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C Obi
Physical Chemistry Unit, Department of Pure and Industrial Chemistry, Faculty of Science, University of Port Harcourt, Rivers, Nigeria.

LO Onori-Gudi
Physical Chemistry Unit, Department of Pure and Industrial Chemistry, Faculty of Science, University of Port Harcourt, Rivers, Nigeria.

Correspondence
C OBI
Physical Chemistry Unit, Department of Pure and Industrial Chemistry, Faculty of Science, University of Port Harcourt, Rivers, Nigeria.

Physical nature of *Lycopersicon esculentum*/aluminum interactions in the presence of acidic media

C Obi and LO Onori-Gudi

Abstract
Corrosion inhibition of aluminum in 2M HNO_3 and 2M HCl using *Lycopersicon esculentum* (LE) extract was studied by adopting the gravimetric (weight loss) method at temperatures of 40 ^{0}C and 60 ^{0}C. The results indicated that inhibition of *Lycopersicon esculentum* was more efficient in 2M HNO_3 medium. Temperature studies revealed that the inhibition efficiency increased with inhibitors concentration but decreased at higher temperature. The inhibition process was spontaneous and the inhibition efficiency of the preferred medium (2M HNO_3) followed Langmuir adsorption isotherm model indicating a physical adsorption. The study has shown that the corrosion of aluminum in the presence of acidic media can be inhibited in the presence *Lycopersicon esculentum* extract.

Keywords: Aluminum, thermodynamics, *Lycopersicon esculentum* extract, inhibition, physical adsorption

Introduction
Corrosion is the decay of technical materials with the loss of mechanical workability and therefore is not only of metallic concept. The process occurs in such a way that the metal ion is deposited at a point of lower electron density [1].

Corrosion is a nuisance that has gained a common interest in all areas of metallurgy, petrochemicals and other allied industries. In response to this, there is the exploitation of various inhibitors. Corrosion inhibitors are chemical compounds that when added to a corroding liquid or gaseous medium, decreases the effect of the medium [2]. However many synthetic compounds possess good anti-corrosive properties, most of them are highly toxic to both human beings and environment [3]. This toxic nature is minimized by the adoption of biodegradable, recyclable and environmentally friendly natural products. The natural product extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost, and are biodegradable in nature [4].

Scholarly articles on aluminum corrosion have shown wide applications of natural products as inhibitors [5, 2, 6].

The aluminum metal is passive to corrosion due to the formation of a filmy metal oxide coat on the surface. The metal is very reactive and directly above carbon in the corrosion reactivity series. However, because of the wide applications of the aluminum metals and its alloys in industrial and domestic activities, it is needful to protect the materials by use of biological adsorption inhibitors.

Adsorption inhibitor is influenced by the nature and the surface charge of metal, the type of corrosion environment and molecular structure of inhibitor [7]. The ability of a compound to serve as an Inhibitor is dependent on its ability to form a compact barrier film by nature of adsorption on metal surface. The filming corrosion inhibitor functions by strong adsorption and decrease attack by creating a barrier between the metal and environment rather than reacting with or removing active corrosive specie [8]. The inhibitor adsorption mechanism is necessary to establish the adsorption mode of inhibiting species (molecules or ions) [9].

At efficient inhibitor concentration however, the metal-inhibitor complex becomes insoluble resulting to an improved inhibition due to higher surface coverage [10]. Certain inhibitors function by means of a specific mechanism that depends on electron density and polarizability of functional group [1]. The majority of well-known inhibitors are organic compounds containing hetero-atoms, such as O, N, S, P and multiple bonds [11, 12].

The plant Solanum Lycopersicum is derived from two views: Solanaceae is a Latin referring to all nightshade plants possessing the solanine defense mechanism compound while lycopersicum refers to an abundance of the red coloring lycopene. The plant contains lots of elemental, anti-nutritional and mineral valuables [13].

Nigeria has vast land and good climate for the cultivation of *Lycopersicon esculentum* plant. The leaves after harvest are discarded to the environment without any further use and hence the need for this study.

