Effect of Drying Method on Phytochemical Compositions and Inhibition Efficiency of Alchornea Laxiflora and Mucuna Flagellepes Leaves Extracts in Corrosion Prevention

Adebayo Oluwafemi Lawrence¹, ⁴, *, Emmanuel Folorunso Olasehinde², Labunmi Lajide², Daniel Oloruntoba³

¹Department of Chemical and Process Engineering, University of Strathclyde, Glasgow, United Kingdom
²Department of Chemistry, Federal University of Technology, Akure, Nigeria
³Department of Metallurgical and Materials Engineering, Federal University of Technology, Akure, Nigeria
⁴Chemistry Department, College of Education, Ikere, Nigeria

Email address: femtay41@yahoo.co.uk (A. O. Lawrence)
*Corresponding author

To cite this article:
Adebayo Oluwafemi Lawrence, Emmanuel Folorunso Olasehinde, Labunmi Lajide, Daniel Oloruntoba. Effect of Drying Method on Phytochemical Compositions and Inhibition Efficiency of Alchornea Laxiflora and Mucuna Flagellepes Leaves Extracts in Corrosion Prevention. American Journal of Physical Chemistry. Vol. 8, No. 2, 2019, pp. 32-40. doi: 10.11648/j.ajpc.20190802.11

Received: June 15, 2019; Accepted: July 13, 2019; Published: August 13, 2019

Abstract: This study was aimed at investigating the influence of different drying methods on the phytochemical composition and inhibition efficiency of Alchornea laxiflora and Mucuna flagellepes leaves extracts in corrosion prevention. The fresh samples of the leaves were collected, sorted, dried using two different drying methods viz; air drying and sun drying methods. The dried plant samples were ground separately sieved using 0.25µm and then extracted with ethanol using maceration method and then concentrated the filtrate in a water bath at 60°C to obtained air dried Alchornea laxiflora leaves (AALL), air dried Mucuna flagellepes leaves (AMFL), sun dried Alchornea laxiflora leaves (SALL) and sun dried Mucuna flagellepes leaves (SMFL) extracts. The extract of each sample was analyzed separately for their phytochemical constituents using appropriate methods. From the results, there was variation in the composition in respect of the phytochemical of interest but it could be concluded that the drying methods have little effect on the phytochemical composition of the studied plant but air drying methods could be adopted as it gave highest content (AALL: Saponin 45.55 mg/g, tannin 10.58mg/g, flavnoid 7.49mg/g, Terpenoid 7.06 mg/g, Alkaloid 35.61mg/g, phytobalatin 2.43mg/g and cardiac glycoside 4.72mg/g; AMFL: Saponin 28.55mg/g, Tannin 5.39 mg/g, Flavonoid 6.42 mg/g, Terpenoid 5.94 mg/g, Alkaloid 4.53mg/g, Cardiac glycoside 6.33 mg/g; SALL: Saponin 20.00mg/g, Tannin 4.04 mg/g, Flavonoid 1.91 mg/g, Terpenoid 6.03 mg/g, Alkaloid 12.56 mg/g, Phytobalatin 2.57 mg/g, Cardiac glycoside 3.86mg/g; SMFL: Saponin 15.00 mg/g, Tannin 3.82 mg/g, Terpenoid 4.82 mg/g, Alkaloid 6.25 mg/g and cardiac glycoside 4.93 mg/g. The corrosion inhibition efficiency of the samples extract on mild steel in 1.0M HCl solution was investigated using weight loss measurements. The weight loss measurement indicates an increase in corrosion inhibition efficiencies that reach 90.02% and 84.92% in AALL and AMFL extract and 79.74% and 72.12 in the SALL and SMFL extract respectively. The weight loss data established that the inhibition efficiency on mild steel increases with increase in the concentration of the plant extracts but decreased with increase in temperature. Thermodynamic parameters such as enthalpy change, entropy change, and activation energy were evaluated. Kinetics of the reaction in the presence of the extracts revealed that it follows a first order reaction and the half-life increased as the concentration of the extract increases.

Keywords: Alchornea Laxiflora Leaves, Mucuna Flagellepes Leaves, Phytochemical, Corrosion, Thermodynamics, Kinetics
1. Introduction

The term corrosion can be defined as the interaction (electrochemical reaction) of a metal with the surrounding environment, causing a slow, steady, and irreversible deterioration in the metal, in both physical and chemical properties [1]. The corrosion causes very important material and economical losses due to partial or total replacement of equipment and structures, and plant-repairing shutdowns. Corrosion not only has economic implications, but also social and these affect the safety and health of people either working in industries or living in nearby towns [2].

Mild steel, also known as plain-carbon steel, is now the most common form of steel because its price is relatively low, while it provides material properties that are acceptable for many applications [3]. However, the challenge is that it has low corrosion resistance especially in acidic environments [4]. Industrial processes such as acid cleaning, pickling, descaling, and drilling operations in oil and gas exploration [4]. Industrial processes such as acid cleaning, pickling, descaling, and drilling operations in oil and gas exploration [4]. Industrial processes such as acid cleaning, pickling, descaling, and drilling operations in oil and gas exploration [4]. Industrial processes such as acid cleaning, pickling, descaling, and drilling operations in oil and gas exploration [4]. Industrial processes such as acid cleaning, pickling, descaling, and drilling operations in oil and gas exploration [4]. Industrial processes such as acid cleaning, pickling, descaling, and drilling operations in oil and gas exploration [4]. Industrial processes such as acid cleaning, pickling, descaling, and drilling operations in oil and gas exploration [4]. Industrial processes such as acid cleaning, pickling, descaling, and drilling operations in oil and gas exploration [4]. Industrial processes such as acid cleaning, pickling, descaling, and drilling operations in oil and gas exploration [4]. Industrial processes such as acid cleaning, pickling, descaling, and drilling operations in oil and gas exploration [4]. Industrial processes such as acid cleaning, pickling, descaling, and drilling operations in oil and gas exploration [4]. Industrial processes such as acid cleaning, pickling, descaling, and drilling operations in oil and gas exploration [4].

