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Corrosion Inhibition of Aluminium Alloy in 0.75 M KOH Alkaline Solution Using *Xylopia aethiopica* Seed Extract

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Author's contribution

This work was carried out in collaboration between both authors. Authors OFN and EO designed the research. Author OFN performed the experiment, data collection and analysis. First draft was written by author OFN. Author EO managed the second draft. Both authors read and approved the final manuscript.

Original Research Article

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ABSTRACT

The present study investigated the corrosion inhibition of Al alloy in 0.75 M KOH solution at room temperature using *X. aethiopica* seed extract. Gravimetric technique was employed in the study. It was revealed that the presence of the spice extract in the test solution retards the corrosion rate. The calculated inhibition efficiency from the inhibitor surface coverage was observed to increase linearly with the inhibitor concentration. The consideration of the Langmuir adsorption isotherm indicated that the mechanism of adsorption is Physisorption. Temkin isotherm models explained that there were lateral attractions of the inhibitor molecules on the Al alloy surface. Flory-Huggins isotherm model confirms that there is bulky displacement of water molecules on the metal surface due to the presence of the inhibitor molecules.

Keywords: Corrosion inhibition; Xylopia aethiopica; adsorption isotherm.

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1. INTRODUCTION

Aluminum (Al) is one of the most abundant elements in the earth's crust. Al and its alloys has unique properties such as light weight, high strength, good resistance to corrosion, etc. and these make it ideal for use in convectional and novel applications. The applications site of Al make it to yield to corrosion attack despite its corrosion resistance. The aim of alloying is to enhance the desired properties possessed by the Al.

Corrosion phenomena, control and prevention are unavoidable major scientific issues that must be addressed daily as far as there are increasing needs of metallic materials in all facets of technological development. Corrosion inhibition later formed one of the most practical methods for protecting metals against corrosion [1]. Chemical inhibitors have been very effective in addressing this among other corrosion protection methods although the toxic effects to the environment, have been recorded which opens door to the use of green inhibitors.

Recently, plant extracts have again become important as an environmentally acceptable, readily available and renewable source for a wide range of needed inhibitors [2]. Plants extracts are viewed as an incredible rich source of naturally synthesize chemical compounds that can be extracted by simple procedure with low cost. Thus green plants have gained prominence in corrosion studies. Several investigations have been reported using plants extract. Some of the green plants reported in recent time as corrosion inhibitor of metals include: *Cuminum cyminum* [2], *Uvaria chamea* root [3], *Achyranthes aspera* L [4,5], *Cola acuminata* and *Nicotiana* [6], *Delonix regia* [7], *Euphorbia hirta* [8], *Hibiscus Sabdariffa* [9], *Verninia amygdalina* [10], *Andrographis pa/iculata* [11], Aloe vera [12], *Prosopis cineraria* [13], *Eichhornia crassipes* [14], etc. The common constituents found in those plant extracts investigated as reported by the researchers are: Saponnins, tannins, glycoside, flavoniods, alkaloids, phenols, cardiac, volatile oil, etc.

An attempt at making a contribution to this growing research area has necessitated the present investigation. The present investigation is focused on the use of *Xylopia aethiopica* seed extract as an eco-friendly spice green inhibitor of Aluminum alloy in alkaline environment using gravimetric technique. *Xylopia aethiopica* was considered for the study due to its medicinal value and phytochemical composition. *X. aethiopica* contains the following constituents: cardiac glycoside, flavonoids, phlobatannins, tannins, phenol, anthraquinones, Saponin, steroids, terpenoids and alkaloids [15-17].

2. EXPERIMENTAL DETAILS

2.1 Aluminum Preparation

The aluminum alloy used for the study was obtained form First Aluminum Nigeria Plc. It consist the following element (in %Composition): Al(98.4734), Si(0.45588), Fe(0.75993), Cu(0.06855), Mn(0.11625), Mg(0.01998), Zn(0.05275), Ti(0.01586), Cr(0.00548), Ni(0.00441), V(0.00668), and Pb(0.02079). The metal sheet was cut in to samples of dimension 40 x 20 x 1 mm and used for corrosion studies.