Interestingly, the plant extract (*Lycopersicon esculentum*) used in this study is rich in heterocyclics and therefore the aim is to evaluate the effectiveness and efficiency of the plant extract in the inhibition of aluminum metal corrosion in the presence of 2M HNO_3 and 2M HCl.

Materials and Method

Preparation of *Lycopersicon esculentum* Extracts

Analytical grade reagents were employed to prepare 2M HNO_3 and 2M HCl using de-ionized water. The *Lycopersicon esculentum* leaves used were obtained locally and were dried to a constant weight in an oven at a temperature of 110 ^oC, and then ground to fine powder. The *Lycopersicon esculentum* (LE) extract each was prepared by adding 16g of the powder into 40 0mL of 2M HNO_3 and 2M HCl in around bottom flask. The resulting solutions were heated under reflux for 2 hrs and left to cool overnight, and then filter afterwards. From the respective stock solutions, inhibitor test solutions were prepared in the concentration range of 0.1-0.6ml/ml.

Phytochemical screening for tannins was carried out using the method described by Evans and Trease [14] while glycosides, alkaloids by Sofowora [15] and saponins by Harborne [16].

Preparation of Aluminum Coupons

The pure metal was obtained from First Aluminum of Trans-Amadi Industrial layout Port Harcourt. The sheet was marked at the University of Port Harcourt Engineering workshop into a 4cm by 2cm grid and each unit were mechanically pressed out. A hole of 0.2cm was bore into the mid-top surface of the aluminum coupons. Under specific temperatures seven coupons were used per analysis in acidic media with and without extract.

For each analysis, threads bearing paper tape tags of sufficient length were wound through the hole on each of the seven coupons uppermost surface and used to suspend the immersed coupons in corrosion media-inhibitor extract solutions.

The aluminum coupons were brushed in de-ionized water to reduce the thickness of passivation over the metal surface. The coupons were rinsed in acetone which was evaporated to dryness by sealing rinsed coupons in a dessicator. They were weighed to give the initial weight. The coupons were immersed into the seven 100ml beakers (with and without extract). Time of immersion was noted and the setup was left to heat for 1 hr. The coupons were retrieved at the end of the heating. They were brushed in de-ionized water, dried with acetone, and weighed to give the final weight. The process was repeated five times consecutively. The weight loss in terms of grams of corroded aluminum per milliliter of acid or acid-extract solution was noted by the weight difference of a particular coupon before immersion as to that after brushing and drying. This difference determines the corrosion rate (C_r) and the percentage inhibition efficiency (E_i) is expressed in equation 1 and 2 below:

$$C_r = \frac{W_i - W_f}{W_i} \quad \ldots\ldots 1$$

$$E_i = \frac{W_i - W_f}{W_i} \times 100 \quad \ldots\ldots 2$$

Where W_i and W_f are the initial and final weights in grams

Results and Discussion

The corrosion inhibition of aluminum in acidic media of 2M HNO_3 and 2M HCl has been extensively experimented with *Lycopersicon esculentum* extract. Phytochemical analysis of leaves of *Lycopersicon esculentum* detected the presence of abundant tannins and steroids as compared to glycosides and saponins, these according to Onwukaeme, [17] are known to possess inhibitory properties. The inhibitive effect is best attributed to a net adsorption of organic matter on aluminum-acid interface thereby reducing the surface area available for corrosion reaction [18].

Inhibition Efficiency

The inhibition efficiency as represented in Figures 1 (a-b) – 2 (a-b) were more achieved in the presence of 2M HNO_3 than in 2M HCl over the concentration range of 0.1 to 0.6 ml/ml extract suggesting according to Njoku and his coworkers [7], the influence of acid anions on metal-inhibitor interaction. For an instance, aluminum has a positive surface charge at the corrosion potential. Specific adsorption of chloride ions of HCl results to an electron dense metal surface which is unsusceptible to adsorption of electron dense species. Electron dense active components of *Lycopersicon esculentum* are the conjugated steroids; lycopene and beta carotene.

