

# INHIBITION AND ADSORPTION-KINETIC STUDIES OF *Gmelina arborea* FRUIT EXTRACT ON CORROSION OF ARMOUR STEEL PLATE IN HYDROCHLORIC ACID

JONATHAN M. NWAEDOZIE , EFIOK J. AKPAN\* , ADEYEMI O. OLUFEMI  
Chemistry Department (Materials Science and Explosives), Nigeria Defence Academy, NDA Kaduna.  
Correspondence:jmnwaedozie@gmail.com and efiok-akpan@nda.edu.ng

**Abstract:** The evaluation of inhibitive action of crude *Gmelina arborea* fruit extract (GAFE) on armor steel plate (ASP) in 0.1M HCl solutions has been investigated using different methods viz; weight loss method at temperature 303K-313K, Electrochemical technique (Linear Polarization Resistance) and Surface morphologic examination, using Phenom Prox Scanning Electron Microscope. The inhibitive action is observed to increase with increase in concentration of the extract, but decreases with increase in temperature. The Extract gave highest inhibition efficiency (IE) of 87.50% at 303K and 78.87% at 313K at maximum extract concentration of 0.5g/L. Inhibition efficiency (IE) of extract decreased with increasing temperature for both acids. Thermodynamic parameters evaluated gave heat of adsorption ( $Q_{ads}$ ) range between -24.4904 kJ/mol -16.4337 kJ/mol with an average of -6.1547kJ/mol. The Activation energy parameter ( $E_a$ ) is between 4.11 to 14.76 kJ/mol, which indicates physisorption. Free energy of adsorption process ( $\Delta G^{\circ}_{ads}$ ) showed negatives values, which explained the spontaneous adsorption activity. Adsorption process of GAFE on armor steel plate best fitted and obeyed the El-Awady isotherm. The El-Awady  $1/y$  parameter is  $<1$  at all test conditions. Electrochemical investigations (LPR- curve), reveals that GAFE acts as a mixed inhibitor by retarding the cathodic and anodic reaction. Micrographs from SEM, shows evidence of plant material adsorption on ASP under similar test conditions with near smooth surface. In contrast, Micrographs of ASP after immersion in acids without GAFE shows evidence of general and localized corrosion (pitting).

**Keyword:** *Gmelina arborea*, Armour steel Plate, ductility, Corrosion, Inhibition and toughness

## 1.0 INTRODUCTION

Armor steels are versatile materials alloys of iron used in Military and defense related field in manufacture of combat air craft, Tanks, ships and submarines. They are largely low-carbon, medium-alloy steels of special compositions used for protection from projectiles and ballistics due to its toughness, weldability, and ductility (Laible, 1980; Prifti *et al.*, 1997). Armour Steels like every other material corrodes and poses a major challenge to defence industries fleets against optimum performance and combat readiness. The effect of corrosion can best be appreciated by the annual cost of its prevention, the direct and indirect value of which, survey on the costs of corrosion showed that the direct cost of corrosion was estimated at \$276 billion in the United States for 2002, which is approximately 4% of their Gross National Product (Koch *et al.*, 2002). The Wall Street Journal (1981) estimates it to be over hundreds of millions of US dollars all over the world. In view of the foregoing, corrosion no doubt has proven to be an undesirable

phenomenon that must be arrested or controlled (Buchweishaija , 2010). In order to reduce the metal loss as a result of corrosion, tests and use of suitable inhibiting agents as corrosion inhibitors in different environment is necessary. (NACE, 1984; 2002) defines inhibitor as a chemical substance that, when added in a small concentration to an environment, effectively decreases the corrosion rate of the material.

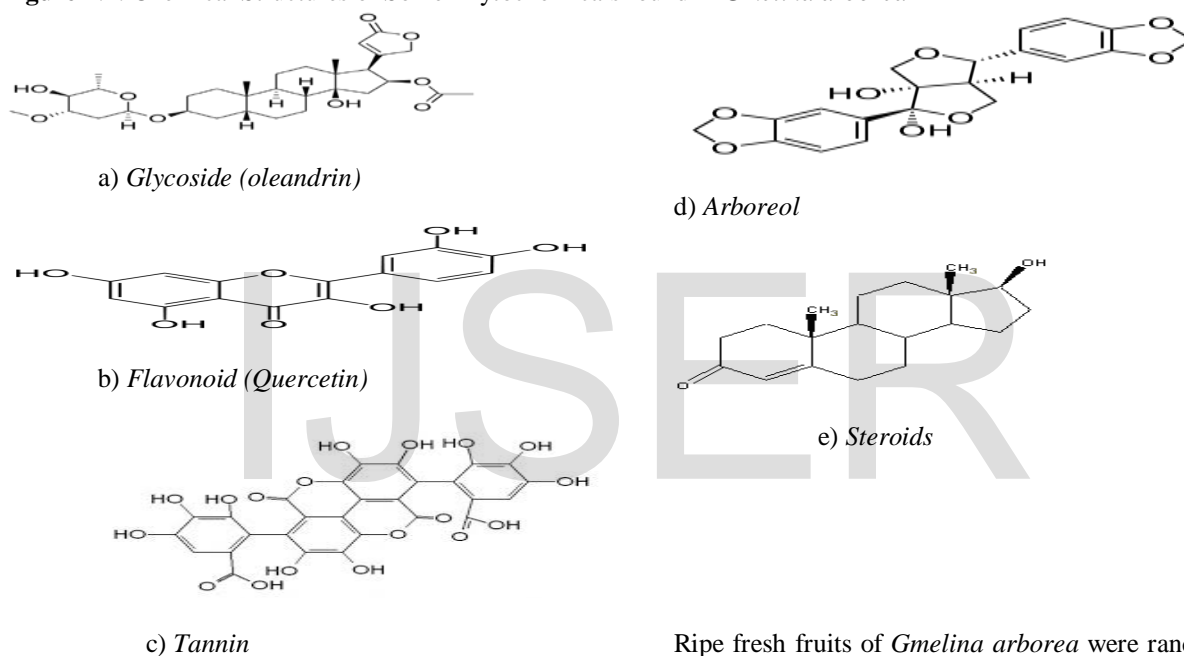
Most of these inhibiting compounds are not only expensive; they are toxic and not environmental friendly. Due to the toxicity of some corrosion inhibitors, there has been increasing search for green or organic corrosion inhibitors (Muthukrishnan *et al.*, 2013). These natural organic inhibitors has been tested and found to be effective in various media and and at same time environmentally friendly, non-toxic, biodegradable, inexpensive, and readily available in nature (El-Etre, 2007; Okafor *et al.*, 2008). These anti corrosion effect has been suggested to be due to the presence of hetero atoms (N, O, and S) as well as

multiple bonds or aromatic rings in these inhibitor (Jayalakshmi, and Muralidharan, 1998)

*G. arborea* is be adaptable and fast growing tree that survives well on a wide range of soil types example; acid soils, calcareous loams, and lateritic soils. It is known to thrive best in fresh, well-drained, fertile soils where rainfall annually varies from 1200 to 4500 mm (Kijkar, 2002). The plant is used for treatment as demulcent, lactagogue, refrigerant, stomachic, galactagogue, laxative, anthelmintic, anti-inflammatory and tonic. The roots alleviate vata and kapha, have hot potency and heavy attribute. It is used against anthrax, blood disorders, cholera, colic,

convulsions, diarrhea, and its decoction is used for abdominal tumors (Banu *et al.*, 2013). Studies and literature survey on different parts of *Gmelina arborea* shows that different classes of secondary metabolites has been identified, example; flavonoids (Kaur *et al.*, 2012), phenolics Shankar (2009), steroids and cardiac glycosides Nayak *et al* (2012) and iridoids (Akhilesh *et al.*, 2008; Neerja *et al.*, 2008; Chugh *et al.*, 2012). Alkaloid, carbohydrates, tannins, mucillages, phenolic and flavonoids has also been extracted from *Gmelina arborea* fruit with Ethanol (Nayak *et al*, 2012)

**Figure 1.1:** Chemical Structures of Some Phytochemicals found in *Gmelina arborea*



The aim of this work is to investigate the corrosion of mild steel in 0.1 M Hydrochloric acid (HCl) using fruit extract of *Gmelina arborea* as corrosion inhibitor by weight loss, Electro analytical and Surface Morphologic investigations. This investigation is predicated upon the fact that the above enumerated bio active phyto-chemicals compounds found in *Gmelina arborea* contains at least one of the numerous known hetero atoms with as the potentials of reducing corrosion activity.

