

# CORROSION INHIBITION AND ADSORPTION CHARACTERISTICS OF *MYRIANTHUS arboreus* LEAVES EXTRACT ON COPPER IN SULPHURIC ACID SOLUTION.

**Abstract:** The inhibiting action of *Myrianthus arboreus* leaves extract on the corrosion of copper in sulphuric acid solution was assessed using weight loss technique at various temperatures. It was observed that the extract inhibited the acid induced corrosion of copper and the corrosion rate decreased in the presence of the inhibitor as compared to the blank. Inhibition efficiency was found to increase with increasing concentration of the extract and temperature. Kinetic study of the data followed a first-order reaction. Thermodynamics study revealed that the corrosion inhibition may be due to spontaneous adsorption of the leaves constituents on the metal surface. The adsorption of the extract on copper surface was found to obey Freundlich and Temkin adsorption isotherms.

**Key words:** Copper, Corrosion inhibition, *Myrianthus arboreus*, Weight loss, Adsorption, Thermodynamic, Kinetics.

## Introduction

Copper is an industrial important metal due to its excellent properties [1]. It is known to be susceptible to corrosion in aggressive media especially in industries where acids are extensively used for cleaning, removal of rust, acid pickling and de-scaling processes [1]. Corrosion is an electrochemical process in which metal surfaces interact with aggressive environments, converting the metal atoms to ions thus causing the breakdown of physical and protective layers of the metal [2]. Acids aggressively enhance metal corrosion. Thus it is important to employ corrosion inhibitors to prevent the dissolution of metal materials such as copper [3]. For economic and environmental benefits, it is vital to use extracts of cheap, easily available biomass as corrosion inhibitors to prevent the problems of metal dissolution [4].

The inhibition abilities of plant parts extract are normally due to the presence of heterocyclic constituents such as flavonoid, tannin, alkaloids, nitrogenous bases, proteins and carbohydrates which usually contain heteroatom like Oxygen, Sulphur or Nitrogen as well as triple or conjugate double bonds with aromatic rings in their molecular structures which are the main adsorption centre [5, 6].

Some reports have been highlighted on the effective application of plants extracts as corrosion inhibitors for copper in different media, such as the inhibitive action of *Morinda tinctoria* leaves extracts in H<sub>2</sub>SO<sub>4</sub> [7]. The influence of aqueous extract of *Cerdtonia siliquaon* corrosion of copper and brass in aqueous 1M nitric acid has been examined [4]. The use of ethanolic extract of capparid seeds in controlling the corrosion of copper in HCl acid has also been reported [3]. [8] reported the inhibitive action of *xanthosoma Spp* leaf extracts (XLE) on the corrosion of copper in seawater. It has been shown that the extract of

39 Azadirachta indica is a good inhibitor for copper corrosion in Nitric acid medium [9].  
 40 Adsorption and inhibitive properties of methanol extract of *Eeuphorbia heterophylla* for the  
 41 corrosion of copper in Nitric acid solutions have been investigated [6]. [10] have reported  
 42 that aqueous extract of *Alhagimaaurorum* is a good inhibitor for copper in H<sub>2</sub>SO<sub>4</sub> acid  
 43 medium. [11]found that fruit extracts of citrus aurantium, *moringa oleifera* and capsicum  
 44 annum are good corrosion inhibitors for copper in Nitric acid solutions. The inhibitive  
 45 efficacy of Emblica officinalis leaves extract on the corrosion of copper and its alloy (Cu-  
 46 27Zn) in natural sea water environment has been studied [12]. IE (%) was observed to be  
 47 markedly higher in natural sea water with the addition of the extract. [13]Found that acid  
 48 extracts of *Gnetum Africana* and Musa acuminate peel have the potential of inhibiting the  
 49 corrosion of copper in Nitric acid. Aloe vera Barbadosensis Gel as effective corrosion inhibitor  
 50 for copper in HCl acid has been reported by [14]. Inhibitive action of cannabis plant extract  
 51 on the corrosion of copper in H<sub>2</sub>SO<sub>4</sub> acid has been carried out by [15]. Corrosion behaviour of  
 52 copper in phosphoric acid containing sodium chloride and its inhibition by Artemisia oil  
 53 extract has been investigated by [16]. Inhibitive effect of *Trigonella stellate* as a good  
 54 corrosion inhibitor for copper in HNO<sub>3</sub> solution was studied by [17]. [18] investigated the  
 55 inhibition potential of *Azardiracha indica* fruit extract on the corrosion of copper in HCl acid  
 56 solution. [19] carried out an investigation on the corrosion inhibition of copper by *Capparis*  
 57 *spinosa* L. extracts in strong acidic medium. It was observed that the extract inhibited the  
 58 acid induced corrosion to maximum IE (%) of 82.7%.

59 The successful results obtained from previous studies on naturally occurring substances to  
 60 inhibit the corrosion of metals in acidic and alkaline environments have motivated this  
 61 investigation on methanol extract of *myrianthus arboreus* as corrosion inhibitor for copper.  
 62 Presently, and to the best of our knowledge, there is no reported work in the open literature  
 63 on *myrianthus arboreus* leaves extract as corrosion inhibitor of copper. This study  
 64 investigated the adsorption and inhibitive properties of methanol extract of *myrianthus*  
 65 *arboerus* leaves for the corrosion of copper in H<sub>2</sub>SO<sub>4</sub> acid solutions using weight loss  
 66 technique. *Myrianthus arboreus* (giant yellow mulberry or bush pineapple) which is of the  
 67 family Ceropiaceae, is a shrub found in the forest zone of tropical Western Africa. Extracts of  
 68 the leaves and leafy shoots are used in the treatment of dysentery, diarrhoea, boils,  
 69 dysmenorrhoea, incipient hernia and vomiting. The bark decoction is used to treat malaria,  
 70 fever, cough and muscular pains.

## 71 2.1 Material & Test Solution Preparation

72 The sheet of copper used for this study was obtained from engineering workshop of the  
 73 University of Port Harcourt, Rivers State, Nigeria. The copper sheet of 0.1cm thickness and  
 74 99.5% purity was mechanically press-cut into 5.0 x 2.5cm coupons. The coupons were  
 75 polished with different grades of emery paper to obtain a clean shiny surface, washed in  
 76 deionized water, degreased in absolute ethanol, dried in acetone and then stored in a moisture  
 77 free desiccator prior to use. 2M H<sub>2</sub>SO<sub>4</sub> solution used as corrodent was prepared from pure  
 78 H<sub>2</sub>SO<sub>4</sub> purchased from Sigma-Aldrich. Deionized water was used for the preparation of all  
 79 reagents used for the study.

