

INHIBITIVE PROPERTIES OF AZADIRACHTA INDICA (NEEM) SEED EXTRACT ON THE CORROSION OF ALUMINUM IN 0.5M HCl MEDIUM

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Abstract— *Azadirachta indica* seed (neem seed) extract was examined as an anti-corrosion agent for aluminum in hydrochloric acid medium. The extract and corrosion products were analyzed using Fourier transform infrared spectrophotometer (FTIR). Thermometric and potentiodynamic polarization methods were employed in the study. Inhibitor concentration was varied from 0.2 g/l to 1.0 g/l while time variation was from 1 hour to 5 hours. It was revealed that stretched C-H and C=C functional groups were predominantly responsible for the corrosion inhibition process. Highest inhibition efficiency of 88.68% was obtained for thermometric method, and 86.36% for potentiodynamic polarization method at inhibitor concentration of 1.0g/l. The extract is a mixed-type inhibitor that can control both cathodic and anodic corrosion.

Keywords—Potentiodynamic polarisation method, Thermometric method, Aluminum, Neem seed Extract,

I. INTRODUCTION

Corrosion remains a major destructive process that affects the performance of metals in their different areas of applications (Yahaya et al., 2017). Aluminum, for example, finds wide use as a construction material in many industries because of its excellent mechanical properties; ductability, weldability and low cost. However, it gets corroded when exposed to the corrosive industrial environment. It has been reported that passive oxide film formed on aluminum surface is responsible for its resistance to corrosion, but the surface film is amphoteric and dissolves substantially when the metal is exposed to high concentrations of acids or bases (El-maghraby, 2009).

Aluminum structure corrodes as a result of electrochemical reaction with its environment. It has been stated that corrosion is one of the major challenges facing oil and gas industries (Unueroh et.al, 2016). Pickling, descaling and cleaning are often carried out to prolong the life span of the aluminum

structures. Acid medium such as HCl used for such maintenance operations often corrodes the structures. The adverse consequences of corrosion are considered a serious problem in industry, constructions and civil services such as electricity, water and sewage systems (Yahaya et al., 2017). The tendency of a metal to corrode depends on the grain structure of the metal, its composition as formed during alloying, or the temperature for deformation of a single metal surface developed during fabrication. Given that the environment plays an important part in corrosion, corrosion mechanisms can be as varied as the environments to which a substance is exposed and thus may be complex to understand. Corrosion prevention and retardation are aimed at addressing these factors. Due to environmental concerns, eco-friendly inhibitors of plant origin are of great interest for corrosion control of metals in corrosive media.

Corrosion inhibition studies on aluminium using plant extracts have been carried out by a number of researchers such as, Abd-El-Nabey (2012), Nnanna et al (2012), Singh et al (2016), Chaubey et al (2017) and Omotoma and Onukwuli (2017).

Research on *Azadirachta indica* (AZI) seed extract is of great interest because it contains several alkaloids and other phytochemicals with important pharmaceutical and industrial applications. Ebenso et al (2004) presented results of corrosion inhibition of aluminum in HCl medium by the use of *Azadirachta indica* extract. Weight loss and thermometric methods were applied. Results obtained indicated that adsorption was exothermic, spontaneous, and obeyed the Freundlich, Temkin, and Flory-Huggins adsorption isotherms. Arab et al (2008) reported that AZI extract with iodide additive shows good inhibition for Al corrosion in HCl medium by the application of the potentiodynamic polarization (PDP) scheme. The synergistic effect enabled spontaneous adsorption and followed the Freundlich adsorption isotherm. Okafor et al. (2010) studied the inhibitive action of leaves (LV), root (RT) and seeds (SD) extracts of *Azadirachta indica* on mild steel corrosion in H₂SO₄ solutions using gravimetric and gasometric techniques. They discovered

that the inhibition efficiency increased with increase in extracts concentration and temperature, and followed the trend: SD > RT > LV. Ethanolic extract of *Azadirachta indica* fruit were reported by Sharma et al. (2013) as good inhibitor for aluminum corrosion in HCl medium by the use of weight loss and thermometric method. Results showed that percentage inhibition efficiency increased with increasing concentration but decreased with rise in temperature and followed Langmuir adsorption isotherm. Ajanaku et al (2015), Abakedi and Asuquo (2016) and Vashi and Prajapati (2019) have also given reports on the corrosion inhibition of aluminum using *Azadirachta indica* leaves.

