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Research Article

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Effect of *Borreria Stachydea* Leaves Extract as Green Corrosion Inhibitor on Al – Si – Mg Alloy in Simulated Seawater Environment

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Abstract Corrosion inhibition effect of *Borreria Stachydea* leaves extract on Al-Si-Mg alloy in simulated seawater environment has been investigated at ambient temperature by gravimetric methods. Extracts of *Borreria Stachydea* leaves in different concentrations were used as 'green' inhibitors. This paper reports the results obtained from the weight loss method, calculated corrosion rates, inhibitor efficiencies and temperature variations. Addition of different concentrations of the plants extracts gave considerable reduction in the weight loss and in the corrosion rate of the test samples. This apparent corrosion inhibition was associated with the protective film provided on the steel's surface by the complex chemical constituents of the plants extracts. The corrosion rates were found to decrease in the presence of the inhibitor, plant extract generally. The inhibition efficiency was found to increase with increasing inhibitor concentration. The effect of temperature on the corrosion inhibition of the alloy indicated an increase in the corrosion rate as temperature increased and subsequent decrease in the inhibition efficiency. The adsorption of the extract molecules on the alloy surface obeys Langmuir adsorption isotherm and occurs spontaneously. The activation energy as well as other thermodynamic parameters for the inhibition process was calculated. These thermodynamic parameters show strong interaction between inhibitor and alloy surface. Thermodynamic data calculated are suggestive of adsorption of inhibitor molecules on the alloy surface.

Keywords Simulated seawater; Al-Si-Mg alloy, *Borreria stachydea* leave, Weight loss method, Adsorption isotherm, Corrosion inhibitor

1. Introduction

Aluminium and its alloys have become significant materials in various applications. It can be alloyed with different elements like copper, zinc, magnesium, manganese, silicon, as well as lithium. Its applications include foil covering, food packaging industry, food and chemical industry, vehicle paneling, marine cages, air frames, chemical plants, pressure vessels, road tankers, transportation of ammonium nitrate, irrigation pipes and window frames.

Al-Si-Mg alloy is an alloy in which silicon is the major alloying element and magnesium as minor. The alloy has moderately high strength with good impact resistance, good corrosion resistance, however upon exposure to aggressive environment the thin films formed that protects it from corrosion get depleted. The marine and pipeline industries have continued to face the problem of corrosion and subsequent deterioration of infrastructure exposed to actual hostile marine environments [1].

Protective oxide films formed on the aluminium surface have a dual nature. These films consist of an adherent compact, and stable inner oxide film covered with a porous, less stable outer layer, which is more susceptible to corrosion [2]. The use of inhibitors is one of the most practical methods for protecting metallic corrosion, especially in hostile environment like seawater. It is well established that inhibitors function in one or more ways to control corrosion; by adsorption of a thin corrosion product, or by changing the characteristics of the environment resulting in reduced aggressiveness [3]. Although many synthetic compounds show good corrosion inhibition ability, the search for most non toxic environmentally friendly inhibitors are the focus now in metallic corrosion prevention *Borreria stachydea* leaves is an erect hairy and weedy herb, about 1ft in height with mauve flowers. It is found in Nigeria, Ghana, Sudan, Malaysia, India and several other nations of the world. *Borreria stachydea* is popularly known and called "alkamar tururuwa" in the Hausa language of northern Nigeria, while the Fulani call it "fairare". From the photochemical investigation of the leaf, it is worthy to note that the leaves of this plant contains hetero atoms (N and O) and the availability of π electrons in the aromatic system which are inherent in its complex mixture of glycosides, saponins, alkaloids, terpenes, tannins, phenolic substances and flavonoids [4]. Not much use of it is made by the locals both for domestic or other purposes.

In the past, human beings have put plants in to several uses such as shelters, production of food stuffs, fertilizers, flavors and fragrance, clothing, medicines and as well as corrosion inhibitors [5]. Their use as corrosion inhibitors found economical and practical method of reducing degradation of metals in aggressive medium. A common definition of corrosion inhibitor is that it's a chemical either synthetic or natural which when added in small quantity to an environment decrease the rate of attack by the environment on metals [6].

