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EXTRACT OF COMBRETUM MICRANTHUM AS CORROSION INHIBITOR FOR Al – Si – Mg ALLOY IN SIMULATED SEA WATER ENVIRONMENT

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ABSTRACT

The leaf extract of Combretum micranthum (CM) was tested as green corrosion inhibitor for Al-Si-Mg alloy in 3.5wt% NaCl solution using gravimetric and linear polarization methods at 30⁰C, 50⁰C and 70⁰C, from 1, 2, 3, 4, 5 hours of exposure time with concentration of the extract 0, 0.2, 0.4, 0.6, 0.8 and 1.0 v/v respectively. The result obtained indicate that the leaf extract of CM is a good corrosion inhibitor in the simulated sea water medium. The inhibition efficiency of the extract increased with an increase in concentration of the CM extract and decreased with increase in temperature. On the other hand, inhibition efficiency (IE%) synergistically decreased on addition of surfactant (Monoethylamine). The adsorption of the inhibitor on Al-Si-Mg surface is exothermic, Spontaneous and is best described by Langmuir, Freundlick and El-Awady adsorption models. The calculated values of activation energy, enthalpy of activation entropy of activation, free energy of process is by physical adsorption. Equally, methanol extract CM is a good adsorption inhibitor for the corrosion of Al-Si-Mg in 3.5wt% NaCl solution. Tafel polarization analysis indicates that the studied plant extract is a mixed type inhibitor.

Keywords: *Al-Si-Mg alloy, inhibitor, adsorption, polarization, Combretum micranthum, gravimetric, monoethylamine*

1. INTRODUCTION

Aluminum is a light weight metal (density = 2.71g/ cm^3) having good corrosion resistance to the atmosphere and to many aqueous media, combined with good electrical and thermal conductivity [1]. Aluminum and aluminum alloys lend themselves to many engineering applications because of their combination of lightness with strength, their high corrosion resistance, their thermal and electrical conductivity and heat and light reflectivity, and their hygienic and non-toxic qualities [2]. Aluminum is considered as an advanced material in many industrial processes due to its relatively low cost, high strength and high corrosion resistance [3]. This metal is however exposed to the action of acids, bases, salt water in industries and marine environment and these medium are generally accompanied by considerable dissolution of the metal, so arises the problem of the material protection.

The use of corrosion inhibitors is a current practice in industry [4, 5]. These inhibitors are chemical compounds usually used in small concentrations wherever a metal is in contact with an aggressive medium. The presence of such compounds retards the corrosion process and keeps the rate of dissolution to a minimum and hence prevents economic losses due to metallic corrosion. The chemical compounds that could be used for this purpose may be organic or inorganic.

An important corrosion inhibition tool is the use of surfactant inhibitors. The most important action of inhibition is the adsorption of the surfactant functional group on to the metal surface [6]. To be effective, an inhibitor must also transfer water from the metal surface, interact with anodic or cathodic reaction sites to retard the oxidation and reduction corrosion reactions and prevent transportation of water and corrosion-active species on the metal

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surface. Monoethylamine (MEA) was employed during the course of study to enhanced the performance of the extract synergistically. These compound has multiple bonds in their molecules that mainly contain nitrogen, sulphur, oxygen atoms through which they get absorbed on the metal surface.

Many industrial processes have put to use inorganic inhibitors for corrosion protection but as a result of cost and toxicity, attention is currently shifted towards the use of more eco-friendly inhibitors [7]. The greatly expanded interest on naturally occurring substances is attributed to the fact that they are cheap, readily available, ecologically friendly, and poses no threat to the environment. In addition, they are biodegradable and renewable source of materials [8].