2.2 Preparation of *X. aethiopica* Seed Extract

The procedure for the preparation of the seed extract is similar to that reported by [18] and [5] after separating the seeds from the husk. The *X. aethiopica* was collected from Uzuakoli forest, in Abia State, Nigeria. The seeds were ground to powder form. 10 g of powder stock was digested in 300 ml of 0.75 M KOH solution. The mixture was refluxed for 3 hrs at constant temperature of 338 K. The solution was cooled under atmospheric pressure. The filtrate measured. Then different inhibitive environment prepared in the range 0.1 to 0.5 mg/L.

2.3 Gravimetric Technique

The prepared metal samples were weighed (using FA2104A analytical electronic digital weighing balance: sensitivity of 0.0001) before immersion in 250 ml beaker containing 240 ml of the respective prepared test solutions (0.0, 0.1, 0.2, 0.3, 0.4, and 0.5 mg/L) at room temperature (303 K). The setups were exposed for a period of 3 hrs. The samples were retrieved eye observation made, corrosion reaction process quench in conc. nitric acid digressed in acetone washed under plenty water and air dried and weighed. Triplicate experiments were performed in each case and the mean value reported.

3. RESULTS AND DISCUSSION

3.1 Mass Loss

The mass losses of Al alloy in 0.75 M KOH solutions, with and without different concentrations of the inhibitor were recorded after 3 hours of immersion at room temperature. The corrosion rates of Al alloy were calculated using eq.1

$$CR = \frac{87.6\Delta W}{At\rho} \tag{1}$$

Where ΔW is the mass lost (in grams), 87.6 is a constant, A is the surface area of the coupon (in cm^2), ρ is the density (in g/cm^3), t is the period of exposure (in hours). The calculated corrosion rate fits into the range (less than 0.50 mm/yr) at which the application is acceptable [19].

Fig. 1 shows the variation in mass loss for Al alloy in the absence and presence of inhibitor. The mass loss in the inhibited set up is much smaller than the uninhibited. The significant difference shows reduction impact on corrosion rate of Al alloy in 0.75 M KOH.

The inhibition efficiency and surface coverage were calculated from the mass loss data according to the Equations 2 and 3, respectively. Fig. 2 show the inhibition efficiency in different concentration of the *X. aethiopica* seed extract and it is seen that the %IE increases linearly with the inhibitor concentration at each exposure period.

$$\Theta = \left(1 - \frac{CR_{inh}}{CR_{blank}}\right) \tag{2}$$

$$\%IE = \Theta.100 \tag{3}$$

Where, CR_{blank} is the corrosion rate in the uninhibited environments. CR_{inh} is the corrosion in the inhibited environment. The high inhibition efficiency as the inhibitor concentration increases could be understood to be due to the reduction in corrosion rate. Thus, *X. aethiopoica* could be considered as inhibitor of Al alloy in 0.75 M KOH solution given the high level of inhibition efficiency. The inhibitor efficiency increased with the inhibitor concentration.

