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A Study of Green Inhibitor for Acidic Corrosion of Mild Steel

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ABSTRACT

The inhibition efficiency of *Euphorbia hirta* leaves on the corrosion of mild steel in hydrochloric acid (1M) was investigated by the weight loss method. Potentiodynamic polarization and electrochemical impedence were studied to evaluate the corrosion inhibition performance of the *Euphorbia hirta* leaf extract. The results revealed that *Euphorbia hirta* acts as a corrosion inhibitor in 1M HCl. The inhibition efficiency increases with increase of extract temperature and contact time but decreases with the concentration of the leaf extract. The inhibition action was attributed to the adsorption of the chemical compounds present in the leaf extract on mild steel. The formation of an adsorbed film on a steel surface was investigated using scanning electron microscopy (SEM) and FT – IR.

Keywords : Corrosion inhibitor, Mild steel, *Euphorbia hirta*, Polarization, 1M HCl, Electrochemical Impedence Spectroscopy.

I. INTRODUCTION

In the Chemical or electro chemical reaction between the materials, usually a metal and its environment that causes a deterioration of the material and its properties. To stop metals (especially steel) from corroding we can try to stop the oxygen and water from coming in contact with the metal. Areas that are humid (more moisture in the air) will have more corrosion than areas that are dry. Corrosion is also faster when there are more ions present in the water. The minimization of corrosion by coating with a protective coating, with an oxide or phosphide or similar substance or with a protective paint or by rendering the metal passive is known as corrosion control. Protective coatings are the most widely used corrosion controlled by modifying the metal and environment. Natural products such as amino acids, proteins, biopolymers and plant extracts have been reported to be efficient corrosion inhibitors [1]. Plant extracts are viewed as rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost [2]. Plants are sources of naturally occurring compounds, some with complex molecular structures and having different chemical, biological and physical properties. The naturally occurring compounds are mostly used because they are environmentally acceptable, cost effective and have abundant availability. These advantages are the reason for use of extracts of plants and their products as corrosion inhibitors for metals and alloys under different environment. Different plant extracts can be used as corrosion inhibitors commonly known as green corrosion inhibitors [3-16]. Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds.

In this view, we have chosen *Euphorbia hirta* as green inhibitor for mild steel in 1 molar hydrochloric acid. The corrosion rate was studied by weight loss method. To ascertain the inhibition efficiency of the leaf extract, we have varied the concentration of the extract, temperature and time duration.

II. EXPERIMENTAL PROCEDURE

About 10g of powdered leaves of *Euphorbia hirta* was boiled in 100mL of water for 1 hr. Then it was cooled and filtered. The extract was used to prepare various concentrations of inhibitors by diluting 2, 4, 6, 8, 10 mL and blank in 1M HCl in 50 mL SMF. About 25mL of made up solution was taken and the mild steel was dipped in different concentrations in the beaker.

2.1. Weight loss measurements

Mild steel specimens of size 2.5 cm, with a small hole of about 1 cm diameter near its upper edge were used for weight loss studies. The specimens were cut abraded with scrubbed, rinsed with water before they were dried. The pre-cleaned and weighed specimens were suspended in beakers containing the test solutions. Tests were conducted under immersion test in 150 mL of the aerated and unstirred test solutions. Immersion of time was varied from 5 hrs to 72 hrs (3 days) in 1M HCl. The specimens were retrieved from test solutions after 5, 10, 24, 48, 72 hrs appropriately cleaned, dried and reweighed. The weight loss was taken to be the difference between the weight of the specimens at a given time and its initial time. The effect of temperature on mild steel corrosion and corrosion inhibition was investigated by repeating experiments 303, 313, 323, 333, 343K respectively. All tests were run in duplicate and the data obtained showed good reproducibility.

Corrosion rate (mmpy) = $87.6 \times \frac{W}{DAT}$ (1)

Where, mmpy - millimeter per year; W - Weight loss in mg; D - Density in gm/cm^{-3};

A - Area of specimen cm^2;

T - Time in hours;

R_{corr} - Corrosion Rate

The inhibition efficiency (% IE) and degree of surface coverage (ϴ) were calculated using equations below respectively.

% IE = W_1-W_2/ W_1× 100 **(2)**

ϴ = W_1-W_2/ W_1 **(3)**

W_1 and W_2 are weight losses in the absence and presence of the inhibitor respectively.

