

# Manihot Esculentum Root Peels Ethanol Extract as Corrosion Inhibitor of Aluminium in 2 M H<sub>2</sub>SO<sub>4</sub>

Sylvester O. Adejo, Joseph A. Gbertyo\*, John U. Ahile and Tyohemba T. Gabriel

**Abstract:** The inhibition of aluminium corrosion by the ethanol extract of *Manihot esculentum* peels in 2 M H<sub>2</sub>SO<sub>4</sub> solution was studied by weight loss method at the temperature range of 303 K to 315 K. It was observed that the percentage inhibition efficiency, IE % and surface coverage,  $\theta$ , increased with increase in the inhibitor concentration and when temperature was raised. The increase in IE% with rise in temperature suggests that the inhibitor followed chemical adsorption pathway. The highest inhibition efficiency was 43.33 at 315K, a comparatively low value of IE% at the highest studied temperature indicating that desorption processes were higher in the adsorption-desorption equilibrium process. Free energy of adsorption,  $\Delta G_{ads}$ , ranged from -11.63 kJmol<sup>-1</sup> to -13.90 kJ/mol<sup>-1</sup>, indicative of spontaneous adsorption process and these values are supportive of a physical adsorption mechanism, granting a basis for mixed inhibition process. The heats of adsorption values were +11.39 kJmol<sup>-1</sup>, +11.73 kJmol<sup>-1</sup>, +7.271kJmol<sup>-1</sup>, +5.40 kJmol<sup>-1</sup>, and +3.254 kJmol<sup>-1</sup> implying endothermicity. The values of activation energy,  $E_a$  ranged from 45.90 kJmol<sup>-1</sup> to 52.77 kJmol<sup>-1</sup>, further supporting that some constituents of the extract were physically absorbed. The mean entropy value of -131.41 Jmol<sup>-1</sup> suggests that the entire adsorption process might be controlled by the activation complex. More so, the data obtained fitted best to Freundlich, El-Awady and to some extent, Langmuir adsorption isotherms.

**Keywords:** Corrosion, inhibition, *Manihot esculentum*, root peels, Weight loss method, aluminium, Adsorption isotherms.

## 1. Introduction

The wastage of metal due to corrosion has become an important engineering problem. Probably, no other source of waste except that affecting human life is of greater concern to all. It has well been said that only through the elimination of waste caused by corrosion and the increase in our national efficiency we can hope to lower the cost of living on one hand, and raise our standard of living on the other. The elimination of waste is a total asset. It has no liabilities [1], [2], [3].

Corrosion, an irreversible interfacial physicochemical interaction of a material (metal, alloy, ceramic, glass, wood, polymer and concrete) with its environment [4], [5] which results in consumption of the material or dissolution of the material's components, changes in the properties of the material leading to the impairment of its function; the environment, or the technical system of which it forms a part, has generated serious concern in the industry [6]. Cassava, *Manihot esculenta* Crantz, is a perennial woody shrub with an edible root, which grows in tropical and sub-tropical areas of the world [7].

Cassava is one of the most important food crops in the tropics and serves as a food security and income generation crop for many millions of people in the developing countries [8].

It is grown widely in Nigeria and in many regions of the tropics, where it serves as one of the basic food source for about 200 to 300 million people. In 1999, Nigeria produced 33 million tonnes making it the world's largest producer [9]. During fermentation of grated cassava tuber (fufu - local food popular among South Western Nigerians made from cassava tuber), lactic acid bacteria, yeast and other bacteria contribute significantly to starch breakdown, acidification, detoxification and flavour development [10]. Lactic acid bacteria are found to be useful in flavouring foods, in inhibiting spoilage bacteria and pathogens, in intestinal health and other health benefits related to blood cholesterol levels, immune competence and antibiotics production.