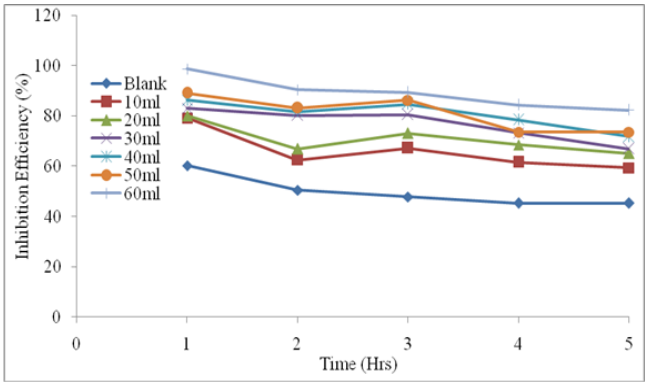

Fig 1a: Inhibitive effect of LE at various concentrations in 2M HNO_3 at 40 ^oC

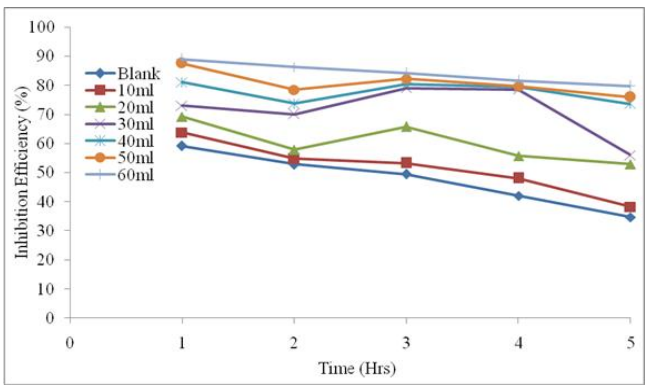

Fig 1b: Inhibitive effect of LE at various concentrations in 2M HNO_3 at 60 ^oC

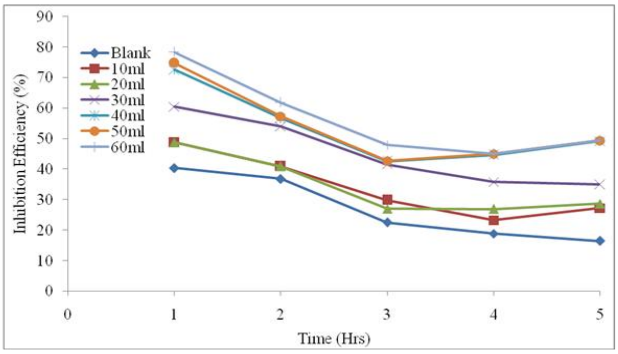

Fig 2a: Inhibitive effect of LE at various concentrations in 2M HCl at 40 °C

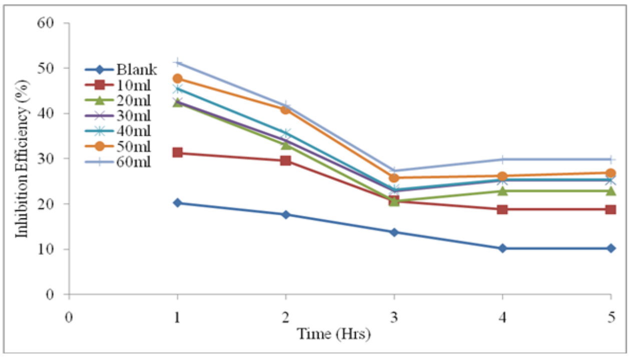

Fig 2b: Inhibitive effect of LE at various concentrations in 2M HCl at 60 °C

Adsorption Isotherm Behavior

The linear regression from the plot of concentration per surface coverage (C/θ) against concentration takes the path of Langmuir adsorption isotherm model. By Langmuir adsorption isotherm expressed in equation 2, the intercept is an inverse of adsorption equilibrium constant which is used in the derivation of the Gibb's free energy (ΔG) which is expressed in equation 3.

