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Electrochemical Investigation of the Anti-corrosive Effect of *Spondias mombin* Leaves Extract on the Corrosion of Aluminium Alloy (AA2024) and Mild Steel in 0.5 M NaCl

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

The inhibiting effect of *Spondias mombin* (SM) leaves extract on the corrosion of AA2024 and mild steel in 0.5 M NaCl environment was investigated using electrochemical techniques. Tafel plots obtained from the potentiodynamic polarization (PDP) experiments indicate that for both metals, the curves shifted toward more negative values of the corrosion current density (I_{corr}) as the inhibitor concentration increased. More so, for all concentrations of the inhibitor, the values of maximum displacement shift in corrosion potential (E_{corr}) were found to be less than 85 mV. This shows that

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SM behaves like a mixed-type corrosion inhibitor. The electrochemical impedance spectroscopy (EIS) study shows that for both metals, the charge transfer resistance (R_{ct}) values increased with an increase in concentration of the inhibitor. The increase in values of R_{ct} can be attributed to the formation of protective film at the metal-solution interface. The Nyquist plots show semi circles whose diameter increased as the inhibitor concentration is increased and this is suggestive of retardation in corrosion process. The inhibition efficiency values obtained in the EIS experiment were found to be in close conformity with those of the PDP experiment.

Keywords: Electrochemical; anti-corrosive; Spondias mombin; aluminium alloy.

1. INTRODUCTION

Aluminium and its alloys have wide range of applications in naval, aerospace, and oil and gas industries. Aluminium alloy AA2024 has unique physical properties which include; high strength, fatigue resistance, light weight, anti-corrosive and workability. The physical features of AA2024 make it suitable for use to manufacture some special airplane parts such as wing structure, gears and shafts, as well as the fuselage [1].

Mild steel also known as low carbon steel contains approximately 0.05 - 0.15 % carbon and has a density of approximately 7.85 g/cm^3. Mild steel properties (high yield and tensile strength, ductility, malleability and weldability) make it useful in the construction of oil and gas pipe line as well as automobile parts. Mild steel also have application in aviation industry as it is used to construct ship hull. However, exposure of sea planes and ships to certain atmospheric conditions and saline sea water wears off their material protective layer and make them susceptible to corrosion. Salt water's salinity approximates to 3.5% of NaCl. Salt solutions act as an electrolyte whose free ions initiate oxidation in metals and alloys which subsequently lead to corrosion.

“Corrosion is a surface electrochemical phenomenon common to all base metals in aqueous or humid environments whereby metal ions are developed at a cathodic site and the electrons associated with this dissolution are accepted at an anodic site” [2,3]. “However, corrosion processes can be controlled or inhibited by employing organic or inorganic inhibitors. Inorganic substances suitable as metal corrosion inhibitor must easily oxidize the metal to form an impervious layer which prevents direct ions-metal interaction and hence retard the rate of metal dissolution in the medium” [4]. Over the years, inorganic inhibitors such as; chromate [5] and phosphate [6] compounds were employed to check corrosion process. The high toxicity of these inorganic compounds posed both health and environmental risk and as a result, international laws recommended cessation of their use as corrosion inhibitor [7]. “The ban on some inorganic compounds as inhibitors led to search for environmentally friendly alternatives such as green (organic) inhibitors. The corrosion of metals and alloys exposed to corrosive environment has been investigated by researchers [8,9,10,11,12] employing organic or inorganic inhibitors”. “Organic compounds capable of serving as inhibitors must have active adsorption centers and should also possess hetero-atoms such as oxygen, sulphur, phosphorous, chlorine, bromine, iodine and nitrogen” [13]. “The inhibitive effect of plants extracts can be attributed to the presence of organic species such Carbohydrates, tannins, alkaloids and nitrogen bases, amino acids and proteins” [14,15]. Aside the use of organic inhibitors, other corrosion control means are; use of protective paints or protective metal, control of aqueous solution pH values toward slightly alkaline and application of electric potential to equipment.