Organic inhibitors generally have heteroatoms, O, N, and S are found to have higher basicity and electron density and thus act as corrosion inhibitor, O, N and S are the active centers for the process of adsorption on the metal surface. The inhibition efficiency should follow the sequence $O < N < S < P$ [9]. In recent years, a lot of research efforts have gone into the search for non-toxic naturally occurring substances for use as metal corrosion inhibitors. In this regard, a number of amino acids [10, 11] as well as extracts from leaves, roots and stem barks of plants (biomass) and even fruits or fruit peels have been reported as effective inhibitors of metal corrosion [12]. The crucial property of the plant extracts is because they contain phytochemical compounds such as tannis, saponins, alkaloids, flavonoids, amino acids, phenolic compounds, glycosides, pigments, resins, triterpenoids with molecular electronic structures close to conventional corrosion inhibitors. In the presence study, the inhibitive property of CM leaves extract have been investigated for Al-Si-Mg in sea water environment using gravimetric and linear polarization techniques.

2. MATERIALS AND METHODS

2.1Materials and Sample Preparation

Material used for the study is Sand cast A356.0 type Al-Si-Mg alloy of composition as presented in Table 1. Other materials include crucible furnace, polishing machine, digital weighing balance, corrosion bath, potentiostat corrosion kit and scanning electron microscopy. After casting, the Al-Si-Mg was mechanically cut into different coupons each of dimension 10mm x 15mm. each coupon was polished with different size of emery papers grids (600-1200), and was later degreased by washing with ethanol, rinsed with acetone and air dried before they were preserved in a desiccator.

Table 1: Elemental composition of the alloy Al-Si-Mg

Element	Si	Mg	Cu	Zn	Al
Composition (wt.%)	7.0	0.35	0.20	0.10	Bal

2.2. Plant Extraction

Samples of CM leaves were obtained from Malunfashi Local Government Area, Katsina State, Nigeria. The samples were taken to Herbarium in Biological Science Department, Ahmadu Bello University, Zaria, Nigeria for identification and were assigned a batch number. The leaves were shade dried, ground, and soaked in a solution of methanol for 72hrs. After 72hrs, the samples were filtered. The filtrates were further subjected to evaporation at 343k in order to make it free of methanol using Rotary evaporator. The stock solutions of the extracts so obtained were used in preparing different concentration of the extract by dissolving 0.2, 0.4, 0.6, 0.8 and 1.0g of the extract in 1L of 3.5wt% NaCl solution respectively, for gravimetric analysis and as well as linear polarization analysis.

2.3. Phytochemical Screening of the Plant

Phytochemical analysis of the methanol and aqueous extract of the sample was carried out in the Department of Pharmacognosy and Drug Development, Faculty of Pharmaceutical Science, Ahmadu Bello University, Zaria, Nigeria. Frothing and Wagner's tests were used for the identification of saponin, glycoside and alkaloids. Bromine water and ferric chloride tests were used for the identification of tannin and a few drop of 10% NaOH added to the extract reveals the presence of flavonoids [13].

Phytochemical screening was performed using simple chemical tests to detect the presence and relative amounts of tannins, saponins, flavonoids and alkaloids in the plant extracts by standard laboratory procedures as follows:

- For Tannins:- To a portion of the extract, 3-5 drops of ferric chloride solution was added. A greenish-black precipitate indicates the presence of condensed tannins while hydrolysable tannins gives a blue or brownish-blue precipitate.
- For Saponins:- About 10ml of distilled water was added to a portion of the extract and was shaken vigorously for 30 seconds. The tube was allowed to stand in a vertical position and was observed for 30 minutes. A honey comb froth that persists for 10-15 minutes indicates presence of saponins.

- For Flavonoids:- A few drops of 10% NaOH were added to the extract. Yellow colouration indicates presence of flavonoid.
- For Alkaloids:- Few drops of Wagner's reagent were added to a portion of the extract. Whitish precipitate
- indicates presence of alkaloids.