## 2.0 MATERIALS AND METHODS

### 2.10 COLLECTION AND EXTRACTION OF THE PLANT SAMPLE

Ripe fresh fruits of *Gmelina arborea* were randomly collected from Nigerian defense academy old site Kaduna (10.558°N and 7.428°E) and identified with dedicated Voucher 210. The fruits mechanically macerated and allowed to stand for one day, and later sun dried for two weeks under normal atmospheric condition. Plant sample were pulverized/homogenized with the aid of clean mortar and pestle. 100g of dried plant was measure using analytic balance of dried fruit was dissolved in 200ml of (1:1 Volume ratio of both Acetone and Ethanol). The filtrate was distilled in a water bath that was maintained at 60±5°C in order to leave the extract free of solvent. Plant extract was used in the preparation of the test solutions by dissolving 0.1g, 0.2g, 0.3g, 0.4g, 0.5g of the extract in 1L of 0.1M HCl and then used to test for corrosion inhibition

properties. Double distilled water and analar grades reagents were used in the studies. The prepared coupons were then subjected to corrosion testing using (Gravimetric, Electrochemical and Surface morphological Techniques).

The concentrations of the inhibitors were within the range, 0.1 to 0.5g/L. Each of these concentrations were used to prepare different test solutions by dissolving them in 0.1M HCl and used in the various tests.

## 2.20 ARMOR STEEL PREPARATION

Armor steel plate was obtained from machined and cut away products from fabrication works of Amor personnel carrier from mechanical workshop of Defense Industry Corporation of Nigeria (DICON). Elemental analysis was carried out using Optical emission spectrometer (Shimadzu PDA 7000). All Corrosion tests were performed on the ASP of the same composition following percentage composition:

0.19714 % C, 0.25974 % Si, 0.66418 % Mn, 0.02426 % P, 0.95733 % Ni, 0.42712 % Cr, 0.34352 % Mo, 0.15558 % Cu, 0.9582 % Ti, 0.02922 % Al, 0.07648 % Co, 0.04753%,96.7221%Fe.

Amor steel plate (ASP) were pressed cut with the aid of precision cutting and grinding machine and polished with silicon carbide abrasive paper of grits (260-1,200) to dimension (18.25 mm X 10.00 mm) with 6.00 mm thickness and polished to mirror surface for weight loss, while specimens of 2 mm X 2 mm dimension was prepared to fit into phenom prox SEM sample holder. Similarly, Copper wire of 40cm long whose both ends were made bare was mounted on working electrode (ASP) with the aid of Aluminum electrochemical adhesive tape.

The other end was connected to one of the three terminals of the potentiostat. The working electrode (ASP) and then covered with a Polytetrafluoroethylene (PTFE) ribbon and an epoxy resin such that an area of 1 × 1 cm was left exposed at one side for electrochemical measurement where all the electrodes were immersed in 200 ml corrodent Absolute ethanol and acetone was used to degrease the polished coupons. (Oguzie *et al.*, 1994; Umoren *et al.*, 2008).

## 2.30 WEIGHT LOSS MEASUREMENTS.

Gravimetric experiments were carried out in a heating test tube containing test solution in semi enclosed thermostatic water bath. A weighed metal (ASP) coupon was completely immersed in test tube in the inside the water bath that was maintained at 303K and 313K. The experiment was conducted at 2hour intervals over 10 hours immersion time. The corrosion product was removed intervals by washing each coupon (withdrawn from the test solution). The experiment was repeated at 313K with triplicate measurement in the absence and presence of various concentrations of GAFE in 0.1M HCl solution. The weight loss, corrosion rate of ASP and the degree of surface coverage and efficiency were calculated using the Equation (1), (2) (3) and (4) respectively (Ebenso, 2009)

$$W_L = W_i - W_f \quad (1)$$

$$\text{Corrosion Rate (CR)} = \frac{\Delta W_L}{A T} \text{ (g/cm}^2 \cdot \text{hr)} \quad (2)$$

The degree of surface coverage ( $\theta$ ) is given by:

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

The efficiency percentage of inhibitors (IE %) was computed using the relationship

$$\text{IE} \% = \left[ 1 - \left( \frac{\Delta W_{inh}}{\Delta W_{blank}} \right) \right] \times 100 \quad (4)$$

Where  $W_1$  and  $W_2$  are the weight losses (g) for ASP in the presence and absence of the inhibitor respectively, CR is the corrosion rate of mild steel in  $\text{gcm}^{-2} \cdot \text{h}^{-1}$ , A is the area of the mild steel  $\text{cm}^2$ , t is the total period of immersion (in hours) and  $\theta$  is the degree of surface coverage of the inhibitor.

## 2.40 ELECTROCHEMICAL STUDIES

Representative Samples from weight loss experiment were further subjected to electroanalytical investigations by immersing the ASP in 0.1M HCl in the absence and presence of 0.5g GAFE for two hours at 303K. Open circuit measurement was conducted with and without inhibitors at 303K using Potentio-static and Galvanostatic AUTOLAB AUTO50280 in combination with NOVA 1.10.1.9 software following a complete set up and test initiated over a Direct Current. Investigation on measurement of open circuit Potential followed

immediately after immersion of all the electrodes, at the following sets of electrochemical conditions;  $\pm 1.500$  V with Scan rate of 0.0120000(V/s) at 0.083333 interval time (sec). Linear potentiodynamic polarization measurement was automatically initiated immediately after OCP measurement at same set electro analytical conditions as was earlier reported in this work for OCP determination. The parameters measured includes; the values of corrosion current densities ( $I_{corr}$ ), corrosion potential ( $E_{corr}$ ), cathodic ( $\beta_c$ ) and anodic ( $\beta_a$ ). The linear Tafel segments of the anodic and cathodic curves were selected with point marker on the logic chart display from points showing linearity and automatically extrapolated to corrosion potential ( $E_{corr}$ ) to obtain the corrosion current densities ( $I_{corr}$ ), and other corrosion parameter directly from the NOVA 1.10.1.9 software. In each measurement, a fresh working electrode was used. The inhibition efficiency (IE) values were calculated from the  $I_{corr}$  values from equation 5 below [oguzie *et al.*, 2004].

$$IE\% = \left[ 1 - \left( \frac{I_{corr}(inh)}{I_{corr}(blank)} \right) \right] \times 100 \quad (5)$$

Where;  $I_{corr}(Blank)$  = Corrosion current density in the absence of inhibitors and  $I_{corr}(inh)$  = Corrosion current density in the presence of inhibitors.

The linear Tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities.

### 2.50 SURFACE MORPHOLOGICAL STUDIES

Representative Samples from weight loss experiment were further subjected to Surface analysis was performed using scanning electron microscope. SEM images were obtained from ASP surface after the immersion in 0.1 HCl in the absence and presence of GAFE for two hours at 303K.. This was done in order to assess the extent of acidic attack on ASP by micro-structural examination and the effect of the addition of the extract as an inhibitor.

## 3.0 RESULTS AND DISCUSSION

### 3.10 WEIGHT LOSS MEASUREMENT

#### 3.11 Effect of Variation of Time with Weight Loss and Inhibitor Concentration

The rate of weight loss with time of metal samples (ASP) in constant concentrations of 0.1 M HCl with varying inhibitor concentration was monitored using weight-loss method. The data of weight-loss with corresponding calculated corrosion rate of ASP in 0.1M HCl are presented in (Table 3.1). The Variations of weight-loss with time and Inhibitor concentration in (Figures: 3.1 and 3.2) shows that, weight loss and corrosion rate of ASP increased with increasing immersion time but decreased with increasing inhibitor concentration in all test conditions in 0.1 M HCl media.

