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Electrochemical Study of Zinc Plate in Acid Medium: Inhibitory Effect of Bitter Leaf (Vernonia Amygdalina)

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Vernonia amygdalina (bitter leaves) was tested as a green inhibitor for zinc-plate in 2M hydrochloride solution by means of weight loss, gasometric principle and potentiostatic polarization at 313-343K. Increasing rate of hydrogen gas during the chemical reaction was examined in gasometric studies. Inhibition feasibility was explained by formation of insoluble complex adhesion on the surface of metal. However, results obtained indicated that, percentage of extract concentration increased due to the volume of $H_{2\ gas}$ generated. Extract in acid medium retard corrosion degradation of the deposited zinc- plate and forcefully reduce corrosion rate. Micro-structural examination through AFM revealed the morphology and evaluation performance of vernonia amygdalina. Polarization results obtained showed that performance efficiency of vernonia amygdalina was outstanding and the inhibitory effectiveness was as a result of increase in vernonia amygdalina concentration.

Keywords: Morphology, Corrosion, green inhibitor, zincplate, vernonia amygdalina

1. INTRODUCTION

Steel exhibits a wide range of useful forms and mechanical properties thereby finding applications in almost all industries. However, it is highly susceptibility to corrosion attacks [1-4] Zinc plate on the other hand is a thin sheet of steel plated with zinc to prevent corrosion, mostly used in a metal manufacturing sectors like petrochemical industry. [2-6]. The electrochemical behaviour of zinc plate in acidic and alkali environment are function of several factor such as surface characteristic of the material, the temperature range, pH value and the concentration of the solution [5-7]. Several studies have shown that the dissolution mechanism of zinc and the appearance of pitting on the surface of zinc-plate are due to the presence of saline and acidic medium. However, due to corrosion attack, the high toxic nature and cost of some chemicals used as inhibitors, the development of environmentally acceptable and inexpensive green inhibitors have been strengthened [8-11]. Extracts from different parts of plants such as Henna, *Lawsonia inermis* [7], Rosmarinous officinalis, *Carica papaya*, *cordia latifolia* and curcumin date palm, *phoenix dactylifera,* henna, *lawsonia inermis,* corn, *Zea mays* [9-15] and many more, have been found to be good corrosion inhibitors for metals and alloys [16-20]. The anticorrosion activity of onion, garlic, and bitter gourd for mild steel in HCl media have been shown to exhibit good result in various research articles. Oil extracts of ginger, jojoba, eugenol, acetyl-eugenol, artemisia oil, and Pennyroyal (*Mentha pulegium*) are used for corrosion inhibition of steel in acid media [20-24].

In this study, the corrosion inhibition performance of vernonia amygdalina leaves solution extract on the corrosion of zinc-plate test specimens in 2M HCl will be carried out at both the ambient temperature of 40^oC and elevated temperature of 70^oC. These acids were selected for investigation because of their known and strong corrosive action. A positive result from this investigation could lead, later to the identification of the specific compound(s)/active constituents in the leaves that cause(s) corrosion inhibition. This could be economically and technologically beneficial.

2. EXPERIMENTAL PROCEDURE

2.1. Plant collection and extracts preparation

Fresh vernonia amygdalina leaves *were* collected at Ota, Nigeria, and oven dried for two hour, thirty minutes at 1120^oC. The dried leaves were then separately grounded into powdery form and put in different beakers. Ethanol was added to each container. The resulting solutions were boiled for two hours and then left overnight to settle while being cooled down also. Each solution was filtered with the aid of filter papers after it was refluxed. From each of these solutions, varying extract concentration of 25, 55, 75 and 100 cm^3 at 50^oC elevated temperature and at duration of 56 minutes were made for further use as estimated concentration in order to study the corrosion inhibitory effect.

2.2. Substrate Preparation

The material for this study is zinc plate coupons' of 5 cm by 2 cm. It has been selected based on its industrial application and economic usage. The test sample for electrochemical analysis and corrosion investigation was rinsed with acetone, thereafter with distilled water before being immersing into the prepared solution; and the electrochemical method assigned.

2.3. Media Preparation

The chemicals made use of were of AR grade and are easily soluble in water. For the preparation of solutions, distilled water was used. The dried leaves were grounded into powdery form; while a small amount of 10 g powder was soaked in 250 ml distilled water and refluxed for 3 h. The aqueous solution was filtered; an estimated concentration of 120 ml was use for the study of corrosion inhibition properties. Five different concentrations of vernonia amygdalina leaf extract were made in sequence of 25, 55, 75 and 100 cm^3 for the 2M hydrochloric media.