2. Experimental

2.1. Preparation of Plant Extract

Borreria stachydea leaves were obtained from a farm centre in Okene Local Government area of Kogi State and identified at the Biological Science Department, University of Nigeria Nsukka. The *Borreria stachydea* leaves were dried under shade and ground to powder, and then dissolved in 500 ml of distilled water and heated in a water bath at 60 ^{O}C Thereafter the solution was filtered and the filtrate concentrated to 200 ml in a water bath at 100 ^{O}C. The stock solution of the extract so obtained was used in preparing different concentrations of the extract 0.1, 0.2, 0.3, 0.4, and 0.5 g respectively [7].

2.2. Materials

The Al-Si-Mg alloy with chemical composition (wt.%) as follows: Si = 7.0; Mg = 0.35; Cu = 0.20; Zn = 0.10 and balance Al was produced according to the method described elsewhere [8]. Coupons were cut into 10 x 15 mm size and were used for weight loss measurement. Specimens were mechanically abraded with 400, 600, 800 and 1000 grade of emery papers and thereafter degreased with acetone, washed with distilled water and dried in air before immersing in the medium.

2.3. Phytochemical screening

The phytochemical screening of the plant was carried out at Chemistry Department of the University of Nigeria, Nsukka using standard procedure [9 - 10]..

2.4. Weight Loss Measurement

Al-Si-Mg alloy coupons were immersed in five beakers containing various concentrations of the corrosion inhibitor (0.1, 0.2, 0.3, 0.4, and 0.5) g/l and a sixth beaker without the inhibitor which was used as the control. For the experiment at 303K, the coupons were retrieved after 24 hours. They were thoroughly cleaned and washed with distilled water, degreased with acetone and weighed with an electronic balance. The same experiments were repeated at 313k, and 323k respectively and the same process of weighing was applied. The difference between the present and previous weights were computed and recorded as the weight loss. From the weight loss, the corrosion rates (CR) were calculated using the equation:

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

Where W= weight loss in mg
D= density g/cm^3
A= area in cm^2
T= exposure time in hours

From the corrosion rate, the inhibition efficiency, (IE %) was calculated using the equation

$$IE\% = \frac{CRo - CR}{CRo} \times 100 \qquad (2)$$

Where 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:

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

3. Results and Discussion

3.1. Phytochemical screening

Table 1 shows the phytochemical screening of methanol extract of *Borreria stachydea* leaves. The results obtained indicate that Tannins, Saponins, Flavonoids, Glycosides, Phytosterols and Alkaloids are present in the methanol extract of *Borreria stachydea* leaves extracts, hence the inhibition efficiency of methanol extract of plant may be attributed to the phytochemical constituent of the extract.

Table 1: Phytochemical Screening of *Borreria stachydea* leaf extract by methanol

Substances	Presence
Glycosides	+
Flavanoids	+
Tannins	+
Saponins	-
Alkaloids	+
Carbohydrates	+
Triterpenes	+

Key: + = present; - = absent

3.2. Effect of inhibitor concentration on corrosion rate

The corrosion rate with exposure time at different temperature is shown in Figure 1 and from the result obtained; it was observed that the corrosion rate of the alloy in simulated seawater environment decreased with addition of inhibitor. At 303 k, the corrosion rate for the control is 15.71 mm/yr but this value was reduced to 5.42 mm/yr in the presence of inhibitor. Similar trend was observed with increase in temperature. This may be due to the increased protection offered by the inhibitor as concentration increases, thereby preventing the breakdown of the passive films leading to an increase in the corrosion resistance of the alloy compared with the uninhibited samples [11]. The least corrosion rate was obtained at 303 k, in 0.5 g/l concentration, while the highest was at 323k from control. However, as the temperature increased, the corrosion rate increase with 313 k having the highest values of corrosion rates. This could be that there is desorption of inhibitor from the alloy surface or break down of protective film formed earlier due to increase in temperature thereby exposing it to the aggressive environment.