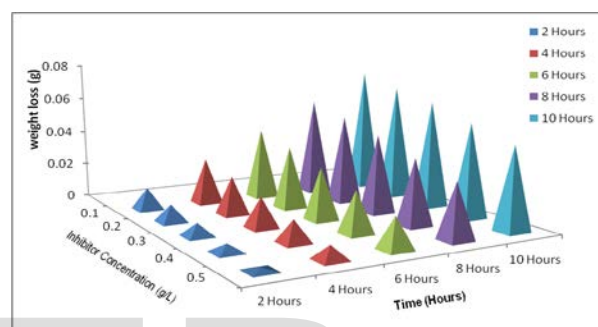


Figure 3.1: Variation of weight loss with time and various concentrations of GAFE in 0.1M HCl at 303K

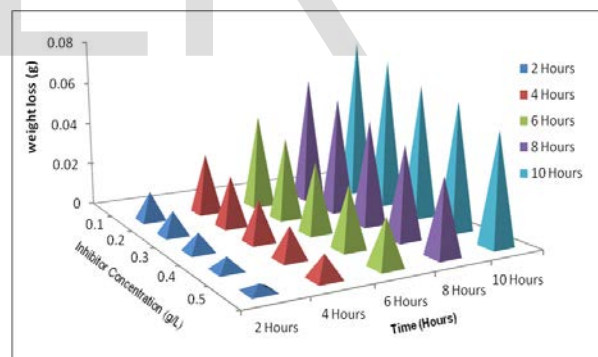
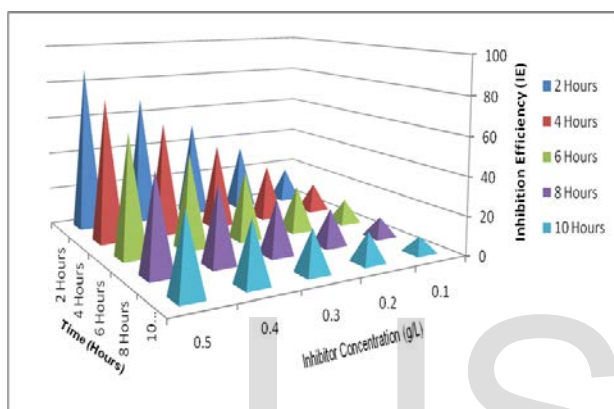


Figure 3.2: Variation of weight loss with time and various concentrations of GAFE in 0.1M HCl at 313K

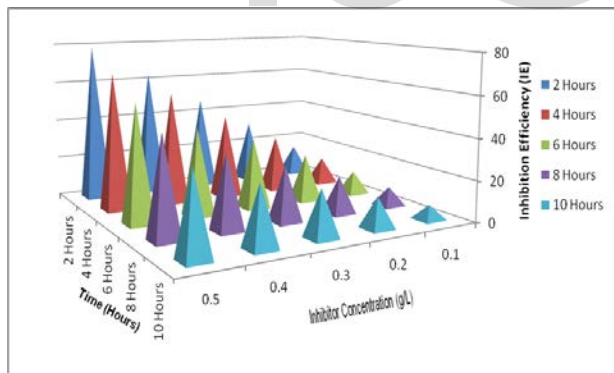
#### 3.12 Variation of Inhibition Efficiency with Inhibitor Concentration and Time

Result obtained presented in (Table 3.1) shows a general trend of decrease in Efficiency with increasing immersion time and increase efficiency with increase inhibitor in all test conditions shown in (Figures: 3.3 and 3.4). The reduced inhibition efficiency as time increased is suggested to be as a result of desorption activity as of GAFE from the

ASP surface as time increased, which subsequently resulted in higher values of weight loss and corresponding corrosion rate due to exposure of more surface area to corrodant attack. Highest efficiency of the entire weight loss investigation is observed in 0.1M HCl + 0.5g/L GAFE systems with 87.50 % at 303K and 78.87% for 0.1M HCl + 0.5g/L GAFE for 2hours immersion time at 313K systems respectively . Lowest of all efficiencies was observed with 7.10% for 0.1M HCl+ 0.1g/L GAFE after 10 hours at 313K and 8.04% for 0.1M HCl+ 0.1g/L GAFE after 10 hours at 303K respectively.



**Figure 3.3: Variation of inhibition efficiency with GAFE concentration and time in 0.1M HCl at 303K**



**Figure 3.4: Variation of inhibition efficiency with GAFE concentration and time in 0.1M HCl at 313K**

### 3.13 Effects of Temperature on Corrosion Rate and Efficiency

The effect of temperature on the inhibitive action of GAFE on the corrosion of ASP was monitored at various Inhibitors concentrations and temperatures of 303 K and 313 K. The calculated data in (Table 3.1)

reveals that, as the concentration of Inhibitor (GAFE) increased, the corrosion rate decreased for both temperatures, with lowest corrosion rate record of  $1.3479 \times 10^{-4} \text{g/cm}^2 \cdot \text{hr}$  for HCl +0.5g/L GAFE while efficiency in same condition is 87.50 % at 303K. This shows the propensity of the extract to get adsorbed and inhibit the corrosion of the metal (Umoren and Ekanem, 2010; Obot *et al.*, 2011). Higher efficiencies are observed in all test conditions at 303K than at 313K, this variations is suggestive of desorption of GAFE from the ASP, probably due to acceleration of initiation reaction at 10K rise in temperature resulting in destabilizing GAFE molecules and decreasing the its activity, this in turn results in reduced efficiency for either chemo/ and or physical adsorption activity on active ASP site Corrosion rate and weight loss was observed to increase with increasing temperature for all conditions with given GAFE concentration in the corrodant under study. The maximum corrosion rates and weight loss are  $1.4601 \times 10^{-3} \text{g/cm}^2 \cdot \text{hr}$  and 0.1027g for blank at 313K during the tenth hour immersion period for HCl system.

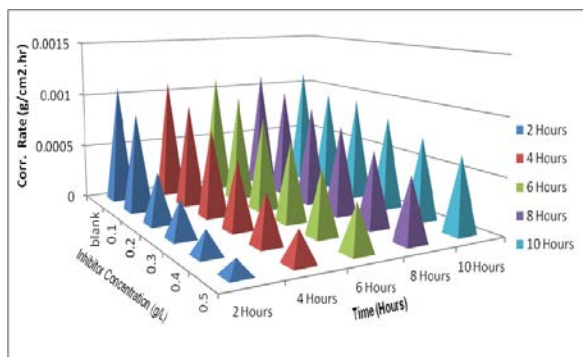
The increase in Corrosion rate as temperatures increases in given Inhibitor concentration for 303K and 313K, can be explained on the basis of desorption and the unstable nature of active phytochemicals of GAFE molecules on ASP when temperature was increased, thus reduced adsorption potential (desorption favored) on the active sites of ASP surface, which results in the exposure of more surface area of the metal surface to acid attack. Plants Phytochemical activities have been reported to show reduced activity at certain temperatures while others are optimal at same or other temperatures (Ruenroengklin *et al.*, 2008)

In view of the foregoing, it is inferred that the plant may not be a good inhibitor in higher temperature. The decreased in the adsorption at higher temperature provides a clue to suggesting possible physical adsorption process of inhibitor (Maayata and Al-Rawashdeh, 2004).

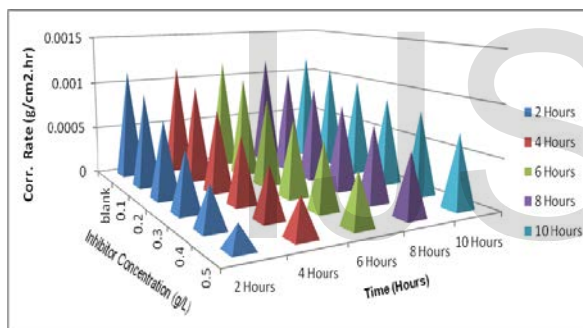
### 3.14 Variation of Corrosion Rate with Inhibitor

The corrosion rate was observed to decrease as the inhibitor concentration was increased, where as corrosion rate increased as time increased with same inhibitor concentration at all test conditions as shown

in (Figures:3.5 and 3.6). This is consistent with report of investigation by Adeyemi and Singh (1998), who opined that some inhibitors are known to be effective at short period of time interval because of Maximum Efficiency of 87.50% presented in (Table 3.1) and shown in in (Figures 4.9, 4.1), at maximum GAFE concentrations of 0.5g/L at 303K.



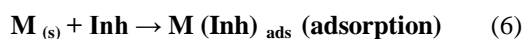
**Figure 3.5: Variation of Corrosion Rate with GAFE concentration and time in 0.1M HCl at 303K**



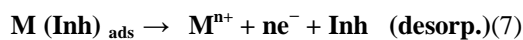
**Figure 3.6: Variation of Corrosion Rate with GAFE concentration and time in 0.1M HCl at 313K**

This indicates that the inhibitors were adsorbed onto the metal surface and thereafter, inhibits the corrosion process (El-Mahdy and Mahmoud, 1995). The inhibitive action requires understanding of the inhibitor at the electrode-solution interface. In acid solution, the chemical compounds of GAFE may have been Protonated.

The surface charge of ASP in HCl solutions is known to be positive (Deng and Li, 2012). Farhat and Quraishi (2010) showed that the mechanism of adsorption for the adsorption process to the metal surface can be best described using a general equation as:



autoanalysis. The inhibition Efficiency is also observed to increase with increasing concentration of GAFE with



Where;  $M(Inh)_{ads}$  and  $Inh$  are the organo-metallic complex and the inhibitor.

### 3.20 Adsorption and Thermodynamic Characterization

In order to obtain the adsorption isotherm, the surface coverage  $\Theta$  is calculated using the weight loss and electrochemical measurements by the ratio following the expression,  $\Theta = \%IE/100$ .