2.4. Weight loss experiment

Weighed test specimens were totally immersed in each of the test media contained in a 250 ml beaker of extract in HCl solution for 24 days. Experiments were performed with acid test media of 2M in which some had the solution extract added. The specimens were taken out of the test media every 4 days, washed with distilled water, rinsed with methanol, air dried, and re-weighed. The surface coverage (θ) and inhibition efficiency (I.*E* %) were determined by using the following equations

$$\text{I-E (\%)} = \frac{w - wo}{w} \; x\; 100 \qquad (1)$$

Where w_o and w are the weight loss values in the presence and absence of inhibitor respectively. Hence, the corrosion rate (C_R) of zinc plate was calculated using the relation:

$$C_R = \Delta w/ST \qquad (2)$$

Where Cr is corrosion rate, Δw is change in weight loss of the sample (mg), T is the exposure time (hrs), and S is the surface area of mild steel.

Plots of weight loss versus the exposure time are showed in Figure 1. All the experiments were performed at a temperature of 50°C. The percentage inhibitor efficiency, I.E, was calculated from relationship written in equation 1 at the 24th day of the experiment, and the results are presented in Table 1.

2.5. Gasometrical Technique

In gasometric measurements, after vernonia amygdalina was extracted from the fresh state, various serial extract concentrations of 25, 55, 75 and 100 cm^3 were added into 250 cm^3 flask containing 2M HCl solutions at 343 K. The efficiency of the inhibitor using gasometrical method was determined by Tafel method taking into consideration the volume of hydrogen gas evolved with or without inhibitor.

$$(\%)\ \text{I.E} = \frac{vo - v1}{vo}\ \text{x}\ 100 \qquad (3)$$

Where vo is the volume of hydrogen gas without Inhibitor and v_1 is the volume with extracts.

2.6. Electrochemical Measurements

The Electrochemical study was carried out using PGZ100 potentiostat/Galvanostat having three electrode configurations at room temperature. The zinc plate is the working electrode, platinum electrode as auxiliary electrode while standard calomel electrode (SCE) was used as the reference electrode. The potentiodynamic polarization data was acquired at an average polarization scan of 0.5 mV/s. Prior to the measurement, the potential was made to stabilize at 30 minutes. Measurement was taking in 2M HCl for a period of 30 minutes in the absence and presence of inhibitor.

2.7. Surface Characterization

To investigate the surface morphology and topography of zinc-plate after deposition, Atomic Force Microscopy {AFM} was employed.

3. RESULTS AND DISCUSSION

3.1. Effect of Inhibitor Concentration

The effect of inhibitor concentration on the corrosion rate of zinc plate in 2M HCl in the presence and absence of different concentration of vernonia amygdalina using weight loss method is shown in Figure 1. The extract shows maximum inhibition efficiency of 100% in HCl at 313K. Further increase in extract concentration did not cause any change in the performance. The percentage inhibition efficiency (*E* %) and corrosion rate obtained from weight loss method at different concentrations of the extract are shown in Table 1. Gasometric results from Table 2 revealed that the percentage inhibitor for the 100% extract addition performance evaluation was more effective than others, reason being that with higher corrosion inhibitor, less corrosion rate was generated with lower volume of H gas evolved as shown in figure 2.

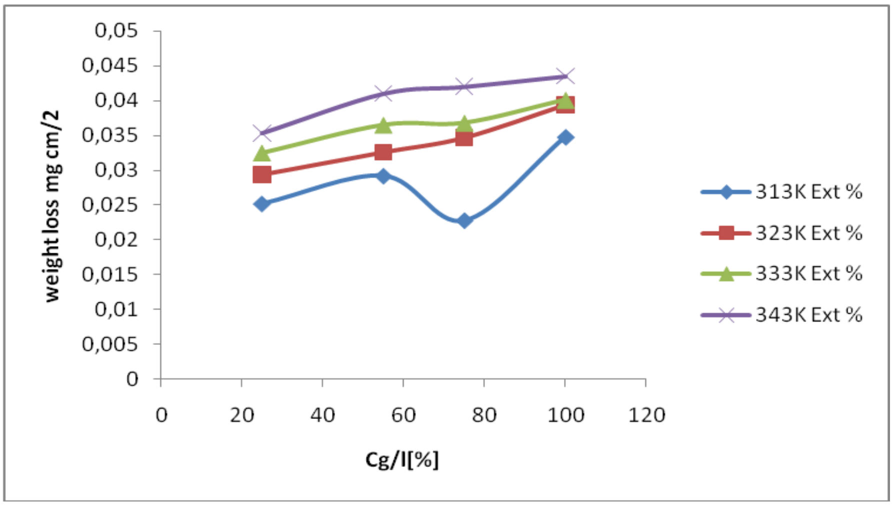

Figure 1: Inhibitive curve for the zinc-plate in 2M HCl in the presence of varying concentration of inhibitor

Hence, less hydrogen gas evolves during kinetic reaction between HCl and deposited metal unlike the control specimen. However, rate of corrosion reaction can be traceable to the function of hydrogen gas evolving with time.