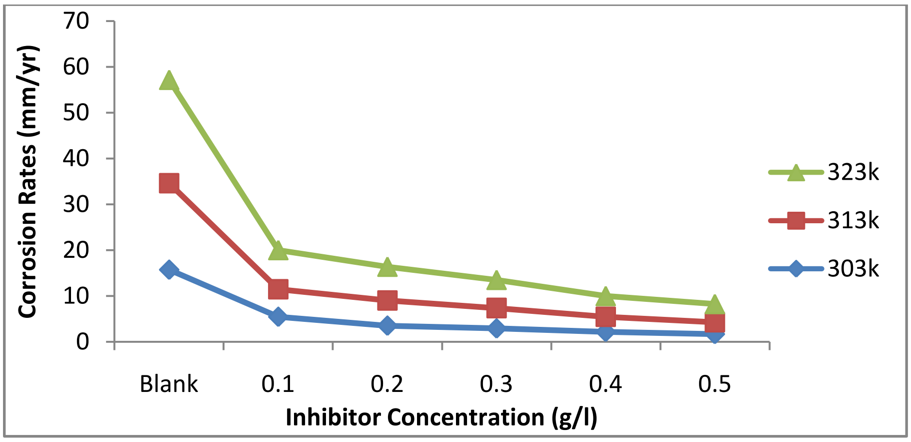

Figure 1: Variation of Corrosion Rate against Inhibitor Concentration of Al-Si-Mg Alloy in the Presence and Absence of Borreria stachydea leaves extract

3.3. Effect of inhibitor concentration on inhibitor efficiency

The inhibitor efficiency with inhibitor concentration is shown in Figure 2. The inhibition efficiency increased with increase in the concentration of *Borreria stachydea* leaves extract. A maximum inhibition efficiency of 89.49 % was obtained at 0.5 g/l inhibitor concentration with the least temperature of 303k. The reduction in inhibition efficiency at 313 k and 323 k can be attributed to the acceleration of the breakdown of the passive film at higher temperature.

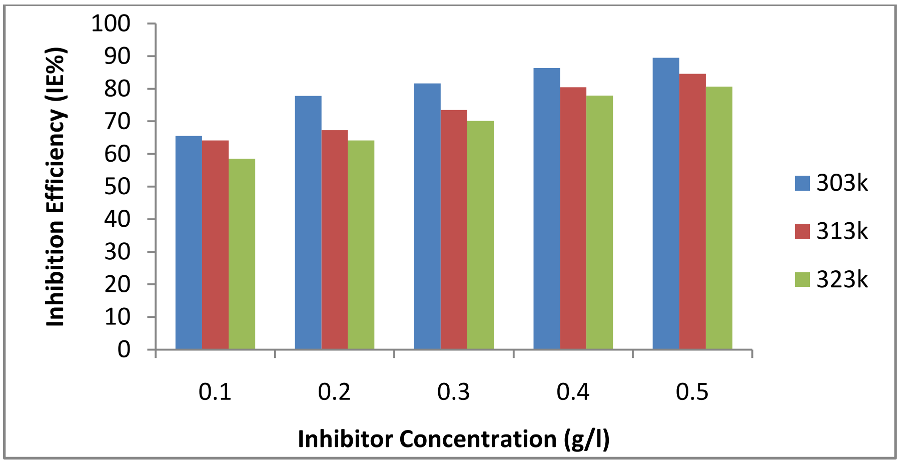

Figure 2: Variation of Inhibitor Efficiency against Inhibitor Concentration of Al-Si-Mg Alloy in the Presence and Absence of Borreria stachydea leaves extract

3.4. Effect of Temperature

The effect of temperature on the corrosion of Al-Si-Mg alloy in the absence and presence of *Borreria stachydea* was studied using the Arrhenius state equation as shown in Equations (4) and (5) [12].

$$\log CR = \log A - Ea/2.303RT \quad (4)$$

$$\log\left(\frac{CR}{T}\right) = \{\log(R/N\,Ah) + \Delta Sa/2.303R\} - \Delta Ha/2.303R \quad (5)$$

Where CR = corrosion rate of the metal, A = Arrhenius or pre-exponential factor, E_a = activation energy, R = universal gas constant and T = temperature of the system, N_A = Avogadro's constant, ΔSa = entropy of activation and ΔHa = enthalpy of activation. From Equation 4, plot of log CR versus reciprocal of absolute temperature, 1/T is as presented in Figures 3, which 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, $1/T$, as shown in Figures 4 gives a straight line with slope equal to - $\frac{\Delta Ha}{2.303R}$ and intercept of $\left[Log\frac{R}{NAh} + \frac{\Delta Sa}{2.303R}\right]$, from which the enthyalpy and entropy of activation for the corrosion process can be calculated. Values of Ea, ΔSa, and ΔHa are presented in Table 2. The values of the extrapolated activation energy, Ea were found to be greater where corrosion rate were inhibited than those obtained where there were no inhibition indicating that the extracts of *Borreria stachydea* retarded the corrosion of the alloy in the studied medium. It was also found that the activation energy was lowered than the value of 40 kJ/mol. which confirmed that adsorption occurs through the mechanism of physical adsorption [13]. The formation of thin film on the metal surface that has become a barrier to both energy and mass transfer led to the increase in activation energy. On the other hand, the solution temperature increased it weakens the efficiency of the extract thereby enhancing the counter process of desorption. Hence the inhibition efficiency values decreased with increase in temperature.