Natural products such as plant extract, amino acids, proteins, and biopolymers have been reported to be efficient corrosion inhibitors [7]. Plant extracts are viewed as rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost [8]. These natural extracts are analogues to the synthetic organic inhibitors and are being proven to work as much as their synthetic counterparts. However, the drying techniques are important in sample preparation and preservation. By reducing the moisture content less than 15%, drying helps to prevent any microbial growth. In fact, efficient drying techniques will enhance the quality of dried and the filtrate obtained was put in a vacuum rotary evaporator at a temperature of 54-60°C to obtain both the air dried and sun dried Alchornea laxiflora and Mucuna flagellepes concentrate which was kept in a brown bottle prior for use.

2.2. Plants Extraction with Ethanol

The Alchornea laxiflora and Mucuna flagellepes leaves were obtained from the vicinity of Federal Polytechnic Ado, Ekiti State, Nigeria and were authenticated at the Department of Biology, College of Education, Ikere, Ekiti State, Nigeria. The leaves were washed, some section of it were air-dried at room temperature while the remaining ones were sun dried. Both air and sun dried leaves were ground and sieved through a 850µm mesh. The samples were later extracted with Ethanol by Maceration method [13]. After three days, the mixture was pressed by filtration through a 0.25µm mesh and the filtrate obtained was put in a vacuum rotary evaporator at a temperature of 54-60°C to obtain both the air dried and sun dried Alchornea laxiflora and Mucuna flagellepes concentrate which was kept in a brown bottle prior for use.

2.3. Weight Loss Measurement

In weight loss experiment, a previously weighted metal coupon was completely immersed in 100 ml of 1.0 M HCl in the absence and presence of different concentration of the inhibitors with the aid of glass hooks at room temperature. After every 4 hours each coupon was withdrawn from the test solution, and the corrosion product was removed by washing each coupon in distilled water, rinsed in acetone and dried completely using nitrogen gas before re-weighing. From the initial and final weights of the mild steel, the weight loss, corrosion rate (CR, g/hr/cm²) in absence and presence of inhibitors, inhibition efficiency (%) of the inhibitors and the degree of surface coverage (θ) were calculated using equations 1, 2 and 3 respectively [14]. The experiment was repeated at different temperature (303, 313, 323 and 333K).

\[
CR = \frac{\Delta w}{At} \quad (1)
\]

Inhibition Efficiency = \left[1 - \left(\frac{CR_2}{CR_1}\right)\right] \times 100 \quad (2)

Surface Coverage (\theta) = \left[1 - \left(\frac{CR_2}{CR_1}\right)\right] \quad (3)

Where \Delta w is the weight loss in grams, CR1 and CR2 are...
the corrosion rates of the mild steel strip coupons in absence and presence of inhibitor, A is the cross-sectional area of the mild steel in cm² and t is the exposure time in hours.

2.4. Determination of the Phytochemical Constituents

The phytochemical screening of the plants extracts was carried out by simple qualitative and quantitative methods used by earlier researchers [15-19].

3. Results and Discussion

3.1. Phytochemical Analysis

| Phytochemicals      | AALL | AMFL | SALL | SMFL |
|---------------------|------|------|------|------|
| Saponin (mg/g)      | 45.55| 28.55| 20.00| 15.00|
| Tannin (mg/g)       | 10.58| 5.39 | 4.04 | 3.82 |
| Flavonoid (mg/g)    | 7.49 | 6.42 | 1.91 | -    |
| Terpenoid (mg/g)    | 7.06 | 5.94 | 6.03 | 4.82 |
| Alkaloid (mg/g)     | 35.61| 4.53 | 12.56| 6.25 |
| Anthraquinone       | -    | -    | -    | -    |
| Cardiac glycoside   | +    | -    | +    | +    |
| Legal test          | +    | +    | +    | +    |
| Killiani test       | +    | +    | +    | +    |
| Lieberman test      | -    | -    | -    | -    |
| Salkowski test      | -    | +    | +    | +    |

Table 2. Quantitative phytochemical screening of air and sun dried Alchornea laxiflora and Mucunna flagellepes leaves extracts.

| Phytochemicals      | AALL | AMFL | SALL | SMFL |
|---------------------|------|------|------|------|
| Saponin (mg/g)      | 4.72 | 6.33 | 3.86 | 4.93 |
| Tannin (mg/g)       | -    | -    | -    | -    |
| Flavonoid (mg/g)    | -    | -    | -    | -    |
| Terpenoid (mg/g)    | -    | -    | -    | -    |
| Alkaloid (mg/g)     | -    | -    | -    | -    |
| Anthraquinone       | -    | -    | -    | -    |
| Cardiac glycoside   | +    | -    | +    | +    |

Figure 1. Plot of corrosion rate of mild steel in 1.0 M HCl against different concentrations of the leaves extract.

