



CORROSION INHIBITION PERFORMANCE OF *ACACIA NOLITICA* POD EXTRACT ON ALUMINIUM ALLOY IN 1M ALKALINE SOLUTION

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ABSTRACT

The effect of extract of *Acacia Nolitica* pod on the corrosion inhibition of LM 6 aluminium alloy in 1M NaOH was studied using weight loss, gasometric, and open circuit potential techniques. Corrosion rates were found to reduce in the presence of the inhibitor. The inhibition efficiency was found to increase with increase in the concentration of the inhibitor and decreased with increase in the temperature. Thermodynamic parameters showed that the adsorption of the inhibitor on the metal surface is a spontaneous process and that the adsorption was via a physisorption mechanism. The adsorption process fitted perfectly with the Langmuir adsorption isotherm indicating that the extract was strongly adsorbed on the aluminium alloy surface. Morphology of the surface was examined by scanning electron microscopy (SEM) in the absence and presence of 0.5%v/v of the used inhibitor which confirmed the existence of a protective film of inhibitor molecule on the metal surface.

Keywords: Adsorption, Physisorption, *Acacia Nolitica* Pod Extract, Corrosion.

INTRODUCTION

Corrosion studies of aluminium and aluminium alloys have received considerable attention by researchers because of their wide industrial applications and economic considerations (Oguzie, 2007). Aluminium and aluminium alloys have emerged as alternative materials in aerospace and in some chemical processing industries. Due to their wide applications, aluminium alloys frequently come in contact with aggressive medium such as: acids or bases during pickling, de-scaling, electrochemical etching and extensively used in many chemical process industries.

Alkaline solution is more corrosive in nature for aluminium than other corrosive media (Padmalatha & Deepa, 2017; Qurashi *et al.*, 2017). Therefore, it is desirable to study the corrosion and protection of aluminium in alkaline medium. Aluminium has been reported to have high resistance to corrosion as a result of the oxide film on its surface and this gives it stability (Qurashi *et al.*, 2017). It is reported that due to the presence of OH⁻ ion protective oxide film dissolves in alkaline solution and negative potential develops on the aluminium surface (Abiola & Otaigbe, 2008).

The shift towards green technology has helped to sustain the growing interest in the use of agricultural plants and their derivatives as sources for the development of inhibitors (Alaleme *et al.*, 2012; Alaleme *et al.*, 2016). Their advantages include low cost of processing, availability, and biodegradability (Loto *et al.*, 2014). Also, some of the plants used as green inhibitors are weeds with very little economic or established medicinal values (Hui, *et al.*, 2013). From literature, the corrosion inhibition characteristics of several plants have been explored as reported elsewhere (Belkhaouda *et al.*, 2013; Loto *et al.*, 2014; Alaneme, 2014; Alaneme & Olusegun, 2012; Deepa *et al.*, 2013; Johnsirani *et al.*, 2013; Alaneme *et al.*, 2015; Shalabi *et al.*, 2014; Abubakaret *et al.*, 2013; Alaleme *et al.*, 2016; Chaubey *et al.*, 2016). In the present work, aqueous extract of the pods of *Acacia Nolitica* (AN) was selected for the corrosion inhibition study on LM 6 aluminium alloy in 1M NaOH solution using gasometric, open circuit potential and weight loss measurement respectively. The experimental results were supported by SEM investigations.

MATERIAL AND METHODS

Chemicals and reagents

All chemicals and reagents used in this study were of analytical grade. LM 6 aluminium alloy was supplied by Orkila chemicals Ltd, Ikeja, Lagos State, Nigeria. The 1M NaOH solution was prepared by dissolving 40 g of sodium hydroxide pellets in 1000 ml of double distilled water as reported elsewhere (Chaubey *et al.*, 2016).

Preparation of pod extract

Acacia Nolitica (AN) Pods were obtained within the environs of Ahmadu Bello University, Zaria, Nigeria. The pods of the plant were gathered, sun dried and pulverized. 40 g of the pulverized pods were taken into 400 ml of prepared 1M NaOH solution in a reagent bottle. The mixture was immersed in a water bath maintained at 70°C for 3 hours, after which it was removed from the water bath and allowed to stand for some time before filtered to obtain the extract. Stock solutions of inhibitors of 0.1, 0.2, 0.3, 0.4, and 0.5%(v/v) AN pod extract in 1M NaOH were prepared from the filtrate.

