated values of  $\Delta G_{\text{ads}}$  are recorded in Tables 4 and 5. The results indicated that  $\Delta G_{\text{ads}}$  values are negatively less than the threshold value of  $-40 \text{ kJ/mol}$  required for chemical adsorption. Therefore the adsorption of the acid extracts of *Gnetum africana* and *Musa acuminata peel* on the surface of copper is spontaneous and supported the mechanism of physical adsorption [3, 11-13]. The activation energy, ( $E_a$ ) of the corrosion process in the absence and presence of the acid extracts of the inhibitors was evaluated using Arrhenius equation, expressed as Eq. 6.

$$\text{Log } \frac{CR_2}{CR_1} = \frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (6)$$

Where  $CR_1$  and  $CR_2$  are the corrosion rates at temperatures,  $T_1$  (303 K) and  $T_2$  (333 K), respectively,  $R$  is the gas constant. Values of  $E_a$  calculated from Equation (6) are presented in Tables 4 and 5. Calculated values of  $E_a$  are lower than the threshold value of  $80 \text{ kJ mol}^{-1}$  required for chemical adsorption, hence the adsorption of acid extract of *Gnetum africana* and *Musa acuminata peel* occurred according to the mechanism of physical adsorption.

The heat of adsorption ( $Q_{\text{ads}}$ ) of acid extracts of *Gnetum africana* and *Musa acuminata peel* on the surface of copper was calculated using Eq. (7).

$$Q_{\text{ads}} = 2.303R \left[ \text{Log } \frac{\theta_2}{1-\theta_2} - \text{Log } \frac{\theta_1}{1-\theta_1} \right] \times \frac{T_1 T_2}{T_2 - T_1} \quad (7)$$

Where  $R$  is the gas constant,  $\theta_1$  and  $\theta_2$  are the degrees of surface coverage of the inhibitor at temperatures,  $T_1$  (303 K) and  $T_2$  (333 K), respectively. Calculated values of  $Q_{\text{ads}}$  are also presented in Tables 4 and 5. These values range from  $-2.64$  to  $-3.37$  for *Musa acuminata peel* and from  $-3.42$  to  $-4.32$  for *Gnetum africana* which indicate that the adsorption of acid extracts of the both inhibitor on copper surface is exothermic.

### D. Corrosion Kinetics

Data obtained from weight loss measurement were fitted into equation 8 to test for the order of corrosion reaction in the

presence of acid extracts of *Gnetum africana* and *Musa acuminata* peel.

$$\ln(\text{weight loss}) = k_1 t \quad (8)$$

Where  $k_1$  is the first order reaction constant and  $t$  is time.

Representative plots for the first order reaction in different concentrations of the inhibitors are shown in Fig. 2 and Fig. 3. The tests revealed the plots of  $\ln(\text{weight loss})$  versus time (in days) were linear with  $R^2$  close to unity. This indicates that a first order kinetic is applicable to the corrosion of copper in the presence of acid extracts of the inhibitors [14]. Therefore, the corrosion of copper in the acid extracts of the inhibitors can be significantly represented by Eq. (8).

In addition, the half lives ( $t_{1/2}$ ) of the corrosion of copper in various media were calculated using Eq. (9).

$$t_{1/2} = \frac{0.693}{k_1} \quad (9)$$

Values of rate constant ( $k_1$ ) obtained from the slope of the plots of Eq. (8) and the half life calculated from Eq. (9) is presented in Tables 6 and 7. From the results obtained it is significant to note that half life increases with increase in concentration of acid extracts of *Gnetum africana* and *Musa acuminata* peel. This suggests that half life of copper in  $\text{HNO}_3$  increases with increasing concentration of the inhibitors. Also from Tables 6 and 7, it can be shown that the half life of the acid extracts of the inhibitors at 333K is lower than that at 303K. This indicates that inhibition efficiency is inversely related to temperature.

#### E. Phytochemical Constituents

Tables 8 and 9 show the phytochemical composition of *Gnetum africana* and *Musa acuminata* peel. The results obtained, indicate that saponnin, tannin, phlobatin, anthraquinone, cardiac glycosides, flavanoid, terpene, and alkaloid are present in acid extracts of *Gnetum africana* and *Musa acuminata* peel. Hence, the inhibition efficiency of the inhibitors may be attributed to the phytochemical constituent of the extract [15]. Differences in the inhibition efficiency of the inhibitors can be attributed to the variations of these phytochemicals among the inhibitors.