## 80 2.2 Preparation of Extract

81 Fresh leaves of *Myrianthus arboreus* plants were obtained from Ukanafun in Akwa Ibom  
82 State, South-South Nigeria. The leaves were washed thoroughly and rinsed with deionized  
83 water to remove impurities; sun-dried to constant weight and pulverized to using a blender.  
84 The extract was obtained using 99.8% methanol in a soxhlet extractor. The resulting solution  
85 was evaporated to dryness in an oven at 40°C, weighed and stored in sample container before  
86 being used for phytochemical analysis. Different concentrations of the extract were prepared  
87 by dissolving 0.5g of the dry *Myrianthus arboreus* in 2.0M H<sub>2</sub>SO<sub>4</sub> acid solution for weight  
88 loss measurements.

### 89 2.3 Weight loss Technique

90 A known weight of copper coupon was suspended in 60ml of the test solution in an open  
91 beaker in the absence and presence of the extract (inhibitor) between the temperatures of  
92 303–303K. Thermostated water bath was used to regulate the temperatures. After every 2  
93 hours progressively for 18 hrs, each sample was retrieved from the test solution, washed with  
94 deionized water, rinsed in acetone, dried in air and reweighed. The difference in weight after  
95 immersion and drying was taken as the total weight loss of each copper coupon. This  
96 procedure for weight loss determination was similar to that reported by [20] and stated in  
97 Equation 1.

$$98 \quad \Delta W = W_i - W_f \quad (1)$$

99 where,  $\Delta W$  is the change in weight of the copper coupons,  $W_i$ , weight before immersion,  
100 while  $W_f$  is the weight after immersion in the test solution.

101 From the weight loss results, the percentage inhibition efficiency (%IE), corrosion rate (CR),  
102 surface coverage ( $\theta$ ) and rate constant (k) were calculated using Equations, 2, 3, 4 and 5  
103 respectively.

$$104 \quad IE\% = \Delta W_B - \Delta W_{inh} \times 100 \quad (2)$$

105 where  $W_B$  and  $W_{inh}$  are the weight losses of copper in absence and presence of *Myrianthus*  
106 *arboreus* leaves extract in H<sub>2</sub>SO<sub>4</sub> acid solution at a particular temperature.

107 The degree of the adsorbent surface covered by the adsorbate ( $\theta$ ) was calculated using  
108 Equation 3.

$$109 \quad \theta = \left[ 1 - \frac{\Delta W_{inh}}{\Delta W_B} \right] \quad (3)$$

110 Corrosion rates (gcm<sup>-2</sup>h<sup>-1</sup>) of copper in different corrosion media were determined using  
111 Equation 4

$$112 \quad CR = \frac{\Delta W}{At} \quad (4)$$

where,  $\Delta W$  = weight loss (g),  $A$ , surface area ( $\text{cm}^2$ ) of adsorbent and  $t$ , time of immersion (hours).

### 3 RESULTS AND DISCUSSION

#### 3.1 Effect of time and Extract concentration on weight loss

The variation of weight loss of copper in 2M  $\text{H}_2\text{SO}_4$  acid medium in the absence and presence of different concentrations of the *Myrianthus arboreus* leaves extract as a function of time at temperatures of 303–333K is shown in Figure 1.

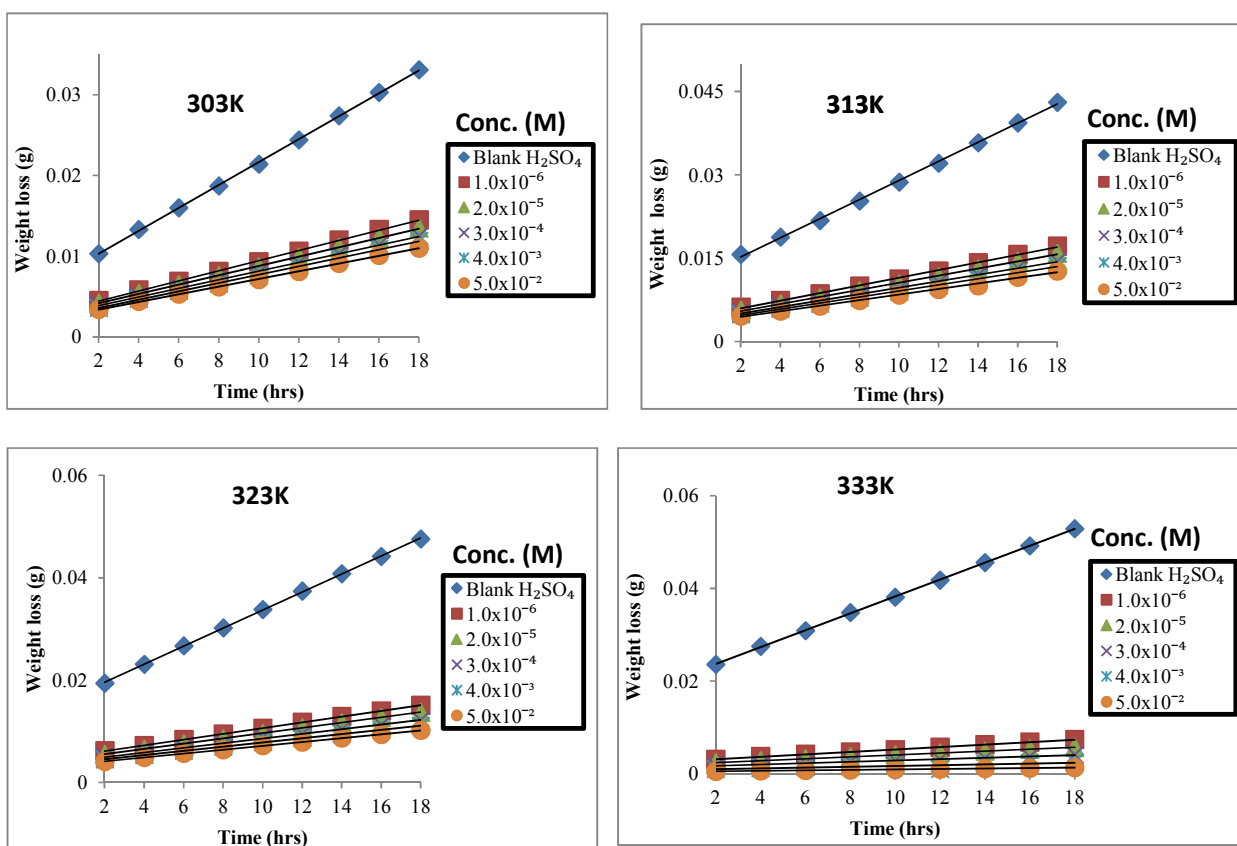
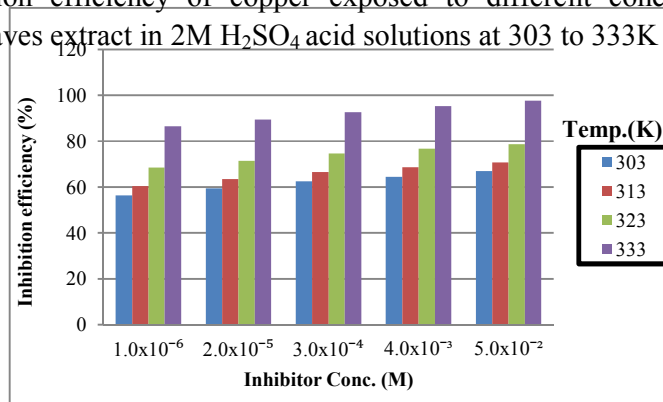