3.2. Effects of Extracts Concentration on Corrosion Rate

The loss in weight which is expressed as the corrosion rate of the mild steel in 1.0 M HCl solutions in the absence and presence of different concentrations of air dried and sun dried Alchornea laxiflora and Mucunna flagellepes leaves extract as a function of inhibitor concentration is presented in Figure 1. These plots are in accordance with the works of earlier researchers [24 –26]. It was observed that the corrosion rates of the mild steel decreased with respect to the quantity of the phytochemical composition of the extracts and its concentration, indicating that the extent of inhibition is dependent on the amount of extract present [27].

3.3. Effect of Extract Concentrations on Inhibition Efficiency

As observed in Figure 2, that the inhibition efficiencies of the extracts increases with increase in both air dried and sun dried sample concentration. This indicates that the phytochemical components of the extracts are adsorbed onto the metal surface resulting in the blocking of the reaction sites, and protection of the mild steel surface from the attack of the corrosion active ions in the acid medium [28, 30]. Comparing the maximum inhibition efficiencies of the extract on the mild steel, it is observed that the efficiencies follow the trend: AALL (90.02%) > AMFL (84.92%) > SALL (79.74%) > SMFL (77.12). This shows that the yield of the phytochemicals in the plant extracts responsible for the inhibition of the corrosion reactions depend not only on the plant type but also on the drying method. This finding is in line with previous reports [4, 31, 32].
3.4. Effect of Temperature on Inhibition Efficiency

The effects of temperature on the inhibition efficiency of all the samples extract on mild steel are shown in Figure 3. It is evident from the figure that as the reaction temperature increases from 303-333K, the inhibition efficiency decreases. This is expected because many changes may occur on the metal surface, such as rapid etching, rapture, desorption of the inhibitor, decomposition or rearrangement of the inhibitor [33]. This phenomenon is consistent with the mechanism of physical adsorption as reported by earlier researchers [34, 35]. The highest inhibition efficiency recorded at the lowest temperature and highest concentration studied for all the extracts are 88.67, 84.00, 79.87 and 71.70 for AALL, AMFL, SALL and SMFL extracts respectively.

3.5. Effect of Temperature on Corrosion Rate

The effect of temperature on the inhibited acid–metal reaction is very complex, because many changes occur on the metal surface such as rapid etching, desorption of inhibitor and the inhibitor itself may undergo decomposition [36]. The effect of temperature on the corrosion rate of mild steel in

![Figure 2. Plot of Inhibition Efficiency of the air dried and sun dried leaves extracts against their Concentrations at room Temperature.](image)

![Figure 3. Plot of inhibition efficiency of (a) AALL and AMFL (b) SALL and SMFL leaves extract against their Concentration at different temperature.](image)

![Figure 4. Plot of Corrosion rate of mild steel in 1.0M HCl in the absence and presence (a) AALL and AMFL (b) SALL and SMFL leaves extract at different Temperature.](image)
blank solution and in the presence of different concentrations of the inhibitors at the temperature range 303K–343 K is shown in Figure 4. It was found that the rate of corrosion of mild steel in the blank and inhibited acid solution in all the ethanol extract increases with increase in temperature. However, the corrosion rate is much retarded in the solution containing the inhibitor than the blank solution. This is expected because as temperature increases, the rate of corrosion of mild steel also increases as a result of increase in the average kinetic energy of the reacting molecules and the corrosion rate is more pronounced in the sun dried samples than air dried sample. The decrease in the corrosion rate in the solution containing the inhibitor is as a result of the mitigating effect of the phytochemical constituents of the extracts on the corrosion rate of the mild steel [23].

3.6. Effect of Immersion Time

Weight loss measurement was performed in 1.0 M HCl in the absence and presence of the extracts concentration (0.2-1.0g) for 7 days at room temperature. The plot of weight loss against time for all the dried sample extracts (Table 3 and 4) shows that weight loss increases as the immersion time increases in all the ethanol extract but the weight loss is much more pronounced in the ethanol extract of sun dried samples. However, the weight loss is much reduced in the presence of the inhibitor compared to the blank solution. The decrease in weight loss in the presence of inhibitor may be due to the adsorption of the phytochemical constituents in the extract on the surface of the mild steel [23].

3.7. Kinetic Study

The kinetics of the corrosion process acquires the character of a diffusion process, in which at higher temperature, the amount of inhibitor present on the metal surface is much reduced than that present at lower temperature [37]. It is on this basis that kinetic analysis of the data is considered necessary. In this present study, the initial weight of mild steel coupon at time t, is designated Wi, the weight loss is W, and the weight change at time t, (Wi-W,W,) while k, is the first order rate constant.

\[
\ln (Wi - WL) = -kt + \ln WL
\]

According to equation 4, the plots of ln (Wi –WL) against time (days) at room temperature showed a linear variation and the first order reaction rate constants (k) calculated from the slope of the graph and the half-life (t_{1/2}) were presented in Table 5. As observed from the table, there is an increase in the half-lives (t_{1/2}) of all the samples with air dried sample of *Alchornea laxiflora* leaves extracts having the highest values. This finding also aligned with our findings that the mode of drying plant leaves contributes to its efficiency in corrosion prevention. It should also be noted that as the concentration of the extract increases, the half-life also increases which results into a decrease in the corrosion rate suggesting that more protection of the mild steel by the air dried sample of the *Alchornea laxiflora* leaves extract has been established.