For wider utilization, cassava products can be a catalyst for rural industrial development and raise the incomes of producers, processors and traders. It can also contribute to the food security status of its producing and consuming households [11]. Besides starch, the cassava tuber contains some soluble carbohydrates, that is glucose and sugar, which can be inverted poisonous prussic acid. The nutritive value for cassava tuber is estimated at 127 calories per 100 g to contain protein.

The exploration of natural products of plant origin as inexpensive eco-friendly inhibitors is an essential field of

---

S.O Adejo and J.U. Ahile are Lecturers with the department of Chemistry, Benue State University, Makurdi-Nigeria; J.A. Gbertyo is a Postgraduate student and G.T. Tyohemba has been recently awarded a Master of science degree, all from the same University.

J.A. Gbertyo\* is the corresponding author: [ja.gbertyo@gmail.com](mailto:ja.gbertyo@gmail.com) Mobile: +2348062919604

study in corrosion science and engineering. In addition to being environmentally friendly and ecologically acceptable, plant products are of low cost, readily available and renewable sources of materials. Extracts from their leaves, barks, seeds, fruits and roots contain mixtures of organic compounds which function as effective inhibitors of metals and their alloys corrosion in different aggressive media [12].

This research, reports the use of ethanol extract of peels of *Manihot esculentum* as eco-friendly inhibitor for the corrosion of aluminium in 2 M H<sub>2</sub>SO<sub>4</sub> medium within the temperature range of 303 K to 315 K.

## 2. Materials and Methods

### 2.1. Materials

Aluminium wires were obtained commercially and taken to the Department of Mechanical Engineering, University of Agriculture, Makurdi-Nigeria, where they were melted to give metal of very high purity and then re-moulded into desired sheets. The sheets were mechanically press-cut to form coupons, each of dimension 2.1 cm x 2.1 cm and 0.35 cm, with a tiny hole drilled at the edge of each coupon for suspension in the corrodant. The coupons' surfaces were thoroughly polished to mirror finish using emery paper of different grades, and then degreased by washing in absolute ethanol, dried with acetone, and preserved in a desiccator. Subsequently, the initial weight of each coupon was carefully measured [12], using an ADAM Electric Weighing Balance (model AFP-4100L Max: 4100, d = 10mg). A 2 M H<sub>2</sub>SO<sub>4</sub> solution was prepared which served as corrodant. All reagents used were of analytical grade, while doubly distilled water was used for the preparation of the solutions.

20.0 g of shade-dried *Manihot esculentum* peels were soaked in 200 cm<sup>3</sup> of absolute ethanol for 48 hours, with occasional shaking and filtered, thereafter, using cotton wool, and the ethanol evaporated from the filtrate using thermostated water bath maintained at 321 K to avoid any possible structural changes to the components of the extract. The residue obtained, therefore, was the preserved in a desiccator. Stock solutions containing 0.1, 0.2, 0.3, 0.4, and 0.5 gdm<sup>-3</sup> in the 2 M H<sub>2</sub>SO<sub>4</sub> were prepared from the extract [13], [14].

### 2.2 Weight Loss Measurement method

50 mL of the 2 M H<sub>2</sub>SO<sub>4</sub>, which served as the corrodant, was taken into a 100 mL beaker and placed in the thermostated water bath maintained at 303 K. A coupon of known initial weight was wholly immersed in the corrodant suspended with the aid of a thread tied to a retort stand for 8 hours. At retrieval it was immediately dipped into a saturated solution of ammonium acetate to quench the corrosion reaction, and carefully washed in absolute ethanol, rinsed in distilled water and then kept the desiccator and allowed to stand to constant weight and re-

weighed [15], [16]. The weight loss of the coupon was obtained as the difference in the weight before and after the immersion. Triplicate results were used in each case and the mean values

reported. This procedure was repeated at 307 K, 311 K, and 315 K which served as the blank at these temperatures. The same procedure was repeated after the introduction of various concentrations of the extract into the corrodant maintained at same temperatures. The weight loss was calculated thus,

