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Eco-Friendly Corrosion Inhibition of Aluminum Alloys with *Acacia nilotica* in Acidic Media

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Abstract

Gravimetric analysis was used to examine the corrosion inhibitory effects of Acacia nilotica extract in 0.5 N H_2SO_4 on aluminum alloy at different concentrations and at 303 K. At a corrosion inhibitor concentration 0.45% at 303 K, the inhibition efficiency is found to be remarkably high (52.25%). Results show that the extract's capacity to inhibit was caused by its adsorption onto the metal surface via the Langmuir adsorption process. For characterization of the Al alloy, the Scanning Electron Microscope (SEM) was employed. It was discovered that the extract gets adsorbed spontaneously on the aluminum or Al alloy surface. As the concentration of extract increases, so does the efficiency of inhibition. Thermodynamic and kinetic parameters including entropy, free energy, and enthalpy of adsorption, were ascertained. It was shown to be exothermic, physical, and spontaneous. The phytochemical components of the Acacia nilotica extract were found to have a high protective influence and are probably responsible for forming a barrier of protection on the metal surface. The best-fitting Langmuir adsorption isotherm on the surface of aluminum has been determined to be an inhibitor adsorption. Thermodynamic and kinetic characteristics showed that the inhibitor and metal surface interacted strongly. The fruit extract of Acacia nilotica contains a high level of protection due to the presence of phytochemicals such as terpenoids, alkaloids, glycosides, saponins, tannins, nitrogen, phosphorus, gallic acid, chlorogenic acid, alkylated flavan-3,4-diol (leucoanthocyanidin), and catechin. Because the fruit extract from Acacia nilotica is non-toxic and biodegradable, its use could lower the financial burden of corrosion monitoring while also lessening the environmental risks that follow. It was discovered that in a sulfuric acid solution, Acacia nilotica extract effectively protects aluminum or aluminum alloy from pitting corrosion.

Keywords: *Acacia nilotica*, adsorption, aluminium, SEM, sulphuric acid

INTRODUCTION

Aluminum is the sole metal that, although being thermodynamically reactive, can shield itself from corrosion by creating an amphoteric oxide coating, which shields it from additional assault when exposed to aggressive media. When exposed to extremely hostile media with a pH of either less than 5 or more than 9, the protective oxide coatings on aluminum and its alloys dissolve and cause corrosion [1, 2]. Aggressive media may encounter aluminum due to a variety of industrial applications. A few of these include the processes of pickling, anodizing (surface treatments), and metal cleaning/descaling, which call for the use of acids such as H_2SO4, HCl, and H_3PO_4 [3, 4].

Studies show that phytochemicals containing heteroatoms like S, O, and N are abundant in plant extracts, which makes them active in generating inhibitory characteristics [5].

The progressive and spontaneous breakdown of a substance caused by an electrochemical or chemical

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oxidizing process is known as corrosion. We must believe in deterioration in its authentic or fundamental form since the process of corrosion returns metal to its initial state. Corrosion failure is thus defined as the degradation of metals due to factors other than mechanical causes [6].

"Corrosion is an irreversible interfacial reaction among the material [metal, polymer (rubber, plastic, etc.) and ceramic (bricks, concrete, etc.)] and its surrounding corrosive environment which results in its disintegration or consumption into the component material of the environment," states the International Union of Protected Polymers (IUPAC) the chemical or electrochemical reaction that breaks down metal when it comes into contact with chemicals, moisture, weathering, or other agents or media.

Corrosion is the destructive attack that a metal or metal alloy undergoes due to a chemical or electrochemical reaction with its environment [7].

According to the NACE International definition, corrosion is the unfavorable response (process) between a material, usually metal, and its surroundings that deteriorates the material or its qualities. From being irreversible and degenerative, it also affects the Second Law of Thermodynamics.