$$C/\theta = \frac{1}{K} + C \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 3$$

$$K = \frac{1}{55.5} \exp(-\Delta G/RT) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 4$$

The plots of C/θ versus Conc. for 2M HNO_3 and 2M HCl are shown in Figures 3(a-b) and 4(a-b), respectively, and the values of K_{ads} subsequently calculated from the intercept are shown in Tables 1(a-b) and 2(a-b) respectively. The correlation coefficient (R^2) values of 2M HNO_3 at 40 °C and 60 °C which are 0.990 and 0.993 revealed a good fit of the experimental data and suggests that the adsorption of LE extract on metal surface followed the Langmuir adsorption isotherm model. The results showed that the adsorption equilibrium constant (K_{ads}) decreased with increasing temperature, indicating better adsorption of LE extract onto the aluminum surface at lower temperature.

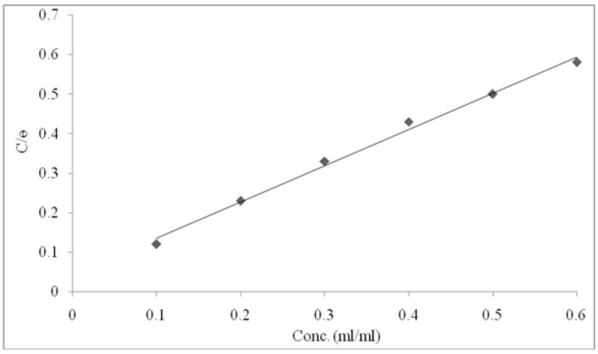

Fig 3a: Plot of concentration per surface coverage against concentration at 40 °C in 2M $HN0_3$

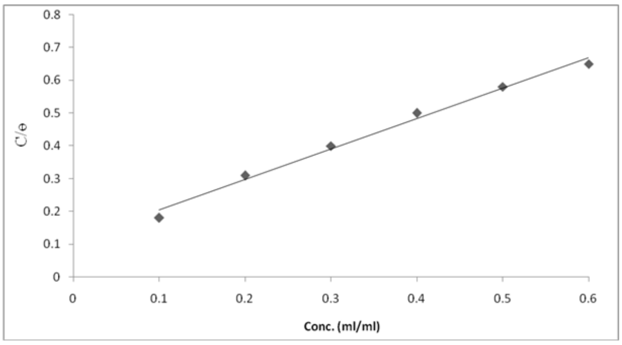

Fig 3b: Plot of concentration per surface coverage against concentration at 60 °C in 2M $HN0_3$

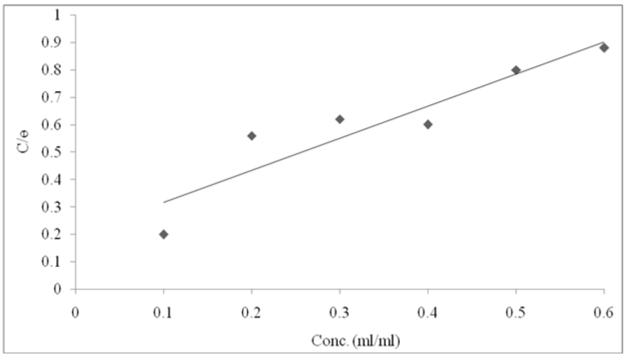

Fig 4a: Plot of concentration per surface coverage against concentration at 40 °C in 2M HCl

