

Performance of Mild Steel in Nitric Acid/*Carica Papaya* Leaf Extracts Corrosion System

Makanjuola Oki^{1*}, Paul A. L. Anawe² and John Fasakin³

¹ Landmark University, Department of Mechanical Engineering
PMB 1001, Omu-Aran, Kwara State, Nigeria

² Covenant University, Department of Petroleum Engineering
Ota, Ogun State, Nigeria

³ Covenant University, Department of Petroleum Engineering
Ota, Ogun State, Nigeria

* Corresponding author's email: [makanjuolaoki \[AT\] justice.com](mailto:makanjuolaoki [AT] justice.com)

ABSTRACT— *Corrosion inhibition efficiency of leaf extracts from Carica papaya has being investigated using gravimetric, gasometric and thermometric techniques. Carica papaya leaf extracts reduced the corrosion rate of mild steel in 2.5M nitric acid by interfering with both anodic and cathodic reactions. The corrosion rate in the absence of the inhibitor was 840 mmpy while at 60% inhibitor concentration, it was 60 mmpy. The corrosion rate decreased rapidly initially as the concentration of the inhibitor increased and attained an efficiency of 93% at a concentration of 60%. The complimentary inhibition efficiencies, E%, obtained from thermometric and gasometric techniques are similar in values and range from about 93% to 96%. The adsorption of the active components of the leaf extracts follows the Langmuir adsorption isotherm*

Keywords— *Carica papaya*, corrosion inhibitor, weight loss, gasometry.

1. INTRODUCTION

Corrosion inhibitors find application in industrial process streams and especially in primer coatings where they give a level of protection to metals/alloys in constant contact with corrosive environments. Their mode of operation depends on their origin amongst other characteristics. Most inhibitors of organic origin perform by adsorbing on corroding metal surfaces [1-6] where they affect either the anodic or cathodic reactions in one manner or the other. On the other hand, those of inorganic origin tend to form insoluble thin films on corroding metal surfaces and thereby forming a passivating layer which significantly reduce the corrosion of the underlying metal [1, 7-10].

Most proprietary corrosion inhibitors are mixtures of organic and inorganic compounds which in most cases have negative environmental impacts and are expensive. As a result of these, researchers [11, 12] have in recent times, beamed search lights on alternatives from various plant extracts which are considered environmentally clean, biodegradable and renewable.

The evaluation of corrosion inhibitors of plants' origin has been performed by various methods such as electrochemical impedance spectroscopy (EIS) and time tested gravimetric methods with a very good degree of reliability and correlation [13, 14]. Other researchers [15] have made use of weight loss and gasometric techniques, the results of which showed a good degree of correlation. Yet others [16] have made use of EIS and potentiodynamic polarisation techniques which results showed close similarities in corrosion rate values. Although, inhibitor performance evaluation by these various methods gave similar results with good degree of correlation when performed in hydrochloric acid and sulphuric acid solutions of various strengths, however, results for the performance of corrosion inhibitors of plant extracts origin in Nitric acid are limited. Nitric acid is extensively used in the oil/gas and related industries for cleaning as sludge heel removers, descaling and other applications where the protection of the underlying metals are usually of paramount importance.

Thus, in this study nitric acid was employed as test solutions for the evaluation of leaf extracts of *Carica Papaya* as corrosion inhibitor for mild steel specimens using reaction number, gravimetric and gasometric techniques.

2. EXPERIMENTAL

2.1 Materials

Mild steel specimen which contained, Carbon, 0.16%; Magnesium 0.53%; Silicon 0.16% and Iron 99.25% was made out into electrodes with a notch at one end unto which a 10mm copper wire was fastened with the aid of araldite. The final dimension of each of the specimen was 5 x 2.5 x 0.02 cm. All chemicals used were of laboratory grade by BDH Chemicals, UK, while inhibitor of interest was extracted from dried pawpaw leaves. Double distilled water was used throughout the experiment.

2.2 Methods

2.2.1 Coupon preparation

The mild steel electrodes were successively polished with different grades (320–600) of emery papers, washed with double distilled water, degreased with acetone, dried and stored in desiccators.