III. RESULT AND DISCUSSION

3.1. Weight loss method

The weight loss method of monitoring corrosion rate is useful because of its simple application and reliability. Several authors have been reported on comparable agreement between weight loss technique and the other technique of corrosion monitoring. The corrosion rate can be determined by using equation (1). The effect of addition of inhibitors at different concentration on the corrosion of mild steel in 1M HCl studied by weight loss method at blank HCl and HCl with the leaf extract for immersion period of 5 hours. A decrease in corrosion rate is observed in the presence of inhibitor to the blank.

Table: 1 Effect of leaf extract on corrosion rate

Medium used	**Weight loss (g)**	**Corrosion rate (g/cm^2)**
1M HCl	0.23	0.0410
HCl with extract	0.14	0.0267

3.1.1 Effect of concentration of extract

The effect of concentration of the leaf extract was studied by varying the concentration from 2, 4, 6, 8, 10 ppm in 1 M HCl at room temperature for 5 hrs. The corrosion rate decreases and then increases, so that inhibition efficiency increases and then decreases with decrease in inhibitor concentration. This is better because it means low concentration of green inhibitors can be used, thus making them cheaper and eco-friendly. By using equations (2) and (3), inhibition efficiency (IE) and the degree of surface coverage (Ɵ) can be calculated respectively. Table 2 depicts the value of corrosion rate, weight loss, IE and Ɵ. The trend of IE with concentration of leaf extract is given by figure 1.

Table 2 Effect of concentration of *Euphorbia hirta* leaf extract

Concentration of inhibitor ppm	**R_{Corr}** g/cm²	**Weight loss** g	**I.E** %	**Ɵ**
2	0.0374	0.21	14.4827	0.1448
4	0.0267	0.15	11.1111	0.1111
6	0.0339	0.19	12.8378	0.1283
8	0.0339	0.19	12.9251	0.1292
10	0.0310	0.16	10.6771	0.1006

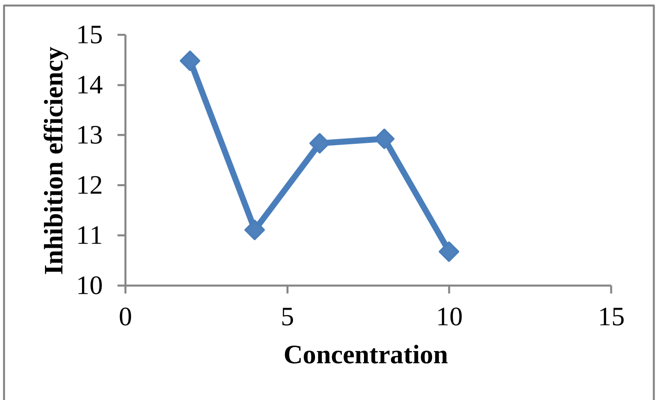

Figure 1 Plot of Inhibition Efficiency (%) vs Concentration of leaf extract

3.1.2 Effect of Temperature

The inhibition efficiency increased with an increase in temperature. This is an advantage, where mild steel can be used in high temperature applications. The corrosion rate, weight loss, percentage inhibition efficiencies and surface coverage for different temperatures in 2 ppm of the leaf extract concentration for 5 hours are given in Table 3. With an increase in temperature, more active molecules of the reactants (acid and mild steel surface) become available for the reaction. Thus, the observed trend may also be due to the fact that rates of chemical reactions generally increase with temperature (Figure 2).

Table 3 Effect of temperature on corrosion rate

Temperature ˚C	**R_{corr}** g/cm²	**Weight loss** g	**IE** %	**Ɵ**
30	0.0267	0.15	10.6771	0.1006
40	0.0339	0.19	12.4183	0.1241
50	0.0374	0.21	14.4827	0.1448
60	0.0553	0.31	21.2328	0.2123
70	0.0607	0.34	23.2876	0.2328