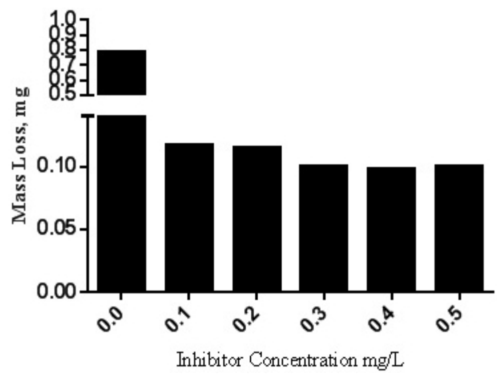

Fig. 1. Mass loss against inhibitor concentration

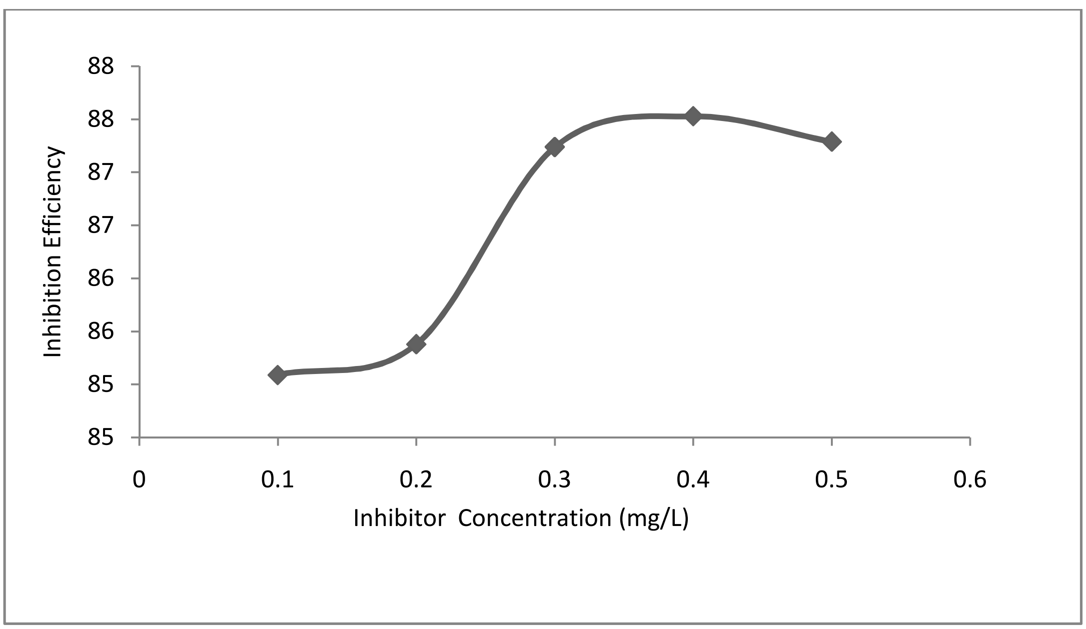

Fig. 2. Variation of inhibition efficiency with inhibitor concentration of *X. aethiopica* on al alloy in 0.75 M KOH

3.2 Adsorption Mechanism

The high efficiency of the inhibitor gives room to the study of the mechanism of inhibition. Adsorption isotherms provide information about the interaction of the adsorbed molecules with the metal surface [20]. Adsorption depends mainly on the charge and nature of the metal surface, electronic characteristics of the metal surface, adsorption of solvent, other ionic species and temperature of corrosion reaction [21,27].

Adsorption of the inhibitor involves the formation of two types of interactions responsible for bonding inhibitor to the metal surface namely: physical adsorption and chemical adsorption. Physical adsorption is weak indirect interaction and is due to electrostatic attraction between inhibiting organic ions or dipoles and the electrically charged surface of the metal. While chemical adsorption occurs when direct forces govern the interaction between adsorbate and adsorbent. Chemical adsorption involves charges charge transfer from adsorbate to the metal surface atoms in order to form a coordinate type bond. Chemical adsorption has a free energy of adsorption higher than physical adsorption and hence, usually it is irreversible [1]. Thus, the inhibition of metal corrosion by organic compounds is attributed to either the adsorption of inhibitor molecule or the formation of a layer of insoluble complex of the metal on the surface which acts as a barrier between the metal surface and the corrosive medium [18].

The relationship between the surface coverage and the inhibitor concentration forms a basis to the study of the mechanism of adsorption isotherm. Attempts were made to fit the Θ values to various isotherms including Langmuir, Temkin, Flory-Huggin, Frumkin and Freundlich. The value of the correlation (R^2) was used to determine the best fit which Langmuir, Temkin and Flory-Huggins reported.