The present work employed the thermometric and potentiodynamic polarization methods/analyses to the corrosion inhibition of aluminum in HCl medium using *azadirachta indica* seeds alone.

II. EXPERIMENT AND RESULTS

A. Material preparation

The aluminum sheet of compositions Si (0.25%), Fe (0.02%), Zn (0.05%), Mn (0.04%) Mg (0.03%), V (0.04%), Ti (0.02%), Cu (0.03%), Cr (0.02%) and Al (99.5%), that was used for this study was mechanically cut into coupons of dimension $3 \times 3 \times 0.035\text{cm}$. The coupons were washed in distilled water, degreased in absolute ethanol, dried in acetone and preserved in a moisture-free desiccator.

B. Extract preparation

Mature seeds of *Azadirachta indica* were harvested from the neem Garden of Federal University of Technology Owerri, Imo State. The obtained seeds were washed and sun-dried for 9 days, and further crushed using electric grinder. 500g of the ground seeds were soaked in 1000ml of analytical grade ethanol in a 2-liter container for 48 hours. The resulting mixture was filtered using whatman No. 42 grade filter paper. The solution of the neem seeds extract and the solvent was heated in a constant temperature water bath set at 80°C to recover the neem seed extract. Five inhibitor test samples were prepared by dissolving 0.2g/l, 0.4g/l 0.6g/l, 0.8g/l, 1.0g/l of the extract in 200ml of 0.5M HCl respectively.

Fourier transform infrared spectrophotometer (FTIR) was then used to study the functional groups of the pure extract and corrosion product. Comparative analysis of various FTIR-produced peaks was carried out to obtain the appropriate functional groups for the corrosion inhibition process. Thermometric and potentiodynamic polarization methods were then applied in the corrosion inhibition study.

C. Thermometric method

The method of the thermometric measurement used by Omotoma and Onukwuli (2017) was adopted in this study. The thermostat was set at 30 °C for the initial temperature of the system. The temperatures of the system containing the aluminum and 0.5M HCl, in the absence and presence of various concentration of the inhibitor, were recorded regularly until a steady temperature value was obtained in each case. The reaction number (RN) was determined using Equation (1).

$$RN = \frac{T_m - T_i}{t} \quad (1)$$

where T_m and T_i are the maximum and initial temperatures in °C respectively, and t (mins) is the time it takes to reach T_m .

The inhibitor efficiency (IE) of the Neem seed extract was calculated using Equation (2).

$$IE\% = \left(1 - \frac{RN_{inh}}{RN_{free}}\right) * \quad (2)$$

where RN_{free} and RN_{inh} are the reaction numbers for the aluminum in free and inhibited HCl respectively.

D. Potentiodynamic Polarization method

Electrochemical tests were conducted to further verify the inhibition efficiency of the *Azadirachta indica* seed extract. In this test analysis, a potentiostat/ galvanostat electrochemical system workstation, with a conventional three electrode corrosion cell were used. A graphite rod and a saturated calomel electrode (SCE) were used as a counter and reference electrodes, respectively. A metal specimen (aluminum coupon) was fixed in epoxy resin with a surface area of 1cm² exposed to the test solution (HCl). This served as the working electrode. The electrochemical measurements were carried out in aerated and unstirred solution at the end of 1800s of immersion; this allowed the open circuit potential (OCP) to attain steady state. Temperature was fixed at 30±1°C. Potentiodynamic polarization studies were conducted in the potential range ±250 mV versus corrosion potential at a scan rate of 0.333mVs⁻¹. After the measurement, the inhibition efficiency was determined using equation (3):

$$IE = \frac{I_{corr_{uninh}} - I_{corr_{inh}}}{I_{corr_{uninh}}} \times 100 \quad (3)$$

where $I_{corr_{uninh}}$ and $I_{corr_{inh}}$ are corrosion current density values with and without inhibitor.