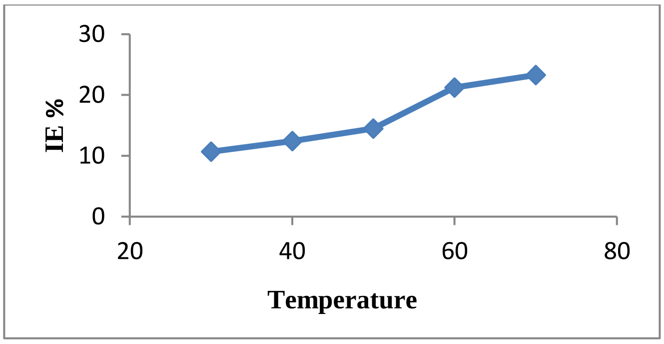

Figure 2 Plot of Inhibition Efficiency (%) vs Temperature

3.1.3 Effect of Contact time

The effect of contact time on inhibition efficiency was carried out in 2 ppm leaf concentration at 308K for 5 to 72 hours. It can be seen that inhibition efficiency (%) increases with increasing time. This shows that the inhibitors are adsorbed on the surface when it is in contact with the mild steel for a long time (Table 4). Figure 3 gives the trend of corrosion rate with time.

Table 4 Effect of contact time on corrosion rate

Contact Time Hours	**R_{Corr}** g/cm²	**Weight loss** g	**IE** %	**Ɵ**

5	0.0267	0.15	10.6771	0.1006
10	0.0178	0.20	14.0845	0.1408
24	0.0085	0.23	15.7534	0.1575
48	0.0042	0.23	15.8620	0.1586
72	0.0032	0.26	17.8082	0.1780

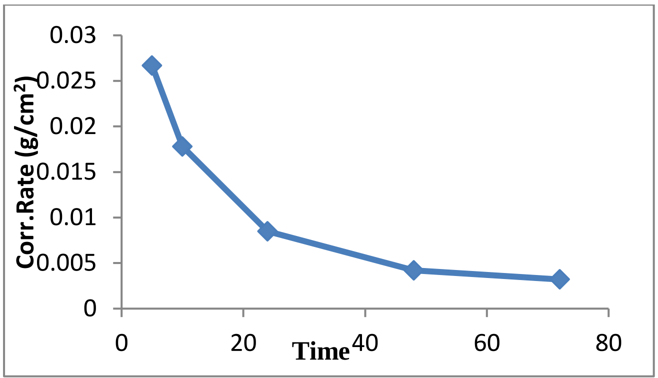

Figure 2 Plot of Corrosion Rate vs Time

3.2. Adsorption Isotherm

The nature of corrosion inhibition has been deduced in terms of the adsorption characteristics of the inhibitors. The adsorption of an organic compound adsorbed and a metal surface is regarded as a substitution adsorption process between the organic molecule in the aqueous solution and water molecule adsorbed on the metallic surface.

$Org_{(sol)} + x\ H_2O_{(ads)} \rightarrow Org_{(ads)} + x\ H_2O$

Where, x is the size ratio representing the number of water molecule replace by one molecule of organic compound adsorbed. The adsorption of organic compounds can be described by two main types of interaction. They are physisorption and chemisorption.

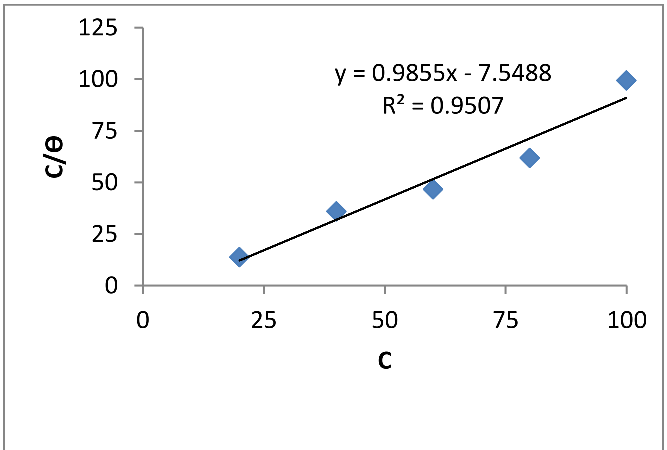

Figure 3 Plot of C/Θ vs C (Langmuir adsorption isotherm)

3.3. Electrochemical Impedence study

The impedence measurement has been applied to the study of pitting and other localized corrosion. Polarization resistance R_p can be used to determine the resistance of the metal under investigation against corrosion. From the impedance and polarization study, we get the polarization resistance value. From that value we can calculate C_{dl} value using the formula

$C_{dl} = 1/2\ \pi\ f_{max}\ R_{ct}$

Where, C_{dl} – Double layer capacitance; f_{max}- Maximum frequency; R_{ct} - Charge transfer C_{dl} values are used to study about corrosion efficiency. The values obtained for the bare (1M HCl) corresponds to 0.2345, bare (1M HCl), with extracts corresponds to 1.7483.The AC impedance spectra of mild steel immersed in HCl, in the presence and absence of inhibitors, are shown in Figure 4. The AC impedance parameters namely charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) are given in Table 5. When the mild steel is immersed in acid, the R_{ct} values are 0.561 Ω cm² in 1M HCl and the C_{dl} values are 0.2345 Fcm^{-2} in 1M HCl. When the leaf extract is added to HCl, the R_{ct} value is increased to 1.549 Ω cm² for 1M HCl. The increase in R_{ct} value confirms that a protective film is formed on metal surface.