Fig.1: Variation of weight loss (g) with time (hrs) for Copper coupons in 2M  $\text{H}_2\text{SO}_4$  at different concentrations of extract and temperatures.

Results obtained depict increase in weight loss with immersion time and decrease in concentration of extract, with highest value of weight loss for the blank which probably was due to increase in corrosion rate. The decrease observed in weight loss with increase in concentration of the extract suggests an increase in surface coverage on the metal and the adsorption of the extract constituents on the metal surface which may have created a barrier between the metal and the acidic medium. Similar observations have also been reported [2, 21].

### 3.2 Effect of extract concentration on Inhibition efficiency

The inhibition efficiency of copper exposed to different concentrations of *Myrianthus arboreus* leaves extract in 2M H<sub>2</sub>SO<sub>4</sub> acid solutions at 303 to 333K is shown in Figure 2.

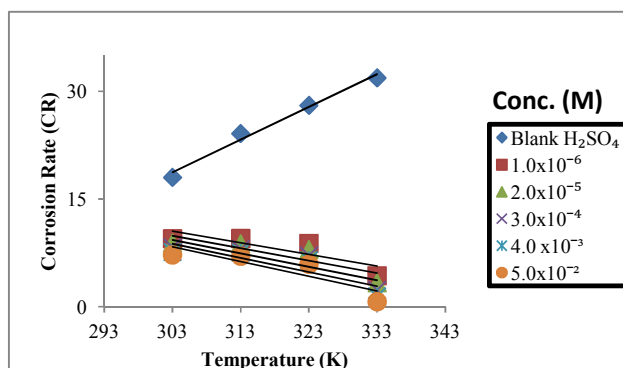


**Fig. 2: Variation of Percentage inhibition efficiency (%) with inhibitor Concentration (M) for the corrosion of copper coupons in 2M H<sub>2</sub>SO<sub>4</sub> at different temperatures.**

The inhibition efficiency values were observed to increase with increase in concentration of *Myrianthus arboreus* extract from 1.0 x 10<sup>-6</sup> to 5.0 x 10<sup>-2</sup> M. The maximum percentage inhibition of 97.67% was recorded at highest concentration studied. Hence, increase in the concentration of the inhibitor appears to have significantly increased the adsorption of its molecules on the metal surface and subsequently retarded the dissolution of the metal in acidic medium, as has also been reported elsewhere [22, 23].

### 3.3 Effect of temperature on corrosion rate

The effect of temperature on corrosion rate of copper in the absence and presence of different concentrations of *Myrianthus arboreus* leaves extract was carried out at the temperature range of 303 -333K as shown in Figure 3 and Table 1.



**Fig. 3: Variation of corrosion rate (CR) of copper with temperature (K) in absence and presence extract.**

It was observed that the corrosion rate of copper increased with rise in temperature for the uninhibited and decreased with rise in temperature for the inhibited system. The effect of temperature on corrosion rate of copper may be attributed to increase in average kinetic energy of the reacting molecules. This decrease in corrosion rate may indicate that the extract

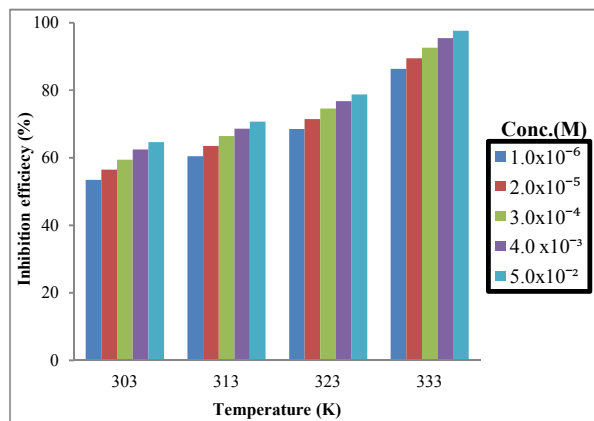
inhibited  $\text{H}_2\text{SO}_4$  acid induced corrosion of copper. This is in accordance with the findings of other authors [24, 25].

**Table1: Corrosion rate (CR  $\text{gcm}^{-2}\text{day}^{-2}\times 10^{-3}$ ), inhibition efficiency (IE%) of extract in 2M  $\text{H}_2\text{SO}_4$  acid solution at different temperatures.**

Temperature (K)	CR ( $\text{gcm}^{-2}\text{day}^{-1}$ ) $\times 10^{-3}$				IE (%)			
	303	313	323	333	303	313	323	333
Extract Conc.(M)								
Blank	18.05	24.24	28.07	31.89	-	-	-	-
$1.0 \times 10^{-6}$	9.52	9.56	8.86	4.36	53.51	60.42	68.51	86.38
$2.0 \times 10^{-5}$	8.92	8.81	8.02	3.39	56.49	63.55	71.48	89.43
$3.0 \times 10^{-4}$	8.29	8.09	7.17	2.38	59.47	66.48	74.62	92.57
$4.0 \times 10^{-3}$	7.69	7.58	6.54	1.48	62.47	68.62	76.72	95.40
$5.0 \times 10^{-2}$	7.25	7.08	5.97	0.75	64.58	70.67	78.74	97.67

### 3.4 Effect of Temperature on Inhibition Efficiency

Results of the present investigations on leaves extract of *Myrianthus arboreus* indicate that the inhibition efficiency increases with increase in both extract concentration and temperatures shown in Figure 4.