3.8. Thermodynamic Studies

Thermodynamic properties such as Activation Energy (Ea), Enthalpy (∆H°) and Entropy of Activation (∆S°) are studied in order to identify the mechanism of adsorption process involved. The activation energy for adsorption of the plant extract with varying concentrations at different temperatures was determined by plotting log corrosion rate (CR) Vs 1/T. From the slope, activation energy (Ea) was calculated using equation 5.

\[
Ea = -2.303 \times R \times \text{Slope}
\]

Where R is the gas constant (8.314J)

The data for Ea, involved in this study are tabulated in Table 6 and 7. From the table, it was revealed that the values of activation energy increases as concentration of inhibitor increases. The value of Ea in blank solution for the air dried and sun dried samples was 17.72 kJ/mol, and 12.50 kJ/mol respectively and the values rises as the concentration of inhibitors increases from 0.2g/l (20.41, 19.95,16.18 and 17.87kJ/mol) to 1.0g/l (25.13, 25.88, 20.41 and 20.62 kJ/mol) for AALL, AMFL, SALL and SMFL extracts respectively. This is due to the physical barrier created by adsorbed molecules on mild steel surface which increased the minimum energy required for corrosion reaction to occurs and the increase in the activation energy values with increasing concentration of the extract further corroborates the fact that inhibition efficiency increases with increase in concentration of the extract. In the present study, a physical adsorption mechanism is proposed since the values of Ea are lower than 80 kJ mol⁻¹ [38], and this happens due to the electrostatic force between negatively charged metal surface and positive charged of organic species The trend of increasing Ea values as with concentration of the inhibitors have been reported by earlier studies on various plant extract such as jujube leaves [39], black pepper [26, 40] sunflower leaves [41], banana peels [42] and *Alchornea laxiflora* leaves [23].

Moreso, from the Errying Transition state plot which involved the plotting of log (CA/CR) Vs 1/T, the enthalpy change (∆H°) for all the samples extract was obtained by using equation 6

\[
\Delta H = \text{Slope} \times R
\]

where R is the gas constant (8.314)

The enthalpy (∆H°) values calculated for all the dried samples are positive and it increases with increase in concentration of the inhibitor. The positive signs of the enthalpies reflect the endothermic nature of the mild steel dissolution process. The increase in the values of enthalpy change with increase in concentration indicate that the addition of inhibitors retard the corrosion process and more energy is needed for it to break the film barrier and react with mild steel surface.

The entropy change (ΔS) values for the samples extract was also obtained from the Errying transition state plot by
using equation 8:

$$\text{Intercept} = \log \left( \frac{R}{N} \right) + \frac{\Delta S}{R}$$  \hspace{1cm} (7)

Table 3. Variation of weight loss with respect to time for Corrosion of mild steel in 1.0 M HCl in the absence and presence of ethanol extract of air dried Alchornea laxiflora and Mucuna flagellipes leaves extract.

| Time (days) |空白 | Air dried Alchornea laxiflora leaves extract | Air dried Mucuna flagellipes leaves extract |
|------------|------|---------------------------------------------|-----------------------------------------------|
| 0.2 g/L    | 0.0764 | 0.0712 | 0.0689 | 0.0645 | 0.0593 | 0.2593 | 0.1984 | 0.1012 | 0.0952 | 0.0672 |
| 0.4 g/L    | 1.2247 | 0.1356 | 0.1311 | 0.1283 | 0.0792 | 0.4588 | 0.3662 | 0.2338 | 0.2041 | 0.1241 |
| 0.6 g/L    | 1.7563 | 0.2456 | 0.2248 | 0.1837 | 0.1599 | 0.1363 | 0.5565 | 0.4560 | 0.3564 | 0.2856 | 0.1566 |
| 0.8 g/L    | 1.9878 | 0.3859 | 0.3762 | 0.2649 | 0.2241 | 0.1864 | 0.6584 | 0.5162 | 0.4262 | 0.3969 | 0.2057 |
| 1.0 g/L    | 2.5691 | 0.5163 | 0.4871 | 0.3882 | 0.3162 | 0.2482 | 0.7363 | 0.6152 | 0.5164 | 0.4263 | 0.2851 |
| 2.7706    | 6.0161 | 0.5982 | 0.4737 | 0.3792 | 0.3143 | 0.8619 | 0.7044 | 0.6024 | 0.5166 | 0.3368 |
| 2.8417    | 7.2314 | 0.6893 | 0.5743 | 0.4493 | 0.3741 | 0.9451 | 0.8281 | 0.7156 | 0.5893 | 0.3896 |

Table 4. Variation of weight loss with respect to time for Corrosion of mild steel in 1.0 M HCl in the absence and presence of ethanol extract of sun dried Alchornea laxiflora and Mucuna flagellipes leaves extract.

| Time (days) |空白 | Sun dried Alchornea laxiflora leave extract | Sun dried Mucuna flagellipes leave extract |
|------------|------|---------------------------------------------|-----------------------------------------------|
| 0.2 g/L    | 0.2993 | 0.1852 | 0.1341 | 0.1102 | 0.0744 | 0.3561 | 0.2593 | 0.1532 | 0.1341 | 0.0812 |
| 0.4 g/L    | 1.2247 | 0.4145 | 0.3291 | 0.2354 | 0.1564 | 0.5612 | 0.4764 | 0.3564 | 0.3247 | 0.2067 |
| 0.6 g/L    | 1.7563 | 0.4811 | 0.3911 | 0.3371 | 0.2241 | 0.7259 | 0.6162 | 0.4463 | 0.3791 | 0.2744 |
| 0.8 g/L    | 1.9878 | 0.6391 | 0.4892 | 0.3812 | 0.2691 | 0.8993 | 0.7667 | 0.5951 | 0.3842 | 0.3041 |
| 1.0 g/L    | 2.5691 | 0.7491 | 0.5540 | 0.4391 | 0.2963 | 1.0347 | 0.9021 | 0.6587 | 0.5152 | 0.3563 |
| 2.7706    | 6.0161 | 0.8152 | 0.6541 | 0.5462 | 0.4162 | 1.2491 | 1.0764 | 0.7921 | 0.6044 | 0.5166 |
| 2.8417    | 7.2314 | 0.9511 | 0.7482 | 0.6154 | 0.5064 | 1.4682 | 1.2642 | 0.9651 | 0.7249 | 0.6343 |