Weight loss measurement

Aluminium alloy coupons with dimensions of (2cm×3cm×1.3cm) and chemical composition as per BS1490:1988 of (wt%) 85.95 Al, 0.1 Cu, 0.1 Mg, 12 Si, 0.6 Fe, 0.5 Mn, 0.1 Ni, 0.1 Zn, and 0.45 others, were polished using different grades of silicon carbide impregnated emery paper (120, 400, 800, and 1000 grits). Weight loss studies were carried out under total immersion conditions in beakers maintained at 30°C. In each experiment, 5 cleaned coupons were weighed (m_1) and immersed completely in the inhibited alkaline solution. At ambient temperature (30°C), the coupons were retrieved at intervals of 2 days progressively for 10 days; this is to allow for a measurable amount of the specimen to react in the solution. Finally, the samples were washed with running water to remove any corroded product(s), dipped in acetone, dried and re-weighed (m_2). The weight loss (W) was taken as the difference between the weight at a given time and the initial weight of the test coupon. The corrosion rate (C.R) in

millimeters penetration per year (mm/y) was calculated, from equation 1 (Callister, 1996).

$$C.R = \frac{87.6W}{\rho AT} \quad (1)$$

Where W is the weight loss (mg), A is the total surface area of the coupons in cm², T is time of exposure in hours, ρ is the density of aluminium alloy in g/cm³.

Gasometric measurement

The gasometric setup is basically an apparatus that measures the volume of gas evolved from a reaction as described by Onuchukwu (Njoku, 2014). The reaction vessel was connected to a burette via a delivery tube, which was in turn connected to a reservoir of paraffin oil. 50 ml of the test solution was introduced into the reaction vessel for blank determinations and the initial volumes of air in the burette was taken against that of the paraffin oil and recorded. Thereafter, two aluminium alloy coupons were introduced into the reaction vessel and the flask quickly closed. The volume of hydrogen gas evolved by the corrosion reaction was observed by the drop in the volume of the paraffin oil level in the gasometric gauge. The progress of the corrosion reaction was monitored by careful volumetric measurement of the evolved hydrogen gas at fixed time intervals. The temperature of the experiment was controlled at 30 and 60 °C. The experiments were performed separately employing 0.1 and 0.5% (v/v) inhibitor concentrations in 1M NaOH solution.

Open circuit potential

The potential of aluminium alloy electrode was measured against saturated calomel electrode (SCE) in 1M NaOH solution in absence and presence of 0.5% v/v of the used inhibitors at 30°C. All measurements were carried out using Multi-tester until steady-state potentials are reached; the

experiment was conducted as reported by Abd El-Hameed (2011).

Micrograph examination

The specimens used for surface morphological examination were immersed in the 1M NaOH solution containing maximum concentration of the inhibitor and blank for 10 days, it was then removed, rinsed quickly with running water dipped in acetone and dried. Scanning Electron microscope (SEM) EVO MA-10 with Energy-dispersive X-ray spectroscopy (EDX) manufactured by Carl, at the National Geological Survey Institute, Kaduna, Nigeria, was used for the analysis. Sample coupons were attached to multi-stub specimen holder with the use of double sided conductive carbon tape, after which, they were mounted onto the specimen chamber, while the column was put at vacuum. After reaching the vacuum target, the electron gun was switch on which passed accelerating voltage of 20kV and probe current of 227pA through the samples at a working distance of 7.0mm. Micrographs of the coupons were taken in three magnifications along the span of the specimens (Chaubey *et al.*, 2016).

RESULTS AND DISCUSSION

Weight loss measurement

Effect of inhibitor concentration

Corrosion rate of the aluminium alloy coupons versus time of immersion was plotted in Figure 1. It is evident from the figure that in all cases, the corrosion rate increases with increase in the time of immersion. The curves obtained in the presence of AN additives falls significantly below that in the absence of inhibitor. In this respect, the increase of the additive concentration was accompanied by a decrease of corrosion rate and an increase in the percentage of inhibition as reported by similar observation (Qurashi *et al.*, 2017).