The aim of this work is to investigate the inhibiting effects of *Spondias mombin* (SM) leaves extract on the corrosion of mild steel and AA2024 exposed to 0.5 M NaCl environment using electrochemical techniques. *Spondias mombin* is an ephemeral plant whose height can reach up to 25 m and is mostly cultivated in tropical areas with medium to heavy, well-drained fertile soil.. Its leaf is elliptic in shape. The mineral content and the phytochemical composition of *Spondias mombin* leaves have been intensively investigated by Njoku and Akumefula [16]. The mineral screening result shows the presence of potassium (2.55%), sodium (0.10%), calcium (1.31%), Phosphorus (0.20%) and magnesium (0.30%) while the phytochemical screening result shows the presence of tannins (3.82%), saponins (7.6 %), alkaloids (6.0 %), flavonoids (3%), and phenols (1%).

2. MATERIALS AND METHODS

2.1 Materials

The mild steel and aluminum alloy (AA2024) used for this experiment were respectively obtained from Federal University of Petroleum Resources, Effurun, Nigeria and Kaiser Aluminum, Sokane, USA. The composition of the mild steel is as follows: 0.05 % C, 0.05 % Si, 0.85 % P, 0.15 % Pb, 0.09 % Cu, 1.13 % Mn, 0.85 % S, 0.13 % V, 0.08 % Mo and 96.56 % Fe. The aluminum alloy (AA2024) specimen contains: 0.08 % Si, 0.19 % Fe, 4.61 % Cu, 0.55 % Mn, 1.30 % Mg, 0.11 % Zn, 0.06 % Ti, 0.01 % Cr, 0.05 % V, and 93.13 % Al. The metal samples were press cut to a dimension of 1.0 cm x 1.0 cm. The coupons were polished mechanically with emery paper of different grades. To remove any oil or organic impurities, the coupons were degreased in ethanol, washed with distilled water, air dried and stored in moisture free desiccators prior to use. Accurate weight measurements of the coupons were taken using electronic weighing balance.

2.2 Preparation *Spondias mombin* Leaves Extract

Fresh *Spondias mombin* (SM) leaves were obtained from New Market, Aba, Nigeria. The leaves were washed, air dried and grounded into fine powder. 50g of the ground leaves were placed in soxhlet extractor containing 150 mL mixture of water and ethanol as solvent. The mixture was refluxed several times and the concentrated solution containing the extracts was evaporated at a temperature of 78.5 ^{0}C to obtain a semi solid extract.

2.3 Electrochemical Measurements

Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) were employed to evaluate the corrosion inhibition feature of *Spondias mombin* leaves extract. The electrochemical measurements were conducted in a three-electrode cell (Fig. 1) using a versaSTAT 400 DC Voltammetry system connected to V3 Studio software. The mild steel and AA2024, each with surface area of 1 cm^2 were separately used as the working electrode (WE), a graphite rod was used as counter electrode (CE) and a saturated calomel electrode (SCE) was employed as reference electrode (RE). The experiments were performed thrice to ensure reproducibility.

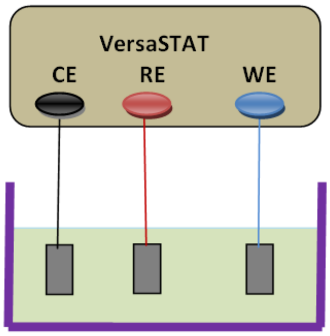

Fig. 1. The electrochemical measurements experimental setup with three-electrode

2.4 Potentiodynamic Polarization (PDP) Measurements

The metal specimens (mild steel and AA2024) were first immersed in blank 0.5 M NaCl solution at room temperature for one hour. The PDP measurements were performed within the potential range of 1000 to 2000 mV at a scan rate of 3 x 10 $^{-4}$ Vs^{-1}. Experimental data obtained can be evaluated using equation (1),

$$\eta = \beta \log\frac{I}{I_0} \quad (1)$$

Where β is the Tafel slope, *I* is the applied current density, and I_0 is the exchange current density. The Tafel slope is obtained when Potential (V) is plotted against logarithm of current density (I) as shown in Fig. 2.