Table 5. Rate Constants and Half-life parameters at various concentrations of air dried and sun dried Alchornea laxiflora and Mucuna flagellipes leaves extracted with ethanol.

| Conc. (g/L) |空白 | AALL | AMFL | ALL | SMFL | AALL | AMFL | ALL | SMFL |
|-------------|------|------|------|-----|------|------|------|-----|------|
| Blank       | 0.2372 | 0.2372 | 0.2372 | 0.2372 | 2.9515 | 2.9215 | 2.9215 | 2.9215 |
| 0.2         | 0.0691 | 0.0967 | 0.1152 | 0.1474 | 10.030 | 7.1646 | 6.0182 | 4.7017 |
| 0.4         | 0.0415 | 0.0783 | 0.0829 | 0.0713 | 16.7173 | 8.8504 | 8.3587 | 9.7070 |
| 0.6         | 0.0369 | 0.0622 | 0.0576 | 0.0645 | 18.8070 | 11.1449 | 12.0365 | 10.7469 |
| 0.8         | 0.0184 | 0.0507 | 0.0553 | 0.0576 | 37.6140 | 13.6778 | 12.5380 | 12.0365 |
| 1.0         | 0.0115 | 0.0230 | 0.0346 | 0.0553 | 60.1824 | 30.0912 | 20.0608 | 12.5380 |

$$\Delta S = \text{Intercept} - \log \left( \frac{R}{N} \right) \times R \times X \times 2.303 \times 10^{-3}$$  \hspace{1cm} (8)

Where: $h$ = plank’s constant $(6.62617 \times 10^{-34})$

$N$ = Avogadro’s number $(6.022045 \times 10^{23})$

$R$ = gas constant $(8.314)$

From the table of the result, the values obtained for entropy ($\Delta S$) change are negative for both air dried and sun dried Alchornea laxiflora and Mucuna flagellipes which indicates that the activation complex in the rate-determining step represents an association rather than dissociation step.

### 3.9. Adsorption Isotherm

The inhibition of the corrosion of mild steel in 1.0 M HCl medium with addition of different concentrations of the extracts can be explained by the adsorption of the components of the plant extracts on the metal surface [43]. Inhibition efficiency (IE) is directly proportional to the fraction of the surface covered by the adsorbed molecules ($\theta$). Therefore, with the extract concentration specifies the adsorption isotherm that describes the system and gives the relationship between the coverage of an interface with the adsorbed species and the concentration of species in solution [44]. The Values of the degree of surface coverage ($\theta$) were evaluated at different concentrations of the inhibitors in 1.0 M HCl solution and were fitted to various adsorption isotherms. Different adsorption isotherms were tested in order to obtain more information about the interaction between the inhibitors and the mild steel surface. The various isotherms tested include Temkin, Freundlich and Langmuir adsorption isotherms and the values obtained are presented in Table 8, 9, 10 and 11. The linear regression coefficients ($r^2$) were used to determine the best fit. Langmuir adsorption isotherms were found to be best fit in which case all the
linear regression coefficients ($r^2$) were close to unity as shown on the tables.

**Table 6.** Values of $E_a$, $\Delta H$ and $\Delta S$ in the absence and presence of air dried Alchornea laxiflora and Macuna flagellepes leaves extracts at different Concentrations.

| Conc. (g/L) | Air dried Alchornea laxiflora leaves extract | Air dried Macuna flagellepes leave extract |
|-------------|-----------------------------------------------|------------------------------------------|
|             | $E_a$(KJ/mol$^1$) | $\Delta H$(KJ/mol$^1$) | $\Delta S$(KJ/mol$^1$) | $E_a$(KJ/mol$^1$) | $\Delta H$(KJ/mol$^1$) | $\Delta S$(KJ/mol$^1$) |
| Blanks      | 17.72            | 15.09                  | -204.63                 | 17.72            | 15.09                  | -204.63                 |
| 0.2         | 20.41            | 15.78                  | -212.88                 | 19.95            | 17.33                  | -207.25                 |
| 0.4         | 21.24            | 16.60                  | -223.97                 | 22.07            | 18.45                  | -217.82                 |
| 0.6         | 23.69            | 19.06                  | -214.45                 | 22.35            | 18.71                  | -217.51                 |
| 0.8         | 23.99            | 21.35                  | -198.86                 | 24.24            | 20.62                  | -209.20                 |
| 1.0         | 25.13            | 21.98                  | -199.31                 | 25.88            | 21.27                  | -198.65                 |

**Table 7.** Values of $E_a$, $\Delta H$ and $\Delta S$ in the absence and presence of sun dried Alchornea laxiflora and Macuna flagellepes leaves extracts at different Concentrations.