It is therefore pertinent to determine empirically the isotherm model that fits best to the adsorption of inhibitors (GAFE) on ASP obtained from experimented data. The effect of the inhibitor (GAFE) on ASP was analyzed and tested with the following isotherms; Langmuir, Freundlich, Temkin, Flory-Huggins, Bockris-Swinkal, El Awardy *et. al.*, and Frumkin) and the values of surface coverage at different concentrations of inhibitor in 0.1M HCl, and was made to fit into the various tested isotherms.

The degree of fit between the experimented data and the isotherm assumptions and equation used in determining the type of adsorption taking place in the system was carried out by choosing particular linear plot with highest correlation coefficient ( $R^2$ ) close to unity (1). From the fit tests results, it was found that the experimental data fits best in the thermodynamic-kinetic model for El awady *et al* (1992) which is a modification advanced to address the limitation from Langmuir isotherm.

It considers inter and intra molecular charge and ion interaction in different reaction phase. The characteristics of the isotherm are given by equation below;

$$\log(\theta/1-\theta) = \log K + y \log C \quad (9)$$

Where;

C is the concentration of the extract,  $\theta$  is the degree of surface coverage,  $K_{ads}$  is the equilibrium constant of adsorption process which is equals to  $K^{1/y}$  that is; ( $K_{ads} = K^{1/y}$ ). This model explains that the number of

active site  $y$  is included, values of  $1/y < 1$  suggest multilayer adsorption while  $1/y > 1$  suggest that a given inhibitor molecule occupied more than one active site (Obot *et al.*, 2009).

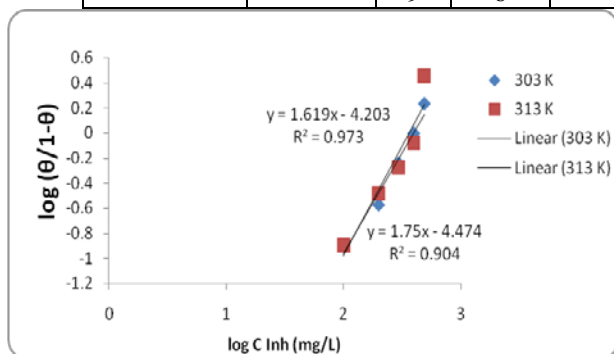
**Table 3.1: Calculated values of variation in Corrosion Rate, Weight loss, Surface Coverage ( $\Theta$ ) and Inhibition Efficiencies (IE) at 303K and 313K in 0.1M HCl with and without inhibitor at different Immersion Time.**

TEMP (303K)/ 0.1M HCl	GAFE Conc (g/L)	W <sub>L</sub> (g)	Corr Rate(g/cm <sup>2</sup> .hr)	$\Theta$ (Surface coverage)	IE % Inhibition efficiency	TEMP (313K) /0.1M HCl	GAFE Conc (g/L)	W <sub>L</sub> (g)	Corr Rate(g/cm <sup>2</sup> .hr)	$\Theta$ (Surface coverage)	IE % Inhibition efficiency
2 hours	Blank	0.0152	1.0810x10 <sup>-3</sup>	NA	NA	2 hours	Blank	0.0159	1.1306x10 <sup>-3</sup>	NA	NA
	0.1	0.0125	8.8905x10 <sup>-4</sup>	0.1776	17.76		0.1	0.0135	9.5992x10 <sup>-4</sup>	0.1509	15.09
	0.2	0.0099	4.5164x10 <sup>-4</sup>	0.3487	34.87		0.2	0.0109	7.7511x10 <sup>-4</sup>	0.3144	31.44
	0.3	0.0073	3.3242x10 <sup>-4</sup>	0.5197	51.97		0.3	0.0084	5.9729x10 <sup>-4</sup>	0.4716	47.16
	0.4	0.0047	2.1402x10 <sup>-4</sup>	0.6907	69.07		0.4	0.0058	4.1244x10 <sup>-4</sup>	0.6352	63.52
	0.5	0.0019	1.3479x10 <sup>-4</sup>	0.8750	87.50		0.5	0.0032	2.2754x10 <sup>-4</sup>	0.7987	78.87
4 hours	Blank	0.0308	1.0958x10 <sup>-3</sup>	NA	NA	4 hours	Blank	0.0324	1.1520x10 <sup>-3</sup>	NA	NA
	0.1	0.0262	9.3172x10 <sup>-4</sup>	0.1493	14.93		0.1	0.0281	9.9912x10 <sup>-4</sup>	0.1327	13.27
	0.2	0.0219	7.7881x10 <sup>-4</sup>	0.2898	28.98		0.2	0.0233	8.2859x10 <sup>-4</sup>	0.2808	28.08
	0.3	0.0172	6.1166x10 <sup>-4</sup>	0.4415	44.15		0.3	0.0188	6.6850x10 <sup>-4</sup>	0.4197	41.97
	0.4	0.0125	4.4452x10 <sup>-4</sup>	0.5941	59.41		0.4	0.0142	5.0492x10 <sup>-4</sup>	0.5617	56.17
	0.5	0.0077	2.7349x10 <sup>-4</sup>	0.7500	75.00		0.5	0.0104	3.6984x10 <sup>-4</sup>	0.6790	67.90
6 hours	Blank	0.0469	1.1119x10 <sup>-3</sup>	NA	NA	6 hours	Blank	0.0495	1.1735x10 <sup>-3</sup>	NA	NA
	0.1	0.0410	9.7202x10 <sup>-4</sup>	0.1258	12.58		0.1	0.0439	1.0407x10 <sup>-3</sup>	0.1131	11.31
	0.2	0.0356	8.4401x10 <sup>-4</sup>	0.2409	24.09		0.2	0.0379	8.9853x10 <sup>-4</sup>	0.2343	23.43
	0.3	0.0300	7.1116x10 <sup>-4</sup>	0.3603	36.03		0.3	0.0322	7.6334x10 <sup>-4</sup>	0.3494	34.94
	0.4	0.0240	5.6896x10 <sup>-4</sup>	0.4882	48.82		0.4	0.0281	6.6611x10 <sup>-4</sup>	0.4323	43.23
	0.5	0.0175	4.1484x10 <sup>-4</sup>	0.6268	62.68		0.5	0.0212	5.0258x10 <sup>-4</sup>	0.5717	57.17
8 hours	Blank	0.0626	1.1129x10 <sup>-3</sup>	NA	NA	8 hours	Blank	0.0662	1.1771x10 <sup>-3</sup>	NA	NA
	0.1	0.0562	9.9926x10 <sup>-4</sup>	0.1022	10.22		0.1	0.0600	1.0668x10 <sup>-3</sup>	0.0936	09.36
	0.2	0.0507	9.0149x10 <sup>-4</sup>	0.0190	19.00		0.2	0.0541	9.6188x10 <sup>-4</sup>	0.1827	18.27
	0.3	0.0449	7.9831x10 <sup>-4</sup>	0.2827	28.27		0.3	0.0482	8.5696x10 <sup>-4</sup>	0.2719	27.19
	0.4	0.0375	6.6674x10 <sup>-4</sup>	0.4009	40.09		0.4	0.0421	7.4851x10 <sup>-4</sup>	0.3640	36.40
	0.5	0.0313	5.5650x10 <sup>-4</sup>	0.5000	50.00		0.5	0.0342	6.0809x10 <sup>-4</sup>	0.4833	48.33
10 hours	Blank	0.0784	1.1145x10 <sup>-3</sup>	NA	NA	10	Blank	0.0830	1.1799x10 <sup>-3</sup>	NA	NA

	0.1	0.0721	9.4109x10 <sup>-4</sup>	0.0804	08.04	hours	0.1	0.0771	1.0960x10 <sup>-3</sup>	0.0717	07.10
	0.2	0.0662	9.4102x10 <sup>-4</sup>	0.1556	15.56		0.2	0.0705	1.0023x10 <sup>-3</sup>	0.1506	15.06
	0.3	0.0613	8.3467x10 <sup>-4</sup>	0.2181	21.81		0.3	0.0624	8.8704x10 <sup>-4</sup>	0.2265	22.65
	0.4	0.0539	7.3381x10 <sup>-4</sup>	0.3125	31.25		0.4	0.0589	8.3733x10 <sup>-4</sup>	0.2903	29.03
	0.5	0.0470	6.6813x10 <sup>-4</sup>	0.4005	40.05		0.5	0.0506	7.1930x10 <sup>-4</sup>	0.3903	39.03