ELECTROCHEMICAL THEORY OF CORROSION

Electrochemical theory has been used by many researchers to assess the efficacy of different corrosion mitigation strategies, and by others to investigate the corrosion activity of different systems [8–11].

The Nearnst and Tafel equations, together with the mixed potential theory of corrosion, provide the foundation of the contemporary electrochemical theory of corrosion [12]. Today, this theory is widely accepted, and its foundations can be used to explain corrosion in most cases.
In line with this theory, it combined two theories.

1. Every electrochemical reaction is divided into at least two fractional processes.
2. There cannot be a net buildup of electric charge during an electrochemical reaction of corrosion.

Consequently, the overall rate of reduction and the overall rate of oxidation must coincide in any corrosion process (reaction). Electrochemical reactions consist of two or more partial oxidation or reduction reactions, according to experimental data. Metal oxidation or de-electronation is defined as an anodic reaction. It can be stated as:

$$M \rightarrow Mn^{+} + n\ e^{-} \quad (1)$$

Cathodic reactions, also known as reduction or electron-consuming reactions, can take many different forms based on the metal's surrounding environmental conditions. A few typical ones are:

$$\text{Hydrogen evolution: } 2\ H^{+} + 2\ e^{-} \rightarrow H_2 \quad (2)$$

$$\text{Oxygen reduction: } O_2 + 4\ H^{+} + 4\ e^{-} \rightarrow 2\ H_2O \quad (3)$$

(In acidic solutions)

$$\text{Oxygen reduction: } O_2 + H_2O + 4\ e^{-} \rightarrow 4\ OH^{-} \quad (4)$$

(In basic or neutral solutions)

$$\text{Metal ion reduction: } M^{3+} + e^{-} \rightarrow M^{2+} \quad (5)$$

$$\text{Metal deposition: } M^{+} + e^{-} \rightarrow M \quad (6)$$

A common cathodic reaction, hydrogen evolution (2) occurs because acidic or acid media are frequently encountered. While metal ion reduction (5) and deposition (6) are less frequent, oxygen reduction reactions (3, 4) are also frequent since any aqueous solution exposed to air is worthy of creating this reaction. An aerated acidic solution can undergo one of two cathodic reactions: the

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evolution of hydrogen or the reduction of oxygen. Thus, aerated solutions become increasingly corrosive, regardless of the dissolution of aluminum (Al) in an acidic aerated solution.

The anodic reaction is

$$Al \rightarrow Al^{3+} + 3\ e^{-} \quad (7)$$

and the reactions occurring at cathodic sites are:

$$2\ H^{+} + 2\ e^{-} \rightarrow H_{2(g)} \quad (8)$$

$$O_2 + 2\ H_2O + 4\ e^{-} \rightarrow 4\ OH^{-} \quad (9)$$

A single Al^{3+} ion enters solution and leaves three electrons on the metal surface, according to equation (7). The characteristic potential for the Al / Al^{3+} is caused by the electrical double layer, which separates the charges.

Equations (8) and (9), which include H_2 / H^+ and O_2 / OH^-, have comparable half-cell relationships. By reversing the process of equation (7), this potential change tends to obstruct the deposition of dissolved metal ions from the solution on the metal. If the metal ions continue to be deposited and disintegrated, they will eventually reach a stable potential where the rate of deposition will equal the rate of dissolution at equilibrium. This will also result in a balancing cathodic current for the reduction of Al^{3+} ions to Al (metal).

$$E_r = E^0 + \frac{RT}{nF} \ln \frac{a_{(oxidized)}}{a_{(reduced)}} \quad (10)$$

where 'T' is the absolute temperature, 'n' is the number of electrons engaged in the reaction, 'R' is the universal gas constant, and 'a' denotes the activity of the corresponding state.