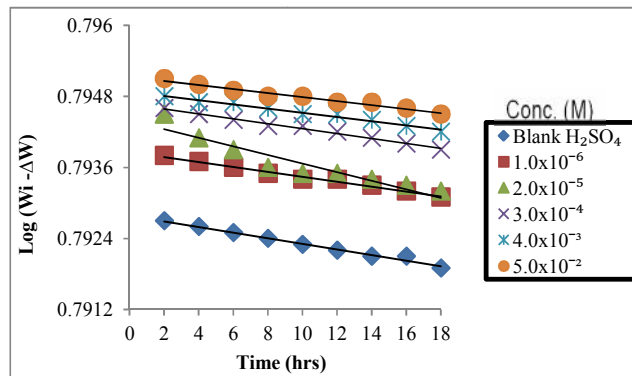
**Fig. 4: Plot of Percentage inhibition efficiency (%) with temperature (K) for copper coupons at different concentrations of the leaves extract.**

Maximum inhibition efficiency of 97.67% was obtained with extract concentration of  $5.0 \times 10^{-2}$  M at 333K. It can be observed from Figure 4 and Table 1 that, as the reaction temperature is increased from 303K to 333K, the inhibition efficiency increases and the corrosion rate decreases for the inhibited systems. Thus, it is appropriate to say that increased temperature favours the corrosion inhibition efficiency of *Myrianthus arboerus* on copper in  $\text{H}_2\text{SO}_4$  acid solution. Similar observations have been reported[26, 27].



### 3.5 Kinetic and Mechanism of Corrosion Inhibition Studies

In order to investigate the order of reaction and assess the weight loss, the experiments were carried out at various inhibitor concentrations of  $1.0 \times 10^{-6}$  to  $5.0 \times 10^{-2}$  M in 2M  $\text{H}_2\text{SO}_4$ . The order of reaction was determined from the plot of  $\log (W_i - \Delta W)$  vs. time in the absence and presence of *Myrianthus arboreus* leaves extract at 303K (Figure 5).



**Fig. 5: The variation of Log (Wi - ΔW) with time (hrs) for the corrosion of copper coupons in 2M H<sub>2</sub>SO<sub>4</sub> solution with and without the leaves extract at 303K.**

The kinetics of the corrosion process is shown in Figure 5 and linear plots of all the data plotted reveal that the corrosion of copper at various concentrations of the extract in H<sub>2</sub>SO<sub>4</sub> follows first order kinetics.

The rate constant,  $k$  and half-life,  $t_{1/2}$  of the corrosion inhibition were calculated from the weight loss data for first order reaction using Equations 5 and 6 respectively.

$$k = \left( \frac{2.303}{t} \right) \log \frac{W_i}{W_f} \quad (5)$$

where,  $W_i$  and  $W_f$  are the initial and final weights of the copper coupons,  $t$  is immersion time of metal.

$$t_{1/2} = \frac{0.693}{k} \quad (6)$$

The calculated values of  $k$  and  $t_{1/2}$  are shown in Table 2.

**Table 2: Rate constant ( $k$ ) and half-life parameters at various concentrations of the extract.**

Temp.(K)	$k$ ( day <sup>-1</sup> ) x 10 <sup>-3</sup>				Half life (days)			
	303	313	323	333	303	313	323	333
Extract Conc. (M)								
Blank	3.29	3.71	4.44	4.37	210.91	186.67	156.14	158.57
1.0 x 10 <sup>-6</sup>	1.53	1.58	1.42	0.57	452.38	438.91	489.23	1210.20
2.0 x 10 <sup>-5</sup>	1.43	1.44	1.27	0.45	483.23	479.98	545.49	1539.11
3.0 x 10 <sup>-4</sup>	1.34	1.29	1.14	0.32	517.98	535.76	609.44	2177.53
4.0 x 10 <sup>-3</sup>	1.23	1.21	1.04	0.19	563.37	571.64	663.79	3512.59
5.0 x 10 <sup>-2</sup>	1.16	1.13	0.95	0.05	596.08	613.11	731.57	6595.60

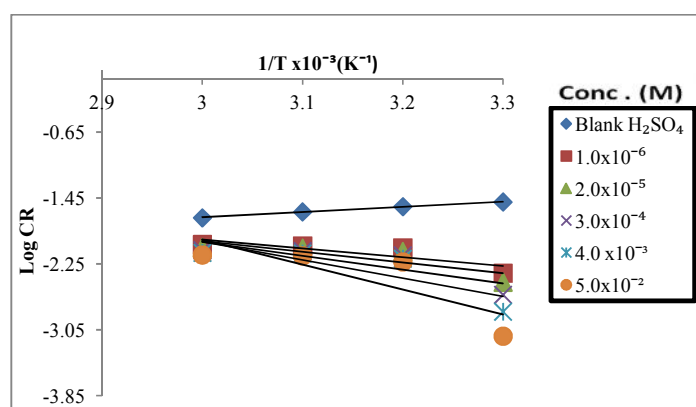
Table 2 indicates that the rate constant of the corrosion process decreases while the half-life increases with increase in the inhibitor concentration. As the  $t_{1/2}$  increases, the rate constant decreases, which indicates that more protection of copper coupons by *Myrianthus arboreus* leaves extract has been established. This is also observed in literature [21,28,23].

### 3.6 Thermodynamics and Adsorption Studies

The values of activation parameters such as activation energy  $E_a$ , for corrosion of copper in the absence and presence of the extract at different concentrations over the working temperature range (303 – 333K) were obtained using Arrhenius equation (7).

$$\text{Log CR} = \log A - \left( \frac{E_a}{2.303RT} \right) \quad (7)$$

where, CR is the corrosion rate at absolute temperature T, R is the universal gas constant,  $E_a$  is the apparent activation energy and A, the Arrhenius pre-exponential factor. The Arrhenius plot of log CR vs  $1/T$  is shown in Figure 6 for the corrosion of copper in the absence and presence of different concentrations of *Myrianthus arboreus*.



**Fig. 6: Arrhenius plot of Log CR vs  $1/T$  at different extract concentrations for the corrosion of copper coupons in 2M  $H_2SO_4$  solution.**

Linear curves were obtained from the Arrhenius plots with slope as  $-(E_a/2.303RT)$ . The values of  $E_a$  calculated from the slopes of the linear plots are given in Table 3.