Table 5 Electrochemical Impedance measurements in 1M HCL

Coating Sample	R_{ct}	f_{max}	C_{dl}	IE %	Surface coverage
Blank (1M HCl)	0.561	0.2663	0.2345	-	-
HCl with extract	1.549	0.7189	1.7483	63.78 %	0.6378

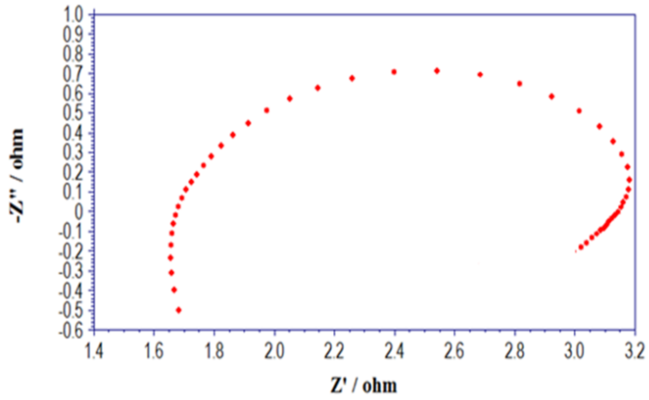

Figure 4 Nyquist plot for Bare 1M HCl with leaf extract

3.4. Potentiodynamic polarization study

The potentiodynamic polarization behaviourof mild steel in 1MHCl . Figure 5 shows that the potentiodynamic polarization behaviour of mild steel in 1MHCl containing different concentration of *Euphorbia hirta* inhibitor and observed data.

Table 6 Potentiodynamic polarization measurements in 1 M HCl with leaf extract

Coating sample	E_{corr}	I_{corr}	PE %
Bare (1M HCl)	-0.9185	0.0274	-
Bare with leaf extract	-0.9205	0.0902	69.62%

The polarization curves of carbon steel immersed in 1M HCl in the presence and absence of inhibitors are shown. The corrosion parameters are given in Table 6. When mild steel is immersed in 1M HCl, the corrosion potential is – 0.9185 V vs saturated calomel electrode (SCE). When the leaf extract is added to 1M HCl, the corrosion potential shifted to the cathodic side (– 0.9205 V vs SCE). That is 0.8944 V to 0.9014 V vs SCE. This suggests that this formulation controls the cathodic reaction predominantly.

When carbon steel immersed in 1M HCl, the corrosion current, I_{corr} from 0.02747 to 0.02902 Acm^{-2}. This indicates that protective film formed on the mild steel strongly in 1M HCl.