The results for the qualitative and quantitative analysis of the plant extracts are presented in Tables 1-2

2.4 Gravimetric measurements

A previously weighed metal coupons (Al-Si-Mg) was completely immersed in 200ml of the test (in a beaker) with and without the addition of different concentrations of CM extracts. The beaker was inserted into a water bath maintained at a temperature of 303k, 323k and 343k over an exposure time of 1hr, 2hrs, 3hrs, 4hrs and 5hrs respectively. After every one hour, each sample was withdrawn from the test solution, washed with water and rinsed with acetone and air dried before re-weighing. The same experiment was carried out with addition of surfactant (MEA) to the existing plant extract (CM) at the same concentration in the ratio 50/50% v/v. The different in weight was recorded as the weight loss. From the weight loss, the corrosion rates (CR) were calculated using the equation

$$CR = \frac{87.6W}{DAT} mm/yr \qquad (1)$$

In (1), W is weight loss in mg, D is the density g/cm^3, A is the area in cm^2, T is the exposure time in hours. From the corrosion rate, the inhibition efficiency, (I.E%) was calculated using the equation

$$\mathrm{I.E\%} = \frac{CRo - CR}{CRo} \times 100 \qquad (2)$$

Here CR$_o$ is the corrosion rate without inhibitor and CR is the corrosion rate in the presence of inhibitor.
The surface coverage, ϴ, was calculated from the corrosion rate as follows:

$$\theta = \frac{CRo - CR}{CRo} \qquad (3)$$

2.5 Electrochemical Measurement

The coupon samples of Al-Si-Mg for electrochemical experiments were of dimensions 10mm x 10mm. these were subsequently sealed with epoxy resin in such a way that only one square surface of area 1.0cm^2 was left uncovered. The exposed surface area degreased in acetone, rinsed with distilled water and dried in warm air. A linear polarization studies was carried out in the potential range from -1500 to 1500mV with a scan rate of 0.012 v/s at room temperature of 303k

2.6 Scanning Electron Microscopy

The SEM analysis was performed using a Jeol JSM-7500F Scanning electron microscope. The morphological studies of the Al-Si-Mg alloy surfaces were exposed to uninhibited and inhibited samples.

3. RESULT AND DISCUSSION

Table 2 shows the phytochemical screening of methanol extract of CM qualitatively and quantitatively. Thin layer chromatography (TLC) was used to detect the presence of each substance in the plant. The results obtained indicate that Tannins, Saponins, Flavonoids and Alkaloids are present in the methanol extract of CM. Each substance appeared on the thin plate in various colour backgrounds while the intensity of the colour appearance indicate the amount. These substances are responsible for the inhibition efficiency of methanol extract of CM.

Table 2: Phytochemical composition of the methanol extract of CM

Phytochemicals	*Qualitative*	*Quantitative*
Tannins	+	1.51%
Saponins	++	23.30%
Alkaloids	+	4.78%
Flavonoids	++	22.50%

Where + means the presence of the chemical constituent and ++ means more of the constituent present.

3.1 Effect of Methanol Extract of CM

Figures 1-3 show the variations of corrosion rates with inhibitor concentrations for the corrosion of Al-Si-Mg in various concentrations of inhibitors in 3.5wt% NaCl solution at different temperatures. The Figures indicate that the rate of corrosion of Al-Si-Mg decreased with increase in inhibitor concentration and exposure time but increase with increase in temperature. This indicates that methanol extract CM is an adsorption inhibitor for the corrosion of Al-Si-Mg. The inhibition efficiency increased with increase in concentration of the inhibitor but also decreased with increase in temperature which is expected to be so because at a higher temperature, desorption is expected.