**Table 3: The Activation Energy ( $E_a$ ) values at the various concentrations of the extract.**

Extract Concentration(M)	$E_a$ (kJ/mol)
Blank	12.31
$1.0 \times 10^{-6}$	20.43
$2.0 \times 10^{-5}$	24.92
$3.0 \times 10^{-4}$	32.17
$4.0 \times 10^{-3}$	42.33
$5.0 \times 10^{-2}$	58.01

Table 3 shows higher values of  $E_a$  in the presence of the extract when compared to that in the absence of the extract. The higher values of  $E_a$  for the inhibited system which increase with increasing concentration of the extract suggest strong inhibitive action of the extracts by



increasing energy barrier for the corrosion process. Thus indicating a strong electrostatic character of the inhibitor's adsorption on the copper surface. The enthalpy and entropy of the adsorption process were calculated using an alternative formula to Arrhenius equation, which is sometimes referred to as Transition state Equation (8), according to [29].

$$\log\left(\frac{CR}{T}\right) = \left[ \left( \log \frac{R}{Nh} \right) + \frac{\Delta S}{2.303R} \right] - \frac{\Delta H}{2.303RT} \quad (8)$$

where,  $h$  is the plank's constant,  $N$ , Avogadro's number,  $R$ , universal gas constant and  $T$  the absolute temperature.  $\Delta H$  and  $\Delta S$  are enthalpy and entropy of activation respectively.

Figure 7 shows the plot of  $\log (CR/T)$  vs  $1/T$  for the corrosion of copper in 2M  $H_2SO_4$  at the different concentrations studied.

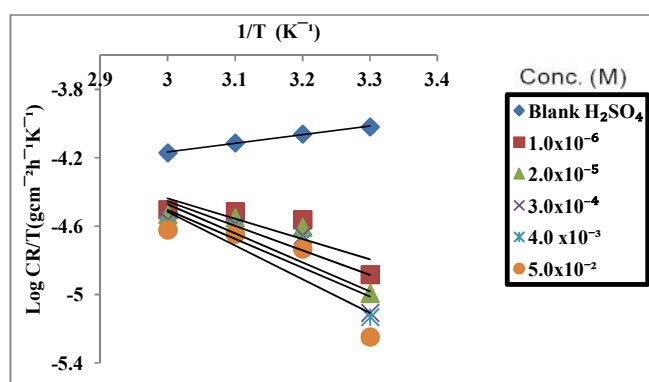


Fig. 7: Plots of Log (CR/T) vs 1/T for the corrosion of copper in 2M  $H_2SO_4$  at different concentrations of the extract.

Straight line graphs were obtained with a slope of  $-(\Delta H/2.303R)$  and an intercept of  $[\log (R/Nh) + \Delta S/(2.303R)]$ , from where the values of  $\Delta H$  and  $\Delta S$  were calculated and shown in Table 4.

Table 4: The Enthalpy ( $\Delta H$ ) and Entropy ( $\Delta S$ ) values of corrosion at the various concentrations of the extract.

Extract Conc.(M)	$\Delta H$ (kJ/mol)	$-\Delta S$ (J/mol)
Blank	11.69	72.68
$1.0 \times 10^{-6}$	22.72	99.51
$2.0 \times 10^{-5}$	27.54	100.61
$3.0 \times 10^{-4}$	34.78	101.53
$4.0 \times 10^{-3}$	44.94	112.94
$5.0 \times 10^{-2}$	60.63	160.49

The positive values of  $\Delta H$  in the absence and presence of the extract reflects the endothermic nature of the copper dissolution process [30] while negative and large values of  $\Delta S$  in both solutions indicate that the activated complex the orbate and adsorbent in the rate determining steps represents association rather than dissociation step. This suggests a decline in disorderliness on going from reactant to activated complex in accordance with some

findings in literature [31, 32, and 17]. Negative value of entropy also signifies no significant change in the internal structure of the copper surface during the adsorption process.

### Adsorption Consideration

Adsorption isotherms are very important in obtaining basic information on the interaction between the inhibitor and the metal surface. The mechanism of organo-electrochemical reactions is also determined through adsorption isotherm [33, 34]. The inhibiting process of the corrosion of copper in 2M H<sub>2</sub>SO<sub>4</sub> medium at different concentrations of the extract can be explained in relation to the adsorption of the components of the extract on metal surface. Three adsorption isotherms were used to describe the adsorption mechanisms [21] of *Myrianthus arboreus* extract on copper coupons in 2M H<sub>2</sub>SO<sub>4</sub> solutions. They are Freundlich (equation 9), Temkin (equation 10) and Langmuir (equation 11). Linearity of curves is an indication that a given isotherm obeys an adsorption process.

$$\log \theta = \log K_f + \frac{1}{n} \log C \quad (9)$$

where  $K_f$  and  $C$ , represents the equilibrium constant of adsorption and extract concentrations respectively,  $\frac{1}{n}$ , the adsorption intensity and  $\theta$ , the surface coverage. The constant  $K_f$  is an approximate indicator of adsorption capacity while  $\frac{1}{n}$  is a function of the strength of adsorption in the adsorption process. The values of  $\frac{1}{n}$  and  $K_f$  can be evaluated from the slope and intercept of such plots respectively. If  $\frac{1}{n}=1$  then the partition between the two phases are independent of the concentration and if value of  $\frac{1}{n}$  is below one, it signifies a normal adsorption (21, 35).

The Temkin isotherm is given as:

$$\exp (-2a\theta) = K_{ad} C \quad (10)$$

The Langmuir is given as:

$$C/\theta = \left(\frac{1}{K_{ads}}\right) + C \quad (11)$$

where,  $a$  is molecular interaction parameter. The values of  $a$  and  $K_{ad}$  can be evaluated from the slope and intercept of such plots respectively. Linear plots in Figures 8 and 9 suggested that the experimental data fits Freundlich and Temkin adsorption isotherm. The estimated values for  $K_f$ ,  $\frac{1}{n}$ ,  $a$ ,  $K_{ads}$  and  $R^2$  for the two isotherms at various temperatures are shown in Table 4a.

**Table 4a: Freundlich and Temkin parameters for the adsorption of *Myrianthus arboreus* leave on Copper surface at 303 – 333K.**

T(K)	Freundlich			Temkin		
	R <sup>2</sup>	K <sub>f</sub>	1/n	R <sup>2</sup>	a	K <sub>ads</sub>
303	0.999	0.6886	0.018	0.998	-0.022	7.7051 x 10 <sup>26</sup>
313	0.995	0.7499	0.015	0.997	0.020	1.8539 x 10 <sup>32</sup>

323	0.991	0.8147	0.012	0.994	-0.018	$1.2209 \times 10^{39}$
333	0.996	1.0069	0.011	0.997	-0.020	$3.6286 \times 10^{43}$

Large  $K_f$  value indicates greater adsorption capacity, low values of  $\frac{1}{n}$  obtained from Freundlich plot shows normal adsorption. The negative values of "a" obtained from Temkin plot showed that repulsion exist in adsorption layer. The values of  $a$  and  $K_{ads}$  obtained signify strong adsorbate – adsorbent molecular attraction and great binding strength (36, 37 and 38).