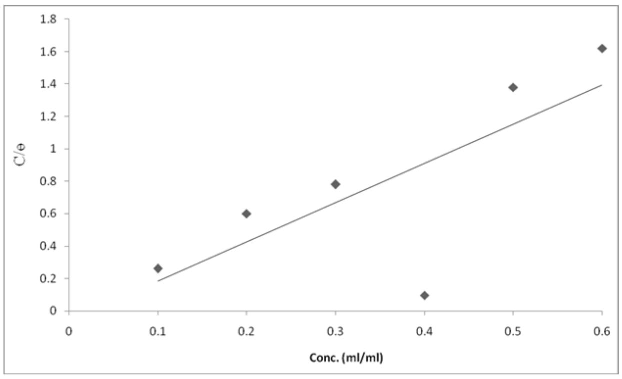

Fig 4b: Plot of concentration per surface coverage against concentration at 60 °C in 2M HCl

Thermodynamic Contribution

The result showed that a decrease in inhibition efficiency with increase in temperature suggests weak adsorption interaction between the metal and the extract organic matter. This behavior corresponds to physical adsorption such that there is a shift to desorption of adsorbed inhibitor as temperature rises [19].

Table 1a: Thermodynamic parameters of LE at 40 ºC in 2M HNO_3

Conc. (ml/ml)	I.E (%)	Surface coverage (θ)	C/θ	K_{ads}	ΔGº (kJ/mol)	R^2
Blank	60.30	0.6030	-			
0.1	65.94	0.6594	0.1517			
0.2	70.87	0.7087	0.2822			
0.3	76.79	0.7679	0.3907	28.57	- 8.72	0.993
0.4	80.57	0.8057	0.4965			
0.5	82.72	0.8272	0.6044			
0.6	89.06	0.8906	0.6737			

Table 1b: Thermodynamic parameters of LE at 60ºC in 2M HNO_3

Conc. (ml/ml)	I.E (%)	Surface coverage (θ)	C/θ	K_{ads}	ΔGº (kJ/mol)	R^2
Blank	47.76	0.4776	-			
0.1	51.61	0.5161	0.1938			
0.2	60.30	0.6030	0.3317			
0.3	71.31	0.7131	0.4207	12.50	- 6.99	0.990
0.4	77.60	0.7760	0.5155			
0.5	80.76	0.8076	0.6191			
0.6	84.18	0.8418	0.7127			

This behavior was noticed as 2M HNO_3 efficiency declined when temperatures of 40°C and 60°C were compared. However, increase in concentration of extract improved the inhibition of extract despite temperature increase.

The result showed that the standard Gibb's free energy change was negative in all the acid media indicating a spontaneous reaction. The values revealed according to Durnie and his coworkers [20] that the inhibition process of *Lycopersicon esculentum* extracts in the acid media indicated possible physiosorption.

Table 2a: Thermodynamic parameters of LE at 40 ºC in 2M HCl

Conc. (ml/ml)	I.E (%)	Surface coverage (θ)	C/θ	K_{ads}	ΔGº (kJ/mol)	R^2
Blank	26.99	0.2699	-			
0.1	33.97	0.3397	0.2944			
0.2	34.45	0.3445	0.5806			
0.3	45.33	0.4533	0.6618	7.69	- 5.13	0.858
0.4	53.13	0.5317	0.7529			
0.5	53.83	0.5383	0.9289			
0.6	56.50	0.5650	1.0619			

Table 2b: Thermodynamic parameters of LE at 60 ºC in 2M HCl

Conc. (ml/ml)	I.E (%)	Surface coverage (θ)	C/θ	K_{ads}	ΔGº (kJ/mol)	R^2
Blank	14.41	0.1441	-			
0.1	23.78	0.2378	0.4205			
0.2	27.68	0.2768	0.7225			
0.3	29.04	0.2904	1.0331	8.33	- 5.52	0.556
0.4	30.05	0.3005	1.3311			
0.5	32.70	0.3270	1.5291			
0.6	34.67	0.3467	1.7306			

Conclusion

The extract of *Lycopersicon esculentum* inhibited corrosion of aluminum in acidic medium of 2M HNO_3 and 2M HCl. The most successful inhibition was noted in 2M HNO_3 at 40°C.

The adsorption process is physical in nature. The presence of *Lycopersicon esculentum* was observed to obey the Langmuir adsorption isotherm model.