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

Where  $W_L$  is the weight loss of the coupon,  $W_i$  the initial weight and  $W_f$  the weight after retrieval. The percentage inhibition was then obtained using equation (2) [17].

$$IE\% = (1 - W_{inh}/W_{blank}) \times 100 \quad (2)$$

Where  $W_{inh}$  and  $W_{blank}$  are the weight losses in grams of the coupon in the presence and absence of the inhibitor respectively. The degree of surface coverage,  $\theta$ , was evaluated using equation (3) [10], [11], [12].

$$\theta = 1 - W_{inh}/W_{blank} \quad (3)$$

The corrosion rate of the metal was determined for the immersion period from weight loss through equation (4).

$$\text{Corrosion rate (mgcm}^{-2}\text{h}^{-1}) = \frac{W_L}{At} \quad (4)$$

where  $W_L$  is the weight loss in milligrams (mg),  $A$  the coupon surface area in cm<sup>2</sup> and  $t$  the immersion time in hours [18].

## 3. Results and Discussion

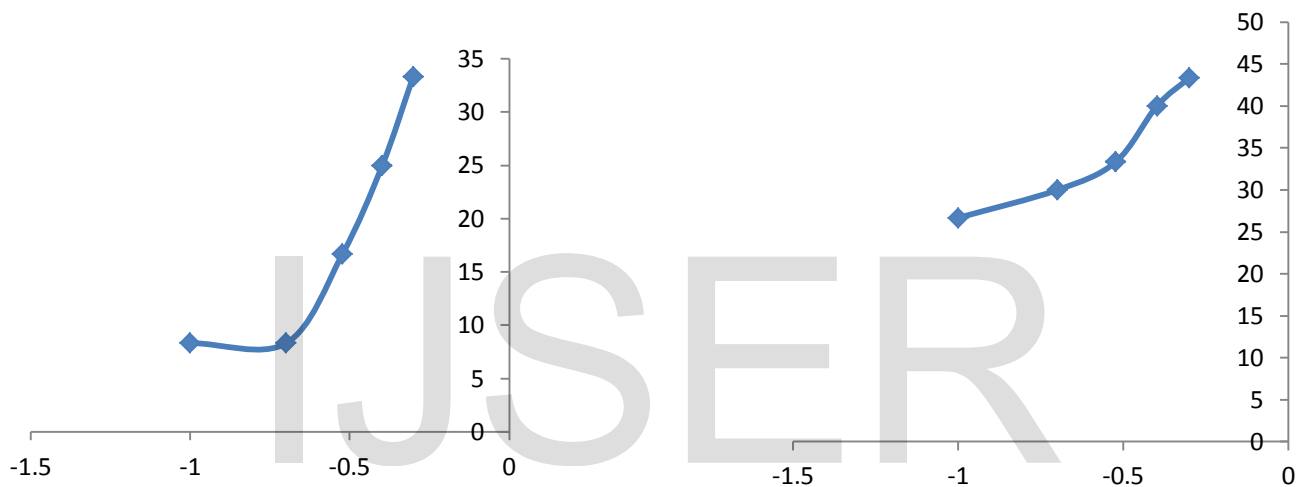
The Table 1 shows the results of weight loss for the corrosion of aluminium in 2 M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of various concentrations of *Manihot esculentum* extract at different temperatures. The results show that *Manihot esculentum* inhibited the corrosion of aluminium the acid medium since there was decrease in weight loss in the presence of the extract comparison with the blank. The weight loss decreased with increase in the extract concentration, but increased with rise in temperature.

The evaluated inhibition efficiency, %IE, also in Table 1 was found to increase with both increase in the concentration of the inhibitor and temperature. This increase in inhibition efficiency with rise in temperature could be suggestive of chemical adsorption as the mechanism of adsorption of the inhibitor onto the surface of the metal [19]. The rate of corrosion that was observed to be high in the blank came down considerably when the inhibitor was introduced.