E. EXPERIMENTAL RESULTS

FTIR for the neem seed extract and corrosion product measures a sample's absorbance of infrared light at various wavelengths to determine the material's molecular composition and structure. The FTIR converts the raw data from the broad-band light source to actually obtain the absorbance level at each wavelength. From figures 1-2, the x-

axes represent the infrared spectrum, which plot the intensity of infrared spectra. The peak which are also called the absorbance bands, correspond to the various vibrations of the sample's atoms when it's exposed to the infrared region of the electromagnetic spectrum. The absorbance band is of group frequency type. From the shifting mechanism of the neem seed extract and the corrosion product, the dominant compounds as shown in Tables 1 and 2 are the C=C and C-H group.

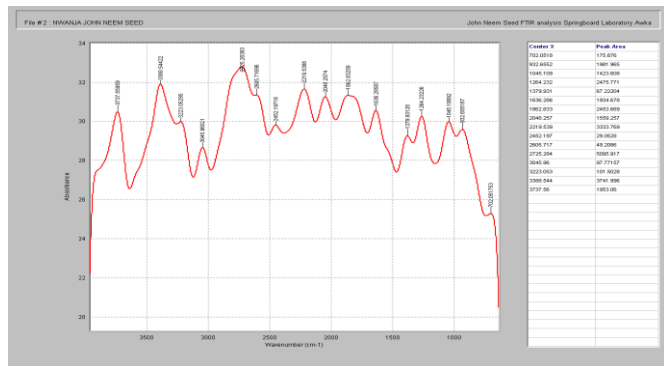


Fig. 1: FTIR spectrum of the neem seed extract; absorbance versus wave number (1/cm).

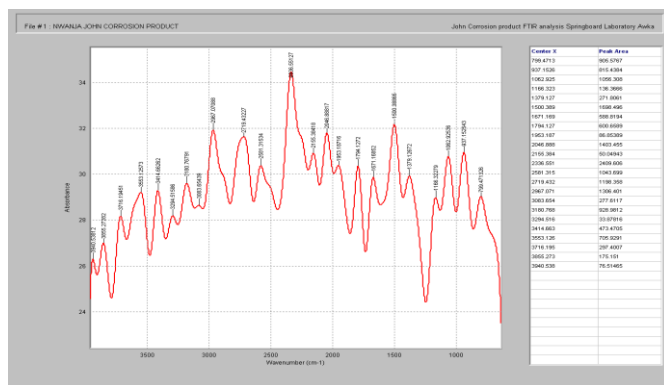


Fig. 2: FTIR spectrum of corrosion product; absorbance versus wave number (1/cm).

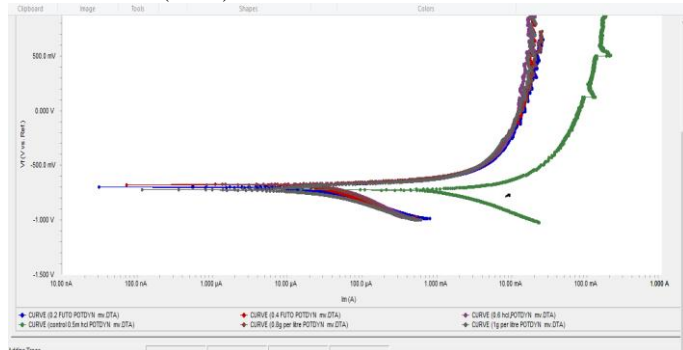


Fig 3: Potentiodynamic polarization result for neem seed extract inhibition of Al corrosion in 0.5M HCl medium/

Table 1: FTIR spectrum analysis for neem seed extract

Peak (cm ⁻¹)	Assignment
1636.286-2219.539	OH bend in plane
2352-2605.7170	Sp ³ , CH stretch
2725.284-3223.053	C=O stretch
3388.54	NH bend out
35500	SP, C-H, C=C bend in

Table 2: FTIR spectrum analysis for corrosion product with inhibitor.