In this study, Langmuir adsorption isotherm was found to be suitable for the experimental findings and has been used to describe the adsorption characteristic of this inhibitor. The Langmuir isotherm is represented in eq. 4 [24,27].

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{4}$$

Where θ is the degree of surface coverage, C is the inhibitor concentration and K_{ads} is the equilibrium constant of the adsorption process. The corresponding Langmuir isotherm is obtained by plotting C/Θ versus C (Fig. 3). The linear relationship of the plot shows that the *X. aethipica* obeys the Langmiur adsorption isotherm. Here, the line has a slope of 1.13, the calculated equilibrium constant of adsorption is 200.0 and correlation (R^2) of 0.9999. The deviation of the slope from unity is indicative of heterogeneous adsorbing species occupying more or less a typical adsorption site at the metal/solution interface [22]. And the value of R^2 is very close to unity indicating a strong adherence to the Langmuir adsorption Isotherm [23]. The equilibrium constant for the adsorption process from Langmuir isotherm is related to the standard free energy of adsorption by the expression [24,21,25,26].

$$\Delta G^0_{ads} = -RTIn(55.5K_{ads}) \tag{5}$$

Where R is the gas constant (8.314 kJ/mol); and T is the temperature (K). The constant value of 55.5 is the concentration of water in solution in mol/l. The value of ΔG^0_{ads}1239 for the inhibitor on the surface of Al alloy is given -23.471kJ/mol. Since ΔG^0_{ads} is very below 40kJ/mol, it explains that the adsorption process is physisorption. The negative value of ΔG^0_{ads} indicated spontaneity adsorption of the inhibitor on the Al alloy surface. The inhibition of the plant molecules could be attributed to the presence of Temkin is an extension of the

Langmuir adsorption isotherm. It elucidates the nature of the interaction on the metal/solution interface. Temkin adsorption isotherm assumes a uniform distribution of adsorption energy which increases with increase of the surface coverage. The characteristics of Temkin isotherm model are given by the eq. 6a.

$$\exp(\mathrm{f}, \Theta) = \mathrm{K_{ads}C} \tag{6a}$$

And it is rearranged

$$\theta = (1/f)LogC + (1/f)LogK_{ads} \tag{6b}$$

Where K_{ads} is the equilibrium constant, C is the inhibitor concentration, Θ is the surface coverage, f is the interaction term parameter (if f > 0, there is a lateral attraction, if f <0, there is a lateral repulsion between the adsorbing molecules). The plot of surface versus Logarithm of the inhibitor concentration (Fig. 4) yields *S*-Shape curve with linear correlation coefficient R^2 = 0.828 close to unity. The obtained value of K_{ads} = 1.3154 x 10^{10}. *f* = 26.3 indicating a very strong lateral attraction between the adsorbing molecules of *X. aethiopica* extract and the surface of the Al alloy.