| Conc. (g/L) | Sun dried Alchornea laxiflora leaves extract | Sun dried Macuna flagellepes leave extract |
|-------------|-----------------------------------------------|------------------------------------------|
|             | $E_a$(KJ/mol$^1$) | $\Delta H$(KJ/mol$^1$) | $\Delta S$(KJ/mol$^1$) | $E_a$(KJ/mol$^1$) | $\Delta H$(KJ/mol$^1$) | $\Delta S$(KJ/mol$^1$) |
| Blanks      | 12.50            | 9.870                  | -220.94                 | 12.50            | 9.870                  | -220.94                 |
| 0.2         | 16.18            | 18.29                  | -205.45                 | 17.87            | 15.25                  | -209.74                 |
| 0.4         | 16.38            | 18.96                  | -217.82                 | 18.97            | 16.35                  | -206.89                 |
| 0.6         | 17.39            | 20.76                  | -215.52                 | 18.99            | 17.46                  | -214.22                 |
| 0.8         | 18.28            | 22.66                  | -213.24                 | 19.27            | 19.63                  | -223.78                 |
| 1.0         | 20.41            | 23.80                  | -207.73                 | 20.62            | 20.99                  | -213.95                 |

**Table 8.** Adsorption isotherm parameters obtained from the Corrosion data for mild steel in 1.0 M HCl containing AALL extract.

| Temp.(K) | Langmuir adsorption | Freundlich adsorption | Temkin adsorption |
|----------|---------------------|-----------------------|-------------------|
|          | Slope               | $r^2$                 | $K_{ads}$         | $r^2$ | $1/n$ | $K_t$ | $r^2$ | Constant b.  |
| 303      | 1.062               | 0.997                 | 12.50             | 0.981 | 0.123 | 1.1402| 0.973 | 22.2738     |
| 313      | 1.150               | 0.997                 | 13.70             | 0.958 | 0.100 | 1.2218| 0.946 | 27.2795     |
| 323      | 1.184               | 0.997                 | 14.09             | 0.957 | 0.095 | 1.2560| 0.947 | 29.5622     |
| 333      | 1.203               | 0.998                 | 12.82             | 0.988 | 0.115 | 1.2735| 0.985 | 25.5046     |

**Table 9.** Adsorption isotherm parameters obtained from the Corrosion data for mild steel in 1.0 M HCl containing AMFL extract.

| Temp.(K) | Langmuir adsorption | Freundlich adsorption | Temkin adsorption |
|----------|---------------------|-----------------------|-------------------|
|          | Slope               | $r^2$                 | $K_{ads}$         | $r^2$ | $1/n$ | $K_t$ | $r^2$ | Constant b.  |
| 303      | 1.145               | 0.998                 | 16.1290           | 0.953 | 0.087 | 1.2028| 0.944 | 30.3726     |
| 313      | 1.172               | 0.997                 | 13.6986           | 0.977 | 0.103 | 1.2417| 0.971 | 26.3811     |
| 323      | 1.237               | 0.999                 | 14.7058           | 0.981 | 0.097 | 1.3002| 0.977 | 28.6445     |
| 333      | 1.255               | 0.998                 | 12.9870           | 0.961 | 0.105 | 1.3243| 0.957 | 27.1167     |

**Table 10.** Adsorption isotherm parameters obtained from the Corrosion data for mild steel in 1.0 M HCl containing SALL extract.

| Temp.(K) | Langmuir adsorption | Freundlich adsorption | Temkin adsorption |
|----------|---------------------|-----------------------|-------------------|
|          | Slope               | $r^2$                 | $K_{ads}$         | $r^2$ | $1/n$ | $K_t$ | $r^2$ | Constant b.  |
| 303      | 1.290               | 0.993                 | 7.0922            | 0.964 | 0.161 | 1.4289| 0.947 | 16.0973     |
| 313      | 1.390               | 0.981                 | 6.135             | 0.824 | 0.150 | 1.5668| 0.805 | 16.4692     |
| 323      | 1.502               | 0.994                 | 6.6667            | 0.965 | 0.150 | 1.5668| 0.951 | 16.4441     |
| 333      | 1.615               | 0.996                 | 6.2893            | 0.977 | 0.153 | 1.7660| 0.967 | 15.3637     |

**Table 11.** Adsorption isotherm parameters obtained from the Corrosion data for mild steel in 1.0 M HCl containing SMF extract.

| Temp.(K) | Langmuir adsorption | Freundlich adsorption | Temkin adsorption |
|----------|---------------------|-----------------------|-------------------|
|          | Slope               | $r^2$                 | $K_{ads}$         | $r^2$ | $1/n$ | $K_t$ | $r^2$ | Constant b.  |
| 303      | 1.178               | 0.994                 | 9.8039            | 0.935 | 0.126 | 1.2823| 0.919 | 20.9648     |
| 313      | 1.122               | 0.993                 | 9.4340            | 0.902 | 0.121 | 1.3366| 0.885 | 22.2072     |
| 323      | 1.306               | 0.997                 | 10.0000           | 0.961 | 0.119 | 1.4028| 0.961 | 22.6367     |
| 333      | 1.336               | 0.992                 | 7.4072            | 0.945 | 0.147 | 1.4028| 0.927 | 18.7616     |
4. Conclusion

This result revealed that the technique used for fresh leaves drying is an important factor which determines the phytochemical constituent of a plant that are responsible for the corrosion inhibition of a mild steel in acidic medium. The air dried *Alchornea laxiflora* leaves extract seem to retain the highest phytochemicals in comparison to the sun dried leaves samples. Their Inhibition efficiency increases as the concentration of the extract increases but decreases with increase in the temperature. Thermodynamic parameters confirm that the adsorption of the extract on the surface of the mild steel is spontaneous and is consistent with the physical adsorption mechanism. The kinetic parameters obtained from the study indicated that the half-life of the mild steel increased with increase in the concentration of the inhibitor with the extract of air dried *Alchornea laxiflora* having the highest half-life. Moreso, the adsorption of the leaves extract on mild steel follows Langmuir adsorption.