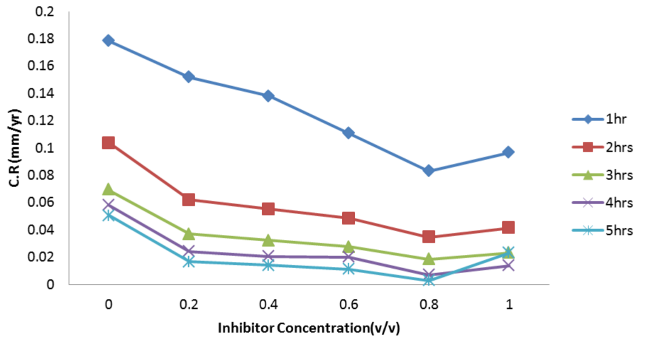

Figure 1: Corrosion Rate against Inhibitor concentration of CM at 30^{0}C

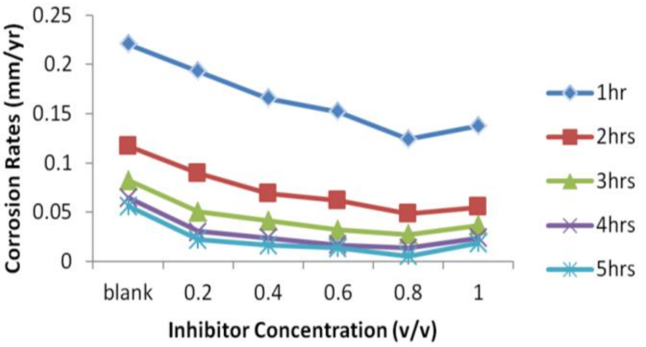

Figure 2: Corrosion rates against inhibitor concentration of CM at 50^{0}C

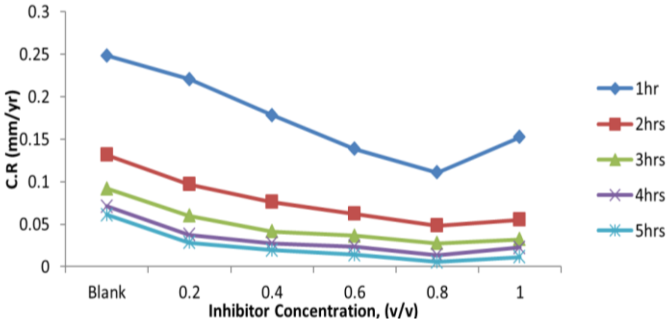

Figure 3: Corrosion rates against Inhibitor concentration of CM at 70^{0}C

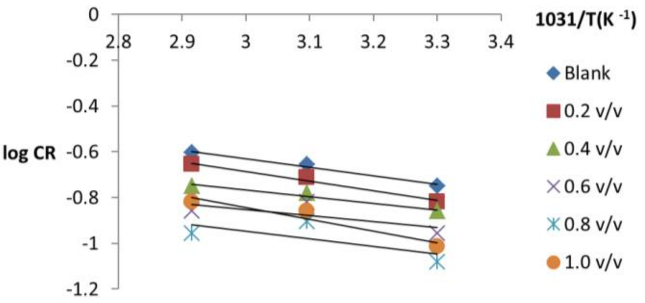

Figure 4: Plot of Log CR against 1/T of C.M in 3.5wt% NaCl of Al-Si-Mg alloy

This also suggests that the adsorption of methanol extract of CM on Al-Si-Mg surface is consistent with the mechanism of physical adsorption [14].The corrosion resistance of the extract was found to be best at lower temperature, 30^{0}C while the corrosion rate increases as the temperature increase indicating desorption of the extract from the surface of the alloy as temperature increases.

3.2 Effect of Surfactant Addition

It was observed that the inhibition efficiency of CM extract alone attains a maximum value of 94.44% at a concentration of 0.8v/v at 30^{0}C. The addition of surfactant was not found to increase the inhibition efficiency of the Al- Si- Mg alloy in 3.5wt % NaCl solution more better than the extract alone, as the maximum inhibition efficiency was 64.45%. This could be that there is no synergy between the plant and the surfactant.

3.3 Effect of Temperature

In order to access the effect of temperature on corrosion inhibition process, gravimetric experiments were performed at different temperatures (30^{0}C, 50^{0}C, 70^{0}C) in the absence and presence of various concentrations of the inhibitor during 5 hours of the relationship between the corrosion rate of Al-Si-Mg and temperature can be expressed by the Arrhenius state equation shown in equation (4) and (5) [15].

$$\text{Log CR} = LogA - \frac{Ea}{2.303RT} \qquad (4)$$

$$\text{Log}\,\frac{CR}{T} = \left[\text{Log}\frac{R}{Nah} + \frac{\Delta Sa}{2.303R}\right] - \frac{\Delta Ha}{2.303RT} \qquad (5)$$

Where CR is the corrosion rate of the metal, A is the Arrhenius or pre-exponential factor, Ea is the activation energy (that is the minimum energy needed before the corrosion reaction of the metal can proceed, R is the universal gas constant, and T is the temperature of the system, Na is the Avogadro's constant, ΔS_a is the entropy of activation and ΔH_a is the enthalpy of activation.