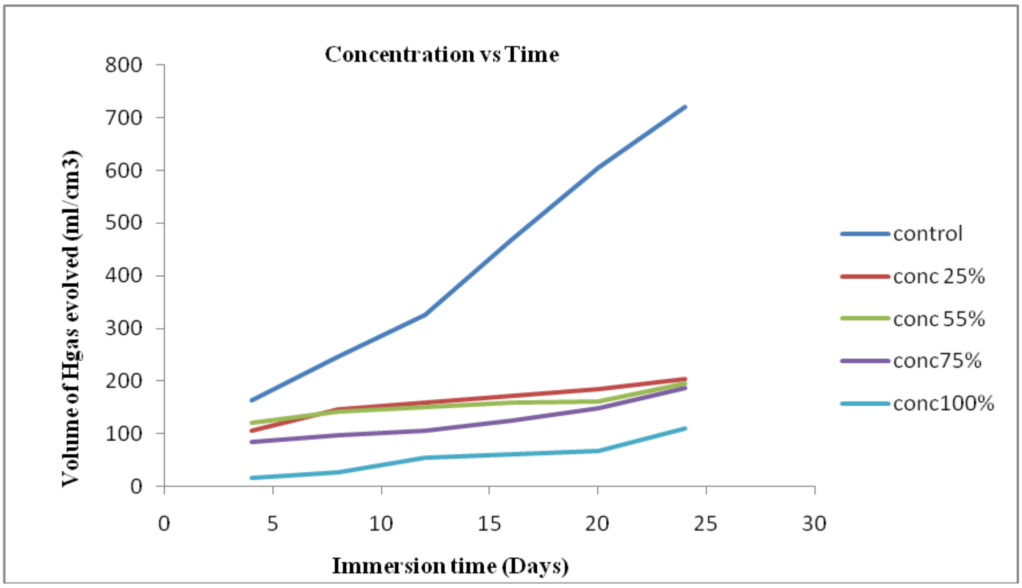

Figure 2: Relationship between the volume of hydrogen gas evolved and immersion time for zinc-plate in the presence of extract concentration at 313 K

3.2. Effect of Immersion Time

For the performance evaluation and stability of inhibitive influence of the extract at different period (time), weight loss measurements and gasometric analysis were performed in 2 M HCl in the absence and presence of the extract, varying concentration at 313 K for 3 hours immersion time. Concentrations of inhibitor were plotted against immersion time as shown in Figure 2. This figure shows that inhibition efficiency of the extract increase with increasing immersion time – 24 days. The increases in inhibition efficiency suggest the strong adsorption of constituents present in the extract on the zinc-plate surface, resulting in a more protective layer. This implies that vernonia amygdalina leaves extract effectively inhibits the zinc-plate corrosion in 2 molar hydrochloric acid solutions.

3.3. Effect of Temperature

Weight loss measurements were carried out in the range of temperature from 313–343 K in the absence and presence of extract at optimum concentration during the 3 hour immersion time. The aim was to evaluate the thermodynamic stability of the absorbed film of inhibitor on zinc plate. Taking a critical look at table 2, the result indicates that as temperature increases, the rate of corrosion increases while the inhibitory efficiency reduces. This practically shows that the rise in temperature decreases the inhibitive process; hence the highest inhibition efficiency is at 313K. Taking reference from 100%

inhibitive effect, the log of corrosion rate is a linear function of temperature effect using Arrhenius equation [Abdullahi et al., 2008].

$$logRcorr = logA - Ea/2.303Rt \quad (4)$$

Where R_{corr} is the rate of corrosion from weight loss; A is Arrhenius factor/constant; R is the gas constant; T is absolute temperature; and Ea is the apparent activation corrosion energy. Figure 3 shows variation of Log Icorr versus Log1/T in a graphical representation while Figure 4 depicts Arrhenius plot of [log R_{corr} vs 1/T] in the presence of inhibitor. From Figure 4, it can be deduced that corrosion reaction can be regarded as Arrhenius-type process. Also of note is that increase in the active passive energies in the solution with inhibitor is a function of decrease in adsorption inhibitor process on the surface metal with temperature increase. Consequently, it is evident that inhibition efficiency decreases with increasing temperature as shown by the result obtained in Table 2.

Table 1: The effect of temperature on the corrosion parameter of zinc-plate in 2M HCl with different concentrations using weight loss measurement

Concentration (g/L)	T (K)	Weight loss (mg)	(θ)	E (%)
25	313	0.0252	0.760	76
	323	0.0294	0.540	54
	333	0.0325	0.345	35
	343	0.0353	0.314	31
55	313	0.0292	0.791	79
	323	0.0326	0.715	71
	333	0.0365	0.636	64
	343	0.0410	0.628	63
75	313	0.0228	0.885	89
	323	0.0347	0.764	76
	333	0.0368	0.727	73
	343	0.0420	0.650	65
100	313	0.0348	0.927	93
	323	0.0394	0.813	81
	333	0.0410	0.736	74
	343	0.0435	0.678	68
Control	313	0.0820	-	-