**Table1. Weight loss (WL) and inhibition efficiency (%IE) for the inhibition of aluminium corrosion by peels extract of *Manihot esculentum* at various temperatures**

Concentration (g/dm <sup>3</sup> )	WL (g)				%IE			
	303 K	307 K	311K	315 K	303 K	307 K	311K	315 K
Blank	0.012	0.018	0.027	0.030				
0.1	0.011	0.015	0.020	0.022	8.330	16.57	25.93	26.67
0.2	0.011	0.014	0.020	0.021	8.330	22.22	25.93	30.00
0.3	0.010	0.013	0.018	0.020	16.67	27.78	33.33	33.33
0.4	0.009	0.012	0.017	0.018	25.00	33.33	37.04	40.00
0.5	0.008	0.011	0.016	0.017	33.33	38.89	40.74	43.33

To demonstrate that the extract was adsorbed onto the metal surface for the inhibition process, a plot of inhibition efficiency against the logarithm of concentration was carried out at the two extreme operation temperatures (300 K and 315 K). The S-shaped curve as depicted by figures 1 and 2 clearly shows that a protective barrier was actually formed by the inhibitor molecules on surface of the metal [20], [22], [23].



**Figure 1. Relationship between inhibition efficiency and logarithm of concentration of inhibitor at 303 K**

**Figure 2. Relationship between inhibition efficiency and logarithm of concentration of inhibitor at 315**

Table 2 shows values of activation energy,  $E_a$ , and some thermodynamics parameters. The value of  $E_a$  in the blank was found to be higher than in the inhibited solution and it decreases with increase in the extract concentration. Decrease (or equal to the blank) in the value of  $E_a$  with increase in inhibitor concentration is a feature of chemical adsorption mechanism [24], [25], and this observation supports our earlier proposed chemical adsorption.

Heat of adsorption,  $Q_{ads}$ , values was all found to positive and smaller in the presence of inhibitor, but did not change with the increase in inhibitor concentration. The positive sign of  $Q_{ads}$  is an indication that the process is endothermic and the degree of surface coverage increases with rise in temperature [26], supportive of the chemical adsorption process.

Enthalpy of activation,  $\Delta H^*_{ads}$ , values are positive and are lower than that of the blank, signifying that inhibition

effectiveness increases with increase in temperature. The positive sign is a reflection of endothermic nature of the dissolution process [27]. The average difference in value of the  $E_a - \Delta H^*_{ads}$  (equation 5) was found to be 2.570 kJ/mol, almost same as the value of  $RT$  (2.569 kJ/mol), where T is the average of the temperatures (309 K) at which the work was carried out. This implies that the corrosion process of this metal in the acid medium is a unimolecular reaction [28].

$$E_a - \Delta H^*_{ads} = RT \quad (5)$$

The negative sign of values of entropy of activation,  $\Delta S^*_{ads}$ , shows that the activated complex in the rate-determining step represents an association, rather than dissociation, that is a decrease in disorderliness on going from reactants to the activated complex [28]. This value was observed to increase with increase in concentration, showing increase in the degree of disorderliness.

$\Delta G_{ads}$  values are all negative and increase with rise in temperature. The increase in free energy value with rise in the temperature is an indication that spontaneity of the adsorption process and stability of adsorbed layer increased with rise in temperature. However, the values are

in the physical adsorption mechanism range as they are lower than -20 kJ/mol. This, therefore, can be interpreted to mean that the adsorption process was a mixture of physical and chemical mechanism [28].