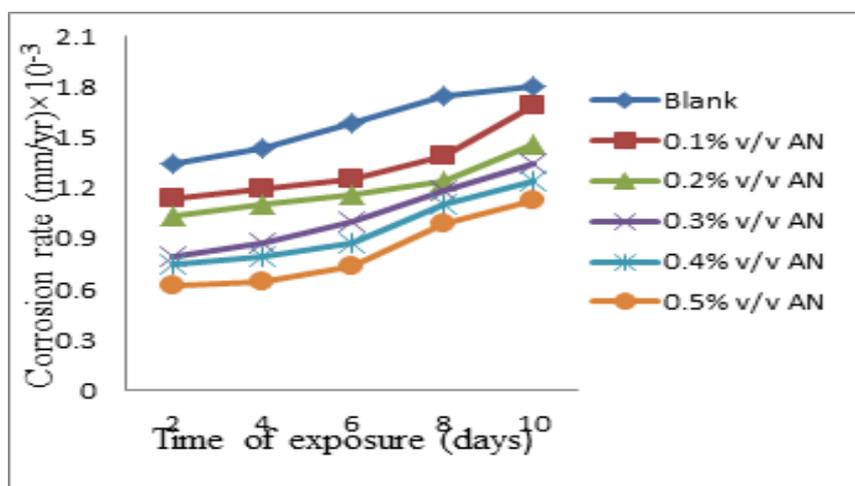


Figure 1: Corrosion rate-time curve of aluminium alloy in 1M NaOH in absence and presence of different concentrations of AN pod.

Effect of temperature

To elucidate the mechanism of inhibition of the corrosion process, weight loss measurements were performed at different temperatures 303, 313, 323, 333K in the presence of 0.5% v/v AN pod extracts in 1 M NaOH. The effect of temperature on the corrosion rate and inhibitor efficiency of the aluminium alloy is graphically represented in Figure 2.

It can be seen in the figure that corrosion rate increased with increase in temperature, which may be due to the desorption

of some adsorbed molecules from the surface of the aluminium alloy at higher temperature due to which greater area of the metal is exposed to the alkaline environment. The inhibitor efficiency decreased with increase in temperature from 303–333K, leading to the conclusion that the protective film of these compounds formed on the aluminium alloy surface is less stable at higher temperature; which may be attributed to desorption of the inhibitor molecules from the surface at higher temperature and agrees with an earlier

research by (Oguzic, 2006).

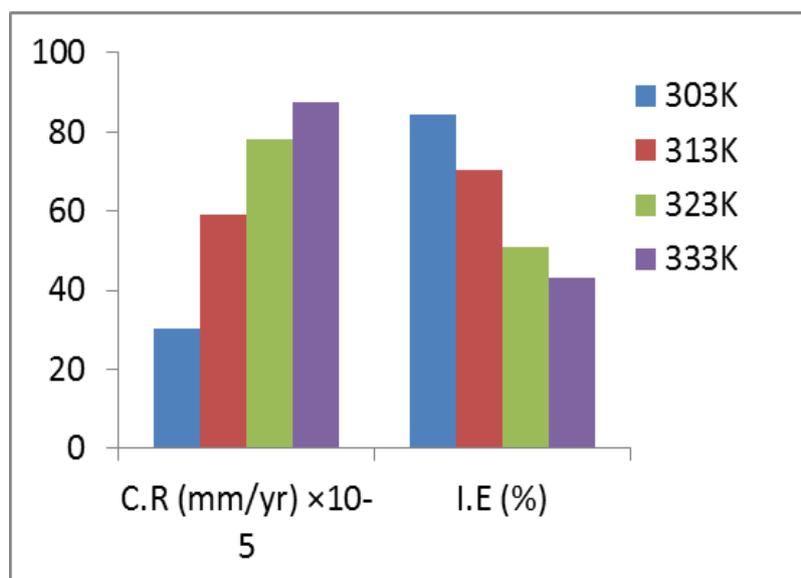


Figure 2: Variation of inhibitor concentration and %IE in 1M NaOH containing 0.5% v/v AN pod extract at different temperatures.

The percentage inhibition efficiency (IE) and degree of surface coverage θ of the AN pod extract at 0.5% v/v was calculated using the following equations:

$$IE = \frac{(C.R)_o - (C.R)}{(C.R)_o} \times 100\% \quad (2)$$

$$\theta = \frac{(C.R)_o - (C.R)}{(C.R)_o} \quad (3)$$

where $(C.R)_o$ and $(C.R)$ are the corrosion rates in (mm/y) without and with different concentrations of the inhibitor.

The apparent activation energy (E_a) was calculated using the Arrhenius equation.

$$\text{Log } C.R = \text{Log } A - \frac{E_a}{2.303RT} \quad (4)$$

where E_a is the activation energy of the reaction, A is the Arrhenius pre exponential factor, R is the gas constant, $C.R$ is the corrosion rate, and T is the absolute temperature. Figure 3 depicts the plots of $\log C.R$ vs $1/T$ and the values of (E_a) obtained from the slope of the plots are given in Table 1.

Table 1: Activation parameters of AN pod extract on the surface of Aluminium alloy in 1M NaOH.