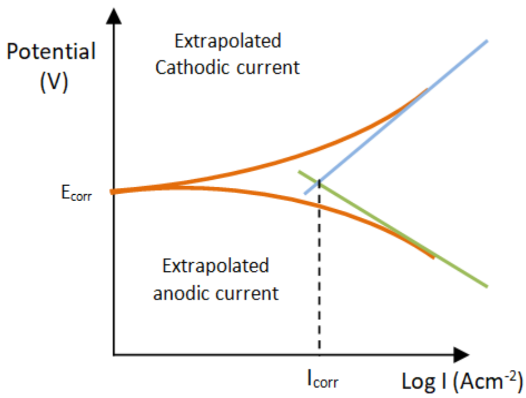

Fig. 2. Potentiodynamic polarization curves

The corrosion potential (E_{corr}) is the potential at which no external current flows while corrosion current density (I_{corr}) is the current density value at which the cathodic reaction rate is equal to the anodic reaction rate. The I_{corr} value can be obtained by extrapolating the linear portion of the anodic and cathodic branches of the polarization curve to the point where their reaction rates are equal [17]. Tafel extrapolation curve has been widely used to measure corrosion rate [18]. The inhibition efficiency can be obtained using equation (2),

$$\text{I.E} = \frac{I'_{corr} - I_{corr}}{I'_{corr}} \times 100\ \% \qquad (2)$$

Where; I'_{corr} is the current density for the uninhibited environment and I_{corr} is current density in the presence of the inhibitor.

2.5 Electrochemical Impedance Spectroscopy (EIS)

The EIS experiments were performed at corrosion potential (E_{corr}) over a frequency range of 1 x 10^5 Hz to 1 x 10^7 Hz with a signal amplitude perturbation of 5 mV. A simple EIS equivalent circuit (Fig. 3a) consists of solution resistance R_s, pure capacitor of double layer C_{dl} and the charge transfer resistances R_{ct} which represents the real impedance value. R_s is associated with the high frequency data while R_{ct} depends on the low frequency data. The obtained impedance data can be analyzed using Nyquist plot (Fig. 3b).

The EIS inhibition efficiency can be obtained using values of the charge transfer resistance as shown in equation (3);

$$\text{I.E (\%)} = \frac{R_{CT} - R'_{CT}}{R_{CT}} \qquad (3)$$

Where; R_{CT} is the charge transfer resistance in the presence of inhibitor and R'_{CT} is the charge transfer resistance in the absence of inhibitor.

3. RESULTS AND DISCUSSION

3.1 Potentiodynamic Polarization Studies

The potentiodynamic polarization curves (Tafel plot) of mild steel and AA2024 exposed to 0.5 M NaCl in the presence and absence of *Spondias mombin* leaves extract (SM) are shown in Figs. 4 and 5. The plots indicate that the curves shifted toward the more negative value of corrosion current density (I_{corr}) as the inhibitor concentration increased. This implies that the anodic dissolution of metals and cathodic reduction of hydrogen ions was inhibited. More so, this is suggestive of reduction of the active surface area and the formation of a protective layer of the inhibitor molecules over the mild steel and AA2024 surface [19]. For all concentrations of the inhibitor, the maximum displacement shift in E_{corr} value was found to be less than 85 mV. This indicates that the inhibitor SM behave like a mixed corrosion inhibitor [20]. Tables 1 and 2 show the PDP experiment parameters for mild steel and AA2024 respectively.

3.2 Electrochemical Impedance Spectroscopy Studies

The Nyquist plot of mild steel and AA2024 exposed to 0.5 M NaCl environment in the presence and absence of *Spondias mombine* (SM) leaves extract is respectively shown in Figs. 6 and 7. It can be observed that the Nyquist plots are characterized by a single capacitive-like semi-circular loop over a frequency range. The diameter of the semicircles was found to increase with increase in concentration of the inhibitors. This signifies that corrosive process was inhibited possibly by charge transfer of the inhibitor molecule onto the metal surface and is in agreement with results reported by some researchers [21,22,23]. Tables 3 and 4 show values of the EIS parameters. The charge transfer resistance (R_{ct}) values were found to increase as the inhibitor concentration increased. The increase in R_{ct} can be attributed to the formation of protective film at the metal-solution interface [24]. The inhibition efficiency values obtained in the EIS experiment were found to be in conformity with those of the PDP experiment.