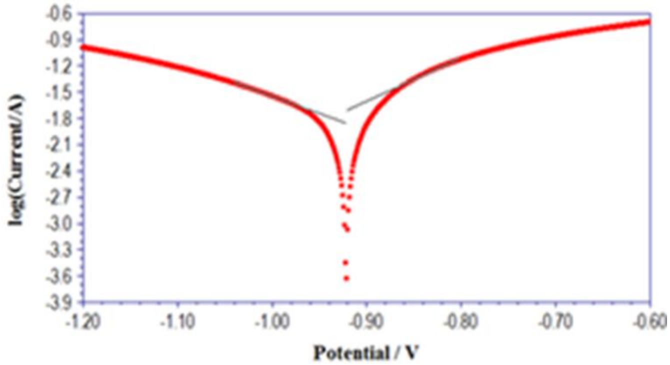

Figure 5 Tafel plot for Bare 1M HCl with leaf extract

3.5. FT-IR Spectroscopy

The peak values obtained from FT-IR analysis are shown in the figure 4.25. The broad peaks are obtained 3695.61 to 3332.99 cm^{-1} assigned to the presence of a superfacial absorbed water, stretching mode of an OH and C-H. The peaks at 3695and 2978 corresponds to stretching vibration of aliphatic aromatic OH and C-H. The peaks at 2978, 2823, 2360, 1627 cm^{-1} corresponds to C-H stretch in the presence of alkanes, C-H stretch in the presence of aldehyde, -NH, -C=O stretching. The peaks at 671, 601, 470, 432 cm^{-1} corresponds to C-Cl stretching in the presence of alkyl halides. The peaks at 948, 1157, 1242, 1512 cm^{-1} corresponds to O-H bend in the presence of carboxylic acids, C-N stretching in the presence of aliphatic amines, $-CH_2X$ in the presence of alkyl halides, -N-O asymmetric stretch in the presence of nitro compound. Almost all the peak observed for plant extract is also noticed in mild steel immersed in 1M HCl acid with plant extract as shown in the figure 6.

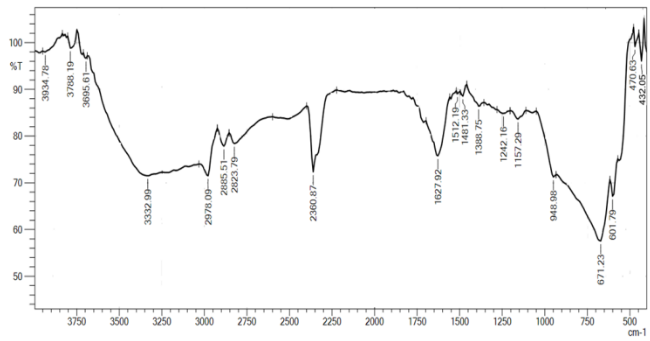

Figure 6 FT-IR Spectrum of leaf extract

3.6. SEM Analysis

Surface morphology of the mild steel surface was studied by scanning electron microscopy. Figure 7 shows that the SEM micrographs of mild steel surface after immersion in 1M HCl respectively. SEM photographs showed that the surface of metal has number of pits and cracks are visible in the surface may be belongs to the plug type of corrosion. But in presence of inhibitor the dissolution process significantly reduced by the formation of thin film covered on the entire surface of the metal.

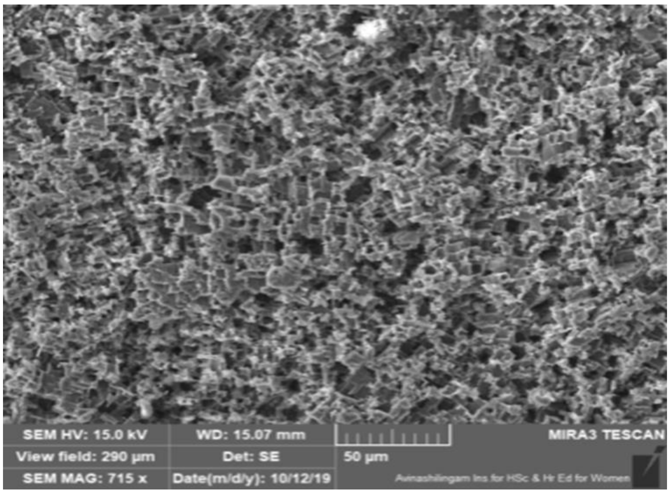

Figure 7 SEM image of leaf extract

IV. CONCLUSION

The current investigation shows that the chosen plant is very effective in inhibiting corrosion of mild steel in 1M HCl. The major conclusions of this experiment are;

- All natural compounds act as inhibitors and the highest efficiency was observed at 1M HCl in the *Euphorbia hirta* leaves.
- The corrosion inhibition process follows Langmuir isotherm suggest that one molecule of the inhibitor occupying one active site.
- Inhibitors of the *Euphorbia hirta* leaves are easily available, non-toxic and eco-friendly as well as having good inhibition efficiency.
- The AC impedence spectra reveal that plant leaves form protective film on mild steel.
- The surface morphology of the corrosion inhibition is characterized by SEM analysis and suggested different morphological structures.
- From the tafel plot, potentiodynamic polarization nature of the corrosion inhibition is examined.

V. REFERENCES

[1]. G. Sıˇgırcık, T. T¨uken, and M. Erbil, Assessment of the inhibition efficiency of 3,4-diaminobenzonitrile against the corrosion of steel, Corrosion Science, vol. 102, pp. 437–445, 2016.