From equation (4), plot of log CR versus reciprocal of absolute temperature, I/T, as shown in Figure 4, gives a straight line with slope equal to $\frac{-Ea}{2.303R}$ from which the activation energy for the corrosion process can be calculated. From equation (5), plot of log CR/T versus reciprocal of absolute temperature, I/T as shown in Figure 5, gives a straight line with slope equal to ΔH_a and intercept of [log R/Nah + ΔSa/2.303R] from which the enthalpy and entropy of activation for the corrosion process can be calculated. Value of Ea, ΔSa and ΔHa are presented in Table 3.

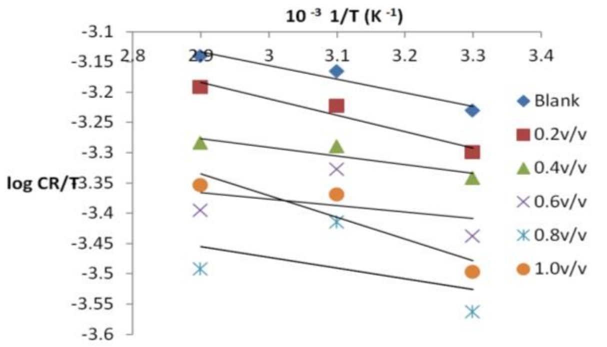

Figure 5: Variation of Log CR/T against 1/T of C.M in 3.5wt% NaCl of Al-Si-Mg alloy.

Table 3: Activation Energy Parameters Ea, ΔHads, ΔSads for Al-Si-Mg Alloy in 3.5wt.% NaCl Solution for CM

Inhibitor Concentration (v/v)		$-E_{ads}$ (KJ/Mol)	ΔH_{ads}.(KJ/Mol)	ΔS_{ads} (KJ/Mol. K)
Blank		7.19	4.30	-0.2452
0.2		8.13	5.21	-0.2435
0.4		5.58	2.76	-0.2524
0.6	CM	8.99	2.06	-0.2562
0.8		10.44	3.40	-0.2539
1.0		9.87	6.82	-0.2435

Values of the extrapolated activation energies Ea were found to be greater where corrosion rates were inhibited than those obtained where there were no inhibition indicating that the methanol extract of CM retarded the corrosion of Al-Si-Mg. it is also found that the activation energy was lowered than the value of 80 kJ/Mol. required for chemical adsorption to take place, confirming that the adsorption of CM extract occur through the mechanism of physical adsorption [16]. Table 3 shows the enthalpies of activation of the corrosion process to be positive which reflect endothermic nature of dissolution process. The entropy of activation in the presence and absence of the inhibitor also has negative values which indicate that the activated complex in the rate determining step represents in association rather than dissociation, implying that a decrease in disordering took place on going from the reactant to the activated complex [17, 18].

3.4 Adsorption Isotherm

The interaction between the inhibitor and Al-Si-Mg surface can be provided by the adsorption isotherm. During corrosion inhibition of Al-Si-Mg, the nature of inhibitor on the corroding surface has been deduced in terms of adsorption behavior of inhibitors.

Many attempts were made to find the best isotherm which describes the study. Langmuir isotherm was found to be the best description for adsorption CM extract on Al-Si-Mg. according to this isotherm Θ is related to the inhibitor concentration, C and adsorption equilibrium constant K_{ads} via:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{6}$$

The plot of C/Θ versus C gave a straight line (Figure 6) with a slope close to unity confirming that the adsorption of CM extracts on Al-Si-Mg surface in 3.5wt% NaCl solution obeys the Langmuir adsorption isotherm. The equilibrium adsorption constant, K_{ads} is related to the Standard Gibb's Free energy of adsorption (ΔE_{ads}) with the following equation.

$$\text{Kads} = \frac{1}{55.5}\exp\left[-\frac{\Delta G_{ads}}{RT}\right] \tag{7}$$