Concentration (% v/v)	E_a (kJ/mol)
Blank	40.05
0.1	51.23
0.2	55.31
0.3	57.26
0.4	60.08
0.5	63.71

It was observed that the value of E_a for uninhibited system is 40.05 kJ/mol, which is lower than values observed for the inhibited system. Higher values of E_a for inhibited system are explained by the formation of a physical barrier to charge and mass transfer created by the adsorbed inhibitor molecules

(Chaubey *et al.*, 2015). The above E_a values in the presence of inhibitors are larger than in the absence, but lower than 80kJ/mol, which is the threshold value for chemical adsorption. This suggests physical adsorption of inhibitor molecules.

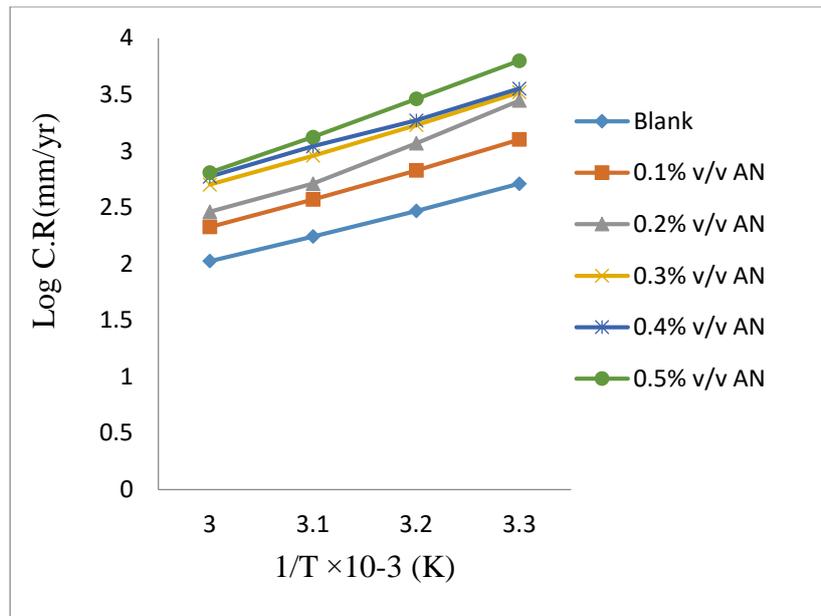


Figure 3: Arrhenius plot for aluminium alloy in 1M NaOH in the absence and presence of AN pod extract.

Adsorption isotherm

Langmuir adsorption isotherm as shown in Figure 4, was employed to determine whether the inhibition of aluminium alloy corrosion is due to either physisorption

which is the adsorption of molecules of AN pod extract or formation of complex insoluble layer of aluminium alloy on the surface which can act as a barrier in between the corrosive medium and the aluminium alloy surface or through chemisorption which involves the displacement of water

molecules from the metal surface and electrons sharing between aluminium alloy and oxygen atom. Langmuir relationship is represented by equation 5.

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (5)$$

where K is the equilibrium constant of adsorption, C is the inhibitor concentration %v/v, and θ is the degree of surface coverage (Okewale & Oliatan, 2017).

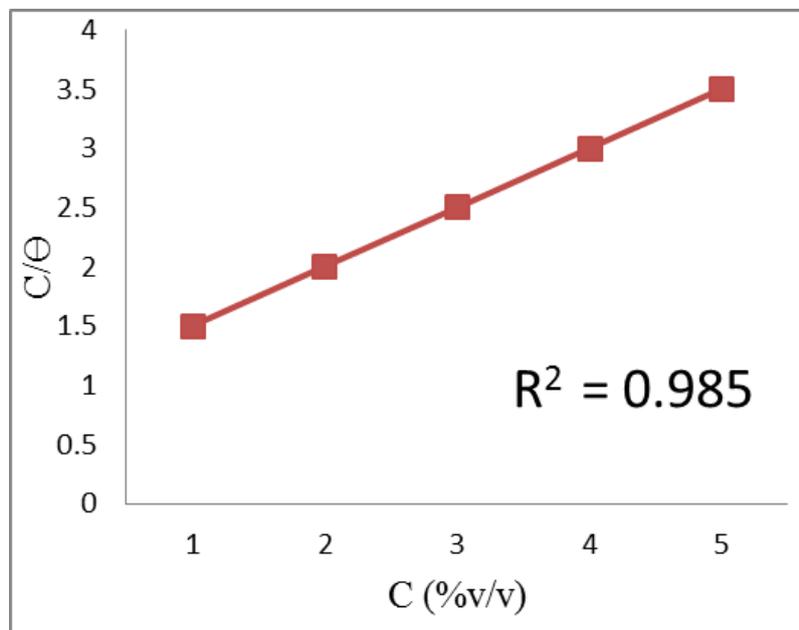


Figure 4: Langmuir adsorption isotherm plot for AN pod extract inhibitor on Aluminium alloy in 1M NaOH.