References

[1] V. S. Sastri, Corrosion Inhibitors Principles and applications. John Wiley & Sons: New York; 1998.
[2] P. B. Raja, M. G. Sethuraman, Mater. Lett. 62 (2008) 113–116.
[3] D. K. Singh, S. Kumar, G. Udayabhanu, and R. P. John, “4(N, N-dimethyl amino) benzaldehyde nicotinic hydrazone as corrosion inhibitor for mild steel in 1M HCl solution: An experimental and theoretical study,” Journal of Molecular Liquids, 2016, vol. 216, pp. 738–746.
[4] K. K. Alaneme, S. J. Olusegun, and O. T. Adelowo, “Corrosion inhibition and adsorption mechanism studies of Hunteria umbellata seed husk extracts on mild steel immersed in acidic solutions,” Alexandria Engineering Journal, 2016, vol. 55, no. 1, pp. 673–681.
[5] M. V. Fiori-Bimbí, P. E. Alvarez, H. Vaca, and C. A. Gervasi, “Corrosion inhibition of mild steel in HCl solution by pectin,” Corrosion Science, 2015, vol. 92, pp. 192–199.
[6] P. Roy, P. Karfá, U. Adhikari, and D. Sukul, “Corrosion inhibition of mild steel in acidic medium by polyacrylamide grafted Guar gum with various grafting percentage: effect of intramolecular synergism,” Corrosion Science, 2014, vol. 88, pp. 246–253.
[7] G. Sigirircik, T. Tüken, and M. Erbil, “Assessment of the inhibition efficiency of 3, 4- diaminobenzoazinitrile against the corrosion of steel,” Corrosion Science, 2016, vol. 102, pp. 437–445.
[8] K. Krishnaveni and J. Ravichandran, “Effect of aqueous extract of leaves of orinda tinctoria on corrosion inhibition of aluminium surface in HCl medium,” Transactions of Nonferrous Metals Society of China, 2014, vol. 24, no. 8, pp. 2704–2712.
[9] M. S. Rabeta, and S. Y. Lai, Effects of drying, fermented and unfermented tea of Ocimum tenuiflorum Linn on the antioxidant capacity. International Food Research Journal, 2013 20 (4): 1601-1608.
[10] B. S. Davi, and S. Rajandran. Influence of garlic extract on the inhibition efficiency of trisodium citrate-Zn2+ system. International Journal of Chemical Science and Technology, 2011, 1: 79–87.
[11] P. C. Okafor, V. I. Osabor, and E. E. Ebensu, Eco-friendly corrosion inhibitor: Inhibitive action of ethanol extracts of *Garcinia kola* for the corrosion of mild steel in HS2O4 solutions, Pigment and Resin Technology, 2007, 35 (5): 299-305.
[12] E. E. Oguzie, Influence of halide ions on the inhibitive effect of Congo red dye on the corrosion of mild steel in sulphuric acid solution. Material Chemistry and Physics, 2005, 87 (1): 212–217.
[13] S. S. Handa, S. P. S Khanuga, G. Longo, D. D. Rakesh: Extraction Technologies for medicinal and Aromatic plants (1st edn.), no. 66. Italy: United Nations Industrial Development Organization and the International Centre for Science and High Technology, 2008: 747–752.
[14] N. O., Eddy Ethanol Extract of Phyllanthus amarus as a green inhibitor for the corrosion of mild steel in H2SO4 Portugaliae Electrochemical Acta, 2009; 27 (5): 579-589.
[15] J. B. Harborne, Phytochemical Methods: A Guide to Modern Techniques of plant Analysis. Chapman & Hall Ltd, London, 1973, 278pp.
[16] D. E. Okwu, Evaluation of the Chemical Composition of indigenous species and flavouring agents. Global Journal of Pure and Applied Science, 2001. 7 (5), 455-459.
[17] O. O. Odeja, G. Obi, C. E. Ogwuue, E. E. Elemike, O. O. Oderinlo. International Journal of Herbal Medicine, 2014; 2 (4): 26-3.
[18] A. Sofowara, Medicinal Plants and Traditional Medicine in Africa, Ibadan, Nigeria, Spectrum Book Ltd., 1993, 289.
[19] O. Odeja, G. Obi, C. Ene Ogwuue,, E. E. Elemike,, and Y. Oderinlo, Phytochemical Screening, Antioxidant and Antimicrobial activities of *Senna occidentalis* (L.) Leaves Extract, Journal of Clinical Phytoscience, 2015, 2-6.
[20] De Souza F. S. and A. Spinelli, “Caffeic acid as a green corrosion inhibitor for mild steel,” Corrosion Science, 2009, vol. 51, no. 3, pp. 642–649.
[21] Abdel-Gaber A. M., B. A. AbdEL-Nabey, M. Saadawy, Corros. Sci., 2009, 51 p. 1038.
[22] Oguzie E. E. Corros. Sci., 2008, 50, p. 2993.
[23] Olasehinde, E. F, Ogunjobi, J. K., Akinlosotu, O. M., Omogbehin, S. A., Investigation of the Inhibitive Properties of *Alchornea laxiflora* leaves on the Corrosion of Mild Steel in HCl: Thermodynamics and Kinetic Study ‘Journal of American Science, 2015; 11 (1s).
[24] A. Tosun, M. Ergun: Protection of Corrosion of Carbon Steel by Inhibitors in Containing Solutions, G. U. Journal of Science, 2006, 19 (3), 149-154.
[25] P. R. Vijayalakshmi, R. Rajalakshmi and S. Subhashini, Corrosion Inhibition of Aqueous Extract of Cocos nucifera - Coconut Palm-Periolo Extract from Destructive Distillation for the Corrosion of Mild Steel in Acidic Medium. Portugaliae Electrochemical Acta, 2011; 29 (1): 14-15.
[26] M. Lebrini, F. Robert, A. Lecante, C. Roos Corrosion inhibition of C38 steel in 1M hydrochloric acid medium by alkaloids extract from Oxandra asbeckii plant. Corrosion Science. 2012; 53 (2): 687–695.