2.2.2 Preparation of leaf extracts and test solutions

The dried leaves were blended into powdery form, 40g each was refluxed in 400ml 2.5M nitric acid in two separate round bottom flasks for 3 hours each. They were left to stand for 5 days thereafter and then filtered using suction pump and sieves. From the stock solution, test solutions containing 10, 20, 30, 50 and 60 percent of the inhibitor of interest were prepared by serial dilution. All corrosion testing procedures were carried out in a fume cupboard.

2.2.3 Gravimetric measurements

Gravimetric experiments were carried out in 250 ml beaker containing 150 ml of the 2.5M HNO₃ without and with different percentages of inhibitors. The beakers were kept on a thermostat maintained at 30° C. The polished rectangular specimens were weighed accurately and immersed in the solution of interest for various times and their potentials monitored with a high impedance voltmeter. The specimens were then removed from the test solutions, brushed under running double distilled water, washed thoroughly with acetone, dried and re-weighed. The mean of weight loss values of duplicate identical experiments was used to calculate the corrosion rates of the specimens and inhibition efficiency of the leaf extracts. The corrosion rate was obtained in millimetre penetration per year (mmpy) with the relationship in equation 1 as demonstrated by Aiman Eid Al-Rawajfeh and Ubeidulla Al-Qawabeha [17].

$$\text{Corrosion rate (mmpy) [CR]} = \frac{(543 \times \Delta W)}{\text{Area (A)} \times \text{Time (t)} \times \text{Metal density } (\rho)} \quad \dots\dots\dots (1)$$

where, mass loss, ΔW , is expressed in mg, area in cm², time in hours of exposure and metal density, expressed in gm/cm³. The degree of coverage, Θ , of the inhibitor is given by:

$$\Theta = \frac{\Delta W_u - \Delta W_i}{\Delta W_u} \quad \dots\dots\dots (2),$$

where ΔW_u is the change in weight of specimen in uninhibited test solution and ΔW_i is the change in weight in the inhibited test solution. Also percentage inhibition efficiency, E% is given by:

$$E\% = \frac{CR_u - CR_i}{CR_u} \times 100 \quad \dots\dots\dots (3),$$

where CR_u and CR_i are the corrosion rates in uninhibited and inhibited test solutions respectively.

2.2.4 Gasometric measurements

The gasometric measurements were carried out in the manner described by Ekpe et al [18] and by Umoren and others [19]. This involved the collection of gases evolved in a graduated burette initially filled with water and inverted over the gasometric apparatus containing test solutions in flasks into which the specimens were immersed. The volume of the gases evolved was monitored over time. The rate of gas evolution is proportional to the rate of corrosion and it is given by the relationship,

$$RV_G = \frac{\Delta V}{\Delta t} \quad \dots\dots\dots (4),$$

where RV_G is the rate of gas evolution, ΔV is change in the volume of gas within a time interval, Δt . In addition, surface coverage and inhibition efficiency can be obtained as in equations 2 and 3 above, in which cases, rates of gas evolution in uninhibited, RV_{G_u} and inhibited, RV_{G_i} test solutions respectively replaced ΔW_u , ΔW_i , CR_u and CR_i in their respective equations.

2.2.5 Measurement of Reaction Numbers.

The reaction number, RN , is defined as: $RN = \frac{T_m - T_o}{t} \quad \dots\dots\dots (5)$

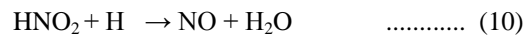
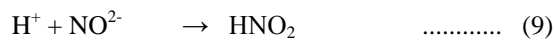
Where, T_m and T_o are the maximum and the initial reaction temperatures respectively and t is the time to attain the maximum temperature.

Thus, at the immersion of the specimens in the test solutions in the absence and presence of inhibitors, the reaction temperatures were monitored at one minute interval using a thermometer with a precision of $\pm 0.5^\circ\text{C}$.