Corrosion product of Al in HCl (with inhibitor)	
Peak (cm ⁻¹)	Assignment
1500.389-1671.1685	C=O stretch
1671.169-1930	C=C bend
1953.187-2336.55	NH stretch
2581.3153-2967.071	C= C bend
3083.054-3553.126	Sp ² , C=H stretch
3716.1945-3940.54	SP, CH, stretch

Table 3: Results for thermometric method

Inhibitor conc. (g/l)	Reaction Number, RN	IE (%)
0.0	0.17667	
0.2	0.09310	47.31
0.4	0.05617	68.21
0.6	0.03810	78.44
0.8	0.02888	83.66
1.0	0.02000	88.68

Table 4: Potentiodynamic Polarisation analysis

Concentration of Plant Extract (g/l)	E_{corr} (mV)	I_{corr} (uA/cm ²)	Surface Coverage (θ)	Inhibitor Efficiency (%)
Blank	-7.00E-01	5.5E-02	-	
0.2	-7.00E-01	9.2E-03	0.8327	83.27
0.4	-7.00E-01	9.00E-03	0.8364	83.64
0.6	-7.00E-01	8.9E-03	0.8382	83.82
0.8	-6.50E-01	9.00E-03	0.8364	83.64
1.0	-7.00E-01	7.5E-03	0.8636	86.36



Table 3 further validates the inhibitive properties of *Azadirachta indica* seed extract. The result of the thermometric method in Table 3 shows that inhibition efficiency of the neem seed extract increased as the inhibitor concentration increased. The optimum inhibition efficiency of 88.68% was obtained at the inhibitor concentration of 1.0g/l. The potentiodynamic polarization curves are presented in Figure 3. The electrochemical parameters associated with the polarization measurements such as corrosion potential, E_{corr} and corrosion current density, I_{corr} , are presented in Table 4. Figure 3 shows the tafel curves for the analyses. The plot indicates that in the presence of the inhibitor (at various concentrations), the curves shift towards lower corrosion current density. This shows that the inhibitor is adsorbed on the metal surface. Again, a difference in the value of corrosion potential, E_{corr} in the absence and presence of an inhibitor higher than 85mV is indicative of the fact that the inhibitor is either of cathodic or anodic type (Ansari and Quraishi, 2015). Since this difference between the blank solution and the various concentrations of the extract is much lower than 85mV, the inhibitor is therefore, a mixed type inhibitor. The results provide an understanding of the effects of the inhibitor on the anodic and cathodic corrosion reactions (Ihebrodike et.al, 2011). The extract was found to inhibit the corrosion of the aluminum in the HCl medium with optimum inhibition efficiency of 86.6% at extract concentration of 1.0g/l.

III. CONCLUSION

From the analysis of the shifting mechanism of the functional groups, stretched C-H and C=C functional groups were predominantly responsible for the corrosion inhibition process. Furthermore, the result of the thermometric method showed an optimum inhibition efficiency of 88.68% at extract concentration of 1.0g/l while that for the potentiodynamic polarization method was 86.36% at 1.0g/l. The potentiodynamic polarisation studies also indicated that the extract is a mixed-type inhibitor that can control both cathodic and anodic corrosion.

It is therefore recommended that *Azadirachta indica* seed extract be applied as additive for acidic cleaning of aluminum structures.

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