One species of acacia tree in the Leguminosae family is *Acacia nilotica*. The plant extract from *Acacia nilotica*, which tested positive for tannins, showed corrosion inhibition intensities comparable to those of gallic acid. These organic plant ingredients have a wide range of applications as corrosion inhibitors due to their non-toxicity, anti-microbial qualities, and sustainable sources of production. It offers aluminum effective corrosion protection. The pod of *Acacia nilotica* contains terpenoids, alkaloids, glycosides, tannins, saponins, nitrogen, and phosphorus in an alcoholic extract. The pods have been shown to contain gallic acid, chlorogenic acid, alloylated flavan-3, 4-diol (leucocyanidin), and catechin [13–14].

Because the extract from the fruits of *Acacia nilotica* is non-toxic and biodegradable, its usage could potentially lower the financial burden of corrosion monitoring while also lessening the ensuing environmental risks.

Numerous scientific investigations have been conducted about the corrosion of aluminum and the use of natural products, such as *Tamarindus indica* [15], *Piper nigrum* [16], *Acacia nilotica* [17], and *Azadirachta indica* [18], as corrosion inhibitors for aluminum in acidic media.

In the current work, a 12-hour immersion period's impact on the inhibitive tendency of *Acacia nilotica* extract for acid corrosion of aluminum has been examined.

EXPERIMENTAL

Preparation of Test Coupons

To hang in the test solution, a 0.12 mm diameter hole was positioned near the upper edge of a 2.54 × 1.52 cm^2 coupon made from a locally produced aluminum sheet with a thickness of 0.18 cm, which was mechanically cut. Emery paper was used to polish coupons to a mirror shine.

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Test solutions & Experimentation

By using bi-distilled water, electrolytic solutions of 0.5N H_2SO_4 were created. Every chemical used was a reagent of analytical purity. The dried fruits were refluxed in a Soxhlet extractor to obtain the ethanolic extract of *Acacia nilotica*. Every specimen was suspended using a glass hook and submerged in a beaker that had 50 milliliters of the test solution and various inhibitor concentrations. The experiment was carried out in an immersion tank at 303 K for 12 hours. Test specimens were rinsed under running water after predetermined exposure times, and they were allowed to dry by hanging them in desiccators for an adequate amount of time [19, 20].

RESULTS AND DISCUSSION

Weight Loss Studies

Table 1 indicates the value of inhibition efficiency (η%), fractional surface coverage (θ), corrosion rate (ρ_{corr}), Adsorption equilibrium constant (K_{ads}) obtained at varying concentration of the inhibitors in 0.5N H_2SO_4 acid solution for an immersion period of 12 hours at 303 K temperature.

From the mass loss value (ΔM), the inhibition efficiency (η%) was calculated applying the following equation (Figure 1).

$$\eta\% = [\ (\Delta M_u - \Delta M_i) / \Delta M_u] \times 100$$

where ΔM_u is mass loss without inhibitor and ΔM_i is weight loss with inhibitor.

The following equation [21] can be used to calculate the corrosion rate (ρ_{corr}) in millimeter penetration per year (mmpy).

$$\rho_{corr} = (\Delta M \times 87.6) / \text{area} \times \text{time} \times \text{metal density}.$$

where the metal density is expressed in gm/cm^3, the time of exposure is expressed in hours, the area of exposed metal surface is expressed in cm^2, and the weight loss in mg is expressed as ΔM.

Table 1. Kinetic parameters on corrosion of aluminum in 0.5N H_2SO_4 with ethanolic extract of varying concentration of fruit, stem bark and root bark of *Acacia nilotica* at 303 ± 0.1 K.