**Table 2. Values of activation energy ( $E_a$ ) and thermodynamic parameters for extract of Manihot esculentum peels as inhibitor for aluminium corrosion**

Conc. (g/dm <sup>3</sup> )	$E_a$ (kJ/mol)	$+Q_{ads}$ (kJ/mol)	$+\Delta H^*_{ads}$ (kJ/mol)	$-\Delta S^*_{ads}$ (J/mol)	$-\Delta G_{ads}$ (kJ/mol)			
					303 K	307 K	311K	315 K
Blank	63.11		60.58	81.30				
0.1	47.36	11.39	44.76	134.26	9.877	12.02	13.62	13.90
0.2	45.90	11.73	43.37	139.01	8.131	10.25	11.83	12.52
0.3	48.04	7.271	45.46	132.92	9.097	10.89	11.71	11.86
0.4	48.56	5.400	45.96	132.01	9.659	10.82	11.38	11.86
0.5	52.77	3.254	50.23	118.87	10.12	10.87	11.21	11.63
Average	48.53	7.809	45.96	131.41	9.377	10.97	11.95	12.35

The inhibition of metal corrosion by organic additives has been attributed to their adsorption onto metal surface. This can be usually confirmed from the fitness of the experimental data to various adsorption isotherms, and the most frequently used adsorption isotherms are Temkin, Frumkin, Langmuir, Freundlich, Hill de Boer, Parsons, Flory - Huggins, Dhar-Flory Huggins, El-Awady and Bockris-Swinkels' isotherms. All of these isotherms are of the general form [12],

$$f(\theta, x) \exp(-2\alpha\theta) = KC \quad (6)$$

where  $f(\theta, x)$  is a configurational factor, which depends upon the physical model and assumptions underlying the derivative of the isotherm,  $\theta$  the surface coverage,  $C$  the inhibitor concentration,  $x$  is the size ratio, ' $\alpha$ ' is the molecular interaction parameter and  $K$  the equilibrium constant of adsorption process [29].

The data best fitted Freundlich, El-Awady, Temkin and to some extent, Langmuir adsorption isotherms, judging from the value of the regression coefficient,  $R^2$  as reflected in Table 3. The adsorption equilibrium constant  $K$  values are positive, indicative of favourable adsorption. The

parameters,  $n$  in the Freundlich isotherm is related to intensity of adsorption and it varies with heterogeneity of the material [30]. The value of  $n$  is always positive, but not an integer, and the typical value is 0.6 [30]. The fact that the obtained average value of  $n$ , is 0.5100, which is not too far from the typical value of 0.6 suggests that this adsorption process can reasonably be modelled by this isotherm and is heterogeneous.

The adsorption also follows the kinetic-thermodynamic model of El-Awady isotherm as a plot of  $\log \frac{\theta}{1-\theta}$  versus  $\log C$  gave straight curve with slope equal to  $y$ . It has been argued that  $y < 1$  implies single inhibitor molecule occupies more than one active sites on the metal surface and for  $y > 1$ , it means a formation of multilayer [31], [32], [33]. Table 3 clearly reveals that values of  $y$  are 1.0990, 0.7070, 0.4400 and 0.4600 at 303 K, 307 K, 311 K and 315 K, respectively, 303K shows formation of multilayer while 307, 311 and 315 imply that a single inhibitor molecule occupies more than one active site.

**Table 3.** values of Parameters of linearised various Adsorption isotherms

Isotherm	Temperature (K)	Slope	Intercept	R <sup>2</sup>	K	-ΔG <sub>ad</sub> kJmol <sup>-1</sup>
Langmuir	303	-	-	-	-	-
	307	1.6710	0.5110	0.9400	1.957	11.97
	311	1.9910	0.2750	0.9510	3.636	13.72
	315	1.8910	0.2510	0.9610	3.984	14.14
Freundlich		n				
	303	0.9110	-0.270	0.8440	1.8621	11.68
	307	0.5230	-0.269	0.9880	1.8578	11.83
	311	0.2980	-0.319	0.8500	2.0845	12.28
	315	0.3080	-0.287	0.9350	1.9364	12.25
	Average	0.5100				
El-Awardy		y				
	303	1.0990	-0.070	0.8380	1.1749	10.52
	307	0.7070	-0.018	0.9760	1.0423	10.36
	311	0.4400	-0.064	0.8470	1.1588	10.77
	315	0.4600	0.9140	0.9140	1.0257	10.59
	average	0.6765				
Temkin	303	2.267	-0.999	0.7950	9.977	15.91
	307	3.058	-1.433	0.9470	27.10	18.67
	311	3.827	-1.831	0.8430	67.76	21.29
	315	3.780	-1.894	0.8960	78.34	21.94