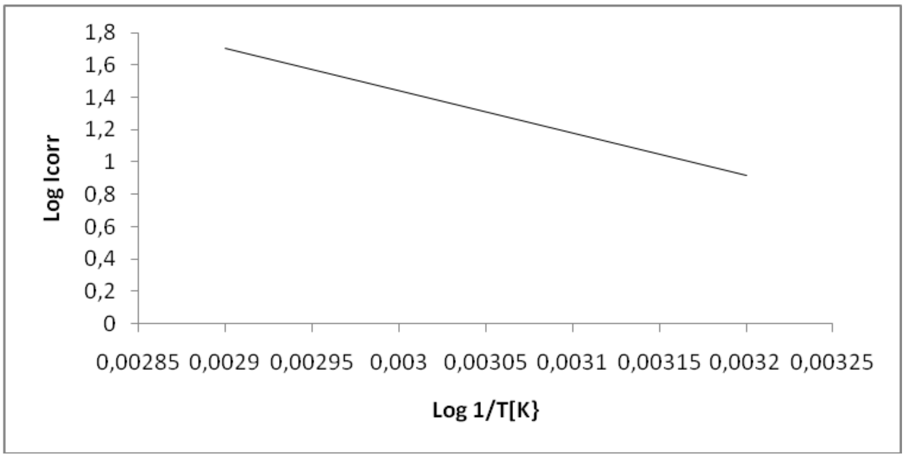

Figure 3: Variation of Log Icorr versus Log1/T

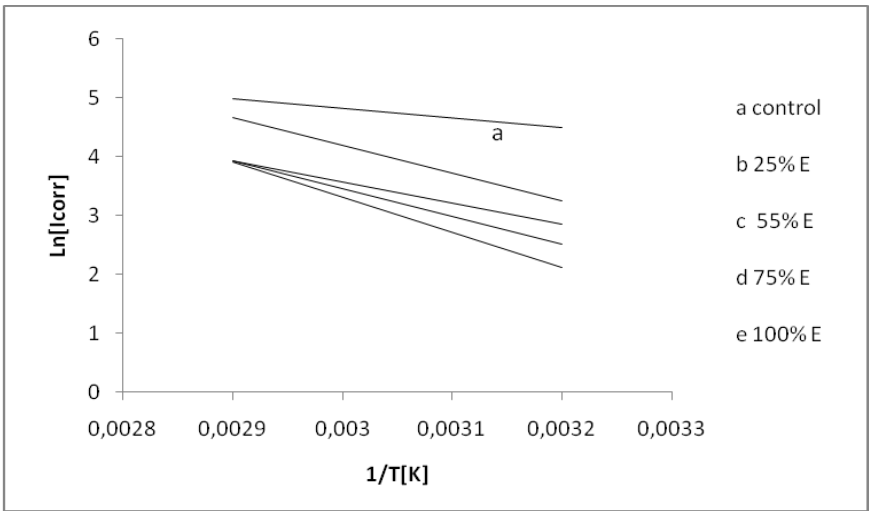

Figure 4: Arrhenium plots of ln[Icorr/T] versus 1/T at various concentration.

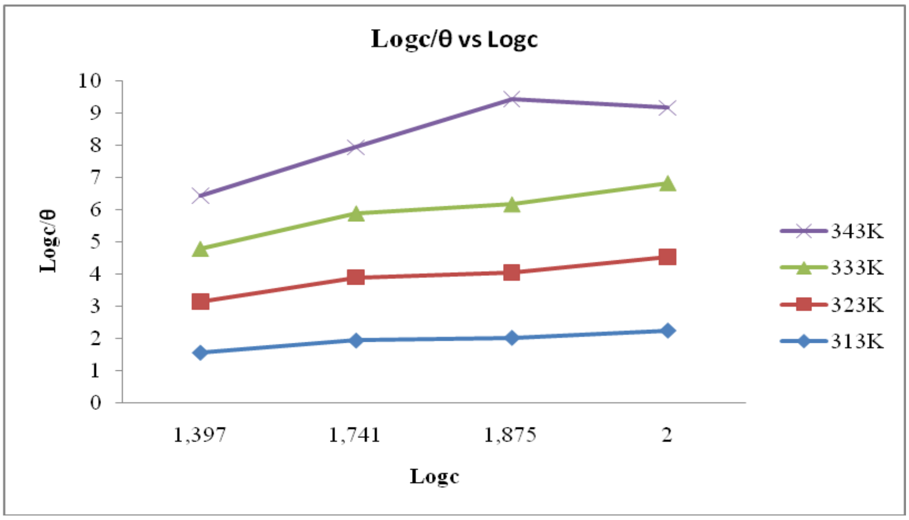

Figure 5: Variation of logc/θ versus log c

Table 2: Effect of corrosion parameter obtained from potentiostatic polarization at different temperature for zincplate in the presence of vernonia amygdalina extract in 2M HCl