3.5. Adsorption Isotherm

The adsorption behavior of *Borreria stachydea* extract was investigated. The test revealed that adsorption of leave extract on the surface of the alloy is constant with Langmuir adsorption isotherm. The isotherm model can be represented as follows:

$$\frac{c}{\theta} = \frac{1}{K} + c \qquad (6)$$

where c is the inhibitor concentration and K is the adsorption equilibrium constant representing the degree of adsorption. θ is the degree of surface coverage [14]. Taking the

$$log \frac{c}{\Theta} = c + 1/k \qquad (7)$$

Logarithm of equation 6, equation 7 is obtained. The plot of log c / ϴ versus log c as shown in Figure 5 gave linear plots indicating that Langmuir adsorption isotherm is applicable to the adsorption of *Borreria stachydea* extracts on the surface of the alloy.

Thermodynamic parameters play an important role in studying the inhibitive mechanism. The standard adsorption free energy (ΔG^o_{ads}) was obtained according to [15].

$$\Delta Gads = -RT \ln(55.5\ K) \qquad (8)$$

Where R is the molar gas constant, T is the temperature in Kelvin, 55.5 is the molar concentration of water and

$$K_{ads} = \Theta/(1 - \Theta)\ C. \qquad (9)$$

Calculated value of the free energy is presented in Tables 3. Generally, values of ΔG^o_{ads} around -20 kJ / mol or lower are consistent with the electrostatic interaction between the charge molecules and the charged metal (physisorption); those around -40 kJ / mol or higher involve charge sharing or charge transfer from organic molecule to the alloy surface to form a coordinate type of bond (chemisorptions) [16]. From the result obtained, the values were found to be negative, physisorption, and a suggestion that the adsorption of *Borreria stachydea* extracts onto the alloy surface is a spontaneous process and adsorbed layer is stable.

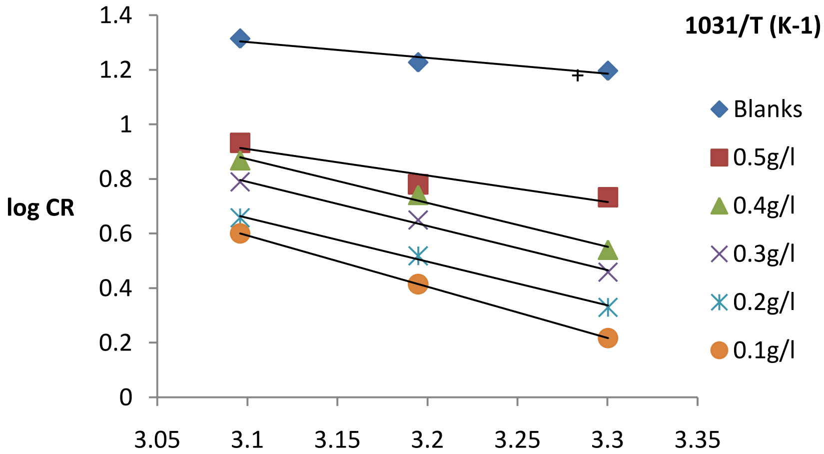

Figure 3: Arrhenius plots of log CR versus 1/T for Al-Si-Mg alloy in the absence and presence of Borreria stachydea leave extract