#### 4. Conclusion

The ethanol extract of root peels of *Manihot esculentum* was found to have inhibitory effect on the corrosion of aluminium in 2 M H<sub>2</sub>SO<sub>4</sub>. The adsorption process which was found to be favourable followed the Freundlich, El-Awardy, Temkin and to some extent Langmuir isotherms.

#### References

[1] E.E. Oguzie, B.N. Okolue, E.E. Ebenso, G.N. Onuoha, A.I. Onuchukwu, *Material Chem. and Phy.* **1994**, *401*, 187- 190.  
 [2] S.O. Adejo, J.A. Gbertyo, and U.J. Ahile Inhibitive properties and adsorption consideration of ethanol extract of *Manihot esculentum* leaves for corrosion inhibition of aluminium in 2 M H<sub>2</sub>SO<sub>4</sub> . *Int'l J. of Modern Chem.*, **2013**, *4(3): 137-146*

[www.modernScientificPress.com/Journals/IJMChem.aspx](http://www.modernScientificPress.com/Journals/IJMChem.aspx)

[3] S.O. Adejo, M.M. Ekwenchi, E.O. Odiniya, J.P. Acholo, S.P. Banke, Ethanol extract of leaves of *Portulaca oleracea* as green inhibitor for corrosion of mild steel in H<sub>2</sub>SO<sub>4</sub> medium. Proc. Inter. Conference on Research. Dev., Accra, Ghana, **2010**, *3(10)* 113-118  
 [4] [www.corrosion-doctors.org/modulus/mod-prevention.htm](http://www.corrosion-doctors.org/modulus/mod-prevention.htm) retrieved 13/10/2012:50pm  
 [5] [www.iso.org/iso/home/store/catalogue](http://www.iso.org/iso/home/store/catalogue) retrieved 1/10/2012, 6.00pm  
 [6] I.B. Obot, N.O. Obi-Egbedi, *Sur. Rev. and Lett.* **2008**, *15*, 903-911.  
 [7] S.O. Adejo, M.M. Ekwenchi, S.P. Banke, Ethanol extract of leaves of *Manihot esculentum* as eco-friendly inhibitor for corrosion of mild steel in H<sub>2</sub>SO<sub>4</sub> medium. Proc. 33<sup>rd</sup> Annual Inter. Conference Chem. Soc. Nigeria, Ogun, 2010, 240-244  
 [8] S.O. Adejo, S.G. Yiase, U.J. Ahile, T.G. Tyohemba, and J.A. Gbertyo, Inhibitory effect and adsorption parameters of extract of leaves of *Portulaca oleracea* for corrosion of aluminium in H<sub>2</sub>SO<sub>4</sub> solution. *Scholars*