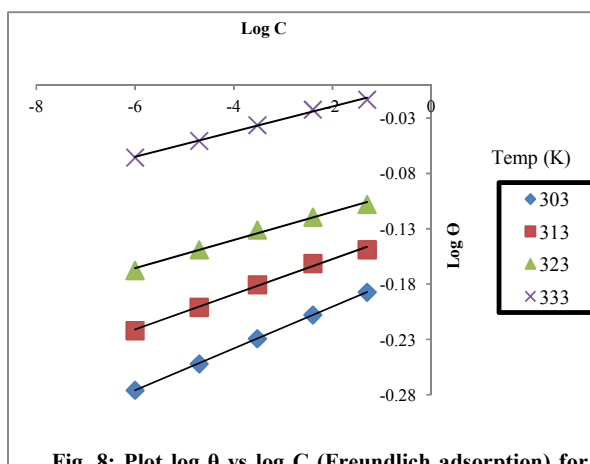


Fig. 8: Plot log  $\theta$  vs log C (Freundlich adsorption) for the inhibition of copper corrosion in 2M  $H_2SO_4$  by different concentrations of extract at temperatures of 303-333K.

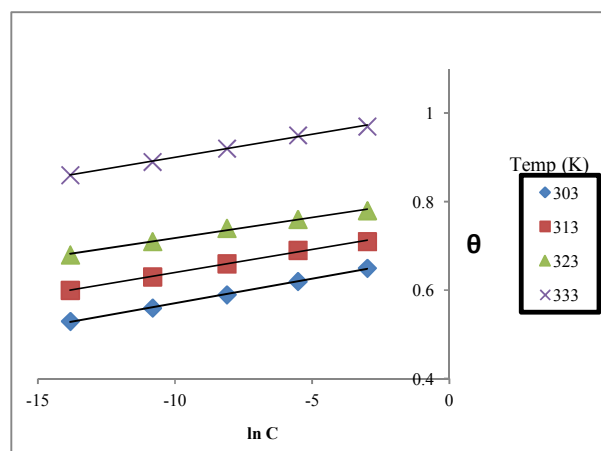


Fig. 9: Plot  $\theta$  vs ln C (Temkin adsorption) for the inhibition of copper corrosion in 2M  $H_2SO_4$  by different concentrations of extract at temperatures of 303-333K.

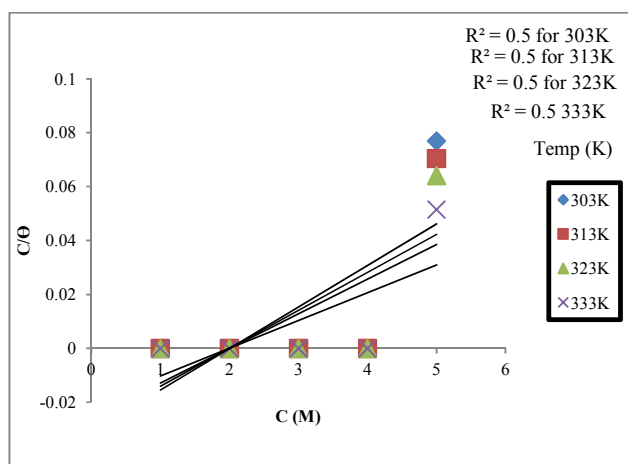


Fig.10 : Langmuir adsorption plot ( $C/\theta$  vs C) for inhibition of copper corrosion in 2M  $H_2SO_4$  by different concentrations of extract at temperatures of 303-333K.

The equilibrium constant of adsorption ( $K_{ads}$ ) obtained from the intercepts of  $\theta$  vs log C plot is related to the free energy of adsorption ( $\Delta G_{ads}$ ). The ( $\Delta G_{ads}$ ) which characterizes the

interaction of adsorption between the molecules of leave extracts and metal surface was calculated using Equation 12 and also presented in Table 5.

$$\Delta G_{ads} = -2.303RT \log(55.5K_{ads}) \quad (12)$$

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

**Table 5: The calculated values of Free Energy of adsorption at various temperatures.**

Temperature (K)	$-\Delta G_{ads}$ (kJ/mol)
303	9.1546
313	9.6833
323	10.2670
333	11.1541

Table 5 shows that the values of  $\Delta G_{ads}$  are negative at all temperatures, indicating spontaneous adsorption of the leaves extract and good stability of the adsorbed layer on the copper surface [39]. The negative values of  $\Delta G_{ads}$  for the extracts are signifying that the adsorption mechanism of the extract on copper in 2M  $H_2SO_4$  acid solution at the temperatures studied may be **Physisorption**. Similar results have also been reported [40] on the inhibitive action of *delonixregra* extract on the corrosion of aluminium in acidic medium.

Literatures reviewed reveal that negative values of  $\Delta G_{ads}$  up to  $-20$  kJ/mol or lower are consistent with electrostatic interaction between charged molecules and a charged metal (indicating physical adsorption) while those around or more than  $-40$  kJ/mol involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type bond (indicating chemisorption) [41, 42]. The mechanism of adsorption observed from this study could be attributed to the fact that *Myrianthus arboreus* leaves extract contains many **Phyto-constituents** in which some have the ability to absorb chemically and others physically. Similar observations have been reported [27, 21].

#### **Phytochemical Constituents of *Myrianthus arboreus* leave extract.**

Qualitative phytochemical screenings of *Myrianthus arboreus* leaves extract revealed the presence of some chemical constituents according to [43, 44 and 45]. The chemical structures of most of these phyto-constituents contain electron rich bond or hetero atoms that facilitate their electron donating ability. The presence of secondary metabolites in plants extracts has been identified as the factor responsible for the corrosion inhibitory properties on metal surface [25]. Hence, the inhibition of the corrosion of copper by methanol extracts of *Myrianthus arboreus* is attributed to the phyto-constituents of the extract. Similar inferences have been reported by some researchers for their inhibition. The corrosion inhibition of copper using three different types of flavonoid was studied and inhibition efficiency of 92% was obtained. This indicates a good corrosion inhibitor [46]. The corrosion inhibition of mild steel in sulphuric acid solution by flavonoid separated from *Nypa fruticans* wurmb leaves extract was reported to be a good and efficient corrosion inhibitor [47].

**Table 6: The phytochemical Results for Methanol extract of *Myrianthus arboreus* leaves.**

Phytochemical Constituents	Results
Alkaloid	+++
Flavonoid	+++
Saponin	+
Tannin	+
Terpenoids	+
Carbohydrates	+
Cardiac glycosides	+
protein	+
steroids	-
Anthraquinone	-
Fixed oils	-

— = Absent, + = present,  
 ++ = moderately present,  
 +++ = in high concentration.