Where 55.5 is the concentration of water in solution (mol/L), R is the universal gas constant and T is the absolute temperature. The negative values of standard free energy of adsorption ΔG_{ads}., confirm the spontaneity of adsorption process [19, 20] and stability of the adsorbed layer on the Al-Si-Mg surface. The obtained values are listed in table 2. Generally, the negative are consistent. -20KJ/Mol. or less negative are consistent with physisorption, while those around -40KJ/Mol. or more negative involve chemisorption [21, 22]. The values found for Al-Si-Mg alloy indicate that the adsorption is physisorption (electrostatic interactions). The relation between ΔG^0_{ads} $\Delta H^0_{ads}$and $\Delta^0 S_{ads}$ is given by the following basic equation:

$$\Delta G^o{}_{ads} = \Delta H^o{}_{ads} \quad T\Delta G^o{}_{ads} \tag{8}$$

3.5 Polarization Study

Linear polarization curves obtained for Al-Si-Mg in 3.5wt% NaCl solution at various concentrations of CM extracts ranging from 0.2, 0.4, 0.6, 0.8 and 1.0 v/v are shown in Figure 6. It can be observed that the addition of CM extracts at all the studied concentrations decreased the anodic and cathodic current densities and resulted in significant decline in the I_{corr}. This indicates that CM extracts shifted to smaller I_{corr}. Values in both anodic and cathodic branches of the curves, thus acting as a mixed type inhibitor [23] and the decrease is more pronounced with the increase in the inhibitor concentration by comparing polarization curve in the absence and in the presence of various concentration of CM extracts. It is observed that, increase in concentration of the inhibitor shift the corrosion potential (E_{corr}.) in the positive direction and reduces both anodic and cathodic process [24]. The Polarization parameters are presented in Table 4 while the polarization curve is presented in Figure 6.

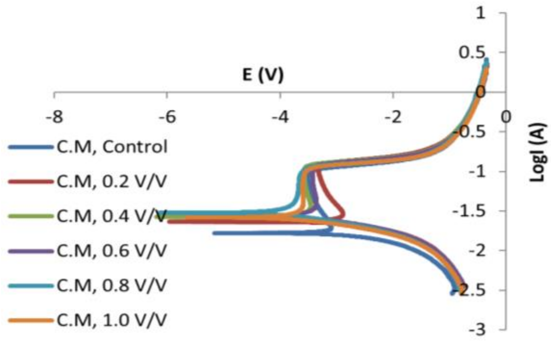

Figure 6: Polarization curve of Al-Si-Mg alloy in 3.5wt% NaCl solution in the absence and presence of C.M

Table 4: Polarization parameters for Al-Si-Mg in 3.5wt%NaCl solutes in the presence and absence of CM

Plant extract (C.M)	E_{corr} (v)	I_{corr} (A)	η %
Blank	-1.7818	0.0040	-
0.2	-1.6418	0.0025	80.62
0.4	-1.5820	0.00063	84.33
0.6	-1.5752	0.00068	83.05
0.8	-1.5275	0.00015	96.15
1.0	-1.5898	0.00027	93.50

From Table 1, the inhibition efficiency was calculated using the equation given as:

$$IE\% = \frac{1 - I_{inh}}{I_{corr}} \times 100 \qquad (9)$$

In (9), I_{inh} and I_{corr} are the corrosion current densities in the absence and presence of inhibitors.

3.6 Scanning Electron Microscopy

The protective layer that formed on the metal surface was characterized by SEM analysis. Morphologies of Al-Si-Mg alloy in the absence and presence of optimum concentration of CM extracts at 30^0C are shown in Plates 1 and 2. Plate1 shows SEM microstructure of the control Al- Si- Mg alloy with the lowest C.R in the absence of inhibitor. Plate 2 shows evidence of some film on the surface of the alloy and it is more pronounce in x1500 magnification.