Concentration (g/L)	T (K)	E_{Corr} (mV/SEC)	I_{Corr} (mV/dec)	βc (mv/dec)	βa (mV/dec)	E (θ)	E (%)
25	313	-420	23	-92	26	0.760	76
	323	-412	46	-86	20	0.540	54
	333	-434	72	-42	18	0.345	35
	343	-448	96	-82	15	0.314	31
55	313	-390	20	-96	30	0.791	79
	323	-405	29	-74	25	0.715	71
	333	-407	40	-50	16	0.636	64
	343	-414	52	-32	14	0.628	63
75	313	-440	11	-85	21	0.885	89
	323	-432	24	-41	19	0.764	76
	333	-429	30	-18	16	0.727	73
	343	-428	49	-16	12	0.650	65
100	313	-360	7	-92	23	0.927	93
	323	-345	19	-75	20	0.813	81
	333	-340	29	-70	17	0.736	74
	343	-348	45	-62	14	0.678	68
Control	313	-450	96	-105	30	-	-
	323	-454	102	-85	21	-	-
	333	-459	110	-81	24	-	-
	343	-461	140	-71	20	-	-

3.4. Adsorption Isotherm

In order to explain the adsorption isotherms for the interaction between the inhibitor and the zinc-plate by applying the Langmuir Adsorption Isotherm, surface coverage θ at different concentrations of vernonia amygdalina leaves extract in acid solution with temperature range of 313 to 343K was used.

The value of θ was found to increase, with increase in the inhibitor concentration as shown in Figure 5. The adsorption of an organic adsorbate on the surface of the metal is achieved by substitution adsorption process between the organic particles in the aqueous solutions and the adsorbed on the metal surface. However, Langmuir Adsorption Isotherm equation 4 and 5 by Abdullahi, et al., 2008 and Bammou et al., 2011 is given as:

$$\frac{\theta}{1-\theta} = AC\left[\frac{-\Delta H}{RT}\right] \quad (5)$$

In relation to:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (6)$$

Where A is the Arrhenius constant; C is the concentration of inhibitor; ΔH is the heat of adsorption; and θ is the surface coverage. The Langmuir isotherm relationship was applied in Figure 6, and especially in Figure 7 where a linear relationship is depicted on a straight line. This implies that the adsorption of vernonia amygdalina on zinc-plate provides a strong adsorb and coherent effect thereby overcoming the action of acid solution.

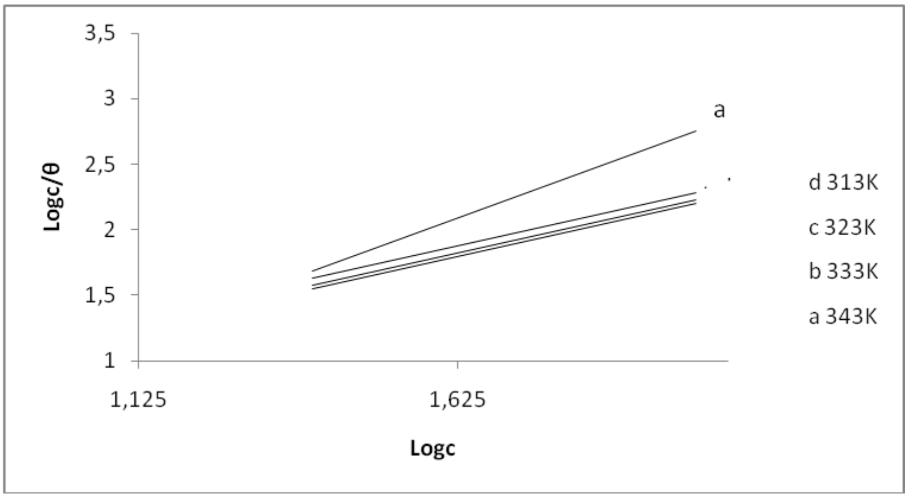

Figure 6: Langmuir Adsorption Isotherm plotted as log c/θ versus log c variation of extract in 2M HCl at different temperature