It is seen that the corrosion rate data of AN pod extract fitted to Langmuir adsorption isotherm strongly, this is very obvious from the correlation co-efficient (R^2) value of 0.985 this suggests that *Acacia Nolitica* pod extract molecules form a monolayer on the aluminium alloy surface.

Gasometric measurements

Effect of immersion time on corrosion rate

Gasometric measurements of aluminium alloy subjected to the effect of alkaline media in the absence and presence of AN pod extract were made at various time intervals. Figures 5(a)

and 5(b) present plots of evolved hydrogen gas as a function of time for aluminium alloy corrosion in 1M NaOH in absence and presence of AN pod extract at 303K and 333K, respectively. The plots in Figures 5 show a remarkable decrease in hydrogen evolution with the introduction of the inhibitor indicating that AN pod extract inhibits corrosion of aluminium alloy in alkaline medium. The rates of hydrogen evolution were observed to decrease with increasing inhibitor concentration, suggesting that the inhibiting effectiveness of AN pod extract depends on the inhibitor concentration. However, the kinetic parameters indicate satisfactory

inhibitor efficiencies even at low concentration of AN pod extract. In all the cases, the dissolution of aluminium alloy was characterized by a linear increase in the evolution of hydrogen with time. The reaction rate was characterized by differentiating the volume of hydrogen evolved with time and was obtained from the slope of the linear portions of Figure 5(a) and 5(b). Table 2 shows the values of corrosion rates obtained for the test solution. The result shows that corrosion rate reduced in the presence of the inhibitor and was found to decrease with increasing AN pod extract concentration as reported elsewhere (Alaneme & Olusegun, 2012).

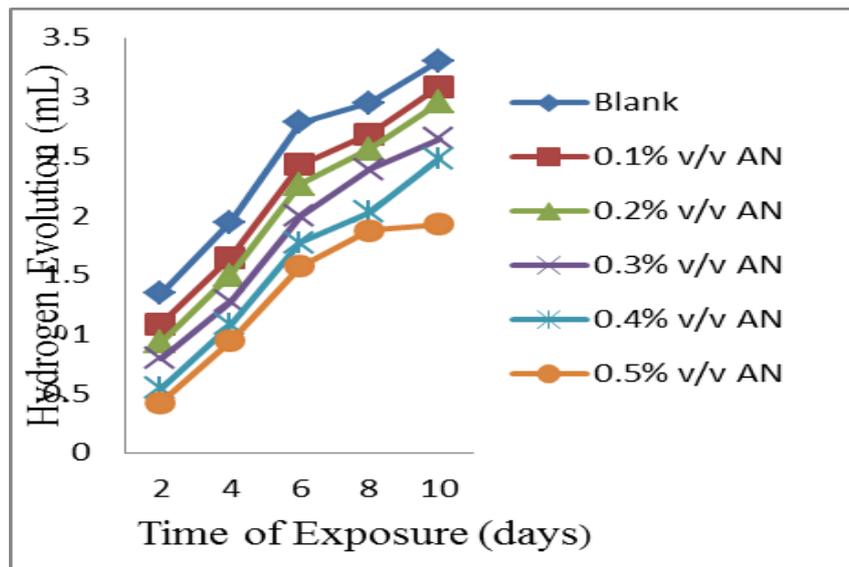


Figure 5a: Hydrogen evolution time curve for Aluminium alloy in 1M NaOH in the absence and presence of AN pod extract at 303K.

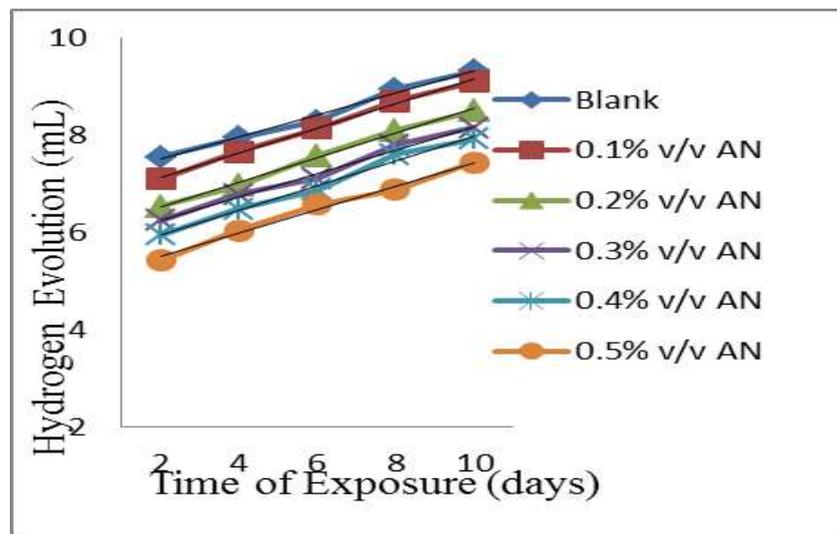


Figure 5b: Hydrogen evolution time curve for Aluminium alloy in 1M NaOH in the absence and presence of AN pod extract at 333K.