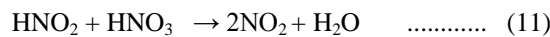
3. RESULTS AND DISCUSSION

3.1 Potential-time measurement

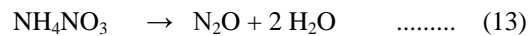
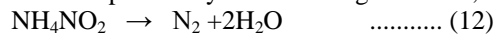
Irrespective of time and concentration of inhibitor, the potential of the mild steel specimens in 2.5M nitric acid in the presence and absence of the inhibitor fluctuated between -0.584 mV to -0.574 mV. Potential fluctuations of this manner may suggest crack and heal events occurring on the surface of the electrode in the aggressive, nitric acid medium. The cathodic corrosion reaction of nitric acid has been described to occur in stages. While the anodic reaction is the oxidation of iron to its oxidation state of +2, the cathodic reactions occur in steps thus [20]:



The nitrous acid (HNO_2) formed in equation (9) regenerates NO_2 by an interaction with the nitric acid by the reaction,



Thus the reaction becomes autocatalytic. Ammonia salts are also formed during the cathodic reactions. The ammonia salts decompose to form N_2 and NO_x compounds by the following reactions,



Hence formation of a gas made up of the following gases NO_2 , NO , N_2O and N_2 are emitted due to the cathodic reactions. Nitric acid is highly oxidising and may encourage oxide formation on mild steel [21]. The extent of passivation depends on the concentration of the acid and at 15M, the induced passive film may reduce the corrosion rate to 0.508 mm per year. Hence with the probability of formation of passive film in addition to multiple stepped cathodic reactions, an incubation period prior to occurrence of rapid corrosion reactions is expected for steel in nitric acid. Thus such oxide film with inherent flaws at the bottom of which the substrate may be transiently exposed will give rise to potential fluctuations of the manner observed. Moreover, for the difference in potential between the noblest and the most active values to fall within 0.01 millivolts, may suggest a combined anodic and cathodic inhibition actions.

3.2 Gravimetric studies

Table 1 summarises the results obtained from the gravimetric studies during exposure of mild steel specimens to 2.5M nitric acid in the presence of various concentrations of *Carica papaya* leaf extracts.

Table 1: Summary of results obtained from weight loss measurements for mild steel in 2.5 M Nitric acid.

Conc. % of leaf extracts, C	Weight loss, $\Delta w(\text{mg})$	% Inhibition, E%	Corrosion rate, CR (mmpy)	Surface coverage, Θ
Blank, 0	3455.35	0	840.34	0
10	574.75	83.7	139.78	0.8337
20	472.70	86.32	114.96	0.8632
30	375.44	89.13	91.31	0.8913
50	308.25	91.08	74.97	0.9108
60	248.90	92.80	60.53	0.9280

From the Table, 1 and from Figures 1 and 2, the corrosion rates for mild steel in nitric acid/ *Carica papaya* corrosion system decreased with increase in concentration of mixtures of inhibiting species in the leaf extracts, whereas the efficiency and surface coverage increased with increase in the inhibitors' concentrations. These are expected since the number of inhibiting species will increase in proportion to the concentration of the leaf extracts in the system.

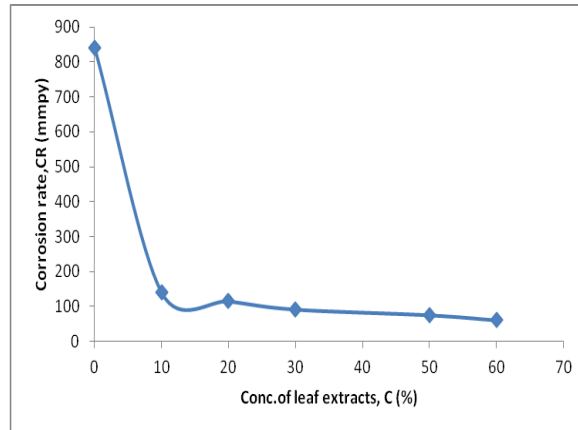


Figure 1: Corrosion rate of mild steel in 2.5M HNO₃ at various concentration leaf extracts.