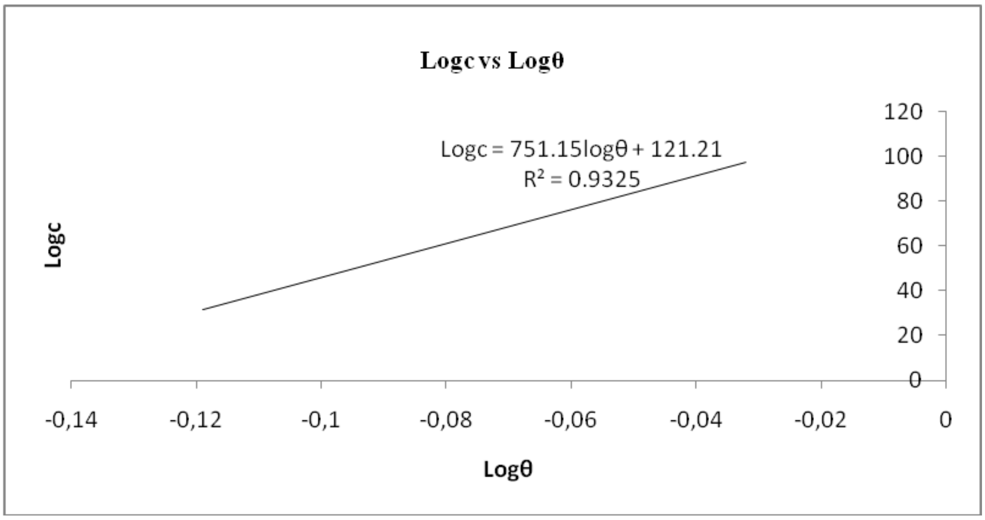

Figure 7: Langmuir adsorption isotherm curve for inhibitor adsorption in 2M HCl on zinc-plate

3.5. AFM Surface characterization measurement

In order to investigate the surface morphology and topography of zinc-plate, AFM was employed. Three surfaces were analyzed as shown in Figure 8a, 8b & 8c, for three different scenarios namely zinc-plate after deposition, zinc-plate when immersed in 2 molar of hydrochloric acid and when inhibitor was added at 25% respectively. Homogeneous structure was observed with perfect crystal and uniform arrangement on the deposit. The surface grain were restructured in Figure 8b, indicating the effect of acid on the zinc-plate. The zinc morphology consists of regular fine grain size. The presence of inhibitor in Figure 8c, retarded greatly the fusion of hydrogen atom into the layer of the substrate, however it gives a surface coverage as possible.