Table 2: Corrosion rates of Aluminium alloy in 1M NaOH in absence and presence of AN pod extract obtained from

Gasometric measurement		
Inhibitor Concentration	Corrosion rate ($\times 10^{-3}$ H ₂ gas vol. mL s ⁻¹)	
	303K	333K
Blank	1.953	9.351
0.1% v/v	0.396	3.358
0.2 % v/v	0.356	3.182
0.3% v/v	0.301	2.986
0.4% v/v	0.212	2.475
0.5% v/v	0.187	2.031

Inhibitor efficiency

For the gasometric experiments, the degree of surface coverage (θ) and the inhibition efficiency (IE, %) of AN pod extract on aluminium alloy in alkaline media was evaluated from equations 6 and 7.

$$\theta = 1 - \frac{V_{inh}}{V_{free}} \quad (6)$$

$$IE = 100 \times \left(1 - \frac{V_{inh}}{V_{free}} \right) \quad (7)$$

where V_{free} and V_{inh} are the corrosion rates in the absence and presence respectively of a given concentration of AN pod extract. Table 3 shows values of the degree of surface coverage (θ) and the inhibition efficiency (IE, %) obtained for different concentrations of AN pod extract using the gasometric technique. The result shows that the extract retarded alkaline corrosion of the aluminium alloy, inhibition efficiencies increased with increasing inhibitor concentration and decreased with increase in temperature.

Table3: Degree of surface coverage and inhibitor efficiencies of different concentrations of AN pod extract on Aluminium alloy in 1M NaOH obtained from Gasometric measurement.

Inhibitor Concentration	Surface Coverage (θ)		Inhibitor Efficiency (IE)%	
	303K	333K	303K	333K
Blank	0	0	0	0
0.1% v/v	0.7969	0.7479	79.7	74.8
0.2 % v/v	0.8171	0.7666	81.7	76.7
0.3% v/v	0.8453	0.7875	84.5	78.8
0.4% v/v	0.8611	0.8050	86.1	80.5
0.5% v/v	0.8952	0.8271	89.5	82.7

Open circuit potential measurement

The potential of aluminium alloy electrodes immersed in 1M NaOH solution was measured as a function of immersion time in the absence and presence of AN pod extract as shown in Figure 6. It is clear that the potential of aluminium alloy electrode immersed in 1M NaOH solution (blank curve) tends towards more negative potential firstly. This behaviour was reported by West (1970), which represents the breakdown of the pre-immersion air formed oxide film presents on the surface.

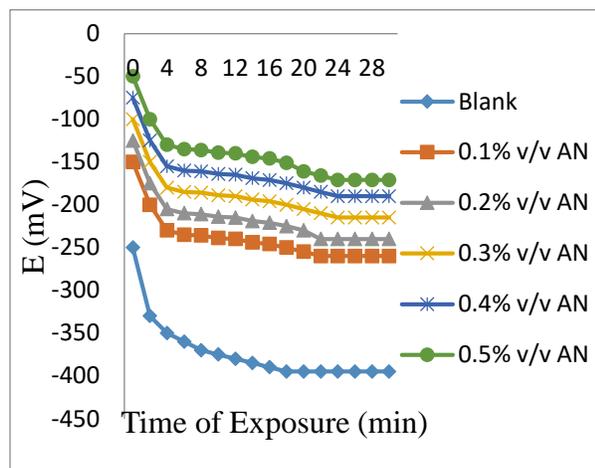


Figure 6: Potential-time curves for aluminium alloy immersed in 1M NaOH solution in the absence and presence of different concentrations of AN pod extract.

It is shown from the figure that addition of the inhibitor molecules shifted the potential to more positive direction (less negative) and as the concentration of the inhibitor increases, the corrosion potential was shifted to more noble direction. In all curves the steady-state values are always more negative than the immersion potential suggesting that before the steady state condition is achieved the aluminium oxide film has to dissolve.