From Figure 1, the corrosion rate decreased rapidly initially, with a rate that decreased with increase in inhibiting species' concentration giving a corrosion rate of 60.53 mmpy at an inhibitor concentration of 60% and it was as low as 140 mmpy at 10% inhibitor concentration. This is envisaged as the incubation period mentioned earlier may have been due to formation of nitric acid induced passive oxide film which partially shielded the substrate from the corrosive species in addition to the multi-stepped cathodic reactions which may be poisoned in one manner or the other by any of the species in the leaf extracts. The inhibitor species, by adsorption, will retard anodic corrosion reactions at the flawed regions in the initial oxide film where the substrate is transiently exposed to the aggressive environment. Thus mixed anodic and cathodic inhibiting effects will occur.

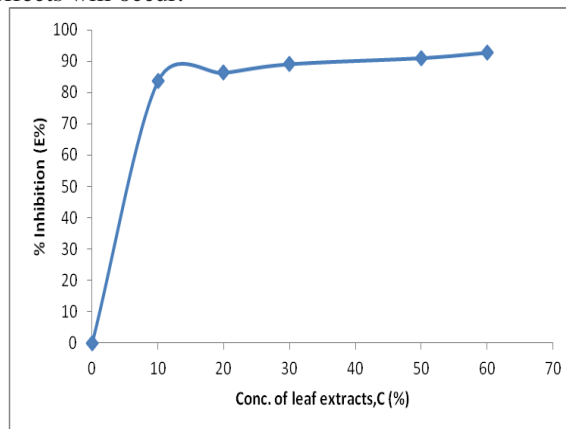


Figure 2: Variation of Inhibition efficiency of leaf extracts for mild steel in 2.5M HNO₃.

Similarly, as displayed in Figure 2, the inhibition efficiency increased rapidly and attained about 93% efficiency at an inhibitor concentration of 60%. Whereas in line with earlier discussions, efficiency of about 84% was achieved at leaf extracts concentration of 10%.

It is usual practice to determine the mode of inhibition action in terms of adsorption isotherms. For the leaf extracts of *Carica papaya*, a linear relationship was obtained when $\frac{\theta}{C}$ was plotted against C, as displayed in Figure 3.

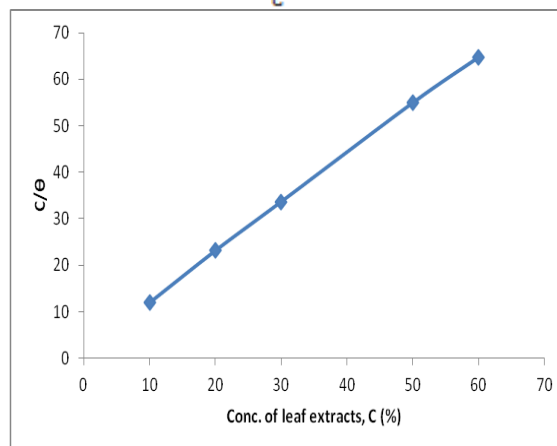


Figure 3: Linear variation of $\frac{\theta}{C}$ versus C, concentration of leaf extracts.

This shows that from the gravimetric data, the adsorption of inhibitor species in the leaf extracts of *Carica papaya* obeys the Langmuir adsorption isotherm which implies that there are no interactions among adsorbed species on the surface of the mild steel.

3.3 Gasometric studies

Table 2 displays data obtained from the gasometric experiments and the data represent the averages obtained from two similar experiments.

Table 2: Summary of data for mild steel specimen in 2.5 M HNO₃ at various concentrations of leaf extracts of *Carica papaya* using gasometric technique.

Concentration of leaf extracts, C (%)	Rate of gas evolution RV_G (cm ³ /min)	% Inhibition (E%)	Surface coverage Θ
Blank, 0	6.250	0	0
10	1.8125	71	0.71
20	1.5625	75	0.75
30	1.3125	79	0.79
50	0.500	92	0.9218
60	0.225	96.4	0.964

The rate of gas evolution is equivalent to the rate of corrosion. During corrosion reactions the rate of anodic reaction is equal to the rate of cathodic reaction because all electrons released in the anodic half reaction are used up in the cathodic half. Hence the rate at which gas is evolved at the cathode is a measure of the rate of corrosion of the mild steel specimens.