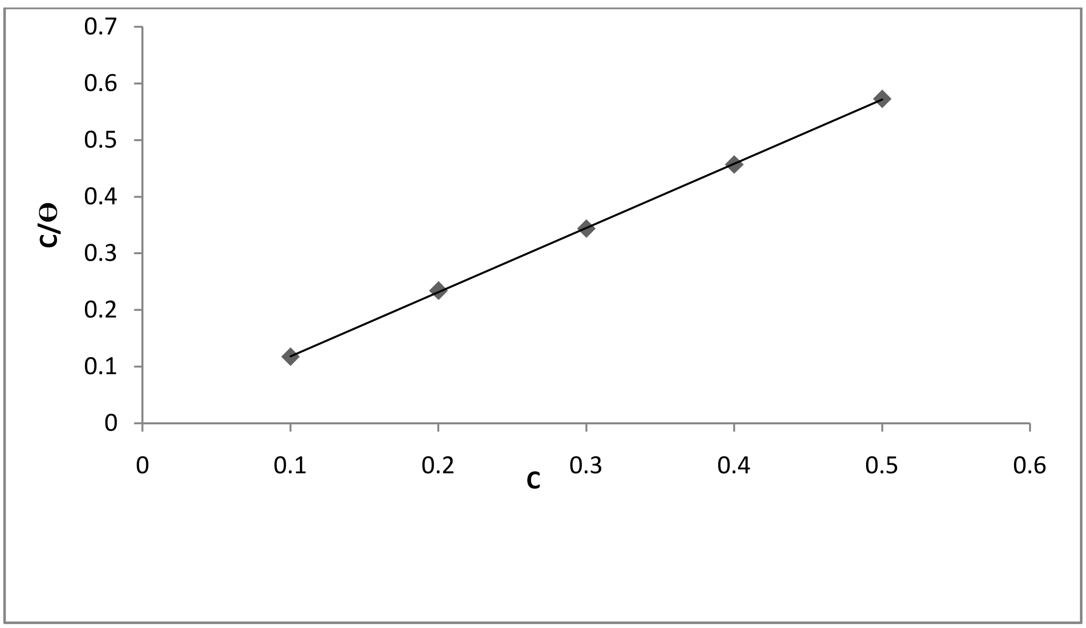

Fig. 3. Langamuir isotherm for the adsorption of *Xylopia aethioipica* seed extract on the surface of al alloy in the alkaline environment

$$Log\ (\theta / C) = Logk + xLog\ (1 - \theta) \tag{7}$$

Flory-Huggins expressed as eq. 7 takes a look at the quantity of the inhibitor molecules that could displace the water molecules from the metal surface [28]. Where 'x' is the size parameter and is a measure of the number of adsorbed water molecules substituted by a given inhibitor molecule. As shown in Fig. 5 the plot of log (Θ/C) against log (1 - Θ) gave a linear relationship (slope 6.587) with R^2 = 0.817, showing that Flory-Huggins isotherm was obeyed. The obtained K_{ads} = 522.69 and the calculated ΔG_{ads}^{0} = -25.885kJ/Mol. The size parameter is approximately 7.