**Table 3.2: El-awady's Kinetic-Thermodynamic, Adsorption Parameters for GAFE+ HCl System**

Conc./Temp	Inhibitor Conc. (mg/l)	log C	Θ	$\frac{\log \Theta}{(1-\Theta)}$	Slope	1/y	R <sup>2</sup>	K <sub>ads</sub>	ΔG <sub>ads</sub> (kJ/mol)
0.1M HCl At 303K	100	2.00	0.1127	-0.8962	1.6195	0.6174	0.9733	0.2974	-
	200	2.30	0.2108	-0.5733					
	300	2.47	0.3645	-0.2415					
	400	2.60	0.4973	-0.0047					
	500	2.69	0.6305	0.2321					
0.1M HCl At 313K	100	2.00	0.1124	-0.8975	1.7500	0.5714	0.9045	0.2546	-7.0925
	200	2.30	0.2325	-0.4828					
	300	2.47	0.3478	-0.2730					
	400	2.60	0.4567	-0.0754					
	500	2.69	0.5846	0.4610					



**Figure 3.7: El-awady's thermodynamic-kinetic Isotherm Plot for 0.1M HCl + GAFE at 303K and 313K**

The equilibrium constant of adsorption process is related to the free energy of adsorption G<sub>ads</sub> as shown in equation 10 (Khamis, 1990)

$$(\Delta G_{ads}) = -2.303RT \log (55.5K_{ads}) \quad (10)$$

Where;

T is the temperature, K<sub>ads</sub> is the equilibrium constant of adsorption, R is the molar gas constant (8.314 kJ/mol); 55.5 is the concentration of water in solution expressed in mol/L. For simplicity, the experimental data are most often described by the isotherm by the use of simplified general thermodynamic-kinetic equilibrium constant of adsorption-desorption (K<sub>ads</sub>) process of mobile adsorption equation adopted by Joseph and co workers (Joseph *et al*, 2014) as equation 11 below;

$$K_{ads} = \frac{\Theta}{[(1-\Theta)c]} \quad (11)$$

Where;

C is the concentration of the extract and Θ is the surface coverage from bulk



The average  $\Delta G^{\circ}_{\text{ads}}$  values obtained is negative (-11.1022 kJ/mol and -7.0925 kJ/mol) both at 303 and 313K. The negative values suggest that the adsorption process of GAFE unto the ASP occurred spontaneously and the adsorption is stable (Ikpi *et al.*, 2012).

Generally, values of  $\Delta G^{\circ}_{\text{ads}} \leq -20\text{kJ/mol}$  are consistent with electrostatic interaction between the charged metals and molecules, which infer physical adsorption, while values more negative than -40kJ/mol signifies chemical adsorption (Obot *et al.*, 2010). It is seen that values of  $\Delta G^{\circ}_{\text{ads}}$  for HCl systems calculated and presented in (Table 3.2) is less than -20kJ/mol and thus, confirms that the adsorption of GAFE on ASP surface is physical adsorption and further corroborate results from adsorption isotherm model fit test of El awady *et al* which corroborates physisorption.

### 3.23 Equilibrium Constant for Adsorption Process ( $K_{\text{ads}}$ )

$K_{\text{ads}}$  represents the strength of adsorption between adsorbate and adsorbent (Adejo *et al.*, 2013; Obot and Obi-Egbedi, 2008). A larger value of  $K_{\text{ads}}$  in GAFE + HCl systems particularly at 303K ( $K_{\text{ads}} = 0.2974$ ) implies favourable adsorption and hence supports better inhibitor efficiency Obot and Obi-Egbedi (2008) and values recorded in (Table 4.3).

The  $K_{\text{ads}}$  values are positive indicating conditions for good adsorption which accounted generally good inhibition efficiency (Abboud *et al.*, 2009). The  $K_{\text{ads}}$  values for  $\text{H}_2\text{SO}_4$  and HCl systems decreased with increase temperature, confirming the observed reduction in inhibition efficiency with rise in temperature (Okafor and Apbende, 2014).

### 3.24 Thermodynamic Heat of Adsorption ( $Q_{\text{ads}}$ )

Computed estimates for the heat of adsorption ( $Q_{\text{ads}}$ ) was calculated from the specific Inhibitor concentration and its corresponding average surface coverage trends in specific experimental duration with temperature  $T_1$  (303K) and  $T_2$  (313K) Using equation (12)

$$(Q_{\text{ads}}) = 2.303R [\log (\Theta_2/1-\Theta_2) - \log (\Theta_1/1-\Theta_1)] \times T_2 T_1 / (T_2 - T_1) \quad (12)$$

Where; R is the molar gas constant, and  $\Theta$  are the degrees of surface coverage of the inhibitor at the temperatures  $T_1$  (303 K) and  $T_2$  (313 K). It is generally accepted that, heat of adsorption value lower than -40kJ/mol is suggestive of physical adsorption (Hosseini *et al.*, 2007).

The calculated value for heat of adsorption showed prevalent exothermic process Table 3.3, with an average of -6.1547kJ/mol. The -6.1547kJ/mol at 303K and 313K respectively.

### 3.25 Entropy Of Adsorption ( $\Delta S_{\text{ads}}$ )

The entropy for reaction of adsorption of GAFE on ASP in this work is investigated by considering absolute temperatures of  $T_1$  (303K) and  $T_2$  (313K) as T, since the experiment was conducted in constant pressure ( $q = \text{approx. } \Delta H$  for isobaric condition). It is believed that in Isobaric condition,  $Q_{\text{ads}}$  approximates those of enthalpy of adsorption ( $\Delta H_{\text{ads}}$ ),  $Q_{\text{ads}} = \Delta H_{\text{ads}}$ ; Sharma and Sharma (1999) and also adopted and advanced by Okafor and Apbende in their work (Okafor and Apbende, 2014). The estimated values of entropy of adsorption ( $\Delta S_{\text{ads}}$ ) is computed by substituting the corresponding values of  $\Delta G_{\text{ads}}$  and  $\Delta H_{\text{ads}}$  into the Gibbs-Helmholtz equation in equation (13) and values presented (Table 3.3)

$$\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T\Delta S_{\text{ads}} \quad (13)$$

When:  $Q_{\text{ads}} = \Delta H_{\text{ads}}$ , (That is  $q = \text{approx. } \Delta H$  for isobaric condition)

Equation 13 becomes;

$$T\Delta S_{\text{ads}} = Q_{\text{ads}} - \Delta G_{\text{ads}} \quad (14)$$

$$\Delta S_{\text{ads}} = Q_{\text{ads}} - \Delta G_{\text{ads}} / T \quad (15)$$

Negative value of average entropies in GAFE+ HCl system at T giving ( $\Delta S_{\text{ads}} = -4.1499$ ) implies that the activated complex in the rate-determining step represents and supports association, meaning that disordering decreased on going from reactants to the activated complex, thereby increasing the probability of GAFE molecules to settle or adsorb on ASP (El-Etre, 2007; Oguzie *et al.*, 2005). It is safe to believe that a far better interaction occurred amongst the GAFE molecules and ASP in the activated complex stage. It is plausible that a large amount of such association with ASP considering its associative tendencies is responsible for the High inhibition

efficiencies recorded in GAFE+ HCl system for all experimental conditions.

### 3.26 Activation Energy Determination

Investigation of temperature dependence inhibition efficiency process when compared to its corrosion activation energy with and without inhibitor provides necessary information on metal-inhibitor adsorption mechanism (chemo or physio-sorption). It has been pointed out that the logarithm of the corrosion rate can be used in computing different values of activation energy ( $E_a$ ) Herrag *et al* (2010), this is a characteristic of the adsorption process with dimensions known as activation energy, which itself describe the kinetics of the *Gmelina arborea* extracts adsorption characteristics on ASP. It is a linear function with the reciprocal of the absolute temperature  $1/T$  in the integrated Arrhenius equation which in turn explains apparent activation energy  $E_a$  for corrosion process with and without inhibitor under study:

$$\log \frac{CR_2}{CR_1} = \frac{E_a}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right] \quad (16)$$

Where;

$CR_1$  and  $CR_2$  (Table 3.1) are rate constants at  $T_1$  and  $T_2$  as temperatures (303K and 313K). Computed values of  $E_a$  are presented in Table 3.4

Before the 0.1 M HCl to attack the ASP, its molecules must be activated over an energy barrier equals to the  $E_a$  of the blank (Table 3.4) and is temperature dependent. The  $E_a$  values obtained in the presence of the extracts are higher than those of the blank acid, indicating deactivation of the acid molecules on collision with the metal surface by the introduction of the extracts thus reducing the rate of acid attack on the metal.  $E_a$  (inhibited) >  $E_a$  (uninhibited) coupled with decrease in inhibition efficiency with increase in temperature have been ascribed to physical adsorption mechanism (Fakrudeen *et al.*, 2012).