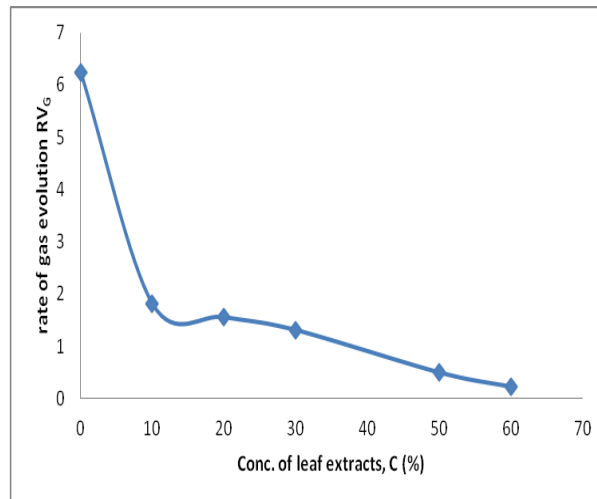


Figure 4: Rate of gas evolution in various concentrations of leaf extracts for mild steel in 2.5M HNO₃

From the data displayed in Table 2 and in Figure 4, a similar trend in the reduction of corrosion activities with increase in the concentration of leaf extracts as discussed for the gravimetric technique can be observed. In addition, the inhibition efficiencies and surface coverage follow similar trends as previously discussed for their values increased as the concentration of inhibitor species was increased. However, at 10% inhibitor concentration, the efficiency observed was 71% as against about 84% observed during gravimetric measurements. Also at 60% inhibitor concentration, efficiencies of 93% and 96% were observed for gravimetric and gasometric techniques respectively which are within limits of experimental errors.

3.4 Thermometric studies

Table 3 displays the summary of the average of two data obtained during thermometric measurements. Whereas the measure of reaction rates, RN , decreases, the inhibition

Table 3: Summary of data obtained from thermometric measurements

Concentration of leaf extracts, C (%)	Reaction number RN (° C/min)	%Inhibition, (E%)	Surface coverage Θ
Blank, 0	0.5580	0	0
10	0.1014	82.8	0.828
20	0.7955	86.07	0.8607
30	0.06555	89.05	0.8905
50	0.05645	91.16	0.9116
60	0.04655	92.66	0.9266

efficiencies and surface coverage increased as the concentration of the inhibitor was increased which showed a similar trend with values obtained during gravimetric and gasometric studies.

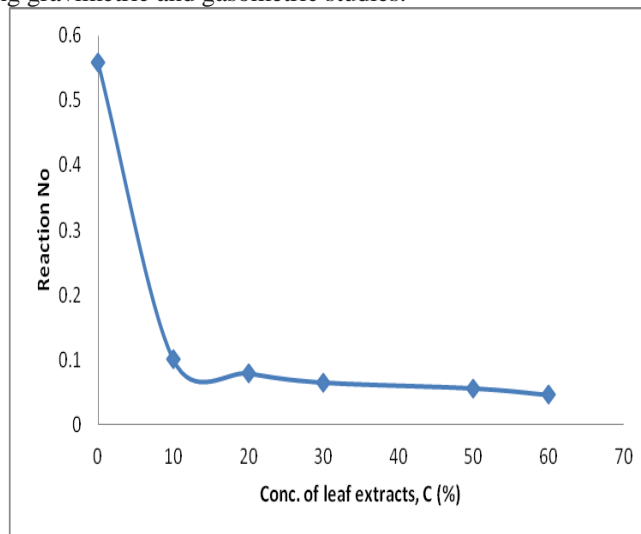


Figure 5: The variation of reaction number for mild steel in 2.5M HNO₃ with various concentrations of leaf extracts.