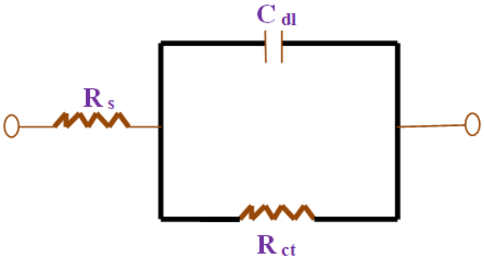

Fig. 3a. EIS equivalent Circuit

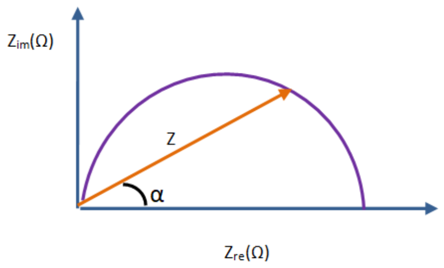

Fig. 3b. Nyquist plot with impedance vector (Z)

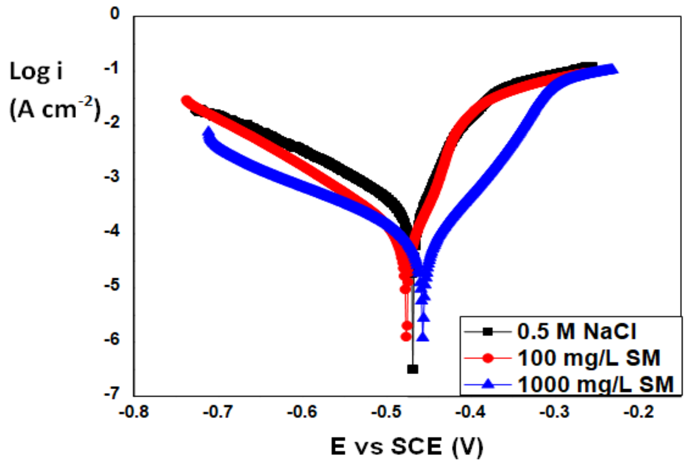

Fig. 4. Potentiodynamic polarization plot of mild steel in 0.5 M NaCl environment in the absence and presence of SM

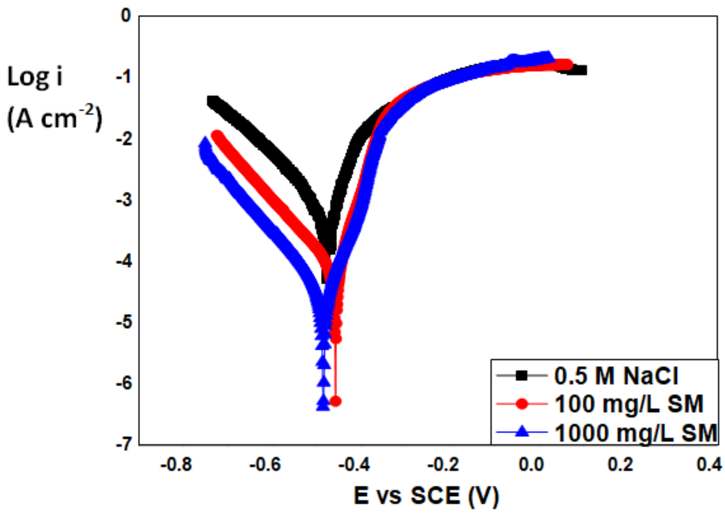

Fig. 5. Potentiodynamic polarization plot of AA2024 in 0.5 M NaCl environment in the absence and presence of SM

Table 1. Potentiodynamic Polarization Parameters for Mild Steel in 0.5 M NaCl in the Absence and Presence of SM

C (mg/L)	E_{corr}(mV/SCE)	I_{corr} (μA/cm^2)	% I.E
Blank	-459.5	198.4	-
100 SM	-424.6	116.4	41.3
1000 SM	-441.6	95.4	52.0