## Conclusion

This study has shown that the methanol extract of *Myrianthus arboreus* leave is a good and efficient inhibitor for the corrosion of copper in 2M H<sub>2</sub>SO<sub>4</sub> solution particularly at increased inhibitor concentration. The maximum inhibition efficiency of 97.67% was obtained. The Ea values obtained were found to be higher for the inhibited system than uninhibited system which shows that the adsorbed organic constituent provided a physical barrier for charge and mass transfer, leading to decrease in dissolution rate of copper. The mechanism of physical adsorption has been proposed and a first order type of reaction was obtained from the kinetic treatment of the experimental data. The adsorption mechanism was observed to obey Freundlich and Temkin adsorption isotherms at all concentrations and temperature ranges studied.

## REFERENCES

- Shah AM, Rahim AA, Hamid SA and Yahya S. Green corrosion inhibitors for Copper corrosion by Mangrove Tannin. International Journal of Electrochemical Science, 2013; 8,2140-2153.
- Mohsin EA, Husam M K and Rasha NA. Inhibition of copper corrosion in H<sub>2</sub>SO<sub>4</sub>, NaCl and NaOH solutions by *Citrullus colocynthis* Fruits Extracts. Journal of Natural Sciences Research, 2014; 4 (17): 60-73.
- Prassan SP, Monika PSV and Alka S. *Capparis decidua* seeds: Potential green inhibitor to combat acid corrosion of copper. RASAYAN Journal of Chemistry, 2015; 8(4):411- 421.
- Fouda AS, Shalabi K. and Idress AA. *Ceratonia siliqua* extract as green Corrosion inhibitor for Copper and brass in nitric acid solutions. Green Chemistry Letters and

- Reviews, 2015;8(3-4): 17-29.
5. Olusegun KA, Abdulraman OCA and Suleiman M. Eco-friendly corrosion inhibitors: Effect of Delonix regia extract on corrosion and kinetics of corrosion process of aluminium alloy 2S in HCl solution. African Corrosion Journal, 2016; 2(2):11-16.
6. Fouda AS, Elmorsi MA and Abou-Elmagol BS. Adsorption and inhibitive properties of Methanol extract of *Euphorbia Heterophylla* for the corrosion of copper in 0.5M nitric acid solutions Polish Journal of Chemical Technology, 2017;19(1):95-103.
7. Krishnaveni K and Ravichandran J. A study on the inhibition of copper corrosion in Sulphuric acid by aqueous extract of leaves of *Morinda tinctoria*. Journal of Failure Analysis and Prevention, 2015;15(5):711-721.
8. Hart, KG, Orubite-Okorosaye K and James AO. Corrosion inhibition of copper in sea water by *Xanthosoma* Spp leaf extracts (XLE). International Journal of Advance Research in Chemical Science (IJARCS), 2016, 3(12):34-40.
9. Patel KK and Vashi RT. *Azadirachta indica* extract as corrosion inhibitor for copper in Nitric acid medium. Research Journal of Chemical Science, 2015, 5(11):59-66.
10. Abd-El-Nabey, El-Housseiny S., El-Naggar GA, Matter EA and Esmail G. Inhibitive Action of *Alhagim aurorum* plant extracts on the corrosion of copper in 0.5M H<sub>2</sub>SO<sub>4</sub> acid. Physical Chemistry, 2015, 5(3):49-62.
11. Savita NC, Punita M, Singh VK and Singh MM. Fruit extract as green inhibitor for copper corrosion in Nitric acid solution. International Journal of Innovative Research in Science, Engineering and Technology, 2015, 4(6): 4545-4553.
12. Deepa R and Selvaraji S. *Emblica officinalis* (AMLA) leaves extract as corrosion inhibitor for Copper and its alloy (Cu-27Zn) in natural sea water. Archives of Applied Science Research, 2010, 2(6):140-150.
13. Nkuzinna O, Menkit MC and Onukwuli OD. Inhibition of copper corrosion by acid extracts of *Gnetum Africana* and *Musa acuminata peel*. International Journal of Multidisciplinary Science and Engineering, 2011, 2(5):6-9.
14. Kalada H and James AO. The inhibitive effect of *Aloe vera Barbadosensis* Gel on copper in Hydrochloric acid medium. Journal of Engineering and Applied Science, 2014, 5(1):24-49.
15. Abd-El-Nabey BA, Abdel-Gaber AM, Said Ali M El, Khamisi El-Housseiny S. Inhibitive Action of Cannabis plant extract on the corrosion of copper in 0.5M H<sub>2</sub>SO<sub>4</sub>. International Journal of Electrochemical Science, 2013, 8: 5851-5865.
16. Mounir F, El Issami S, Bazzi Lh, Salghi R, Bammou L, Bazzi L, Chihab EA and Jbara O. Copper corrosion behaviour in phosphoric acid containing chloride and its inhibition by *Artemisia* oil. International Journal of Research and Reviews in Applied Science (IJRRAS), 2012,13(2):574-587.
17. Fouda AS, Mohamed AE and Khalid MA. *Trigonella stellate* extract as corrosion inhibitor for Copper in 1M nitric acid solution. Journal of Chemical and Pharmaceutical Research, 2016, 8(2):86-98.
18. Swati Y, Arpita S, Guddi C and Monika AS. Inhibitive and adsorption properties of Ethanolic Extract of fruit of *Azadirachta indica* on the corrosion of copper in HCl. International Journal of Innovative Research Science, Engineering and Technology,