The calculated  $E_a$  values in Table 3.4, shows that,  $E_a$  increases with increase in concentration of the extracts, with range  $E_a$  range 4.11-14.76kJ/mol with an average of 12.064kJ/mol. The observed trend from the data is consistent with investigations reported by Obot and Obi-Egbedi (Obot and Obi-Egbedi, 2010).

It is considered as good evidence supporting the higher Inhibition efficiency and lower corrosion rates recorded in the HCl system for weight loss and Linear Polarisation measurements.

Activation energy is also another good tool in the determination and characterization of the type of adsorption taking place. It has been reported earlier that, for an adsorption to be considered as physisorption, it is expected that, the average value of  $E_a$  be  $\leq 80$  kJ/mol. For chemo sorption,  $E_a$  should  $\geq 80$  kJ/mol (Adeyemi and Olubomehin, 2010; Ismail *et al.*, 2011). The Calculated apparent activation energy  $E_a$  from experimented data are all below 80 kJ/mol, for GAFE+ HCl systems at all experimental conditions.

This to a large extent suggests a physical adsorption, which correlates with empirical adsorption isotherm model earlier tested with Highest Regression Coefficient values for kinetic thermodynamic El-awady *et al* model as well as those of  $\Delta G^\circ_{ads}$ ,  $Q_{ads}$ , all inferring a physical adsorption process.

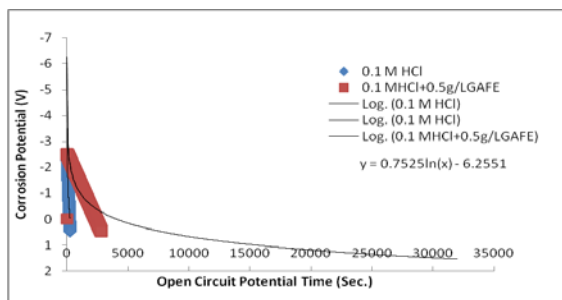
**Table 3.4: Activation Parameters for the Dissolution of ASP With and Without GAFE in 0.1M HCl at 303-313K**

System	Conc of GAFE (mg/L)	( $E_a$ )kJ/mol
0.1M HCl 303-313K	Blank	4.11
	100	6.82
	200	10.35
	300	10.84
	400	14.76
	500	13.44

### 3.30 ELECTROCHEMICAL STUDIES

#### 3.31 Chronopotentiometric-Ocp

The value obtained showed that in all test conditions for chronopotentiometric test, the corrosion potential was observed to have decreased as time increased (Figure 3.8), this trend continued until Open Circuit potential was reached ( $E_{OCP}$ ).



**Figure 3.8: Chronopotentiometric Curve (OCP) with time for 0.1M HCl and 0.1M HCl+0.5g/L GAFE at 303K**

The rate of change of potential with time for inhibited system is lower/slower than those of blank in both acids and at all test conditions. It is believed that the plant extract created a higher resistance polarization across the metal surface (barrier), thereby impeding electron/ charge transfer, which resulted in the lower values of corrosion current  $I_{corr}$  and corrosion potential of inhibited acid systems.

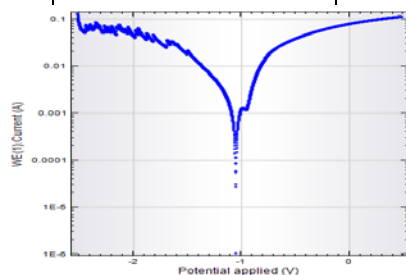
### 3.32 Linear Polarisation Resistance Measurement

Electrochemical corrosion kinetic parameters namely corrosion potential ( $E_{corr}$ ) and corrosion current density ( $I_{corr}$ ) obtained from the tafel extrapolation of the Linear polarization measurement curve (LPR). The polarization parameters obtained from the curves shown in (Figures 3.9, 3.10 and 3.11) are listed in Table 3.5. From the Polarisation logic readout shown in (Figures 3.11), it is seen that Inhibitor (GAFE)

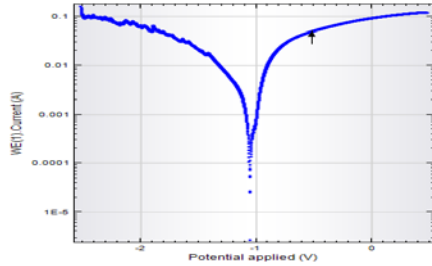
can be best described as a mixed type of inhibitor because of patterns of anodic and cathodic linear polarization shift of potential and current of plot in both acidic media at 303K. This indicates that hydrogen evolution is controlled by activation and the addition of inhibitor does not change the mechanism of cathodic Hydrogen evolution, or may be due to behavior of inhibitor phytochemical under study on ASP having constant activity over a set potential during the anodic or cathodic sweep (Li *et al.*, 2008). There is a slight shift of corrosion potentials ( $E_{corr}$ ) to more negative values and a displacement less than 85 mV with respect to the corrosion potential of blank solution in all cases, indicating that the inhibition property of *Gmelina arborea* extract and primarily affects both cathodic and the anodic processes. This reveals that the studied inhibitor is a mixed type of inhibitor on the ASP in both acidic solutions (Ferreira *et al.*, 2004; Li *et al.*, 2008 and Sastri, 1989).

**Table 3.5: Electro analytical Parameters from Linear Polarisation Resistance Measurement of ASP immersed in 0.1M HCl with 0.5g/L GAFE at 303K**

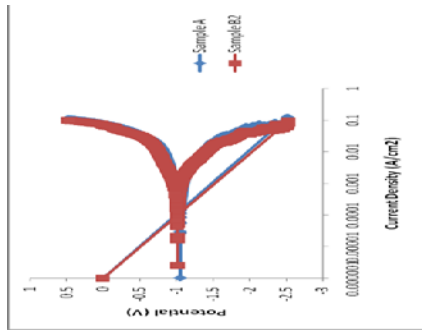
System	$\beta_a$ (V/dec)	$\beta_c$ (V/dec)	$E_{corr, Calc}$ (V)	$E_{corr, Obs}$ (V)	$i_{corr}$ (A/cm <sup>2</sup> )	IE%
0.1MHCl (BLANK)	0.7561	0.54471	-1.0586	-1.0542	0.003629	NA
0.1M HCl+0.5g GAFE	0.14126	0.11885	-1.0215	-1.0168	0.000545	84.98



**Figure 3.9: Linear Polarization curve of ASP in 0.1M HCl at 303K ± 1**



**Figure 3.10: Linear Polarization curve of ASP in 0.1M HCl +0.5g/L GAFE at 303K ± 1**



**Figure 3.11: Variation in Linear Polarization curve between: (A) ASP in 0.1M HCl at 303K ± 1 and (B<sub>2</sub>) ASP in 0.1M HCl + 0.5g/L GAFE at 303K ± 1**

Interestingly also, the inhibition efficiencies from weight loss measurements is found to be in close agreement with values obtained from electro analytical measurements with minor variation as shown in (Table 3.6)

**Table 3.6: Comparative Inhibition Efficiencies from Weight loss and Electrochemical measurements at 303K in 0.1M HCl**

System	Weight Loss At 303k	Electrochemical At 303K
--------	---------------------	-------------------------

	Surface coverage	IE (%)	Surface coverage	IE (%)
0.1 M HCl	NA	NA	NA	NA
0.1M HCl +0.5g/L GAFE	0.8750	87.50	0.8498	84.98

**3.40 Metallographic Examination and Description Of Micrographs**

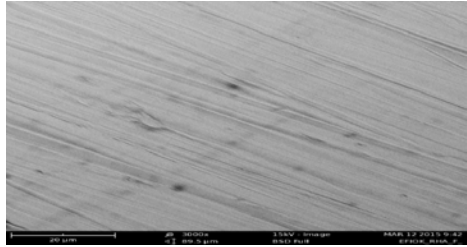
Figure 3.12 a), Shows micrographs of surface condition of ASP before exposure to both acids, the parallel features seen on the clean polished ASP surface which are associated with polishing scratches.

Pore size Histograms values from freshly prepared unexposed ASP is far lower than those for ASP immersed in both the uninhibited and inhibited systems, the uninhibited system is far larger those from inhibited system under same experimental conditions.