Scanning electron microscopy

Morphological images shown in Figure 7a and 7b shows surface corrosion of aluminium alloy decreased remarkably in the presence of the inhibitor. Inspections of the figures reveal that there is severe damage, clear pits and cavities on the surface of aluminium alloy in the absence of inhibitor than in its presence. This confirms that metal surface is fully covered with adsorbed inhibitor molecules.

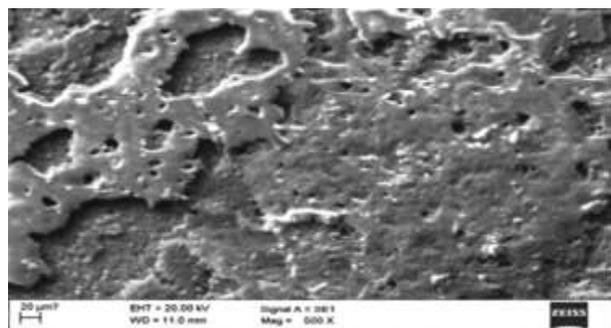


Figure 7a: SEM image of aluminium alloy after immersion in

1M blank NaOH.

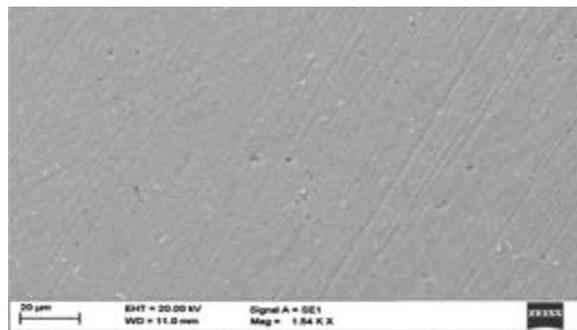


Figure 7b: SEM image of Aluminium alloy after immersion in 0.5% v/v AN pod extract + 1M NaOH.

CONCLUSION

The corrosion behaviour and adsorption characteristics of varied concentrations of *Acacia Nilotica* pod extract in 1M NaOH solution containing aluminium alloy substrate was investigated in this study. From the analyses of the results obtained, Corrosion rates reduced in the presence of the inhibitor and were found to decrease with increasing AN pod extract concentration. Protection efficiency by AN pod extract is found to increase with increase in inhibitor concentration but decreased with increase in temperature, suggesting that the protective film of this compound formed on the aluminium alloy surface is less stable at higher temperature. Activation energies were higher in the presence of the inhibitor suggesting physisorption mechanism in alkaline media. The optical examination of the aluminium alloy specimen show that the inhibitor displayed an effective inhibitive tendency against stress corrosion cracking of the materials in the aggressive solution Considered

REFERENCES

- Abd El-Hameed, R.S. (2011). Aminolysis of polyethylene terephthalate waste as corrosion inhibitor for carbon steel in 1M HCl corrosive medium. *Advances in applied science research*, 2 (3):483-499.
- Abubakar, G., Ibrahim, H., Apugo-Nwosu, T. U., Mustafa, M., Akuso, S. A., Agboun, D. T., Nwobi, B. E., Ayilara, S. (2013). Corrosion Inhibition Studies of *Ficus Abutilifolia* on N-80 Oil Well Tubular Steel In 15% Hydrochloric Acid Solution, *International Journal of Engineering and Computer Science*, 2013, 2(8), p. 2364-2370.
- Abiola, O.K., Otaigbe, J.O.E. (2008). Effect of common water