#### IV. CONCLUSION

Acid extracts of *Gnetum africana* and *Musa acuminata* peel are a good adsorption inhibitor for the corrosion of copper in  $\text{HNO}_3$  at the condition of the experiment. The inhibition potentials of these inhibitors are attributed to the presence of saponnin, tannin, phlobatin, anthraquinone, cardiac glycosides, flavanoid, terpene, and alkaloid in the extract. The inhibition potentials can be optimized by taking advantage of temperature, period of contact, and inhibitors'

concentration. Kinetic, thermodynamic, and adsorption models can sufficiently be used to explain the adsorption behavior of these inhibitors on copper surface. *Gnetum africana* exhibits more inhibitory action than *Musa acuminata* peel.

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Table 1: CR and inhibition efficiency w.r.t extracts of *GA* and *MA peel* on copper surface

Concentration (g/l)	Gnetum Africana				Musa acuminata peel			
	CRx10 <sup>-3</sup> (g/cm <sup>2</sup> .hr)		IE(%)		CR x 10 <sup>-3</sup> (g/cm <sup>2</sup> .hr)		IE(%)	
	303K	333K	303K	333K	303K	333K	303K	333K
Blank	3.9	6.5	-	-	3.9	6.5	-	-
0.001	2.5	5.17	71.1	66	2.78	5.78	68.6	61.9
0.002	1.94	4.78	78	68.6	2.25	5.44	74.5	64.2
0.003	1.72	4.11	80.5	72.9	2.11	4.69	76.1	69.1

Table 2: Langmuir adsorption parameters w.r.t *GA* on copper surface

Temperature(K)	LogK <sub>L</sub>	K <sub>L</sub> (g/l)	Slope	R <sup>2</sup>
333K	0.075	1.188	0.914	0.999
303K	0.187	1.538	0.889	0.999

Table 3: Langmuir adsorption parameters w.r.t *MA peel* on copper surface

Temperature(K)	LogK <sub>L</sub>	K <sub>L</sub> (g/l)	Slope	R <sup>2</sup>
333K	0.069	1.172	0.906	0.998
303K	0.041	1.099	0.936	1.000

Table 4: Thermodynamic parameters w.r.t *MA peel* on copper surface

C(g/l)	Ea(KJ/mol)	Qads(KJ/mol)	$\Delta G$ ( KJ/mol)	
			(303K)	(333K)
Blank	14.05	-		
0.001	17.94	-2.64	-10.4	11.6
0.002	20.83	-4.59		
0.003	21.09	-3.37		

Table 5: Thermodynamics parameters w.r.t *GA* on copper surface

C(g/l)	Ea(KJ/mol)	Qads(KJ/mol)	$\Delta G$ ( KJ/mol)	
			(303K)	(333K)
Blank	14.05	-		
0.001	17.79	-3.42	-11.3	-11.6
0.002	21.56	-4.5		
0.003	21.53	-4.32		

Table 6: Kinetic parameters w.r.t *MA peel* on copper surface

C(g/l)	k <sub>t</sub> (1/hour)		t <sub>1/2</sub> (hour)		R <sup>2</sup>
	(303K)	(333K)	(303K)	(303K)	
Blank	0.259	0.281	2.68	2.46	0.955
0.001	0.238	0.269	2.91	2.54	0.986
0.002	0.194	0.262	3.57	2.64	0.984
0.003	0.182	0.258	3.81	2.65	0.977

**Table 7: Kinetic parameters w.r.t GA on copper surface**

C(g/l)	k <sub>1</sub> (1/hour)		t <sub>1/2</sub> (hour)		R <sup>2</sup>
	(303K)	(333K)	(303K)	(333K)	
Blank	0.259	0.281	2.68	2.46	0.955
0.001	0.207	0.261	3.35	2.66	0.968
0.002	0.186	0.234	3.71	2.96	0.989
0.003	0.177	0.222	3.92	3.12	0.98