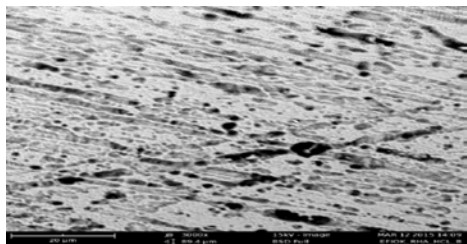
Micrographs from (Figure 3.12 b.), Shows visible pit with dark deposit of corrosion products, this provides physical evidence of acid attack on ASP. These observations can be explained on the basis of Cl<sup>-</sup> ion activity in the uninhibited system (Chin and Nobe, 1972). (Figure 3.12 c) shows GAFE creating a barrier with evidence of plant (Subhashini, 2004). It is also safe to suspect that the plant also showed the potential to prevent possible inter granular, pitting corrosion or any form of localized attack by way of creation of physical barrier (adsorption) as seen in drastic reduction in pore size Histogram from the HCl blank system to the Inhibited system (Figure 3.13 C). This observation is attributable to the absorptive potentials of the plant inhibitor under study to drastically impede oxidative activity which may possibly lead to general, grain boundary or combination of either forms of corrosion.

**3.41 RESULTS FROM METALLOGRAPHIC EXAMINATION USING PHENOM PROX SCANNING ELECTRON MICROSCOPE**

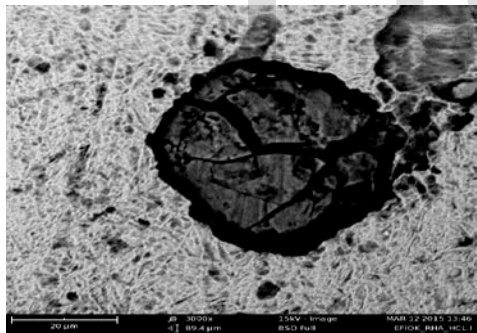
**Figure 3.12:** 15kv, 20µm Micrographs for Polished ASP (a) Before immersion (b) after 2hours immersion in 0.1MHCl at 303K (c) after 2hours immersion in 0.1M HCl+0.5g/L GAFE at 303K.



(a) Before immersion

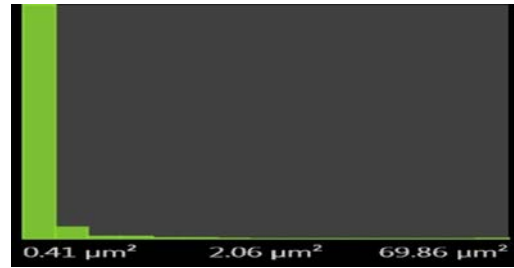


b) After 2hours immersion in 0.1M HCl at 303K

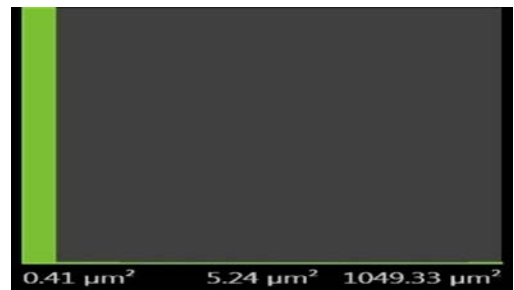


(c) After 2hours immersion in 0.1MHCl+0.5g/L GAFE at 303K

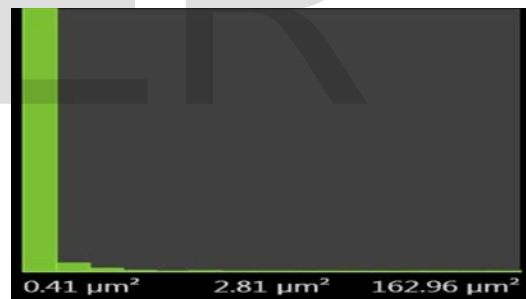
**Figure 3.13:** Pores and Fibre Histograms from SEM Investigation for;



(a)Pore Histogram of ASP before immersion



(b)Pore Histogram of ASP after 2hour immersion in 0.1M HCl At 303K



(c)Pore Histogram of ASP after 2hour immersion in 0.1M HCl+0.5g/L GAFE At 303K

### CONCLUSION

The following conclusions have been drawn from the results of the study;

- Ethanol/acetone (1:1vol/vol) extract from *Gmelina arborea* fruit extract inhibits corrosion process of armor steel in 0.1 M HCl at temperature 303K and 313K.
- The inhibitive action of *Gmelina arborea* fruit extract is due to the adsorption of phytochemical constituents on the armor steel surface going results from investigation

- The thermodynamic adsorption parameters  $\Delta G^{\circ}_{ads}$ ,  $\Delta S_{ads}$ ,  $E_a$ , and  $Q_{ads}$  shows that the studied inhibitor are adsorbed onto armor steel by spontaneous exothermic process.
- The inhibition efficiencies of extract in both acids increased as the extract concentration increased and decreased with increasing temperature, though with generally higher efficiency in HCl system in all test conditions

- Based on trend of inhibition efficiency with temperature and from calculated values from  $\Delta G^{\circ}_{ads}$ ,  $\Delta S_{ads}$ ,  $E_a$  and  $Q_{ads}$ , a physical adsorption of the plants phyto-chemical is suggested.
- The experimental data fitted and obeyed the El-awady's kinetic-thermodynamic adsorption isotherm
- Results from Linear Polarisation Resistance shows that the plant phytochemical is a mixed type of inhibitor capable of reducing anodic and cathodic corrosion process.
- Micrographs, pore size and fibre analysis from Phenom pro x scanning electron microscope (SEM) provides evidence of general and localized (pitting and inter-granular attack) corrosion, as well as physical prove of plant adsorption on the amor steels surface.

#### ACKNOWLEDGEMENTS

Our Profound gratitude is extended to the entire academic and non academic staff of the department of chemistry, Nigerian Defence Academy, NDA Kaduna, for their kind contribution and constructive criticism which culminated in successful execution of this research work.

#### REFERENCES

- Abboud Y., Abouriche A., Aianane T., Charrouf M., Bennamara, A., Tanane O. and Hammouti, B. (2009) Corrosion inhibition of carbon steel in acidic media by *Bifurcaria* extract, *chemical Engineering Communications*, Vol. 196 No.7, pp 788-800
- Adeyemi O. O and Olubomehin O. O. (2010) Investigation of *Anthocleista djalonesis* stem bark extract of corrosion inhibitor for aluminium. *Pacific Journal of Science and Technology* 11(2): 455 – 462.
- Adeyemi O.O and Singh G.(1987) Galvanostatic Polarization and Resistance Studies of Acid

Corrosion of Commercial Copper in the Presence of some Heterocyclic Compounds. *J. Surf. Sc. Tech.*, 3(2) 121-124.;

- Adejo S. O., Gbertyo J. A. and Ahile J. U. (2013) Inhibitive properties and adsorption consideration of ethanol extract of *Manihot esculentum* leaves for corrosion inhibition of aluminium in 2 M  $H_2SO_4$ , *Int'l J. of modern chemistry*. 4(3), 137-146  
[www.modernscientificpress.com/Journals/IJ MChem.aspx](http://www.modernscientificpress.com/Journals/IJ MChem.aspx)
- Akhilesh K. Y., Tiwari N., Srivastava P., Subhash C. S., Shanker K., Ram K. V. (2008) Iridoid glycoside-based quantitative chromatographic fingerprint analysis. A rational approach for quality assessment of Indian medicinal plant Gambhari (*Gmelina arborea*). *J. Pharm Biomed*
- Banu M., Gururaja G M., Deepak M., Roopashree T.S., Shashidhara S. (2013) An overview on Phytochemistry and Pharmacological properties of *Gmelina arborea* *J. Nat. Prod. Plant Resour.*, 3 (4):62-71. (<http://scholarsresearchlibrary.com/archives.html>)
- Buchweishaija J.( 2010). Phytochemicals as Green Corrosion Inhibitors in Various corrosive Media , a Review, Chemistry Department, College of Natural and Applied Sciences, University of Dares Salaam.
- Callister W. D (1997) *Materials Science and Engineering – An Introduction*. 4th Edition, John Wiley and Sons Inc., New York, 550-578
- Chugh C A., Sanjeev M., and Heena D. (2012) Phytochemical Screening and Evaluation of biological activities of some medicinal plants of Phagwara, Punjab. *Asian Journal of Chemistry: Vol 24, No. 12 (2012), 5903-5905.*
- Chin R. J. and Nobe K. (1972) Electrodeposition kinetics of iron in chloride solutions .1.