Inhibitor Concentration (%)	**Mass Loss ΔM (mg)**	**Corrosion Rate (mmy^{-1})**	**Fractional Surface Coverage (θ)**	**Inhibition Efficiency (η %)**	**log $(\frac{\theta}{1-\theta})$**
Uninhibited	83.6	29.27	–	–	–
Fruit extract					
0.09	52.2	18.28	0.3755	37.55	–0.2209
0.18	47.1	16.49	0.4366	43.66	–0.1107
0.27	41.3	14.46	0.5059	50.59	0.0102
0.36	29.4	10.29	0.6483	64.83	0.2655
0.45	19.3	6.75	0.7691	76.91	0.5225
Stem bark extract					
0.09	54.7	19.15	0.3456	34.56	–0.2772
0.18	49.5	17.33	0.4078	40.78	–0.1620
0.27	43.6	15.26	0.4784	47.84	–0.0375
0.36	33.3	11.66	0.6016	60.16	0.1789
0.45	21.8	7.63	0.7392	73.92	0.4524

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Root bark Extract					
0.09	55.3	19.36	0.3385	33.85	–0.2909
0.18	51.6	18.07	0.3827	38.27	–0.2076
0.27	45.8	16.04	0.4521	45.21	–0.0834
0.36	35.7	12.50	0.5729	57.29	0.1275
0.45	24.5	8.58	0.7069	70.69	0.3823

Effective area of specimen: 7.72 cm^2.
Immersion period: 12 hours.

Figure 1 shows variation of inhibition efficiency with concentration of fruit, stem bark and root bark extract of *Acacia nilotica* for aluminum in 0.5N H_2SO_4 at 12 hours immersion period and Figure 2 shows Langmuir adsorption isotherm curve for aluminum in 0.5N H_2SO_4 with fruit, stem bark and root bark extract of *Acacia nilotica* at 12 hours immersion period.

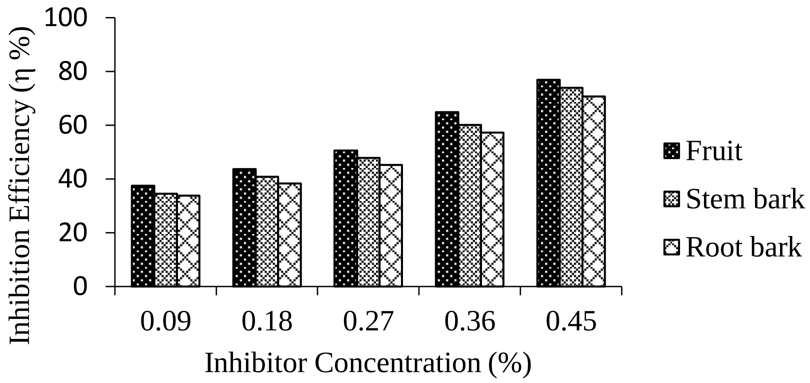

Figure 1. Variation of inhibition efficiency with concentration of fruit, stem bark and root bark extract of *Acacia nilotica* for aluminum in 0.5N H_2SO_4 at 12 hours immersion period.

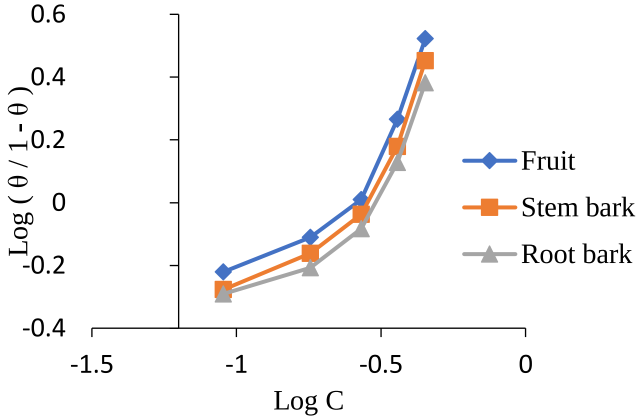

Figure 2. Langmuir adsorption isotherm curve for aluminum in 0.5N H_2SO_4 with fruit, stem bark and root bark extract of *Acacia nilotica* at 12hrs immersion period.

SEM Analysis

The SEM images of pure aluminum metal and aluminum metal in 0.5N H_2SO_4 are shown in Figures 3 and 4 respectively. The SEM image for aluminum in 0.5N H_2SO_4 with *Acacia nilotica* extract is shown in Figure 5.