**Table 8: Phytochemical constituents of acid extract of GA**

Constituents	Value*
Saponnins	++
Terpenes	+++
Tannins	++
Flavonoid	-
Phlobatannins	++
Anthraquinone	++
Cardiac glycosides	+++
Alkaloid	+++

Note: \* + present in trace quantity; ++ moderately present; +++ present in large quantity

**Table 9: Phytochemical constituents of acid extract of MA peel**

Constituents	Value*
Saponnins	+++
Terpenes	+++
Tannins	+++
Flavonoid	++
Phlobatannins	++
Anthraquinone	++
Cardiac glycosides	+++
Alkaloid	+++

Note: \* + present in trace quantity; ++ moderately present; +++ present in large quantity

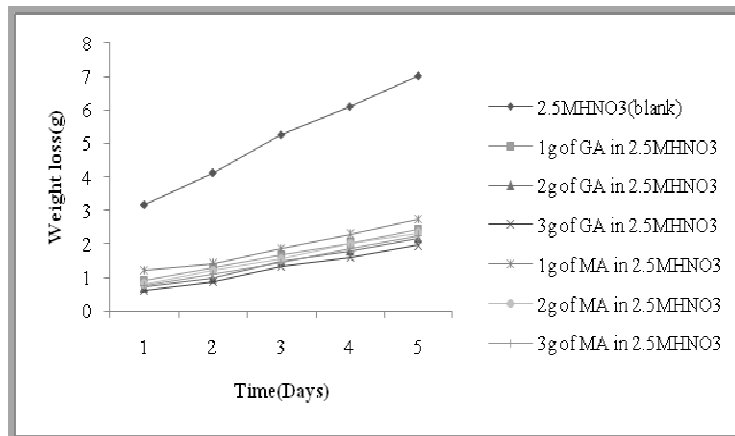


Fig. 1: Weight loss as a function of time at 303K and 2.5M HNO<sub>3</sub> for GA and MA extracts

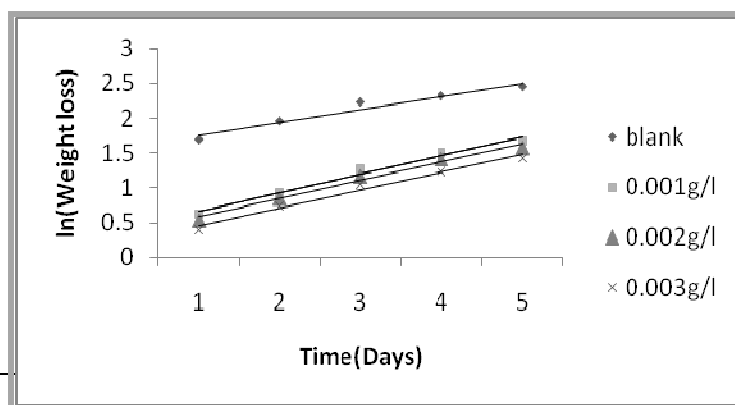


Fig. 2: First order plot w.r.t GA concentrations on copper surface at 303K

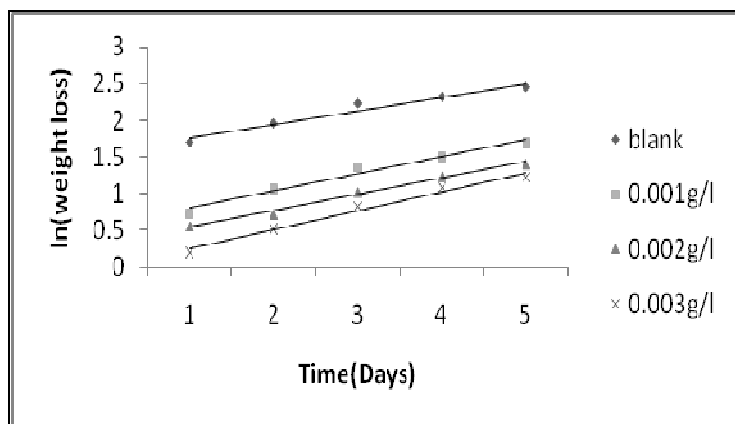


Fig. 3: First order plot w.r.t MA peel concentrations on copper surface at 303K