References

1. Shaw BA, Kelly G. What is Corrosion? Journal of Electrochemical Society Interface Spring, 2006, 24-26.
2. Palou RM, Olivares-Xomelt O, Likhanova NV. Environmentally Friendly Corrosion Inhibitors. Intech, 2014, 432-465.
3. El-Etre AY. Natural onion juice as inhibitors for zinc corrosion. Bulletin of Electrochemistry, 2006, 22(2):75-80.
4. Abdel-Gaber AM, Abd-El Nabey BA, Saadaway M. The role of acid anion on the inhibition of the acid corrosion of steel by lupine extract. Corrosion Science, 2006, 51(3):1038-1042.
5. Cris C. Corrosion: What's eating at Your Metal? Part II, Interface, 2013, 33-36.

6. Vijay R. Corrosion inhibition of Aluminium in Hydrochloric Acid by Natural Plant extracts. Research Paper, 2014, 1-94.
7. Njoku VO, Oguzie EE, Obi C, Ayuk AA. *Baphia nitida* leaves extract as a green inhibitor for the corrosion of mild steel in acidic media. Advances in Chemistry, 2014, 1-10.
8. Khamis A, Saleh MM, Awad MI. Synergistic inhibitor effect of cetylpyridinium chloride and other halides on the corrosion of mild steel in 0.5M H_2SO_4. Journal of Corrosion Science, 2013, 66: 343-349.
9. Onuchukwu AI, Trassatti SP. Hydrogen Permeation into Aluminium AA 1060 as a result Corrosion in an Alkaline Medium: Influence of anions in solutions and of Temperature. Journal of Corrosion science, 1994, 36(1):1815-1817.
10. Ogukwe CE, Onuchukwu AI, Okolue BN, Unaegbu C. Inhibition of aluminium in alkaline solutions by methylene blue. Bulletin of Electrochemical, 2005; 20(9):4.
11. Oguzie EE. Inhibition of acid corrosion of mild steel by Telferia Occidentalis. Pigments and Resin technology 2005; 34(6):321-326.
12. Trinidade LG, Goncalves RS. Evidence of Caffeine adsorption on a Low- carbon steel surface in ethanol. Journal of Corrosion Science, 2009; 51(8):1578-1583.
13. Oyetayo FL, Ibitoye MF. Photochemical and Nutrients/Antintrients Interactions in Cherry Tomato (*Lycopersicon esculentum*) Fruit. International Journal of Advance Biological Research, 2012; 2(4):681-684.
14. Evans WC, Trease GE. A textbook of Pharmacognosy. Edn. 16, Elsevier Ltd. 2009, 135-147.
15. Sofowara A. Medicinal Plants and Traditional Medicine in Africa, 2nd Edn, Spectrum Books Ltd, 1993, 289-300.
16. Harborne JB. Phytochemical methods A Guide to Modern Techniques of plant Analysis, 2nd edition, Chapman and Hall, New York, USA, 1973, 48-189.
17. Onwukaeme ND. Anti-inflammatory activities of flavonoids of Baphia nitida Lodd. (Leguminosae) on mice and rats. Journal of Ethnopharmacology, 1995, 46(2):121-124.
18. Ating EI, Umoren SA, Udousoro II, Ebenso EE, Udoh AP. Leaves extract of *Ananas sativum* as green corrosion inhibitor for aluminum in hydrochloric acid solutions. Green Chemistry Letters and Review, 2010, 3(2): 61-68.
19. Orubite-Okorosaye K, Oforka NC. Corrosion inhibition of Zinc on HCl using *Nypa fruticans* Wurmb extract and 1-5 diphenyl carbazone. Journal of Applied Science and Environmental Management, 2004; 8:56-61.
20. Durnie W, De Macro R, Jefferson A, Kinesella B. Development of a Structure Activity Relationship for Oil Field Corrosion Inhibitors. Journal of the Electrochemical Society 1999; 146(5):1751-1756.