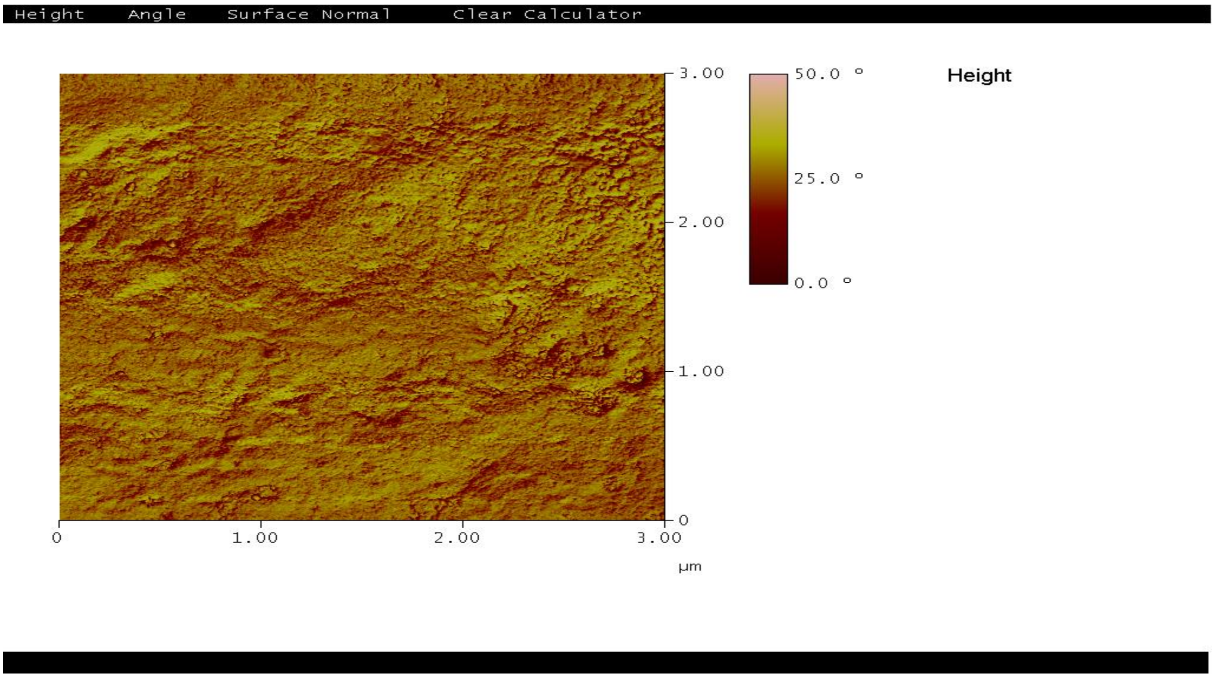

Figure 8a: AFM of zinc-plate before immersion

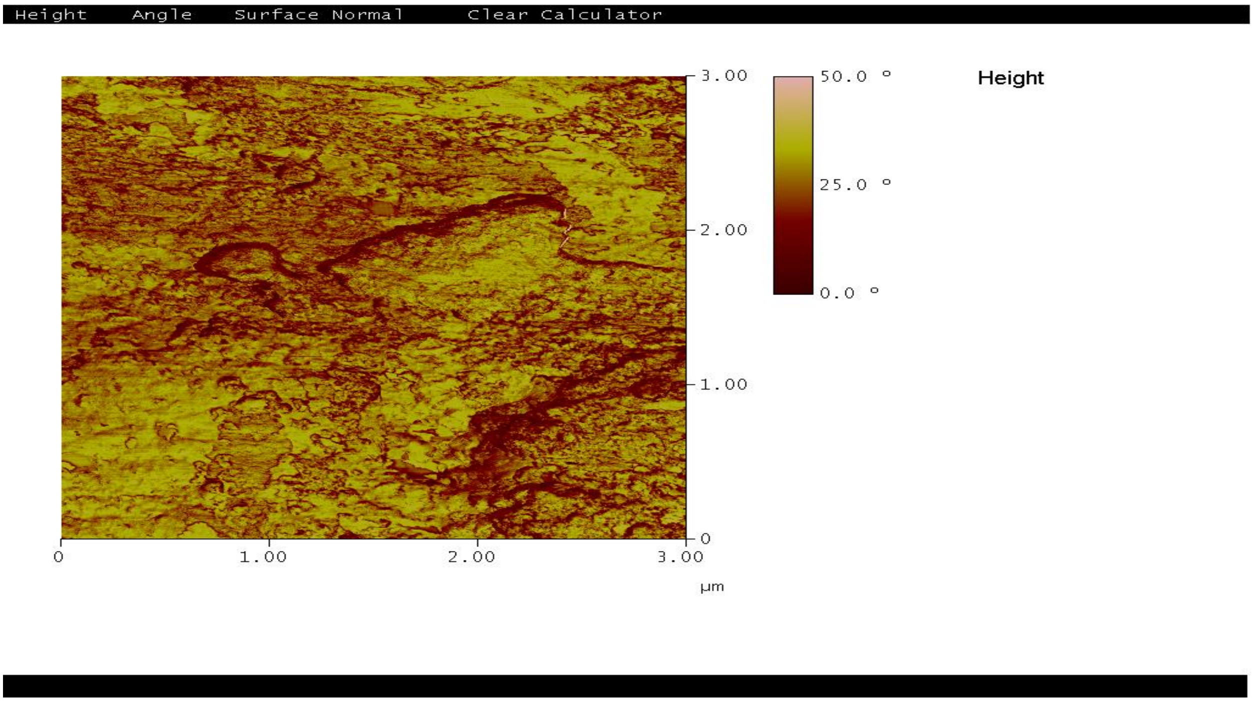

Figure 8b: After immersion in 3hrs in 2M HCl

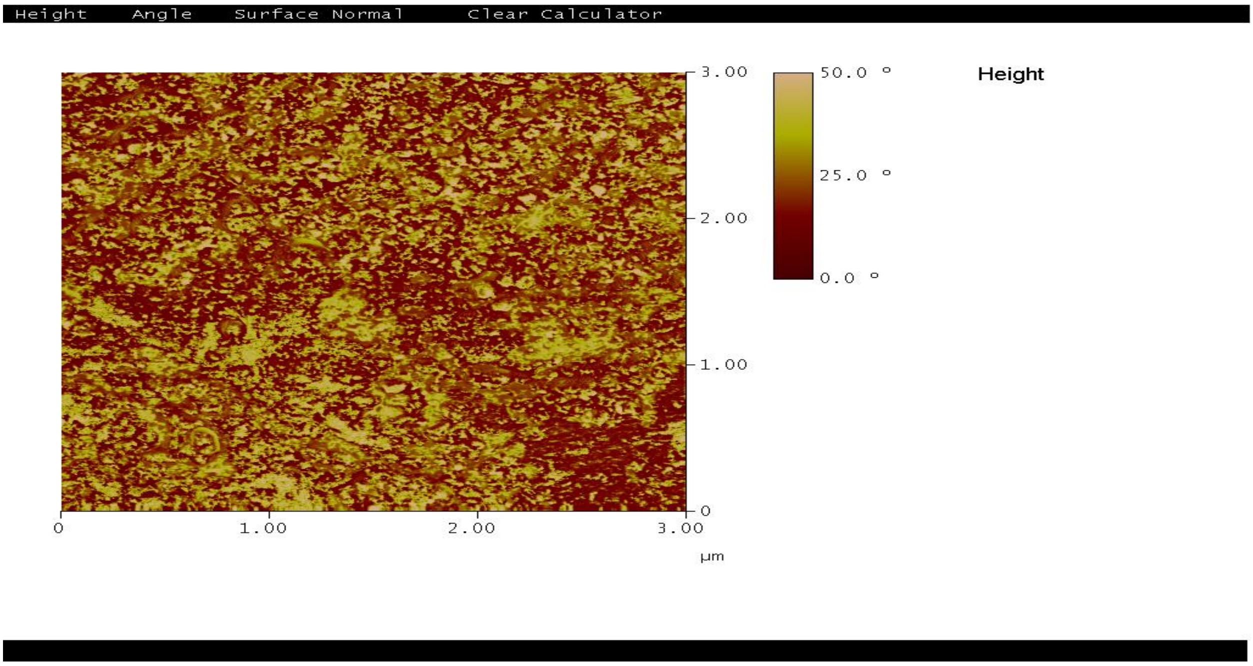

Figure 8c: Immersion in 2M HCl and 25% inhibitor.