As displayed in Figure 5 the reaction number decreased rapidly as the number of inhibiting species in the leaf extracts increased and attained a value of about 0.046 at an inhibitor concentration of 60% from an initial value of about 0.558 °C/min in the absence of inhibitor species. The corresponding efficiency is displayed in Figure 6 where it is observed that the efficiency increases with increase in the concentration of the inhibitor species. As shown earlier the functions of the inhibitor species are by adsorbing on the corroding sites on the surface of the mild steel and the higher the number of

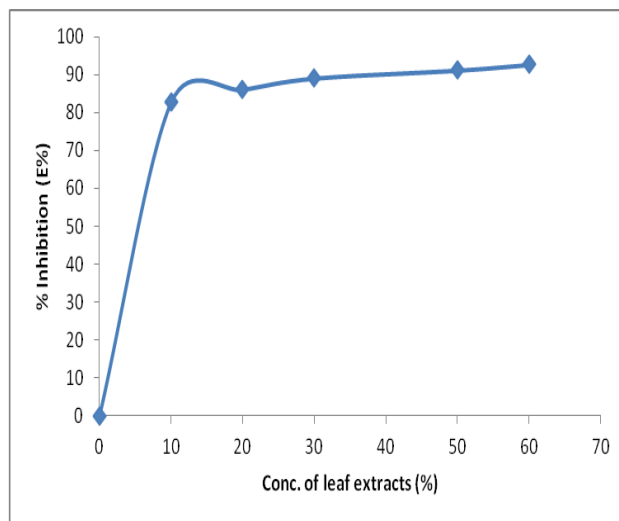


Figure 6: The variation of % Inhibition efficiency of leaf extracts of *Carica papaya* for mild steel in 2.5 M HNO₃ inhibiting species the higher the number available to adsorb at corroding sites which will translate into higher coverage and therefore an improvement in efficiency.

From the data obtained from the three techniques i.e. gravimetric, gasometric and thermometric, the reduction in the values of corrosion activities corroborate each other and the percentages of the efficiency of the inhibitor are similar. These show that the leaf extracts of *Carica papaya* are very effective inhibitors for the corrosion of mild steel in nitric acid.

4. CONCLUSIONS

The leaf extracts of *Carica papaya* reduced the corrosion rate of mild steel coupons in 2.5M nitric acid from 840 mmpy to about 60 mmpy at an inhibitor concentration of 60%.

The inhibition efficiency ranges from 93% to 96% as obtained from the gravimetric, gasometric and thermometric techniques employed in this investigation.

The extracts of *Carica papaya* leaves are good corrosion inhibitors for mild steel in nitric acid.

5. ACKNOWLEDGEMENTS

John Fasakin acknowledges the Heads of Department, Department of Petroleum Engineering and Department of Chemistry, Covenant University, Ota, for the opportunity given to carry out part of the investigation in this report.