- 2014, 3(9):16127-16136.
19. Fadel W, Mahmoud A Al-Qudah and Ghassab M Al-Mazaideh. Corrosion inhibition of copper by *Capparis spinosa* L extract in strong acidic medium: Experimental and Density Functional Theory. International Journal of Electrochemical Science, 2017,12: 4664-4676.
20. Jonathan MN, Efiok JA. And Adeyemi OO. Inhibition and Adsorption-kinetic studies of *Gmelina arborea* fruit extract on corrosion of armour steel plate in hydrochloric acid. International Journal of Scientific and Engineering research, 2015, 6(9):701-717.
21. Fadare OO, Okoronkwo AE. and Olasehinde EF. Assessment of anti-corrosion potentials of extract of *Ficus asperifolia-Miq* (Moraceae) on mild steel in acidic medium. African Journal of Pure and Applied Chemistry, 2016, 10(1):8- 22.
22. Murthy ZVP and Vijayaragavan K. Mild steel corrosion inhibition by acid extract of leaves of *Hibiscus sabdariffa* as a green corrosion inhibitor and sorption behavior. Green Letters and Reviews,2014,7(3): 209-219.
23. Olasehinde EF, Olusegun SJ, Adesina AS, Omogbehin SA and Momoh-YahayahH. Inhibitory action of *Nicotiana tobacum* extracts on the corrosion of mild steel in HCl: Adsorption and thermodynamics study. Nature and Science, 2013,11 (1):83-90.
24. Ismail M, Abdulrahman AS and Hussian MS. Solid waste as environment benign corrosion inhibitor in acid medium. International Journal of Engineering Science and Technology, 2011, 3(2):1742-1748.
25. Okafor PC, Ebiekpe VE, Azike CF, Egbung GE, Brisibe EA and Ebenso EE. Inhibitor action of *Artemisia annua* on the corrosion of mild steel in H<sub>2</sub>SO<sub>4</sub> acid solution. International Journal of Corrosion, 2012, 1-8.
26. Umoh IE and James AO. Inhibition of Zinc corrosion in hydrochloric acid by PyridoxolHydrochloric. International Journal of Pure and Applied Chemistry, 2009, 4(1-2): 55-58.
27. Ating EI, Umoren SA, Udousoro II, Ebenso EE and Udoh AP. Leaves extract of *Anana ssativum* as green corrosion inhibitor for aluminium in hydrochloric acid solutions. Green Chemistry Letters and Reviews, 2010, 3 (2):61-68.
28. Ngobiri NC, Oguzie EE, Oforka NC and Akaranta O.(2015). Comparative study on the effect of Sulfadoxine-Pyrimethamine and an industrial inhibitor on the corrosion of pipeline steel in petroleum pipeline water. Arabian Journal of Chemistry, 2015<http://dx.doi.org/10.1016/jc.2015.04.004>.
29. Noor EA and Al-Moubaraki AH. Thermodynamics study of metal corrosion and Inhibitor adsorption processes in mild steel/1-methyl-4[4'(-x)-styrlpyridinum iodides/ hydrochloric acid systems. Material Chemistry and Physics, 2008, 110, 145-154.
30. Khadom AA, Yaro AS and Kadum AH. Corrosion inhibition by naphthylamine and phenylenediamine for the corrosion of copper –nickel alloy in hydrochloric acid. Journal of Taiwan Institute of Chemical Engineers, 2010, 41(1):122-125.
31. Saedah R and Al-Mhyawi. Corrosion inhibition of aluminium in 0.5M HCl acid solution By Garlic aqueous extract. Oriental Journal of Chemistry, 2014, 30 (2): 541-552.
32. Eduok UM, Umoren SA and Udoh AP. Synergistic inhibition effects between leaves and stem extracts of *Sida acuta* and iodide ion for mild steel corrosion inH<sub>2</sub>SO<sub>4</sub> solutions. Arabian Journal of Chemistry, 2012, 5: 325-337.
33. Larabi L, Harek Y, Benali O, and Ghalem S. Hydrazine derivatives as corrosion inhibition



- for Mild steel in 1M HCl. Progress in Organic Coatings, 2005, 54(3): 256-262.
34. Jeyaprabha CS, Sathiyarayanan SG and Venkatachari G. Effect of Cerium ions on Corrosion inhibition of PANI for iron in 0.5M H<sub>2</sub>SO<sub>4</sub>. Applied Surface Science, 2006, 253, 432-438.
35. Ejikeme P., Umana SG, Alinnor IJ, Onukwuli OD and Menkiti MC. Corrosion Inhibition and Adsorption Characteristics of *Jatropha curcas* leaves extract on Aluminium in 1M HCl solution. American Journal of Material Science, 2014, 4(5):194-201.
36. Ekemini I. and Umoren IS. Solvent effect and Adsorption study of mild steel protection from acid corrosion using Eco-friendly formulations of Annatto extract. Portugaliae Electrochimica Acta, 2014, 35(1): 27-37.
37. Ghazi MBI, Chan NW, Haliza AR and Nor AZ. Freundlich Isotherm Equilibrium Equations in Determining Effectiveness a low cost Absorbent to Heavy Metal Removal in Wastewater (Leachate) at Teluk Kitang Landfill, Pengalan Chapa, Kelantan, Malaysia. Journal of Geography and Earth Science, 2013, 1(1):1-8.
38. Umoren SA, Obot IB, Ebenso EE and OKafor PC. Eco-friendly inhibitors from Naturally occurring Exudate Gums for Aluminium corrosion inhibition in acidic medium. Portugaliae Electrochimica Acta, 2008, 26, 267-282.
39. Shukla SK, Quraishi MA and Ebenso EE. Adsorption and corrosion inhibition properties of Cefadroxil on mild steel in hydrochloric acid. International Journal of Electrochemical Science, 2011, 6, 2912-2931.
40. Abiola OK, Oforka NC, Ebenso EE and Nwinuka NM. Eco-friendly corrosion inhibitors: Inhibitive action of *delonix regia* extract for the corrosion of aluminium in acidic medium. Anti-corrosion Methods and Material, 2007, 54: 219 – 224.
41. Ebenso EE. Synergistic effect of halide ions on the corrosion inhibition of aluminium using 2-acetylphenothiazine. Material Chemistry and Physics, 2003, 79(1):58-70.
42. Oguzie EE, Enenebeaku CK, Akalezi CO, Okoro SC, Ayuk AA. and Ejike EN. Adsorption and corrosion inhibiting effect of *Dacryodis edulis* extract on low carbon–steel corrosion in acidic media. Journal of Colloid and interface Science, 2010, 349: 283-292.
43. Agyare C, Ansah AO, Ossei PPS, Apenteng JA, Boakye YD. Wound Healing and anti-infective Properties of *Myrianthus arboreus* and *Alchorneacordifolia*. Medicinal Chemistry, 2014, 4:533-539.
44. Awodi PI, Abbah CO, Ejembi DO. Phytochemical constituents and Anti-oxidant properties of Aqueous leaf extract of *Myrianthus arboreus*. International Journal of Biomedical Science and Engineering, 2017, 5(1): 9-13.
45. Oyeyemi SD, Arowosegbe S and Adebisi AO. Phytochemical and proximate evaluation of *Myrianthus arboreus* (P.Beau.) and *Sparganophorus Sparganophora* (Linn) leaves. Journal of Agriculture and Veterinary Science, 2014, 17(9):01-05.
46. Al-qudah MA. Inhibition of copper corrosion by Flavonoids in Nitric acid. E- Journal of Chemistry, 2011, 8(1): 326-332.
47. Nwaugbo CM and James AO. The Corrosion inhibition of mild steel in Sulphuric acid solution by flavonoid (catechin) separated from *Nypa fruticans wurmb* leaves extract. Science Journal of Chemistry, 2014, 2 (4): 27-32.