[2]. K. Krishnaveni and J. Ravichandran, Effect of aqueous extract of leaves of Morinda tinctoria on corrosion inhibition of aluminium surface in HCl medium, Transactions of Nonferrous Metals Society of China, vol. 24, no. 8, pp. 2704–2712, 2014.

[3]. Rekha. N Nair, Green corrosion inhibitors for mild steel in acidic medium, International Journal of Modern Trends in Engineering and Research, vol. 04, no. 12, pp. 216-221, 2017.

[4]. Marko Chigondo, Fidelis Chigondo, Recent Natural Corrosion Inhibitors for Mild Steel: An Overview, Journal of Chemistry, Vol. 2016, Article ID 6208937, 1-7.

[5]. M. S. Al-Otaibi, A. M. Al-Mayouf, M. Khan, A. A. Mousa, S. A. Al-Mazroa e H. Alkhathlan, Corrosion inhibitory action of some plant extracts on the corrosion of mild steel in acidic media, Arabian Journal of Chemistry, pp. 1-7, 2012.

[6]. Alfred. I. Onen, Dzaradiya. U. Yakubu, Cleome gynandra and Solanum scabrum Leaf Extracts as Corrosion Inhibitor of Mild Steel in Hydrochloric Acid Solutions, Chem Sci Rev Lett, 4(16), 1069-1078, 2015.

[7]. A. M. Al-Fakih, M. Aziz, H.M. Sirat, Turmeric and ginger as green inhibitors of mild steel corrosion in acidic medium, Journal of Materials

and Environmental Science, vol. 6, no. 5, pp. 1480–1487, 2015.

[8]. K. C. Ajani, A. S. Abdulrahman, and E. Mudiare, Inhibitory action of aqueous Citrus aurantifolia seed extract on the corrosion of mild steel in H2SO4 Solution, World Applied Sciences Journal, vol. 31, no. 12, pp. 2141–2147, 2014.

[9]. E. E. Oguzie,M. A. Chidiebere, K. L. Oguzie, C. B. Adindu, and H. Momoh-Yahaya, Biomass extracts for materials protection: corrosion inhibition ofmild steel in acidic media by Terminalia chebula extracts, Chemical Engineering Communications, vol. 201, no. 6, pp. 790–803, 2014.

[10]. Z. V. P. Murthy and K. Vijayaragavan, Mild steel corrosion inhibition by acid extract of leaves of Hibiscus sabdariffa as a green corrosion inhibitor and sorption behavior, Green Chemistry Letters and Reviews, vol. 7, no. 3, pp. 209–219, 2014.

[11]. K. K. Anupama, K. Ramya, A. Joseph, Electrochemical and computational aspects of surface interaction and corrosion inhibition of mild steel in hydrochloric acid by Phyllanthus amarus leaf extract (PAE), Journal of Molecular Liquids, vol. 216, pp. 146–155, 2016.

[12]. Abeng, F. E., Ekpe, U. J., Ikeuba, A. I., Ugi, B. U., Nna, P. J. Inhibitive action of alkaloid and non-alkaloid fractions of ethanolic extracts of Phyllanthus amarus on the corrosion of mild steel in HCl solution, Global Journal of Pure and Applied Sciences, vol. 19, 2013.

[13]. Kamal, C., Gopalakrishnan, M., A bis-indol alkaloid as a green inhibitor for corrosion of mild steel in HCl solution from Caulerpa racemosa, Journal of Hazardous Materials, vol. 2, no. 3, pp. 54-60, 2012.

[14]. Ghazoui, A., Saddik, R., Benchat, N., Guenbour, M., Hammouti, B., Al-Deyab, S.S., Zarrouk, A. Comparative study of pyridine and pyrimidine derivatives as corrosion inhibitors of C38 steel in molar HCl, Int. J. Electrochem. Sci. vol. 7, pp. 7080-7097, 2012.

[15]. P. M. Ejikeme, S. G.Umana, M. C.Menkiti, O.D.Onukwuli, Inhibition ofmild steel and aluminium corrosion in 1MH2SO4 by leaves extract of African Breadfruit, International Journal of Materials and Chemistry, vol. 5, no. 1, pp. 14–23, 2015.

[16]. M. Prabakaran, S.H. Kim, K. Kalaiselvi, V. Hemapriya, I.M. Chung, Highly efficient Ligularia fischeri green extract for the protection against corrosion of mild steel in acidic medium: electrochemical and spectroscopic investigations, Journal of the Taiwan Institute of Chemical Engineers, vol. 59, pp. 553–562, 2016.