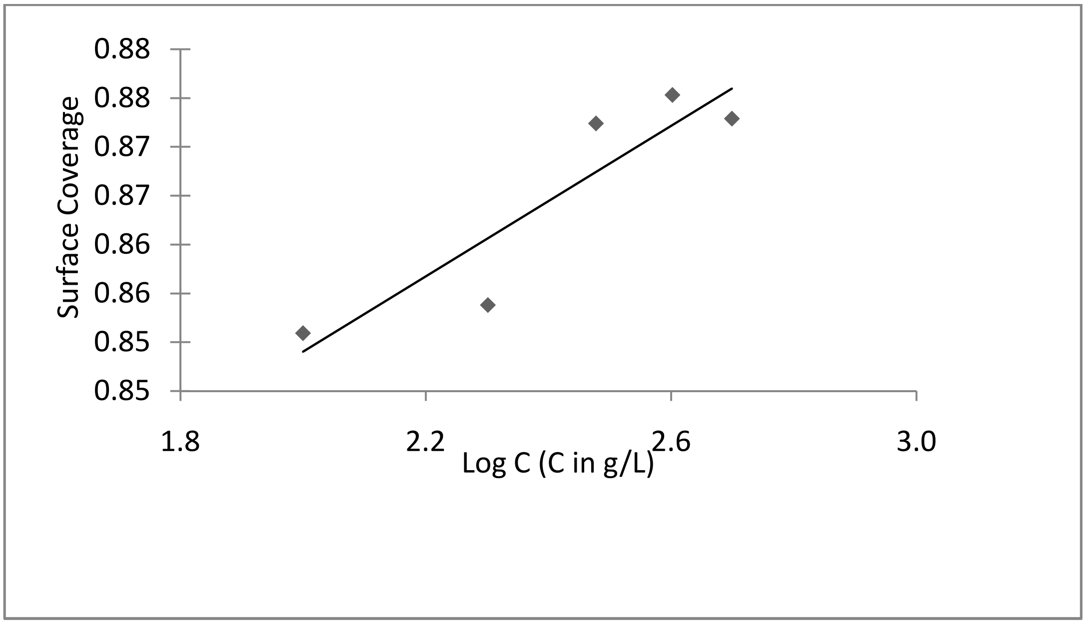

Fig. 4. Temkin isotherm for the adsorption of *Xylopia aethiopica* seed extracts on the surface of Al alloy in the alkaine environment

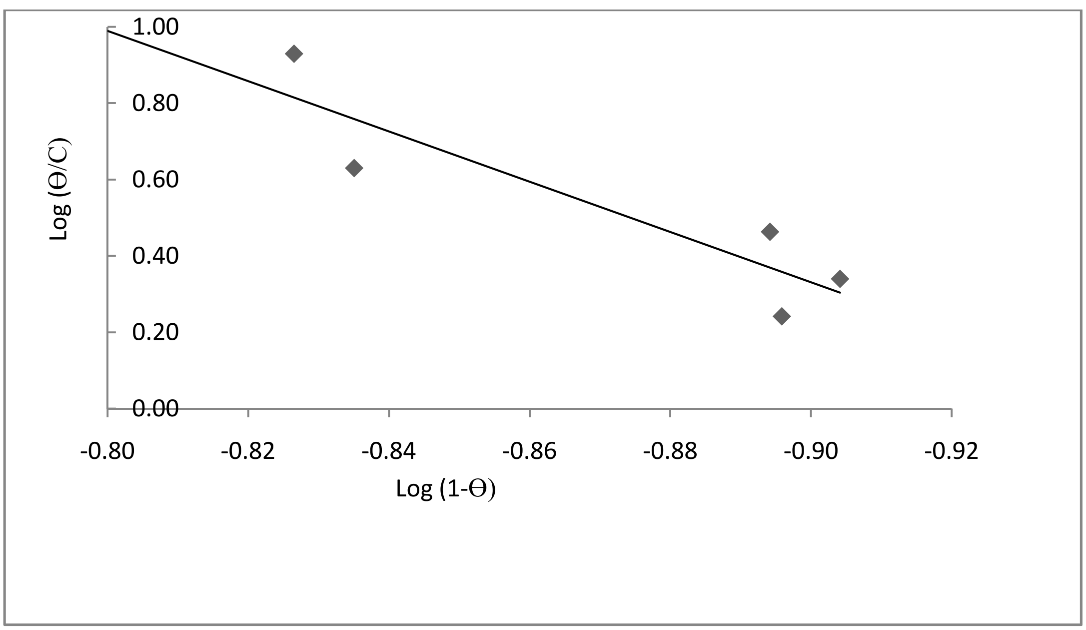

Fig. 5. Flurry-Huggins adsorption isotherm for adsorption of *Xylopia aethiopica* seed extract on the surface of Al alloy in the alkaline environment

4. CONCLUSION

This present study found that *X. aethiopica* seed extract inhibits the corrosion process of Al alloy in 0.75 M KOH solution at room temperature. The inhibition efficiency of the spice extracts increases linearly with the inhibitor concentration. An optimal inhibition efficiency of 84.53% was recorded. The study on the models of adsorption mechanisms revealed that Langmuir, Temkin, and Flory-Huggins adsorption isotherm were obeyed. The experimental data best fit the Langmuir adsorption isotherm. The adsorption mechanism of the inhibitor on the Al alloy surface is through Physical adsorption. The calculated Gibb's free energy showed that the inhibition process is spontaneous. There are lateral attractions between the inhibitor molecules on the Al alloy surface following the Temkin isotherm model. This depicts that the spice constituents clustered on the Al alloy surface preventing contact with the corrosive environment.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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