[27] B. U. Ugi, I. E. Uwah, C. N. Kelvin, Combating corrosion of mild steel in hydrogen tetroxosulphate (VI) acid environment using green corrosion inhibitors: Chrysophyllum albidum plant. Journal of Applied Chemical Science International, 2016, 6 (4): 169–179.

[28] A. O. James, O. Akaranta, Inhibition of Corrosion of Zinc in Hydrochloric Acid Solution by Red Onion Skin Aceton Extract, Res. J. Chem. Sci., 2011, 1 (1): 31-37.

[29] O. O. Adeyemi, O. O. Olubomehin,: Investigation of Anthocleista djalonensis Stem Bark Extract as Corrosion Inhibitor for Aluminium. The pacific Journal of Science and Technology, 2010, 11 (2): 455-462.

[30] L. A. Nnanna, B. N. Onwuagba, I. M. Mejeha, K. B. Okeoma, Inhibition effects of some plant extracts on the acid corrosion of aluminium alloy, African Journal of Pure and Applied Chemistry, 2010, 4 (1), p. 11-16.

[31] M. A. Chidiebere, E. E. Oguzie, L. Liu, Y. Li & F. Wang, Adsorption and corrosion inhibiting effect of riboflavon on Q235 mild steel corrosion in acidic environments. Mater. Chem. Phys. 2015, 156, 95-104.

[32] E. S. Ferreira, C. Giacomelli, F. C. Giacomelli A. Spinelli, Evaluation of the inhibitor effect of ascorbic acid on the corrosion of mild steel. Mater. Chem. Phys. 2004, 83,129–134.

[33] S. Manimegalai and P. Manjul: Thermodynamic and Adsorption studies for corrosion inhibition of Mild steel in Aqueous Media by Sargasam swartzii (Brown algae) j. Mater. Environ. Sci. 2015, 6 (6) 1629-1637.

[34] N. O. Eddy Ethanol Extract of Phyllanthus amarus as a green inhibitor for the corrosion of mild steel in H2SO4 Portugaliae Electrochemical Acta, 2009; 27 (5): 579-589.

[35] E. E. Ebenso, Effect of halide ions on the corrosion inhibition of mild steel in H2SO4 using methyl red. Part 1 Bull. Electrochem. 2003; 19: 209–216.

[36] F. Bentiss, M. Lebrini, H. Vezin, F., Chai, M., Traisnel, M. Lagrene, Enhanced corrosion resistance of carbon steel in normal sulfuric acid medium by some macrocyclic polyether compounds containing a 1,3,4-thiadiazole moiety AC impedance and computational studies. Corr. sci. 2005, 51, 2165–2173.

[37] U. J. Ekpe, P. C. Okafor, E. E. Ebenso. Inhibition of the Acid Corrosion of Aluminium by some derivatives of Thiosemicarbazion, Bulletin of Chemical Society of Ethiopia, 2004; 18 (2): 181-192.

[38] A. L. Obike, C. N. Emeruwa, V. I. Ajije, J. C. Igwe. Corrosion Inhibition and Adsorption Behaviour of Methanol Extract of Spondias cytherea leaves on Mild Steel Corrosion in 5.0MH2SO4, InternationalJournal of Innovative Research in Science, Engineering and Technology, 2016, (5) 2319–8753.

[39] S. S. Shivakumar, K. N. S. Mohana, Ziziphus mauritiana leaves extract as corrosion inhibitor for mild steel in sulphuric acid and hydrochloric acid solution. European Journal of Chemistry. 2012; 3 (4): 426–432.

[40] M. A. Quraishi, D. K. Yadav, I. Ahmad: Green approach to corrosion inhibition by black pepper extract in hydrochloric acid solution. The Open Corrosion Journal. 2009; 2: 56–60.

[41] H. Cang, W. Shi, J. Shao, Q. Xu. Study of Stevia rebaudiana leaves as green corrosion inhibitor for mild steel in sulphuric acid by electrochemical techniques. International Journal of Electrochemical Science. 2012; 7 (4): 3726–36.

[42] R. S. Mayanglambam, V. Sharma, G. Singh: Musa paradisiacal extract as a green inhibitor for corrosion of mild steel in 0.5M sulphuric acid solution. Portugaliae Electrochemical Acta. 2011; 29 (6): 405–417.

[43] H. F. Chahul, C. O. Akalezi, A. M. Ayuba, Effect of adenine, guanine and hypoxanthine on the corrosion of mild steel in H3PO4 Int. J. Chem. Sci. 2015 (7) 2006-3350.

[44] Q. B. Zhang, Y. X. Hua, Corrosion inhibition of mild steel by alkyl imidazolium ionic liquids in hydrochloric acid, Electro. chem. Acta. 2009, (54) 1881-1887.