4. CONCLUSIONS

- CM extracts is a good inhibitor for Al-Si-Mg corrosion in 3.5wt%Nacl solution showing 94.74% inhibition efficiency of exposure time. The results obtained from electrochemical technique were also in good agreement with each other.
- Tafel polarization curves show that the CM extracted as mixed type inhibitor
- The adsorption of CM extracts at Al-Si-Mg NaCl 3.5wt% solution interface obeyed the Langmuir adsorption isotherm model.
- The adsorption characteristics of the inhibitor favour the mechanism of charge transfer from the charged inhibitors molecule to the charged metal surface (physical and sorption).

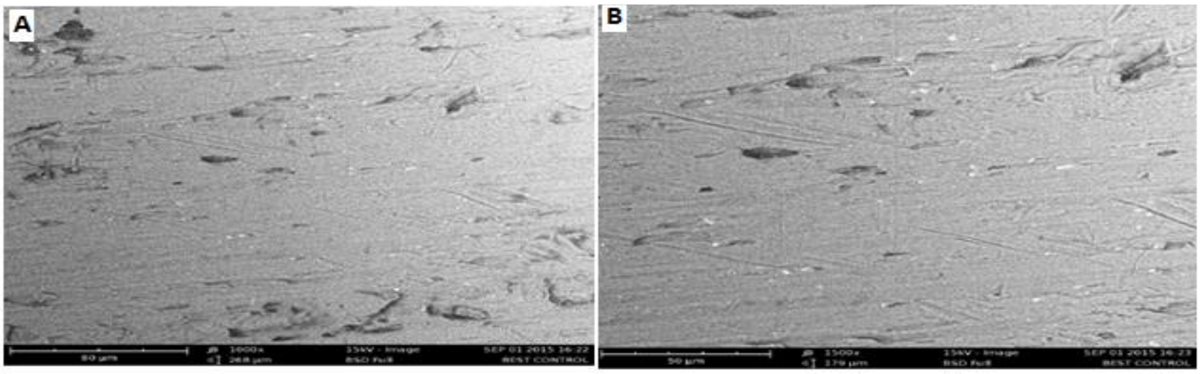

Plate 1: SEM microstructure of control Al-Si-Mg alloy with the lowest corrosion rate without addition of inhibitor using gravimetric method A) x1000 B) x1500

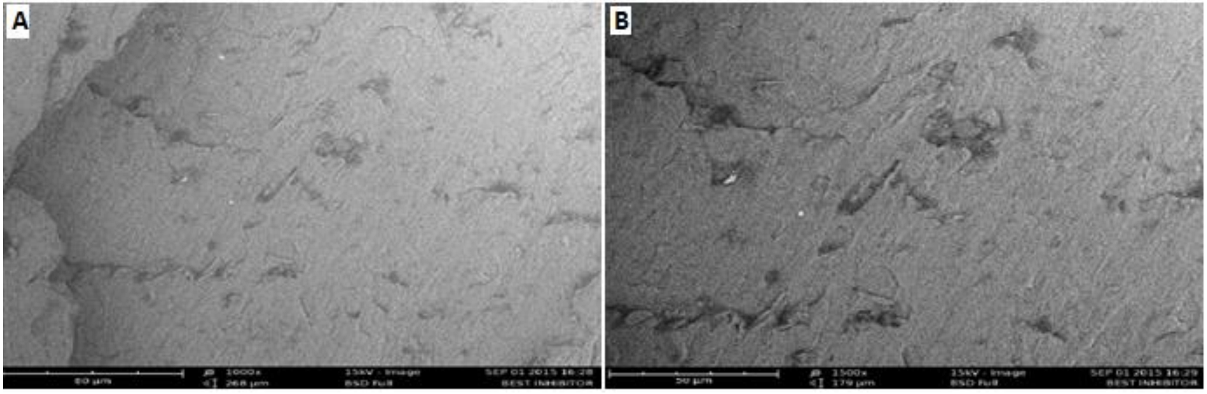

Plate 2: SEM microstructure of Al-Si-Mg alloy with the lowest corrosion rate in the presence of inhibitor using gravimetric method A) x1000 B) x1500

5. ACKNOWLEDGEMENT

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