Table 2. Potentiodynamic Polarization Parameters for Aluminium (AA2024) in 0.5 M NaCl in the Absence and Presence of SM

C (mg/L)	E_{corr}(mV/SCE)	I_{corr} (μA/cm^2)	% I.E
Blank	-485.6	107.5	-
100 SM	-491.6	54.7	49.1
1000 SM	-477.9	36.5	66.0

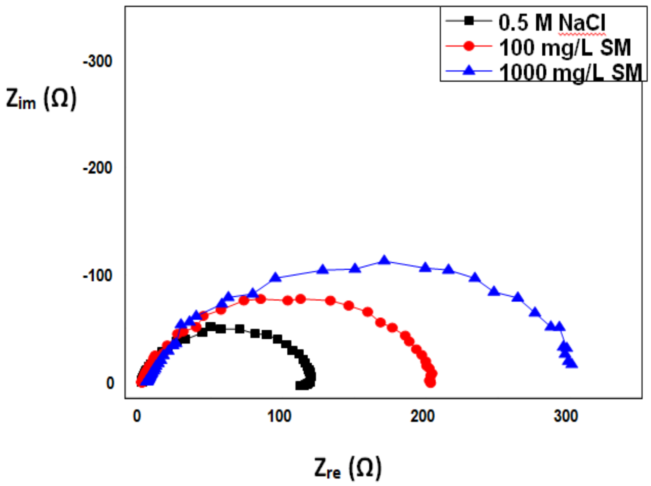

Fig. 6. Nyquist plot of mild steel in 0.5 M NaCl environment in the presence and absence of SM

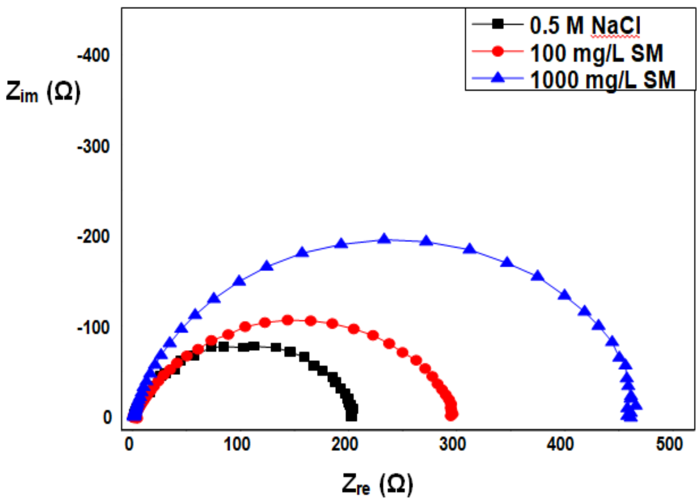

Fig. 7. Nyquist plot of aluminium in 0.5 M NaCl environment in the presence and absence of SM

Table 3. Electrochemical impedance Parameters for mild steel in 0.5 M NaCl in the Presence and Absence of SM

Concentration (mg/L)	N	R_{ct}(Ω-cm^2)	% I.E
Blank	0.89	105.3	-
100 SM	0.88	196.9	46.5
1000 SM	0.89	297.8	64.6

Table 4. Electrochemical impedance Parameters for Aluminum in 0.5 M NaCl in the Presence and Absence of SM

Concentration (mg/L)	N	R_{ct}(Ω-cm^2)	% I.E
Blank	0.88	202.6	-
100 SM	0.88	301.7	32.8
1000 SM	0.89	462.5	56.2

4. CONCLUSION

In this study, electrochemical methods were employed to investigate the corrosion inhibition of mild steel and AA2024 exposed to 0.5 M of NaCl containing various concentration *Spondias mombine* leaves extract as inhibitor. The PDP and EIS results obtained show that the inhibitor extracts retarded the deterioration of the selected metals in the saline solution. The inhibition efficiency values obtained for the PDP experiment were close to those of EIS experiment. There is no significant difference in the inhibiting effect of *Spondias mombin* leaves extract on both metals.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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