- acidic solutions. *journal of the electrochemical society* 119 (11): 1457
- Deng S. and Li X (2012) *corros. Sci.* 55; 40
- Ebenso E. E., Eddy N.O., Odongenyi A.O (2009) Inhibition of the corrosion of mild steel by Methocarbamol. *Portugaliae Electrochimica. Acta.* 27, 1; 13-22
- El-Etre A. Y (2007). Inhibition of acid corrosion of carbon steel using aqueous extract of olives leaves, *J. of Colloid & Interface Sci.* 314, 578-580.
- El-Mahdy G. A and Mahmoud S.S. (1995) Inhibition of Pure Aluminum with 5-Benzylidene-1-Methylthio-4-One. *Corrosion Science*, 51, 436
- El-Awady, A. A., Abd-El-Nabey, B. A., Aziz, S. G., (1992) Kinetic-thermodynamic and adsorption isotherms analyses for the inhibition of the acid corrosion of steel by cyclic and open chain amines. *J. Electrochem. Soc.* 139, 2149-2154
- Farhat A A and Quraishi M. A (2010) Inhibitive performance of gemini surfactants as corrosion inhibitor for mild steel in formic acid, *Electrochimica Acta*, 28, 5; 321-335
- Fakrudeen .P, Lokesh H. B., Amanda Murthy H. C and Bheema R. V. (2012) Electrochemical investigation of corrosion inhibition of AA6063 alloy in 1 M HCl using Schiff base compounds. *IOSR Journal of Applied Chemistry.* 2(5): 37-47.
- Ferreira E.S, Giancomelli C, Giacomelli F.C, Spinelli A (2004): Evaluation of the inhibitor effect of l-ascorbic acid on the corrosion of mild steel, *Mater. Chem. Phys.* 83; 129-134.
- Herrag, L., Hammouti, B., Elkadiri, S., Aouniti, A., Jama, C., Vezin, H., Bentiss, F (2010) Adsorption properties and inhibition of mild steel corrosion in hydrochloric solution by some newly synthesized diamine derivatives: experimental and theoretical investigations. *Corros. Sci.* 52, 3042-3051.
- Hosseini M. Mertens. S.F.L, Ghorbani M, Arshadi M R (2007). *Electrochem. Acta*, 52:3680
- Ismail M., Abdulrahman, A. S., Hussain, M. S. (2011) Solid waste as environmental benign corrosion inhibitors in acid medium. *International Journal of Engineering Science and Technology*, 3(2): 1742-1748
- Ikpi M E, Udoh I I, Okafor P C, Ekpe U J and Ebenzo E E (2012) Corrosion Inhibition and adsorption Behavior of extracts from *Piper guineensis* on mild steel Corrosion in Acidic Media. *Int. J. Electrochem. Sci.*, 7:12193-12206
- Jayalakshmi, M. and Muralidharan, V.S., *Ind. J. Chem. Tech.*, 5, 16 (1998).
- Joseph A. G., Stephen G. Y., Sylvester O. A., Tersoo G. T and Ungwanen J. A (2014) Thermodynamic, Kinetic and Adsorptive Parameters of Corrosion Inhibition of Aluminium Using Sorghum bicolor Leaf Extract in H<sub>2</sub>SO<sub>4</sub>. *International Journal of Advanced Research in Chemical Science (IJARCS)* Volume 1, Issue 2, PP 38-46 ISSN 2349-039X (Print) & ISSN 2349-0403
- Kaur N., Kaur S., Bedi PMS., Kaur R. (2012) Preliminary pharmacognostic study of Gmelina arborea bark. *Int J Nat Prod Sci; 1:184.*
- Kirk O. (1989). *Encyclopedia of Chemical Technology*, 4: 289-3000.
- Khamis E.( 1990,). The Effect of Temperature on the Acidic Dissolution of Steel in the Presence of Inhibitors. *Corrosion* , 46(6), pp. 476-484.
- Koch G.H, Brongers M.P.H, Thompson N.G, Virmani Y.P, and Payer J.H (2002) Corrosion Costs and Preventive Strategies in the United States, U.S. Federal Highway Administration Report, FHWA-RD-01-156.

- Laible, R. C (1980). Ballistic Materials and Penetration Mechanics. New York: Elsevier Scientific Publishing Company.
- Lebrini, M., Lagrene, M., Vezin, H., Traisnel, M., Bentiss, F., (2007) Experimental and theoretical study for corrosion inhibition of mild steel in normal hydrochloric acid solution by some new macrocyclic polyether compounds. *Corros. Sci.* 49, 2254–2269.
- Li, X., Deng, S., Fu, H., Mu, G., (2009) Inhibition effect of 6- benzylaminopurine on the corrosion of cold rolled steel in H<sub>2</sub>SO<sub>4</sub> solution. *Corros. Sci.* 51, 620–634
- Maayata, A.K., Al-Rawashdeh, N.A.F.,(2004). Inhibition of acidic corrosion of pure aluminum by some organic compounds. *Corros. Sci.* 46, 1129–1140
- National Association of Corrosion Engineers (NACE: 1984). Corrosion Basics: An Introduction. Houston, Texas, pp. 214–230.
- National Association of Corrosion Engineers (NACE: 2002) Glossary of Corrosion terms, Mat. Pro., 4(1), 79. NACE
- Nayak B., Subas C. Dinda, Ellaiah P. (2012) Opioid and non opioid analgesic activity of *Gmelina arborea* Roxb fruit extracts. *International journal of Pharmacy and Pharmaceutical Science*. Vol5 (1); 263-266 ISSN 09751491
- Neerja T., Akhilesh KY., Pooja S., Karuna S., Ram KV., Madan M G. (2008) Iridoid glycosides from *Gmelina arborea*. *Phytochemistry*; 69:2387-2390.
- Oguzie E.E., Onuoha G.N., Onuchukwu A.I (2005). Inhibitory mechanism of mild steel corrosion in 2 M sulphuric acid solution by methylene blue dye. *Mater. Chem. And Phys* 89 (2-3): 305-311
- Obot, I.B. and Obi-Egbedi, N.O. (2010,) 2,3-Diphenylbenzoquinoxaline: A new corrosion inhibitor for mild steel in sulphuric acid. *Corrosion Science* 52: 282
- Obot I.B. and Obi-Egbedi N.O (2010) an interesting and efficient green corrosion inhibitor for aluminium from extracts of *Chlomolaena odorata* L. in acidic solution”, *Journal of Electrochemistry* 40, 11; 1977-1984
- Obot I. B. and Obi-Egbedi N. O (2008) Inhibitory effect and adsorption characteristics of 2,3-diaminonaphthalene at aluminium/hydrochloric acid interface: Experimental and theoretical study, *Surface Review and Letters*, 15, 903-911
- Obot, I.B., Obi-Egbedi, N.O. and Umoren, S.A. ( 2009) Adsorption characteristics and corrosion inhibitive properties of clotrimazole for aluminium corrosion in hydrochloric acid, *International Journal of Electrochemical Science*, 4, 863-877
- Obot I. B., Umoren S. A. and Obi-Egbedi N. O., (2011). Corrosion inhibition and adsorption behaviour for aluminium by extract of *Anigeria robusta* in HCl solution: Synergistic effect of iodide ions, *J. of Material and Environmental Sci.* 2(1), 60-71
- Okafor P. C and Apende. E A (2014) Corrosion inhibition characteristics of *Thymus Vulgaris* *Xylopi aethiopia* and *Zingiber officinale* extract on mild steel in H<sub>2</sub>SO<sub>4</sub> solutions. *Pigment and resin Technology*, Volume 43. Number 6. pp354-364
- Okafor P.C., Ikpi M.I., Uwah I.E., Ebenso E.E., Ekpe U.J., and Umoren S.A. (2008) Inhibitory Action of *Phyllanthus amarus* Extract on the Corrosion of Mild Steel in Acidic Media, *Corros. Sci.*, 2008, 50, p 2310–2317.
- Ruenroengklin N, Jia Zhong, Xuewu Duan, Bao Yang, Jianrong Li and Yueming Jiang



- (2008) Effects of Various Temperatures and pH Values on the Extraction Yield of Phenolics from Litchi Fruit Pericarp Tissue And the Antioxidant Activity of the Extracted Anthocyanins *Int. J. Mol. Sci.* 2008, 9, 1333-1341; DOI: 10.3390/ijms9071333
- Sastri V S. (1998) Corrosion inhibitors, principles and applications. New York: John Wiley and Sons
- Shankar S., Girish R., Karthik N., Rajendran R., Mahendran V.S., Allelopathic (2009): Effects of phenolics and terpenoids extracted from *Gmelina arborea* on germination of Black gram (*Vigna mungo*) and Green gram (*Vigna radiata*). *Allelopathy J*; 23:323-32.
- Subhashini S (2004) Corrosion inhibition study of mild steel in acid media by extracts of some *Leguminous* seeds as eco-friendly inhibitors. *J. Camel Pract.Res.* 11(1):27-34.
- Umoren S. A. and Ekanem U. F, (2010) Inhibition of mild steel corrosion in  $H_2SO_4$  using exudate gum from *Pachylobus edulis* and synergistic potassium halide additives, *Chemical Engineering Communication.*197, 1339-1341
- Wall Street Journal (Sept. 11, 1981) 4(2), 111-113

IJSER