- contaminants on the corrosion of aluminium alloys in ethylene glycol–water solution. *Corros. Sci.* 50, p. 242–247.
- Alaneme, K. K., Olusegun, S. J. (2012). Corrosion Inhibition Performance of Lignin Extract of Sun Flower (*Tithonia Diversifolia*) on Medium Carbon Low Alloy Steel Immersed in H₂SO₄ Solution, *Leonardo Journal of Science*, Vol. 20, p. 59-70.
- Alaneme, K. K., Olusegun S. J., Adelowo O.T. (2015). Corrosion inhibition and adsorption mechanism studies of *Hunteria umbellata* seed husk extracts on mild steel immersed in acidic solutions, *Alexandria Engineering Journal*, <http://dx.doi.org/10.1016/j.aej.2015.10.009>.
- Alaneme, K. K., fajemisin, A. V., olusegun, S. J., borode, J. O. (2016). Corrosion inhibition and adsorption characteristics of *Tridax Procumbens L* leaves extract on mild steel immersed in 1M HCl solution, *Leonardo Electronic Journal of Practice and Technology*, Issue 29, p. 43-60.
- Belkhaouda, M., Bammou L., Salghi R., Benali O., Zarrouk A., Ebenso E. E., Hammouti B. (2013). Avogadro Nuts Extract (ANE): An efficient Inhibitor of C38 Steel Corrosion in Hydrochloric Acid, *Journal of Materials and Environmental Science*, 4 (6), p. 1042-1051.
- Callister, W.D. Jnr. (1996). *Material Science and Engineering*, Fourth Edition. New York: John Wiley and Sons. Pp 349-353.
- Chaubey, N., Yadav., Singh, D.K., Quraishi, M.A. (2015). A comparative study of leaves extracts for corrosion inhibition effect on aluminium alloy in alkaline medium. *Ain Shams Eng. J.*
- Chaubey, N., Singh D.K., Quraishi, M.A. (2016). Corrosion Inhibition Performance of Different Bark Extracts on Aluminium in Alkaline Solution, *Journal of the Association of Arab Universities for Basic and Applied Sciences*, 22, p. 38-44.
- Deepa, R. P., Phetchiammal A., Nanthini T., Mariammal S., Selvaraj S. (2013). The Effect of *Eugenia jambolana* on Zinc in 1.0N Hydrochloric Acid Environment, *IJGHC*, 2 (3), p. 510-52.
- Hui, C., Zhenghao, F., Jinling, S., Wenyan, S., Qi, X. (2013). Corrosion Inhibition of Mild Steel by Aloes Extract in HCl solution Medium. *International Journal of Electrochemical Science*, 8, p. 720-734.
- Johnsirani, V., Sathiyabama, J., Rajendran, S., Lydia, S. M., Jeyasundari, J. (2013). The Effect of *Eclipta Alba* Leaves Extract on the Corrosion Inhibition Process of Carbon Steel in Sea Water, *Portugaliae Electrochimica Acta*, 31 (2), p. 95-106.
- Loto, C. A., Joseph, O. O., Loto, R. T., and Popoola A. P. I. (2014). Corrosion Inhibitive Behaviour of *Camellia Sinensis* on Aluminium Alloy in H₂SO₄, *International Journal of Electrochemical Science*, Vol. 9, p. 1221 – 1231.
- Njoku, V. O., Oguzie, E. E., Obi, C., and Ayuk, A. A. (2014). *Baphia nitida* Leaves Extract as a Green Corrosion Inhibitor for the Corrosion of Mild Steel in Acidic Media, *Advances in Chemistry*, p. 1-10.
- Oguzie, E. E. (2006). Studies on the inhibitive effect of *Occimumviridis* extract on the acid corrosion of mild steel, *Materials Chemistry and Physics*, vol. 99, no. 2-3, p. 441–446.
- Oguzie, E.E. (2007). Corrosion inhibition of aluminium in acidic and alkaline media by *Sansevieria trifasciata* extract. *Corros. Sci.* 49, p. 1527–1539.
- Okewale, A. O., & Olaitan, A. (2017). The Use of Rubber leaf Extract as a Corrosion Inhibitor for Mild Steel in Acidic Solution, *International Journal of Materials and Chemistry*, 7(1), p. 5-13.
- Padmalatha, R., Deepa, R. (2017). Corrosion Behaviour of 6063 Aluminium Alloy in Acidic and Alkaline Media. *Arabian Journal of Chemistry*, 10, p. 2234-2244.
- Quarashi, M.A., Chaubey, N., Singh, V. K. (2017). Corrosion Inhibition Performance of Different Bark Extracts on Aluminium in Alkaline Solution. *Journal of the Association of Arab Universities in Basic and Applied Sciences*, 22, p.38-44.
- Sawant, R. S., Godghate, A. G., Sankpal, S. A., Walakiand, S. A. Kankanwadi, S. S. (2014). Phytochemical analysis of bark of *Acacia nilotica*, *Asian Journal of Plant Science and Research*, 4(2), p. 22-24.
- Shalabi, K., Abdallah, Y., Hassan, H. M., Fouda A. S. (2014). Adsorption and Corrosion Inhibition of *Atropa Belladonna* Extract on Carbon Steel in 1 M HCl Solution, *International Journal of Electrochemical Science*, 9, p. 1468 – 1487.
- Sheeja, V. N., Subhashini, S. (2014). *Pavetta Indica* Bark as Corrosion Inhibitor in Mild Steel Corrosion in HCl and H₂SO₄ Medium: Adsorption and Thermodynamic Study, *Chemical Science Transactions*, 3 (1), p. 129-140.
- West, J.M. (1970). *Electrodeposition and corrosion process*, second ed., Van Nostrand Reinhold, London, p.93.



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