6. REFERENCES

- [1] M. Oki, E. Charles, C. Alaka, T. K. Oki, “Corrosion inhibition of mild steel in HCl by tannins from *Rhizophora racemosa*,” *Materials Science and Applications*, vol. 2, pp. 592–595, 2011.
- [2] S. Banerjee, A. Mishra, M. M. Singh, B. Maiti, B. Ray, P. Maiti, “Highly efficient polyurethane ionomer corrosion inhibitor: the effect of chain structure,” *RSC Advances*, vol. 1, pp.199–210, 2011.
- [3] M. A. Amin, S. S. A. El-Rehim, E. E. F. El-Sherbini, O. A. Hazzazi, M. N. Abbas, “Polyacrylic acid as a corrosion inhibitor for aluminium in weakly alkaline solutions. Part I: weight loss, polarization, impedance EFM and EDX studies,” *Corrosion Science*, vol. 51, no. 3, pp. 658–667, 2009.
- [4] S. Banerjee, A. Mishra, M. M. Singh, P. Maiti, “Effects of nanoclay and polyurethanes on inhibition of mild steel corrosion,” *Journal of Nanoscience and Nanotechnology*, vol. 11, no. 2, pp. 966–978, 2011.
- *[5] R. Solmaz, G. Kardas, M. C. ulha, B. Yazici, M. Erbil, “Investigation of adsorption and inhibitive effect of 2-mercaptothiazoline on corrosion of mild steel in hydrochloric acid media,” *Electrochimica Acta*, vol. 53, no. 20, pp. 5941–5952, 2008.
- [6] M. OKI, J.O.E. Otaigbe, T. K Oki, S. Otikor, “Corrosion inhibition of Aluminium in HCl by Amine Modified Epoxy Resin”, *Journal of Materials*. [Online]. (479728). p. 5 pages, 2013. Available from: <http://dx.doi.org/10.1155/2013/479728>. [Accessed: 28 April 2014]
- [7] L. Jin, L. Wang, D. Chen, “Corrosion inhibition on hygroscopic inorganic dust-depressor”, *J. Univ. Sci. Technol. Beijing*, vol.13, No4, pp 368-371, 2006.
- [8] S. K. Boocock, “Non-chromate corrosion inhibitor formulas based on permanganate sodalite compositions” US patent 0075113A1, 2009.
- [9] P. Visser, “Novel chrome-free system resists attack on aluminium alloys”, *European coatings Journal*, vol.12, pp 87-92, 2010.
- [10] M. W. Kendig, R. G. Buchheit, “Corrosion Inhibition of Aluminium and Aluminium Alloys by Soluble Chromates, Chromate Coatings, and Chromate-Free Coatings”, *Corrosion*, 59 (5). pp 379–400, 2003.
- [11] E. Chaaieb, A. Bouyanzer, B. Hammouti, M. Berrabah, “Limonene as green inhibitor for steel corrosion in HCl solution”, *Acta Phys-Chim.*, vol.25 (7). pp. 1254 -1258, 2009.
- [12] A. Y. El-Etre, M. Abdallah, Z. E. El-Tantawy, “Corrosion inhibition of some metals using *Lawsonia* extract”, *Corrosion Science*, 47(2). p. 385–395, 2005.
- *[13] M. A. Amin, S. S. Abd El-Rehim, E. E. F. El-Sherbini, O. A. Hazzazi, “Polyacrylic acid as corrosion inhibitor for aluminium in weakly alkaline solutions. Part I: Weight loss, polarization, impedance EFM and EDX studies”, 51(3). pp. 658-667, 2009.
- [14] S. Senthil Kumaran, Kishore Kumar, “Effect of vegetal and synthetic tannins on the corrosion protection of metals, “Proceedings of the national conference on emerging trends in mechanical engineering 2K13, pp.357-362, 119.18.60.68, 2013.
- [15] P. C. Okafor, E. E. Ebenso, U. J. Ekpe, “Azadirachta Indica extracts as corrosion inhibitor for mild steel in acid medium” *Int. J. Electrochem. Sci.*, 5, pp.978-993, 2010.
- [16] P. Bothi, R. Afidah Rahim, H. Osman, K. Awang, “Inhibitive effect of *Xylopi ferruginea* extract on the corrosion of mild steel in 1M HCl medium” *Int. J of mineral, metallurgy and materials*, 18 (4), pp.413-418, 2011.
- [17] A. Eid Al-Rawajfeh, U. Al Qawabeha “Influence of diamond pressing process on corrosion resistance in steel”, *Materials Science and Engineering A*, 456(1-2), 133.137. DOI: /10.1016/j.msea.2007.01.070.2007
- [18] U. J Ekpe, U. J Ubok, B. I. Ita, O. E. Offiong, E. E. Ebenso, “Inhibitory action of methyl and phenyl thiosemicarbazone derivatives on the corrosion of mild steel in hydrochloric acid” *Mater. Chem. Phys.* 40, pp 87-93, 1995.
- [19] S. A. Umoren, I. B. Obot, E. E. Ebenso, N. O. Obi-Egbedi, Synergistic Inhibition between Naturally Occurring Exudate Gum and Halide Ions on the Corrosion of Mild Steel in Acidic Medium” *Int. J. Electrochem. Sci.*, 3, pp. 1029-1034, 2008.
- [20] U. R. Evans, “Behaviour of Metals in Nitric Acid” in *Trans. Faraday Society*, 40, pp. 120-130, 1944.
- [21] H. H. Uhlig, *Corrosion Handbook*, The Electrochemical Society, New York, NY, pp. 133-134, 1948