4. CONCLUSION

In this investigation, the behavior of zinc-plate in an acid corrosive environment was examined with the influence of vernonia amygdalina extract concentration and temperature variation. Hence, from the result obtained the following conclusions were deduced:

- Inhibitory effect of the extract increases with concentration.
- The increase of temperature enhanced the passive region gradual dissolution of zinc-plate in 2M HCl
- The adsorption of vernonia amygdalina on the zincplate surface at different temperature was found to conform to Langmuir Adsorption Isotherm.
- The inhibitory mechanism / efficiency of this extract is a function of the adsorption of stable insoluble complex on the metal surface.

References

1. Popoola A.P.I and Fayomi O.S.I., 2011. *International Journal of Physical Science* Vol. 6(8).
2. Fayomi, O.S., Tau V.R., Popoola A.P.I., Durodola B.M., Ajayi O.O., Loto C.A., Inegbenebor O.A., 2011. *Journal of Material. Environmental Science*. 2 (3) 271-280.
3. Shivakumara, S., Manohar, U., Arthoba naik, Y., and Venkatesha, T.U., 2007. *Bull. Material Science.*, Vol. 30, No. 5 pp. 455–462. © Indian Academy of Sciences.
4. Ambrish Singh,V. K. Singh, and M.A. Quraishi, 2010 *International Journal of Corrosion*, pp 1155-1162.
5. Popoola A.P.I and Fayomi O.S.I., 2011. *Scientific Research And Essay*. Accepted.

6. Popoola A.P.I and Fayomi O.S., 2011. *International Journal of Electrochemical. Scienc.*, Vol (6) Pp 2264-2273.
7. Al-Sehaibani, H., 2000. *Materialwissenschaft und Werkstofftechnik*, vol. 31, no. 12, pp. 1060–1063.
8. Abdullahi, M. Fouda, A.S., Shama, S.A., and Afifi, E.A., (2008). Africa Journal of Pure and Applied Chemistry, Vol 2(9), pp. 083-091.
9. Abdel-Gaber, A. M. E. Khamis, H. Abo-ElDahab, and S. Adeel, (2008) *Materials Chemistry and Physics*, vol. 109, no. 2-3, pp. 297–305,
10. Ashassi-Sorkhabi H, D. Seifzadeh, and M. G. Hosseini, (2008)" *Corrosion Science*, vol. 50, no. 12, pp. 3363–3370,
11. Abiola O. K. Oforka N. C, Ebenso E. E. Nwinuka N. M., 2007 *Anti-Corrosion Methods And Materials*, vol. 54, No. 4, pp 219-224.
12. Farooqi, I. H. A. Hussain, M. A. Quraishi, and P. A. Saini, 1999. *Anti-Corrosion Methods and Materials*, vol. 46, no. 5, pp. 328–331.
13. James A. O. and O. Akaranta, 2009. African Journal of Pure and Applied Chemistry Vol. 3 (12), pp. 262-268.
14. Kliškić, M, J. Radošević, S. Gudić, and V. Katalinić, 2000. *Journal of Applied Electrochemistry*, vol. 30, no. 7, pp. 823–830.
15. Okafor P. C. and E. E. Ebenso, 2007 *Pigment and Resin Technology*, vol. 36, no. 3, pp. 134–140.
16. Rehan, H. H. 2003 *Materialwissenschaft und Werkstofftechnik*, vol. 34, no. 2, pp. 232–237.
17. Satapathy A. K, G. Gunasekaran, S. C. Sahoo, K. Amit, and P. V. Rodrigues, 2009. *Corrosion Science*, vol. 51, p. 2848,
18. Loto, C.A 1992. *Corrosion***,** 48, 9,759-763.
19. Craig, R.J Wood,L.E 1970 Highway research Record, No. 328.
20. Loto C.A and Odumbo, E.T 1989. *Corrosion*, 45, 7, 553 – 557.
21. Davis, G.D, Fraunhofer, J.A, Krebs,L.A, Dacres, C.M. 2001 *Corrosion*/2001, paper no. 58 Houston, TX: NACE.
22. Loto, C.A, 2003. *Corrosion Prev. & Control*, Vol. 50,1, p.43-49.
23. Bammou L, Mihit M, Salghi R, Bouyanzer A, Al-Deyab S.S , Bazzi L, Hammouti B. 2011. *Int. J. Electrochem. Sci.*, 6 1454 – 1467.