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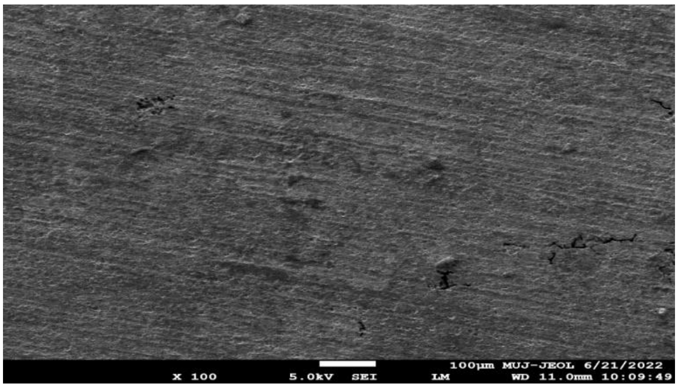

Figure 3. SEM image of pure aluminum metal.

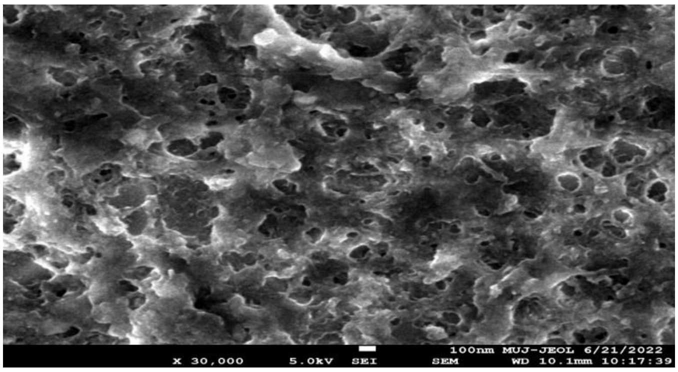

Figure 4. SEM image of aluminum in 0.5N H_2SO_4

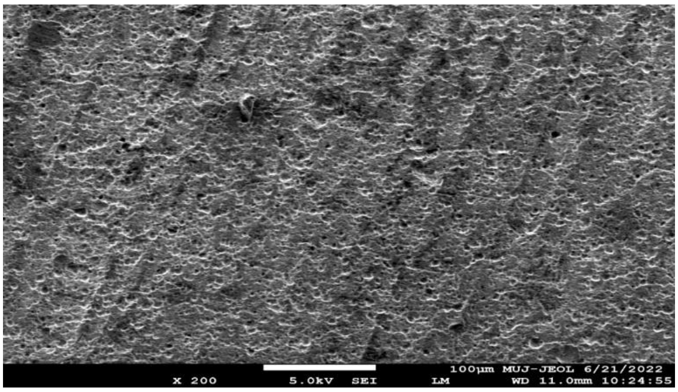

Figure 5. SEM image of aluminum in 0.5N H_2SO_4 with *Acacia nilotica* extract.

CONCLUSIONS

Based on the findings of the investigation of combating aluminum alloy dissolution by using *Acacia nilotica* extract in 0.5N H_2SO_4 acid, the following conclusions may be made.

Fruit extract from *Acacia nilotica* may effectively prevent aluminum from corroding in 0.5N H_2SO_4 acid during a 12-hour immersion period at 303 K. The maximal inhibitory efficiency of the extract is 769.91% at a concentration of 0.45%.

There was an increase in the rate of corrosion at high temperatures, but the addition caused a discernible drop in the rate of corrosion. The extract spontaneously adhered to the Langmuir adsorption isotherm at 303 K when it adsorbs to aluminum.

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Entropy of adsorption decreases with increase in *Acacia nilotica* extract indicates association of inhibitor molecules.

Overall, it can be said that the extract from *Acacia nilotica* can be utilized as a green inhibitor in place of harmful chemicals to stop the corrosion of aluminum in 0.5N H_2SO_4 acid at 303 K.

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