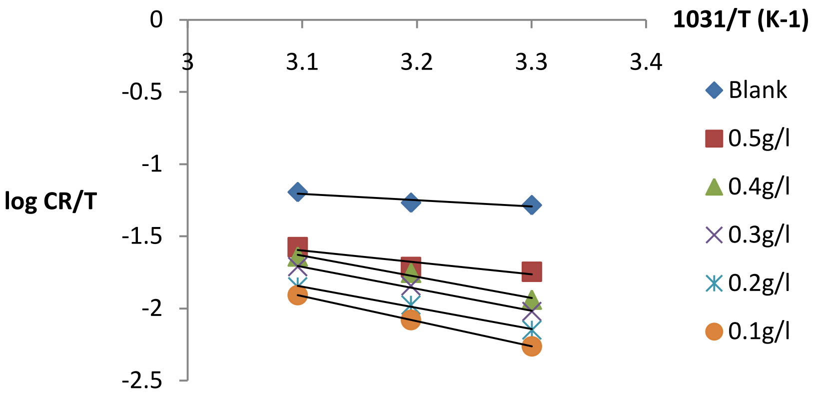

Figure 4: Arrhenius plots of log CR/T versus 1/T for Al-Si-Mg alloy in the absence and presence of Borreria stachydea leave extract

Table 2: Activation energy parameters for for Al-Si-Mg alloy in the absence and presence of *Borreria stachydea* leave extract

Inhibitor Conc. (g/l)	Ea (kJ/mol)	ΔHa (kJ/mol)	ΔSa (kJ/mol)
Blank	13.82	8.41	- 194.68
0.1	35.92	33.32	- 131.01
0.2	30.73	28.13	- 145.86
0.3	30.96	29.08	-140.26
0.4	30.69	28.09	- 141.83
0.5	18.47	15.86	- 179.06

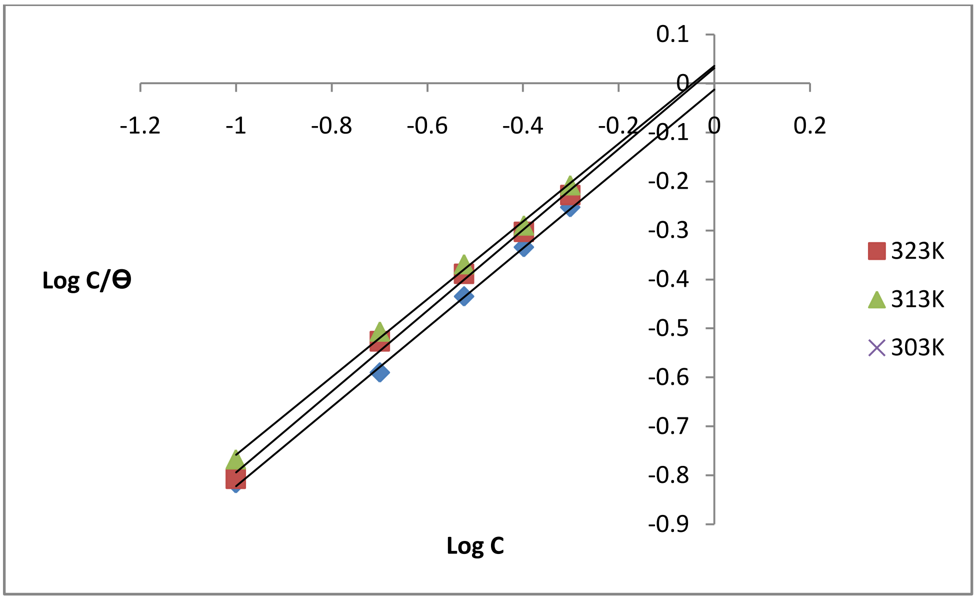

Figure 5: Langmuir Isotherm for the Adsorption of the Inhibitor on the alloy Surface at Various Temperatures

Table 3: Adsorption isotherm parameters for adsorption of *Borreria stachydea* Extract

Inhibitor Concentration (g/l)	ΔG at 303K	ΔG at 313K	ΔG at 323K
0.1	17.53	17.97	17.89
0.2	17.33	16.52	16.67
0.3	16.91	16.24	16.31
0.4	17.08	16.52	16.64
0.5	17.26	16.69	16.48

4. Conclusion

From the results of weight loss of corrosion rate of Al-Si-Mg alloy in simulated seawater using *Borreria stachydea* leave extract as corrosion inhibitor, the following conclusions were drawn:

- The corrosion rate in the presence of *Borreria stachydea* leave extract decreases with increase in the concentration of the inhibitor
- The extract of ***Borreria stachydea* leave** can be used as inhibitor for Al-Si-Mg alloy in simulated seawater environment
- The performance of the extract was found to increase as the concentration of the extract increases, but decreased with temperature rises.
- It has been established that the adsorption process followed a physisorption.

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