- Res. Lib., Archives of Appl. Sci. Research*, (2013), **5(1): 25-32**  
[www.scholarsresearchlibrary.com](http://www.scholarsresearchlibrary.com)
- [9] S.A. Umoren, *the Open Corrosion Journal*, **2009**, *2*, 175–188.
- [10] I.B. Obot, S.A. Umoren, N.O. Obi-Egbedi, *J. Mat. Environ. Sci.*, **2011**, *2*, 60-71
- [11] I.B. Obot, N.O. Obi-Egbedi, S.A. Umoren, *Inter. J. Electrochem. Sci*, **2009**, *4*, 863-877
- [12] M. Lebrini, F. Robert, P. A. Blandinieres, C. Ross, *Intern. J. Electrochem. Sci.*, **2011**, *6*, 2443.
- [13] A.S. Afolabi, *Int'l Research J. Eng. Sci. and Technl.* **2005**, *2(1)*: 156–160.
- [14] S.O. Adejo, M.M. Ekwonchi, F. Momoh, E. Odiniya, *Inter. J. Modern Chem.* **2012**, *1*, 125 - 134
- [15] P.C. Okafor, E.E. Ebenso, E.U. Ekpe, *Int'l J. Electrochem. Sci.*, **2010**, *5*, 978-993
- [16] O.K. Abiola, *J. Chilean Chemical Soc.*, **2005**, *50*, 685-690
- [17] F. Asuke, S.A. Yaro, O.B. Olochej, *J. Applied Sci. Research*, **2010**, *6(11)*: 1759-1765
- [18] S.A. Umoren, I.B. Obot, E.E. Ebenso, N.O. Obi-Egbedi, *Int'l J. Electrochem. Sci.*, **2008**, *3*, 1029-1035.
- [19] K. Lu, L. Ding, H.W. Wang, H.N. Jing, X.N. Zhao, S.B. Lin, Y.D. Li, Y.L. Jin, F.M. Liv, S.R. Jiang, *J. Biomed. Envir. Sci.*, **2006**, *19(2)*: 110 - 117
- [19] E.I. Ating, S.A. Umoren, I.I. Udousoro, E.E. Ebenso, A.P. Udoh, *Green Chem. Lett. Reviews*, **2010**, *3*, 61–68.
- [20] A. Singh, V.K. Singh, M.A. Quraishi, *Inter. J. Corr*, **2010**, *1*, 01–10
- [21] S. Chatterjee, D.S. Lee, M.W. Lee, S.H. Woo, *Bioresource Techn.*, **2009**, *100*, 2803-2809
- [22] M. Lebrini, F. Robert, C. Roos, *Inter. J. Electrochem. Sci*, **2011**, *6*, 2443-2460
- [23] N.O. Eddy, and E.E. Ebenso, *J. Pure Appl. Chem.*, **2008**, *2*, 046–054
- [24] M. Dahmani, A. Touhami, S.S. Al-Deyab, B. Hammouti, A. Bouyanzer, *Int'l. J. Electrochem. Sci*, **2010**, *5*, 1060–1069
- [25] A.A. Khadom, A.S. Yaro, A.H. Abdul, *J. Chilean Chem. Soc.*, **2010**, *55*, 150-152
- [26] E.E. Oguzie, (2005). Inhibition of acid corrosion of mild steel by *Telfaria occidentalis* extract, *Pigment and Resin Technl.*, **34(6)**: 321–326.
- [28] E.E. Oguzie, (2006). Studies on the inhibitive effect of *Occimum viridis* extract on the acid corrosion of mild steel, *Mat. Chem. and Phy.* **99**, 441–446.
- [29] E.E. Oguzie, (2007). Corrosion inhibition of aluminium in acidic and alkaline media by *Sansevieria trifasciata* extract. *Corr. Sci.*, **49(3)**: 1527–1539.
- [30] P.B. Tandel, and B.N. Oza, (2000). Performance of some dyestuffs as inhibitors during corrosion of mild-steel in binary acid mixtures (HCl + HNO<sub>3</sub>), *J. of the Electrochem. Soc. of India*, **49**, 49–128, 2000.
- [31] V.V. Torres, R.S. Amado, Faia de S´a, (2011). Inhibitory action of aqueous coffee ground extracts on the corrosion of carbon steel in HCl solution, *Corr. Sci.*, **53(7)**: 2385–2392.
- [32] M.A. Bendahou, M.B.E. Benadellah and B.B. Hammouti A study of rosemary oil as a green corrosion inhibitor for steel in 2 M H<sub>3</sub>PO<sub>4</sub>, *Pigment and Resin Tech.*, **35(2)**: 95–100, 2006.
- [33] P.R. Deepa and S. Selvaraj, "Inhibitive and adsorption properties of *Punica granatum* extract on brass in acid media", *J. of Phytology*, **2(11)**, 58–64, 2010,